16

OCCURRENCE AND EXTRACTION OF METALS

Metals and their alloys are extensively used in our day-to-day life. They are used for making machines, railways, motor vehicles, bridges, buildings, agricultural tools, aircrafts, ships etc. Therefore, production of a variety of metals in large quantities is necessary for the economic growth of a country. Only a few metals such as gold, silver, mercury etc. occur in free state in nature. Most of the other metals, however, occur in the earth's crust in the combined form, i.e., as compounds with different anions such as oxides, sulphides, halides etc. In view of this, the study of recovery of metals from their ores is very important. In this lesson, you shall learn about some of the processes of extraction of metals from their ores, called metallurgical processes.

OBJECTIVES

After reading this lesson, you will be able to :

- differentiate between minerals and ores;
- recall the occurrence of metals in native form and in combined form as oxides, sulphides, carbonates and chlorides;
- list the names and formulae of some common ores of Na, Al, Sn, Pb ,Ti, Fe, Cu, Ag and Zn;
- list the occurrence of minerals of different metals in India;
- list different steps involved in the extraction of metals;

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* An alloy is a material consisting of two or more metals, or a metal and a non-metal. For example, brass is an alloy of copper and zinc; steel is an alloy of iron and carbon.

- list and explain various methods for concentration of ores (gravity separation, magnetic separation, froth floatation and chemical method);
- explain different metallurgical operations : roasting, calcination and smelting with suitable examples;
- choose the reducing agent for a given ore;
- differentiate between flux and slag, and
- explain different methods for refining of metals : poling, liquation, distillation and electrolytic refining.
- explain the process involved in the extraction of Al, Fe, Cu, and Zn.

16.1 OCCURRENCE OF METALS

Metals occur in nature in free as well as combined form. Metals having low reactivity show little affinity for air, moisture, carbon dioxide or other non-metals present in nature. Such metals may remain in elemental or native (free) state in nature. Such metals are called "noble metals" as they show the least chemical reactivity. For example gold, silver, mercury and platinum occur in free state.

On the other hand, most of the metals are active and combine with air, moisture, carbon dioxide and non-metals like oxygen, sulphur, halogens, etc. to form their compounds, like oxides, sulphides, carbonates, halides and silicates. i.e., they occur in nature in a combined state.

A naturally occurring material in which a metal or its compound occurs is called a *mineral*. A mineral from which a metal can be extracted economically is called an *ore*.

An ore is that mineral in which a metal is present in appreciable quantities and from which the metal can be extracted economically.

The main active substances present in nature, expecially in the atmosphere are oxygen and carbon dioxide. In the earth's crust, sulphur and silicon are found in large quantities. Sea-water contains large quantities of chloride ions (obtained from dissolved sodium chloride). Most avtive metals are highly electropositive and therefore exist as ions. It is for this reason that most of the important *ores* of these metals occur as (i) oxides (ii) sulphides (iii) carbonates (iv) halides and (v) silicates. Some sulphide ores undergo oxidation by air to form sulphates. This explains the occurrence of sulphate ores.

Ores are invariably found in nature in contact with rocky materials. These rocky or earthy impurities accompanying the ores are termed as *gangue* or *matrix*.

Some important ores and the metals present in these ores are listed in Table 16.1

Table 16.1: Some Important Ores

Type of Ore	Metals (Common Ores)
Native Metals	Gold (Au), silver (Ag)
Oxide ores	Iron (Haematite, Fe_2O_3); Aluminium (Bauxite, $Al_2O_3 . 2H_2O$); Tin (Cassiterite, SnO_2); Copper (Cuprite, Cu_2O); Zinc (Zincite, ZnO); Titanium (Ilmenite, $FeTiO_3$, Rutile, TiO_2)
Sulphide ores	Zinc (Zinc blende, ZnS); Lead (Galena, PbS); Copper (Copper glance, Cu_2S); Silver (Silver glance or Argentite, Ag_2S); Iron (Iron pyrites, FeS_2)
Carbonate ores	Iron (Siferite, $FeCO_3$); Zinc (Calamine, $ZnCO_3$) , Lead (Cerrusite, $PbCO_3$)
Sulphate ores	Lead (Anglesite, $PbSO_4$)
Halide ores	Silver (Horn silver, AgCl); Sodium (Common salt or Rock salt, NaCl); Aluminium (Cryolite, Na_3AlF_6)
Silicate ores	Zinc (Hemimorphite, $2ZnO.SiO_2.H_2O$)

16.1.1 Mineral Wealth of India

India possesses large deposits of minerals of some important metals such as iron, manganese, aluminium, magnesium, chromium, thorium, uranium, titanium and lithium. They constitute one-quarter of the world's known mineral resources.Mineral fuels (like coal ,petroleum and natural gas) constitute more than 80% while metallic minerals constitute only about 10% of the total volume of mineral production in a year. In this section, we shall list some of the important minerals of a few common metals such as Fe, Cu, Ag, Zn, Ti, Al Sn, Pb and Na and their locations in India.

Important Ores of Some Common Elements

Iron	Iron ore reserves in the country are estimated at 1750 crore tonnes. Major iron ore mining is done in Goa, Madhya Pradesh, Bihar, Karnataka, Orissa and Maharashtra.
Aluminium	Its chief ore, bauxite is available in India in abundance. The annual production of bauxite is estimated to be more than 2 million tonnes. Important deposits of bauxite in the country occur in Bihar, Goa, Madhya Pradesh, Maharashtra, Tamil Nadu, Gujarat, Karnataka, Orissa, Uttar Pradesh, Andhra Pradesh, Jammu & Kashmir and Rajasthan.

Copper	India does not have rich copper ore deposits. The total reserves of the ore in the country are estimated around 60 crore tonnes. Major ore producing areas are Singhbum district (Bihar), Balaghat district (Madhya Pradesh) and Jhunjhunu district (Rajasthan).
Zinc and Lead	India has no significant deposits of lead ores. Lead and Zinc have been located at Zawar mines near Udaipur (Rajasthan) and at Hazaribagh (Jharkhand), Sargipalli mines in Orissa and Bandalamottu lead project in Andhra Pradesh. Some reserves have been located in Gujarat and Sikkim.The total reserves are estimated at about 360 million tonnes in which lead content is estimated to be around 5 million tonnes and zinc to be around 16 million tonnes.
Tin	Deposits of tinstone $(\mathrm{SnO_2})$ are found in Hazaribagh (Jharkhand) and Orissa.
Silver	India does not possess rich silver deposits. Gold from Kolar fields and Hutti gold fields (Karnataka) and lead-zinc ores of Zawar mines (Rajasthan) contain some silver.
Titanium	Ilmenite $(\mathrm{FeTiO_3})$ is recovered from beach sands of Kerala and Tamil Nadu. The estimated reserves are around 100 to 150 million tonnes.
Sodium :	Tincal or Native borax $(\mathrm{Na_2B_4O_7.10H_2O})$ is found in Ladakh and Kashmir.

16.2 GENERAL PRINCIPLES OF EXTRACTION OF METALS

The process of extracting the metals from their ores and refining them is called *metallurgy*. The choice of the process depends upon the nature of the ore and the type of the metal. The metal content in the ore can vary depending upon the impurities present and chemical composition of the ore. Some common steps involved in the extraction of metals from their ores are :

(i) Crushing and pulverization

(ii) Concentration or dressing of the ore

(iii) Calcination or roasting of the ore

(iv) Reduction of metal oxides to free metal

(v) Purification and refining of metal.

16.2.1. Crushing and Pulverization

The ore is generally obtained as big rock pieces. These big lumps of the ore are crushed to smaller pieces by using *jaw-crushers* and *grinders*. It is easier to work with crushed ore. The big lumps of the ore are brought in between the plates of a crusher forming a jaw. One of the plates of the crusher is stationary while the other moves to and fro and the crushed pieces are collected below (Fig. 16.1).

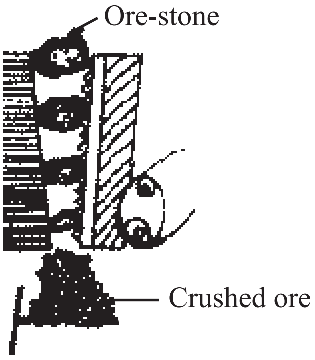


Fig. 16.1 : *Jaw Crusher*

The crushed pieces of the ore are then pulverized (powdered) in a stamp mill shown in Fig. 16.2. The heavy stamp rises and falls on a hard die to powder the ore. The powdered ore is then taken out through a screen by a stream of water. Pulverization can also be carried out in a ball mill. The crushed ore is taken in a steel cylinder containing iron balls. The cylinder is set into revolving motion. The striking balls pulverize the crushed ore into fine powder.

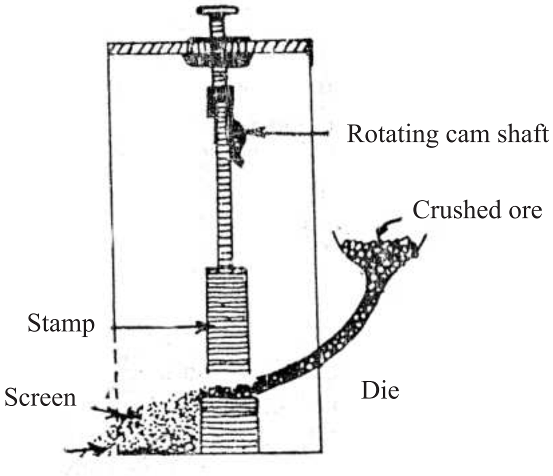


Fig. 16.2 : *The Stamp mill*

16.2.2 Concentration or Dressing of the Ore

Generally, the ores are found mixed with earthy impurities like sand, clay, lime stone etc. These unwanted impurities in the ore are called *gangue* or *matrix.*

The process of removal of gangue from powdered ore is called concentration or ore dressing.

There are several methods for concentrating the ores. The choice of method depends on the nature of the ore. Some important methods are :

(i) **Gravity separation (Hydraulic washing) :** In this method, the light (low specific gravity) earthy impurities are removed from the heavier metallic ore particles by washing with water. It is therefore, used for the concentration of heavier oxide ores, like haematite (Fe_2O_3) tinstone (SnO_2) and gold (Au). In this method, as shown in the Fig. 16.3 the powdered ore is agitated with water or washed with a strong current of water. The heavier ore settles down rapidly in the grooves and the lighter sandy and earthy materials (gangue particles) are washed away.

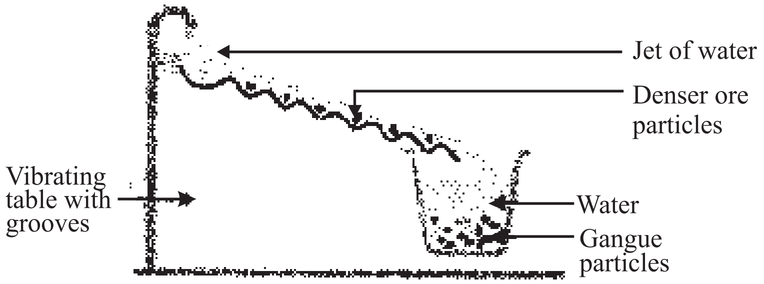


Fig. 16.3 : *Gravity Separation (Hydraulic Washing)*

(ii) Magnetic separation method :

By this method, those ores can be concentrated which either contain impurities which are magnetic or are themselves magnetic in nature.

For example, the tin ore, tin stone (SnO_2) itself is non-magnetic but contains magnetic impurities such as iron tungstate $(FeWO_4)$ and manganese tungstate $(MnWO_4)$.

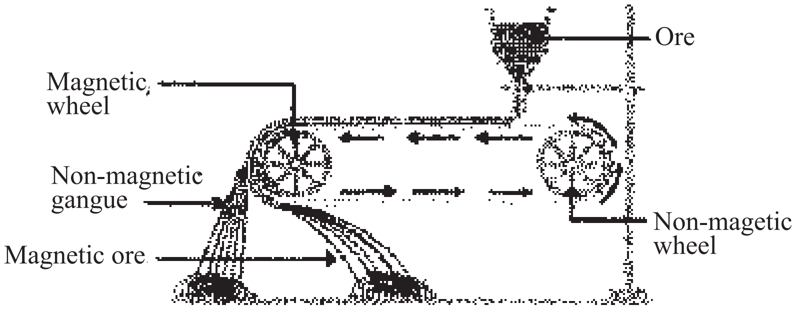


Fig. 16.4. : *Magnetic Separation*

The finely powdered ore is passed over a conveyer belt moving over two rollers, one of which is fitted with an electromagnet (Fig. 16.4). The magnetic material is attracted by the magnet and falls in a separate heap. In this way magnetic impurities are separated from non-magnetic material.

(iii) Froth floatation method :

This method is especially applied to sulphide ores, such as **galena** (PbS), **zinc blende** (ZnS), or **copper pyrites** $(CuFeS_2)$. It is based on the different wetting properties of the surface of the ore and gangue particles. The sulphide ore particles are wetted preferentially by oil and gangue particles by water. In this process, finely powdered ore is mixed with either pine oil or eucalyptus oil. It is then mixed with water. Air is blown through the mixture with a great force. Froth is produced in this process which carries the weted ore upwards with it. Impurities (gangue particles) are left in water and sink to the bottom from which these are drawn off (Fig. 16.5).

(iv) Chemical method :

In this method the ore is treated with a suitable chemical reagent which dissolves the ore leaving behind insoluble impurities. The ore is then recovered from the solution by a suitable chemical method. This is applied for extraction of aluminium from bauxite $(Al_2O_3.2H_2O)$. Bauxite is contaminated with iron (III) oxide (Fe_2O_3), titanium (IV) oxide (TiO_2) and silica (SiO_2). These impurities are removed by digesting the powdered ore with aqueous solution of sodium hydroxide at 420 K under pressure. Aluminium oxide dissolves in sodium hydroxide, whereas, iron (III) oxide, silica and titanium (IV) oxide remain insoluble and are removed by filtration.

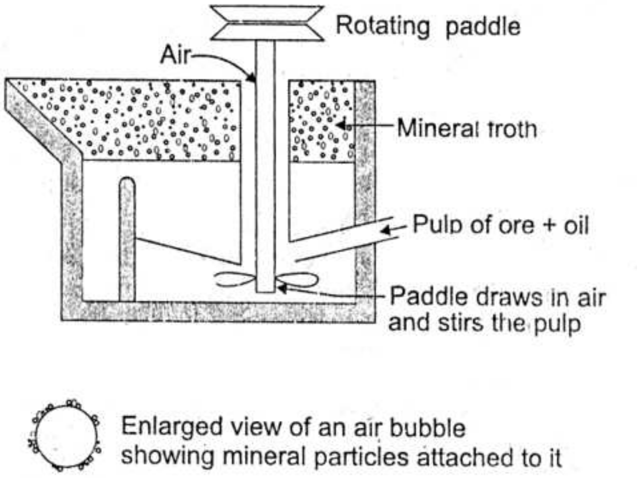


Fig. 18.5 : *Froth floatation*

$$Al_2O_3 + 6NaOH \longrightarrow \underset{\textbf{Sodium aluminate}}{2Na_3AlO_3} + 3H_2O$$

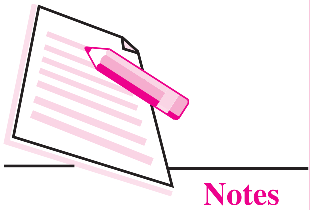
Sodium aluminate is diluted with water to obtain precipitate of aluminium hydroxide. It is filtered and ignited to obtain pure alumina.

$$Na_3AlO_3 + 3H_2O \longrightarrow Al(OH)_3 + 3NaOH$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

INTEXT QUESTIONS 16.1

1. Write the names of eight important metals. Give an example of one important ore of each metal.
2. What is the difference between an ore and a mineral?
3. Name some important methods of concentrating the ores.
4. Which method of concentration is applied in the following cases?
   (i) Magnetic ores (ii) Sulphide ores (iii) Bauxite ore
5. Which metal is extracted from the mineral zinc blede ?



Notes

16.2.3 Calcination and Roasting of the Ore

The concentrated ore is converted into metal oxide by calcination or roasting.

(A) Calcination :

Calcination involves heating of the concentrated ore in a limited supply of air so that it loses moisture, water of hydration and gaseous volatile substances. The ore is heated to a temperature so that it does not melt. Two examples of calcination are given below:

(i) Removal of water of hydration

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

(ii) Expulsion of CO_2 from carbonate

$$ZnCO_3 \longrightarrow ZnO + 2CO_2$$

(B) Roasting :

Roasting is a process in which the concentrated ore is heated in a free supply of air at a temperature insufficient to melt it. The following changes take place during roasting :

(i) Drying of the ore.

(ii) Removal of the volatile impurities like arsenic, sulphur, phosphorus and organic matter.

$$4As + 3O_2 \longrightarrow 2As_2O_3(g)$$

$$S + O_2 \longrightarrow SO_2(g)$$

$$4P + 5O_2 \longrightarrow P_4O_{10}(g)$$

(iii) Conversion of the sulphide ores into oxides

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

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

Calcination and roasting are generally carried out in a reverberatory furnace or in a multiple hearth furnace.

16.2.4 Reduction of the Metal Oxides to Free Metal

This process is carried out after calcination or roasting of ores. In this process called *smelting,* the oxide ores are converted into the metallic state by reduction.

(A) **Smelting** :

Smelting is a process in which the oxide ore in molten state is reduced by carbon or other reducing agents to free metal.

(i) *By using carbon as a reducing agent :*

This method is used for the isolation of iron, tin and zinc metals from their respective oxides. The oxide ores are strongly heated with charcoal or coke. Reduction occurs by the action of carbon and/or carbon monoxide which is produced by the partial combustion of coke or charcoal.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$ZnO + C \longrightarrow Zn + CO$$

Although the ore has been concentrated in an earlier step, it is still contaminated with some gangue material which is finally removed in the reduction process by the addition of *flux* during smelting.

Flux is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called *slag* which is not soluble in the molten metal. Flux are of two types :

Basic Flux :

On heating, lime stone is converted into calcium oxide used as basic flux which combines with acidic impurities like silica in metallurgy of iron and forms fusible calcium silicate $(CaSiO_3)$.

$$\underset{\textbf{(Limestone)}}{CaCO_3} \longrightarrow CaO + CO_2(g)$$

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

Acidic flux :

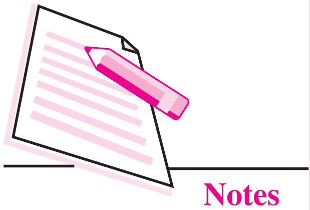
SiO_2 is used as acidic flux to remove basic impurity of FeO in metallurgy of Cu.

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

The fusible slag, such as calcium silicate formed during smelting floats over the molten metal and is thus easily removed. Another advantage is that the slag provides a covering to the molten metal thus preventing it from getting oxidized by air.

(ii) Other reducing agents :

Oxide ores which cannot be reduced by carbon or metals which show affinity to carbon by forming metal carbides, are reduced by reducing agents like



aluminium, sodium, magnesium or hydrogen. *Oxide* like chromium oxide (Cr_2O_3) or manganese oxide (Mn_3O_4) are reduced by aluminium powder is a highly exothermic reaction. This process is known as *Goldschmidt's Alumino-thermite reduction method.*

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

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

Heat is generated in the process due to the formation of Al_2O_3 which is a highly exothermic reaction.

Titanium is obtained by the reduction of $TiCl_4$ (produced by the action of carbon and chlorine on TiO_2) by Mg in an inert atmosphere of argon (Kroll process).

$$TiCl_4 + 2Mg \xrightarrow[1103\ K]{Heat} Ti + 2MgCl_2$$

Titanium can also be obtained by the reduction of TiO_2 by sodium

$$TiO_2 + 4Na \rightarrow Ti + 2Na_2O$$

Tungsten and molybedenum can be obtained by the reduction of their oxides by hydrogen,

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

(iii) *Self-reduction :*

This is applied to the sulphide ores of copper, mercury and lead . The ores are heated in air, a part of these sulphide ores is changed into the oxide or sulphate which then reacts with the remaining part of the sulphide ore to give the metal and sulphur dioxide. The reactions showing their extraction are given below :

(1) $$\underset{\textbf{Copper glance}}{2Cu_2S} + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Copper produced at this stage is called *Blister copper*. The evolution of sulphur dioxide produces blisters on the surface of solidified copper metal.

(2) $$\underset{\textbf{Cinnabar}}{2HgS} + 3O_2 \longrightarrow 2HgO + 2SO_2$$

$$2HgO + HgS \longrightarrow 3Hg + SO_2$$

(3) $$\underset{\textbf{Galena}}{2PbS} + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

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

$$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$$

(B) Reduction of concentrated ores by other methods:

Some metals cannot be obtained from their ores by using common reducing agents such as C, CO, H_2 etc. Other methods of reduction are used for such cases.

(i) *Reduction by precipitation :*

Noble metals like silver and gold are extracted from their concentrated ores by dissolving metal ions in the form of their soluble complexes. The metal ions are then regenerated by adding a suitable reagent. For example, concentrated argentite ore (Ag_2S) is treated with a dilute solution of sodium cyanide (NaCN) to form a soluble complex :

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

This solution is decanted off and treated with zinc to precipitate silver,

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

(ii) *Electrolytic Reduction :*

Active metals like sodium, potassium and aluminium etc., are extracted by the electrolysis of their fused (*molten*) salts. For example, sodium is obtained by the electrolysis of fused sodium chloride (Down's process). The reactions taking place in the electrolytic cell are :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Na^+ ions move towards the cathode and Cl^- ions move towards the anode. Following reactions take place at the electrodes :

At the Cathode $Na^+ + e^- \longrightarrow \underset{\text{(metal)}}{Na}$ (Reduction)
(Negative electrode)

At the Anode $Cl^- \longrightarrow Cl + e^-$ (Oxidation)
(Positive electrode)

$$Cl + Cl \longrightarrow Cl_2$$

Aluminium is extracted from molten alumina (Al_2O_3) by electrolysis. The melting point of alumina is quite high (2323K) which is inconvenient for electrolysis. It dissolves in molten cryolite (Na_3AlF_6) at around 1273 k. The reactions which take place in the cell are:.

At the Cathode $Al^{3+} + 3e^- \longrightarrow Al\,(metal)$

At the Anode $C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

INTEXT QUESTIONS 16.2

1. Explain the following terms :

   Calcination, Roasting, Smelting, Flux and Slag.
2. Which is the cheapest and most abundant reducing agent employed in the extraction of metals ?
3. Name the process which is used for converting sulphide ores into oxides.
4. How are oxide ores reduced ?
5. Name few materials which are used as flux in metallurgical processes.
6. What happens to (i) Bauxite and (ii) Calamine ores during calcination ?

16.2.5 Refining of Metals

Except in the electrolytic reduction method, metals produced by any other method are generally impure. The impurities may be in the form of (i) other metals (ii) unreduced oxide of the metal (iii) non-metals like carbon, silicon, phosphorus, sulphur etc. and (iv) flux or slag. Crude metal may be refined by using one or more of the following methods :

(i) *Liquation :* Easily fusible metals like tin, lead etc. are refined by this process. In this method, the impure metal is poured on the sloping hearth of a reverberatory furnace (Fig.16.6) and heated slowly to a temperature little above the melting point of the metal. The pure metal drains out leaving behind infusible impurities.

Fig. 16.6 : *Liquation*

(ii) *Poling :* Poling involves stirring the impure molten metal with green logs or bamboo. The hydrocarbons contained in the pole reduce any metal oxide present as impurity. Copper and tin are refined by this method (Fig. 16.7).

(iii) *Distillation :* Volatile metals like zinc and mercury are purified by distillation. The pure metal distils over, leaving behind non-volatile impurities.

(iv) *Electrolytic Refining :* A large number of metals like copper, silver, zinc, tin etc. are refined by electrolysis. A block of impure metal is made the anode and a thin sheet of pure metal forms the cathode of the electrolytic cell containing suitable metal salt solution which acts as an electrolyte (Fig. 16.8). On passing current, pure metal deposits at the cathode sheet while more electropositive impurities are left in solution. Less electropositive metals do not dissolve and fall away from the anode to settle below it as *anode mud.*

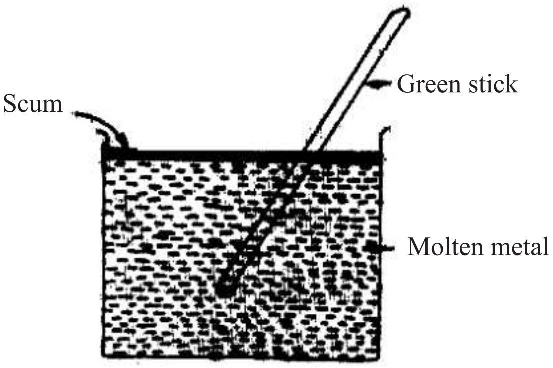


Fig. 18.7 : *Polling*

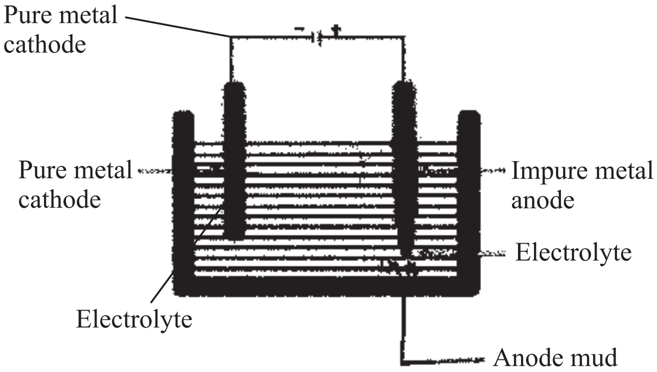


Fig. 16.8 : *Electrolytic Refining*

For example, in the electrolytic refining of crude copper (blister copper), a large piece of impure copper is made anode and a thin piece of pure copper is made the cathode. An acidified solution of copper sulphate is used as an electrolyte. On passing an electric current of low voltage through the solution copper (II) ions obtained from copper sulphate solution go to the cathode where they are reduced to the free copper metal and get deposited.

$$Cu^{2+} + 2e^{-} \longrightarrow Cu \quad \text{(at cathode)}$$

An equivalent amount of the metal from the anode dissolves into the electrolyte as Cu^{2+} ions

$$Cu \longrightarrow Cu^{2+} + 2e^{-} \quad \text{(at anode)}$$

As the process goes on, anode becomes thinner while the cathode becomes thicker. The impurities like silver, gold settle down at the bottom of the cell as *'anode mud'*.

16.3 EXTRACTION OF Al, Fe, Cu AND Zn

Aluminium

Extraction of Aluminium

Aluminium is the most abundant metallic element in the earth's crust, occurring in a variety of aluminosilicatcs such as clay, micas and feldspars. The only ore of aluminium from which it is profitable to extract the metal is bauxite.

The bauxite is first freed from silica and iron (III) oxide impurities by dissolving it in sodium hydroxide (iron(III) oxide remains undissolved) and then precipitating aluminium hydroxide by seeding the solution with a little aluminium hydroxide (silica remains dissolved):

$$A1_2O_3(s) + 2OH^-(aq) + 3H_2O(1) \longrightarrow \underset{\text{aluminate ion}}{2A1(OH)_4^-(aq)}$$

$$Al(OH)_4^-(aq) \longrightarrow Al(OH)_3(s) + OH^-(aq) \text{ (takes place on seeding)}$$

Pure aluminium oxide is now obtained by heating the hydroxide:

$$2A1(OH)_3(s) \longrightarrow A1_2O_3(s) + 3H_2O(I)$$

It is dissolved in molten cryolite, $(Na^+)_3A1F_6^{3-}$, and electrolysed at about 900°C, using a number of graphite blocks as anodes and a graphite lined bath as the cathode. Aluminium is discharged at the cathode and collects at the bottom of the molten electrolyte as a liquid, from where it can be tapped off and allowed to solidify. Oxygen is evolved at the anodes, which are slowly burnt away as carbon dioxide.

The extraction of aluminium is only economic where cheap electricity is available from water power. A low voltage is used to avoid decomposing the molten cryolite which acts as a solvent; a very high current density is used. One theory assumes that aluminium oxide dissociates into $A1^{3+}$ and $A1O_3^{3-}$

$$A1_2O_3 \rightleftharpoons A1^{3+} + A1O_3^{3-}$$

Cathode	**Anode**
$A1^{3+}$ discharged	AlO_3^{3-} discharged
$4A1^{3+} + 12e- \rightarrow 4A1$	$4A1O_3^{3-} \rightarrow 2A1_2O_3 + 3O_2 + 12e-$

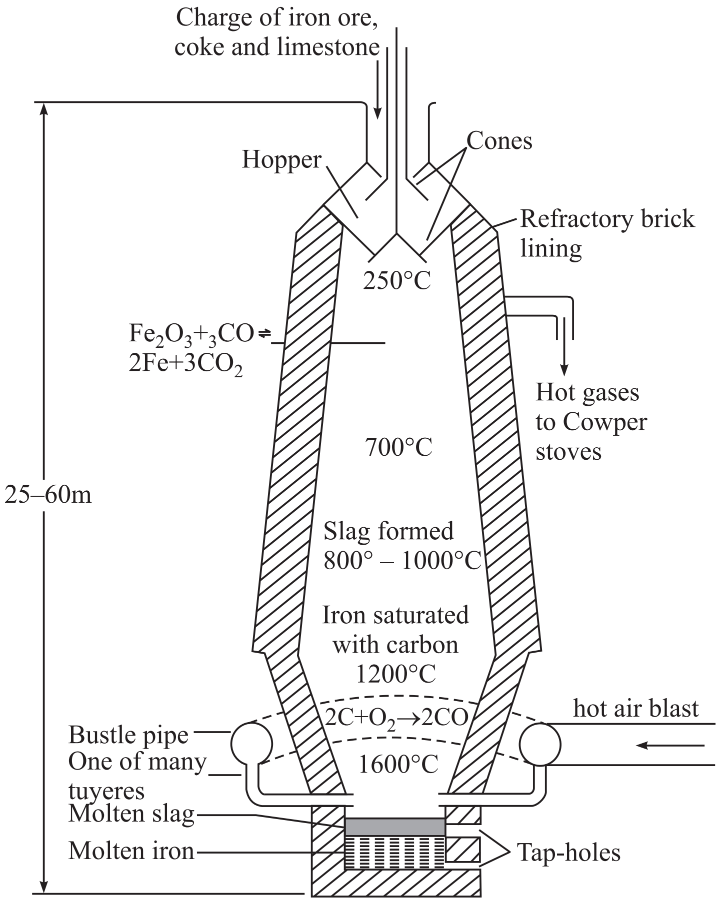
$$\underset{\text{Molten cryolite solvent}}{(Na^+)_3\ A1F_6^{3-}}$$

The process, however, is probably much more complex.

Iron

Iron, which is the second most abundant metal occurring in the earth's crust, is extracted from its oxides, haematite, Fe_2O_3. and magnetite, Fe_3O_4, and also from the carbonate siderite, $FeCO_3$. Iron pyrites, FeS_2, is not considered to be an important ore of iron.

The extraction of iron is carried out in a blast furnace which can vary in size and can be between 25 and 60 metres in height and up to 10 metres in diameter. It is constructed from steel with the inner regions lined with firebricks. A charge of iron ore, limestone and coke in the correct proportions is fed into the top of the furnace through a cone and hopper arrangement. Preheated air at a temperature of about 600°C is injected into the furnace through a number of pipes called tuyeres; the tuyeres are fed from a 'bustle' pipe encircling the blast furnace. The blast furnace is provided with two tap holes which are plugged with clay; molten iron is tapped from the lower one and molten slag from the other. The production of iron is a continuous process and, depending upon its size, a blast furnace can produce from 1000 to 1800 tonnes of iron every twenty-four hours.



The energy and reducing agent required for the smelting of iron are obtained by the combustion of coke, the temperature of the charge increasing steadily as it falls through the ascending combustion gases:

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

Notes

At a temperature of about 700°C the iron ore is reduced to spongy iron by the carbon monoxide:

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$$

Since this reaction is reversible a high CO/CO_2 pressure ratio favours the reduction to iron.

The limestone decomposes at about 800°C and the calcium oxide reacts with sandy impurities to form a slag of calcium silicate. More carbon monoxide is produced by the reduction of carbon dioxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + \underset{\text{impurity}}{SiO_2(s)} \longrightarrow \underset{\text{slag}}{CaSiO_3(l)}$$

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

The reduction of the iron oxide is completed by the coke at a temperature in the region of 1200°C and cementite, Fe_3C, and graphite enter the iron. Other reactions also occur at high temperatures, for instance silica is reduced to silicon and this enters the iron as ferrosilicon:

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

The molten metal is either run out into moulds of sand, when it is known as pig-iron, or more generally conveyed directly in the liquid form to steelmaking plants. The slag is tapped from the furnace as a liquid and can be used in concrete or blown into a ‘woolly’ material and used for insulation.

The hot gases emerging from the top of the furnace contain appreciable amounts of carbon monoxide and are burnt in Cowper stoves to preheat the air for the blast.

Cast iron

Iron castings are made by igniting a mixture of pig-iron, scrap iron and coke in cupola furnaces by a blast of hot air. The molten iron is poured into moulds to make articles such as manhole covers, guttering, machinery frames and drainpipes. Cast iron expands slightly on solidifying and therefore faithfully reproduces the shape of the mould. It is extremely hard, but unfortunately is very brittle and will fracture if struck by a sharp blow. The impurities in cast iron lower the melting point from 1535°C for pure iron to approximately 1200°C.

Wrought iron

This is made by heating impure iron with haematite so that impurities are oxidised. Carbon is converted to carbon monoxide and silicon and manganese to a slag.

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(l) + 3CO(g)$$

As the impurities are removed, the melting point of the iron rises to about 1500°C and the pasty mass is removed from the furnace as balls and worked under a hammer to squeeze out the slag. Wrought iron is tough, malleable and ductile; it can be worked by a blacksmith into chains, railway carriage couplings and ornamental gates, etc.

Copper

Although copper does not occur abundantly in nature, many copper-containing ores are known. It is principally extracted from copper pyrites, $CuFeS_2$, copper glance, Cu_2S, and cuprite, Cu_2O. The extraction of copper from copper pyrites will be considered.

The pulverized ore is concentrated by the froth flotation process and roasted in a limited supply of air to convert the iron into iron (II) oxide :

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

After the addition of silica, SiO_2, the mixture is heated in the absence of air to convert the iron (II) oxide into a slag of iron (II) silicate, $FeSiO_3$,

which is poured away. The copper (I) sulphide is now reduced to copper by heating in a controlled amount of air:

$$Cu_2S(s) + O_2(g) \longrightarrow 2Cu(s) + SO_2(g)$$

Zinc

Zinc is usually extracted from its ore zinc blende, ZnS and calamine $ZnCO_3$. The zinc ores are first concentrated and then roasted in air to convert them into the oxide:

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$$

The sulphur dioxide produced is used to manufacture sulphuric acid. The zinc oxide is mixed with powdered coke and heated to 1400°C. Zinc oxide is reduced by the coke and the mixture of zinc vapour and carbon monoxide pass through an outlet near the top of thee retort:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

Liquid zinc is run out into moulds and solidifies. The hot carbon monoxide is used to preheat the briquettes.

INTEXT QUESTIONS 16.3

1. State the nature of materials used for constructing cathodes and anodes in the electrolytic cell for refining of copper. Write chemical equations for the reactions which take place.
2. Which method is used for the refining of metals that are easily fused ?
3. Which metals are refined by poling ?
4. Name a metal which is purified by distillation.
5. Name any three elements which are refined by electrolytic refining.
6. What is role of cryolyte in the extraction of Al.
7. Which one is responsible to reduce Fe_2O_3 to Fe C or CO.

WHAT YOU HAVE LEARNT

- Metals play an extremely useful role in day-to-day life.
- Most metals are found in nature in combined form. Only a few noble metals such as gold, silver, occur in nature in free state,
- The process of extraction of metals from their ores is called *metallurgical process*.
- A naturally occurring material in which a metal or its compound occurs is called a mineral. A mineral from which a metal can be extracted economically is called an ore. Thus all minerals do not serve the purpose of ores.
- Most active metals are highly electropositive and exist as M^{n+} ions. Therefore, they are found in nature in association with some common anions, i.e., as salts like *oxides, sulphides, carbonates, halides, silicates* etc. Some sulphides slowly undergo oxidation by air to form *sulphates.*
- India possesses rich mineral wealth with abundance of iron, aluminium and some amount of copper, tin, lead, silver and gold.
- Various steps involved in the extraction of metal are :
  - (i) Crushing and pulverization
  - (ii) Concentration or dressing of the ore
  - (iii) Calcination or Raosting of the concentrated ore
  - (iv) Reduction of the oxides to free metal
- The metals thus obtained are then purified by employing some suitable method, viz. *liquation, poling, distillation or electrolytic refining.*
- Metallurgical uperations involved in the extraction of Fe, Al, Cu & Zn.

TERMINAL EXERCISE

1. Name the metal oxides that are not reduced to metallic state by heating with carbon. Which reducing agent is used for these ores ?
2. Which metal sulphide combines with its oxide to form metal ? Give reactions.
3. Name four reducing agents other than carbon, used during smelting.
4. What is the difference between calcination and roasting ?
5. Give the name and formula of at least one ore, of the following metals :

   (i) copper (ii) zinc (iii) iron (iv) tin
6. What happens when
   (i) Calamine is calcined.
   (ii) Zinc blende is roasted.
   (iii) Silica is heated with lime stone.
7. Describe the froth floatation method for the concentration of sulphide ore.
8. Give chemical equations involved in the self reduction method for the extraction of copper.
9. How will you obtain iron from its ore?
10. Explain the process involved in the extraction of al from $Al_2O_3.2H_2O$.

ANSWERS TO INTEXT QUESTIONS

16.1

1. Sodium (Na), Aluminium (Al), Silver (Ag), Iron (Fe), Zinc (Zn), Lead (Pb), Gold (Au), Mercury (Hg).

   Ores : rock salt, bauxite, argentite, haematite, zincite, galena, native gold, cinnabar, respectively.
2. *Mineral* is a naturally occurring material in which a metal or its compound occurs.

   An *ore* is that mineral in which metal is present in large quantity and from which the metal can be extracted in pure and high quality, economically.
3. Gravity separation, magnetic separation, froth floatation and chemical method.
4. (i) Magnetic separation method
   (ii) Froth floatation method
   (iii) Chemical method
5. Zinc.

16.2

1. *Calcination :* it involves heating of the ore in a limited supply of air to a temperature that the ore does not melt.

   Roasting : It involves heating of the ore in a free supply of air to a temperature that the ore does not melt.

   Smelting : The extraction of metal in the fused state is termed smelting. The ore is reduced by carbon to the free metal.

   Flux : it is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called slag.

   Slag is a fusible chemical compound formed by the reaction of flux with gangue. Slag is not soluble in the molten metal and is thus separated.

2. Carbon in the form of coke.
3. Roasting ; $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2(g)$
4. Oxide ores are reduced to metal by heating them with coke.
5. Silica, borax and other non-metallic oxides are acidic fluxes. Lime stone $(CaCO_3)$ is a basic flux.
6. (i) $Al_2O_3.\ 2H_2O \longrightarrow Al_2O_3 + 2H_2O$

   (ii) $ZnCO_3 \longrightarrow ZnO + CO_2$

16.3

1. Cathode : Pure metal   At Cathode : $Cu^{2+} + 2e \rightarrow Cu$

   Anode : Impure metal   At Anode : $Cu \rightarrow Cu^{2+} + 2e$
2. Liquation
3. Copper and tin
4. Zinc
5. Copper, Silver and Tin
6. (i) decrease the melting point of alumino

   (ii) To increase the conductance
7. CO

17

HYDROGEN AND s-BLOCK ELEMENTS

Hydrogen, alkali metals (like sodium and potassium) and alkaline earth metals (like magnesium and calcium) are the essential parts of the world we live in. For example, hydrogen is used in making vanaspati. Yellow glow of street light is due to sodium. Sodium choloride, potassium chloride and compounds of alkali metals are essential for life. Sodium hydroxide sold under the name of caustic soda is used in the manufacture of soap. Plaster of paris, a compound of calcium is used as a building material as well as by doctors in setting of fractured bone.

In this lesson we shall study occurrence, physical and chemical properties and uses of hydrogen and s-block elements (alkali metals and alkaline earth metals).

OBJECTIVES

After reading this lesson, you will be able to:

- explain the unique position of hydrogen in the periodic table;
- list the sources of hydrogen;
- compare and contrast the properties of different isotopes of hydrogen;
- recall the various physical and chemical properties and uses of hydrogen with chemical reactions;
- explain the structure of water molecule and ice;
- list the uses of heavy water;
- list the different methods of preparation of hydrogen peroxide;
- list oxidizing and reducing properties of hydrogen peroxide with at least two examples of each;
- list the uses of hydrogen peroxide;
- explain the different types of hydrides;

- describe the use of hydrogen as fuel;
- recall the names and formulae of some common ores of alkali and alkaline earth metals;
- recall the electronic configuration of alkali and alkaline earth metals;
- write reactions of alkali and alkaline earth metals with oxygen, hydrogen, halogens and water;
- explain the trend of basic nature of oxides and hydroxides;
- explain the solubility and thermal stability of their carbonates and sulphates.
- explain diagonal relationship between Li and Mg;
- describe the biological importance of sodium and potassium;
- explain anomalous nature of beryllium;
- explain the digonal relationship between Be and Al;
- describe the biological role of Mg^{2+} and Ca^{2+}; and
- describe the manufacturing processes for NaOH, Na_2CO_3 and $NaHCO_3$.

17.1 HYDROGEN

Hydrogen is the first element of the periodic table. Hydrogen has the simplest atomic structure and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$.

17.1.1 History and Occurrence of Hydrogen

Turquet de Mayerne (1655) and Boyle (1672) collected an inflammable gas by reacting iron with sulphuric acid. A century later Cavendish investigated the properties of this gas and called it 'inflammable air', but it was Lavoisier who called it by its present name, hydrogen.

Hydrogen occurs in the free state in some volcanic gases and in the outer atmosphere of the sun; other stars are composed almost entirely of hydrogen. The extremely high temperatures that are common place in stars (10^6—10^7°C) enable nuclear fusion of hydrogen atoms to occur, resulting in a colossal liberation of energy; several reaction schemes have been put forward for this process which ultimately results in the formation of helium

$$4\,{}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,\underset{\text{positive electron or positron}}{{}^{0}_{+1}e}\ \text{(energy released)}$$

The hydrogen liberated during chemical reactions is lost very readily, since the mass of the hydrogen molecule is so small and its speed so high that it can escape from the earth's gravitational field. The main sources of hydrogen are water, and petroleum and natural gas, where it occurs in combination with carbon. The element is an essential ingredient in all living matter, being found in proteins and fats.

17.1.2 Position in the Periodic Table

Where is hydrogen placed in the periodic table?

Elements are placed in the periodic table according to their outermost electronic configuration. So hydrogen ($1s^1$) may be placed with alkali metals (ns^1). But hydrogen attains noble gas configuration of helium atom ($1s^2$) by gaining one electron. It forms the hydride ion H^- ($1s^2$) like halogens (ns^2np^5) by gaining one electron. On electrolysis of used alkali hydride, hydrogen is liberated at anode just as chlorine is liberated at anode during electrolysis of sodium chloride. Thus hydrogen ought to be placed in group 17 along with halogens. Hydrogen also resembles group 14 elements, since both have a half filled shell of electrons. So where should hydrogen be placed? This problem is solved by placing hydrogen neither with alkali metals nor with halogens. It has been given a unique position in the periodic table (see Periodic Table in lesson 4).

17.1.3 Isotopes of hydrogen

If atoms of the same element have different mass numbers they are called isotopes. This difference in mass number arises because the nucleus contains a different number of neutrons.

Naturally occurring hydrogen contains three isotopes: protium ${}^1_1H$ or H, deuterium ${}^2_1H$ or D and tritium ${}^3_1H$ or T. These three isotopes contain one proton and 0, 1 and 2 neutrons, respectively in the nucleus (Fig 17.1). Protium is by far the most abundant.

Naturally occurring hydrogen contains 99.986% of the ${}^1_1H$ isotope, 0.014% of D and 7×10^{-16}% of T, therefore the properties of hydrogen are essentially those of the lightest isotope. Tritium is radioactive and emits low energy β particles ($t_{1/2}$ = 12.33yrs).

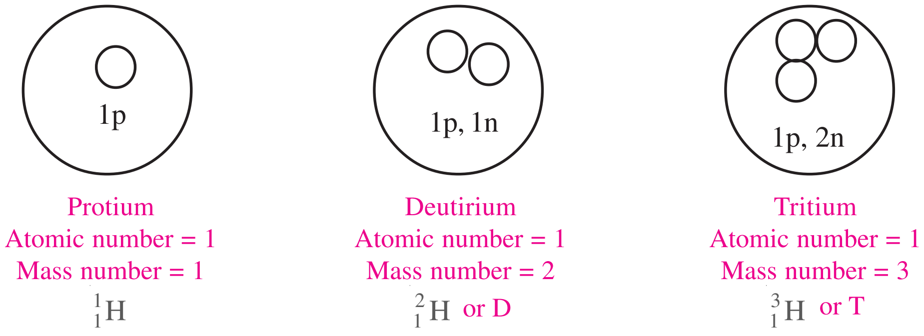


Fig 17.1: *Isotopes of hydrogen*

Due to difference in mass of different isotopes, there arise a few differences in their properties. For example:

1. H_2 is more rapidly adsorbed on the metal surface than D_2.
2. H_2 reacts over 13-times faster with Cl_2 than does D_2.

Notes

Difference in properties that arises from the difference in mass is called *isotope effect*. Since the percentage difference in the mass of isotopes of hydrogen is very large. The difference in properties of isotopes of hydrogen is very large the difference in properties of compounds containing these isotopes is also large.

17.1.4 Physical properties

Hydrogen is a diatomic gas, H_2. It is colourless and has no smell. It is lightest of all the gases known. It is insoluble in water, acids and most of the organic solvents. It is adsorbed when passed over platinum and palladium.

17.1.5 Chemical properties

1. Combustion: Hydrogen is combustible and burns in air with pale blue flame.

$$2H_2 + O_2 \rightarrow 2H_2O$$

2. Reducing property: Hydrogen reduces heated metal oxides to metals.

$$ZnO + H_2 \rightarrow Zn + H_2O$$

$$CuO + H_2 \rightarrow Cu + H_2O$$

3. Reaction with non-metals: Hydrogen combines with nitrogen, carbon, oxygen and chlorine under appropriate conditions to form ammonia, methane, water and hydrogen chloride, respectively.

$$3H_2 + N_2 \rightarrow 2NH_3$$

$$2H_2 + C \rightarrow CH_4$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

Reaction with metals: Hydrogen reacts with highly electropositive metals to from the corresponding hydrides.

$$2Na + H_2 \rightarrow 2NaH$$

$$2Li + H_2 \rightarrow 2LiH$$

17.1.6 Uses

Hydrogen is used:

1. for conversion of coal into synthetic petroleum.
2. in the manufacture of bulk organic chemicals, particularly methanol.
3. in the hydrogenation of oils. Vegetable oils change in to vegetable ghee when hydrogen is passed through the oils at 443K in presence of nickel as catalyst.
4. in the manufacture of ammonia, which is used in the production of fertilizers.
5. as primary fuel for heavy rockets.
6. for filling balloons.

INTEXT QUESTIONS 17.1

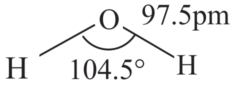
1. Name the isotopes of hydrogen.
2. Name the isotope of hydrogen which is radioactive?
3. Why is hydrogen used for filling balloons?
4. Which gas is produced, when hydrogen combines with carbon?
5. Name the gas which is used for the production of fertilizers.
6. How are vegetable oils changed into vegetable ghee?

17.2 COMPOUNDS OF HYDROGEN

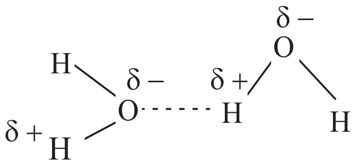
Hydrogen forms a large number of compounds: here we will consider only two of them, namely water (H_2O) and hydrogen peroxide (H_2O_2).

17.2.1 Water (H_2O)

This oxide of hydrogen is essential to all life. It occurs in the form of snow, as water in rivers, lakes, sea etc. and as vapour in the atmosphere. Water is a covalent compound made up of two hydrogen atoms linked with one oxygen atom through covalent bonds. Its Lewis structure and molecular structure are shown below.



Because of the large electronegativity of oxygen, water molecule is highly polar. It has partial negative charge (δ^-) on the oxygen atom and partial positive charge (δ^+) on the hydrogen atom. An electrostatic attraction between H of one molecule with O of other molecule results in the formation of intermolecular hydrogen bonds.



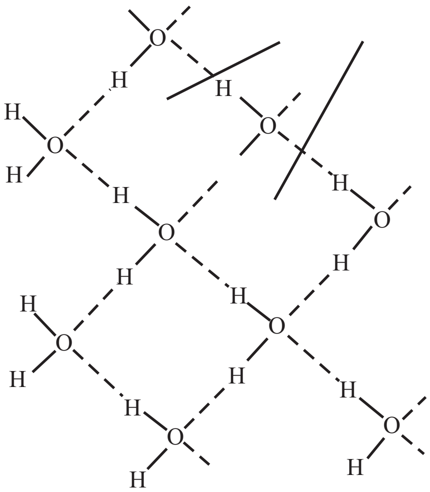
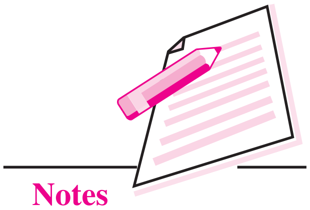


Fig. 17.2: *Tetrahedral arrangement of oxygen atoms in ice.*

Structure of ice:

The remarkable characteristic of water is that in solid form, it is less dense than liquid form. Consequently an ice cube floats on water. Water molecules are joined together in an extensive three dimensional network in which oxygen atom is bonded to four hydrogen atoms, two by hydrogen bonds and two by normal covalent bonds, in a near tetrahedral hydrogen bonded structure (Fig. 17.2), which has got open spaces. This is responsible for low density.



Notes

17.2.2 Heavy water and its applications

Water containing deuterium in place of ordinary hydrogen (protium) is termed as heavy water (D_2O). Heavy water is separated from water by electrolysis. The equilibrium constant for the dissociation of water containing protium is very high (1.0×10^{-14}) as compared to water containing deuterium (3.0×10^{-15}) e.g.

$$H_2O \rightarrow H^+ + OH^-$$

$$D_2O \rightarrow D^+ + OD^-$$

O–H bonds are broken more rapidly than O–D bonds. Thus when water is electrolyzed, H_2 is liberated much faster than D_2, and the remaining water thus becomes enriched in heavy water D_2O. In order to obtain one litre of almost pure D_2O, we have to electrolyze about 30000 litres of ordinary water.

Uses:

1. Heavy water is used as a moderator in nuclear reactors. In this process the high speed neutrons are passed through heavy water in order to slow down their speed.
2. It is used in the study of mechanism of chemical reactions involving hydrogen.
3. It is used as the starting material for the preparation of a number of deuterium compounds, for example:

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

17.2.3 Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is an important compound of hydrogen. Its chemical formula is H_2O_2.

Methods of preparation:

Two methods of preparation of hydrogen peroxide are given below:

1. By the action of dilute mineral acids (H_2SO_4) on metallic peroxides (barium peroxide, sodium peroxide)

$$BaO_2 . 8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

2. By the electrolysis of H_2SO_4 (50% W/W) followed by distillation

At cathode: $2H^+ + 2e^- \rightarrow H_2$

At anode: $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^{-1}$

The anodic solution which contains persulphate ions $(S_2O_8)^{2-}$ is distilled with sulphuric acid at reduced pressure yielding H_2O_2:

$$S_2O_8^{2-} + 2H^+ + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

Properties:

Hydrogen peroxide is a clolourless syrupy liquid and has sharp odour. It has a boiling point of 423K. It is miscible in all proportions with water, alcohol and ether. The oxidation state of oxygen in hydrogen peroxide is –1, a value, which lies between the oxidation state of oxygen in O_2 (zero) and water (–2). Therefore, hydrogen peroxide acts as an oxidizing agent as well as a reducing agent in acidic and alkaline media.

Oxiding Properties:

(a) Oxidizing action in acid solution:

(i) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(ii) $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

(b) Oxidizing action in alkaline solution:

$MnCl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + MnO_2$

(c) Reducing action in acid solution:

$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

(d) Reducing action in alkaline solution:

(i) $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2KOH$

(ii) $Cl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + O_2$

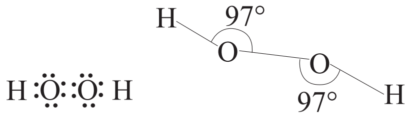
Uses:

Hydrogen peroxide is used:

1. for bleaching hair, leather and wool etc.
2. as a germicide and disinfectant.
3. as an explosive when mixed with alcohol.
4. in the preparation of foam rubber.
5. in pollution control e.g. treatment of drainage and sewage water for dechlorination.

Structure:

The Lewis structure and molecular structure of hydrogen peroxide are shown below:



17.2.4 Hydrides

Hydrogen reacts with metals and nonmetals to forms hydrides. Hydrides can be calssified as:

(1) Ionic hydrides

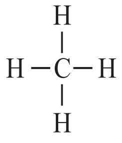
Only the Group 1 and 2 metals are sufficiently electropositive to force the hydrogen atom to accept an electron. These hydrides, which are white crystalline solids, are formed by heating the metal in hydrogen at temperatures up to 700°C. The Group 1 hydrides, e.g. Na^+H^-, have the sodium chloride structure, i.e. each cation is surrounded by six equidistant hydride ions and vice versa; the structures of the Group 2 hydrides, e.g. $Ca^{2+}(H^-)_2$, are more complex.

Except for lithium hydride they decompose before their melting points are reached, and the fact that they contain the hydride ion is proved by electrolysing them in fused alkali halides, when hydrogen is evolved at the anode. The hydride ion is a very reactive entity and all ionic hydrides are decomposed by water and air (probably initiated by traces of water vapour in the air)

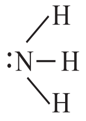
$$H^- + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$$

(2) Covalent Hydrides

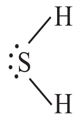
By far the greatest number of hydrides come under this classification and, except for a few, they are gaseous at ordinary temperature. They are formed by the elements from Group 13 to Group 17 in the Periodic Table.



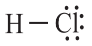
methane



ammonia



hydrogen sulphide



hydrogen chloride

The stability of the hydrides of the elements of a particular periodic group decreases with increasing atomic number (as the element becomes more 'metallic'); thus hydrogen chloride is stable to heat while hydrogen iodide is easily decomposed into its elements. Some are so unstable in the presence of small traces of air, e.g. stannane, SnH_4, that special methods are necessary for their preparation.

In the covalent hydrides, hydrogen is showing its natural tendency to acquire the stable electronic configuration of helium by electron sharing.

(3) Interstitial hydrides

These are ill-defined compounds formed by a number of transition metals in which hydrogen is accommodated in the lattice of the transition element. Some expansion of the metal lattice occurs, since the density of the hydride is less than that of the parent metal. No definite chemical formula can be allocated to these substances, i.e. they are non-stoichiometric. Although the composition can be varied by changes in temperature and pressure, formulae such as $TiH_{1.73}$ and $ZrH_{1.92}$ have been reported. The uptake of hydrogen is reversible and can in all cases be removed by pumping at a sufficiently high temperature. The use of finely divided palladium for making extremely pure hydrogen depends on this reversibility.

17.2.5 The Hydrogen Economy (Hydrogen as Fuel)

The total volume of ocean water is about 1×10^{21} L. Thus, the ocean contains an almost inexhaustible supply of hydrogen.

The world's fossil fuel reserves are being depleted at an alarmingly fast rate. Faced with this dilemma,, scientists have made intensive efforts in recent years to develop a method of obtaining hydrogen gas as an alternative energy source. Hydrogen gas could replace gasoline to power automobiles (after considerable modification of the engine, of course) or be used with oxygen gas in fuel cells to generate electricity. One major advantage of using hydrogen gas in these ways is that the reactions are essentially free of pollutants; the end product formed in a hydrogen-powered engine or in a fuel cell would be water, just as in the burning of hydrogen gas in air:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Of course, success of a hydrogen economy would depend on how cheaply we could produce hydrogen gas and how easily we could store it.

Although electrolysis of water consumes too much energy for large-scale application, if scientists can devise a more practical method of "splitting" water molecules, we could obtain vast amounts of hydrogen from seawater. One approach that is currently in the early stages of development would use solar energy. In this scheme a catalyst (a complex molecule containing one or more transition metal atoms, such as ruthenium) absorbs a photon from solar radiation and becomes energetically excited. In its excited state the catalyst is capable of reducing water to molecular hydrogen.

INTEXT QUESTIONS 17.2

1. Why does ice float on water?
2. What is heavy water? Write its important uses.
3. Give one method of preparation of hydrogen peroxide.
4. Give two uses of hydrogen peroxide.

5. How does hydrogen peroxide decolorize potassium permaganate?
6. Name the types of hydrides
7. NaH is covalent or ionic hydride?

17.3 *s*-BLOCK ELEMENTS

The *s*-block elements have an outer electronic configuration ns^1or ns^2 and are placed in the group 1 and 2 of the periodic table. Group 1 consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals after the Arabic word *al-qis* meaning plant ashes. These ashes are particularly rich in carbonates of calcium, strontium, barium and radium. The elements beryllium, magnesium, calcium, strontium, barium and radium belong to group 2 and are known as alkaline earth metals.

17.3.1 The alkali metals

In this group all the elements are electropositive metals and there exists resemblance between the elements owing to their similar outer electron configuration. The occurrence and properties of alkali metals are discussed below:

17.3.1.1 Occurrence

Sodium and potassium are abundant. Sodium is found as sodium chloride in the sea water and as sodium nitrate (Chile saltpeter) in the deserts of Chile. Potassium too, is found in sea water, and also as carnallite ($KCl.MgCl_2.6H_2O$). Lithium, rubidium and caesium occur in a few rare aluminosilicates. Francium is radioactive; its longest-lived isotope ^{223}Fr has a half life of only 21 minutes.

17.3.1.2 Electronic configuration

The alkali metals with their symbols, atomic numbers and electronic configurations are listed below in Table 17.1:

Table 17.1: Electronic configuration of alkali metals

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2p^6, 3s^2p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Caesium	Cs	55	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^1$

Notes

17.3.1.3 Physical properties of Alkali Metals

Alkali metals are placed in group 1 of periodic table. They readily form unipositive ions. As we go down the group the alkali metals show steady increase in size due to the addition of a new shell at each step. The increase in size of the atoms or ions, directly influences the physical and chemical properties of the alkali metals. Some physical properties are given in Table 17.2.

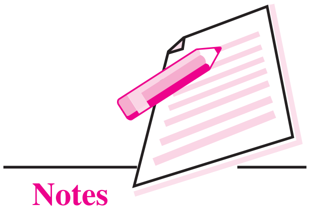
Table 17.2: Physical properties of alkali metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (g cm^{-3})	M.P. K	Electrode Potential (E° volts)
Li	76	520.1	1.0	0.54	454	–3.05
Na	102	495.7	0.9	0.97	371	–2.71
K	138	418.6	0.8	0.86	336	–2.83
Rb	152	402.9	0.8	1.53	312	–2.89
Cs	167	375.6	0.7	1.90	302	–2.93

The trends in physical properties are listed in Table 17.3.

Table 17.3: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +1 oxidation state
2.	Atomic/ionic radii	Li < Na < K < Rb < Cs Atomic and ionic radii increases since number of shells increase as we go down the group.
3.	Ionization energy	Li > Na > K > Rb > Cs As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	Li > Na > K > Rb > Cs The electropositive character increases due to decrease in ionization enthalpy therefore electronegativity decreases.
5.	Metallic character	Li < Na < K < Rb < Cs Metallic character increases as we go down the group due to increase in electropositive character.



6.	Density	Li < Na > K < Rb < Cs Generally density increases from Li to Cs as the atomic mass increases (exception K).
7.	Melting point & boiling points	Li > Na > K > Rb > Cs Decreases down the group because of increasing size and weak intermetallic bond.
8.	Flame coloration	They show characteristic colors in the flame. The outermost electron absorbs energy and is excited to a higher energy level. This absorbed energy is remitted when the electron comes back to ground state. The difference in energy falls in the visible range of radiation hence the colors are seen.
		Li — Crimson red Na — Yellow K — Pale violet Rb — Violet Cs — Violet

17.3.1.4 Chemical Properties

Alkali metals are the most reactive metals in the whole periodic table due to their ease in losing outermost electron hence getting oxidized easily. As the ease of losing electrons increases, the reactivity increases down the group.

(i) Oxides: All alkali metals form oxides, which are basic in nature. Lithium forms only one type of oxide, lithium monoxide Li_2O. Sodium peroxide Na_2O_2 is formed when sodium is heated with oxygen. Other metals of this group also form superoxides MO_2 on reaction with oxygen.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

$$K(s) + O_2(g) \rightarrow KO_2(s)$$

The formation of a particular oxide is determined by the size of the metal ion. Tiny lithium ion is not able to come in contact with sufficient number of peroxo ions. However, the ions of potassium, rubidium, caesium are large enough to come in close contact with peroxo ions and form stable structures as superoxides.

(ii) Reactivity towards water: Although lithium has the most negative E°, its reaction with water is considerably less vigorous than that of sodium which has the least negative E° among the alkali metals (Table 17.2). The low reactivity of lithium is due to small size and high ionization enthalpy. All the metals of the group react with water explosively to form hydroxide and liberate hydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

Notes

Basic character of oxides and hydroxides: The basic character of oxides and hydroxides of alkali metals increases with the increase in size of metal ion. So, lithium oxide and hydroxide are least basic whereas, caesium oxide and hydroxide are most basic in nature.

(iii) Hydrides: The alkali metals react with hydrogen at about 637K to form hydrides (MH), where M stands for alkali metals.

$$2M + H_2 \rightarrow 2MH$$

(iv) Halides: Alkali metals react with halogens to form halides:

$$2M + X_2 \rightarrow 2MX (X = F, Cl, Br, I)$$

17.3.1.5 Diagonal Reltionship between Lithium and Magesium

The similarity between first member of one group and the second member of succeeding group is called diagonal relationship. Thus lithium shows properties similar to magnesium. Likewise Beryllium and aluminium have similar characteristics.

The closeness of the diagonal elements arises due to their comparable polarizing power. Mathematically,

$$\text{Polarizing power} \propto \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

On going from lithium to sodium, the ionic charge remains the same, the ionic radius increases and, therefore, the polarizing power decreases. On going from lithium to beryllium, the ionic charge increases, the ionic radius decreases and, therefore, the polarizing power increases.

On going from beryllium to magnesium, the polarizing power decreases–and becomes comparable to that of lithium.

In other words, the ratio between ionic charge to the square of ionic radius is nearly the same for lithium and magnesium. So are their physical and chemical properties, as shown in the following examples.

1. Both elements have nearly the same values of electronegativities.
2. The melting and boiling points of the two elements are comparable.
3. Lithium and magnesium possess nearly the same degree of hardness.
4. Both the elements form nitrides when heated directly with nitrogen.
5. Both the elements form carbides when heated directly with carbon.
6. Both the elements form normal oxides when heated in air.
7. The carbonates, nitrates and hydroxides of both the elements undergo thermal decomposition to their respective oxides.

8. The halides of both the elements are appreciably soluble in organic solvents.
9. Oxyacid salts of both the elements are sparingly soluble in water.

17.3.1.6 Anamodous behaviour of Lithium

1. Lithium salts of large polarizable anions are less stable than those of other alkali metals, as expected

$Li_2CO_3 \xrightarrow{700°C} Li_2O + CO_2$	Na etc., no reaction below 800°C
$LiNO_3 \longrightarrow Li_2O + NO_2$	$NaNO_3 \longrightarrow NaNO_2 + \frac{1}{2}O_2$
$2LiOH \longrightarrow Li_2O + H_2O$	Na etc., no reaction.

   In each case, the more stable salts of the heavier alkali metals decompose at a temperature higher than that normally obtainable in the laboratory. Lithium forms no solid bicarbonate, triiodide, hydrosulphide, or superoxide. These are unstable at room temperature, whereas those of the other alkali metals require a higher temperature to effect their decomposition.

2. Solubility differences: The lithium salts of anions of high charge density are less soluble than those of the other alkali metals, for example LiOH, LiF, Li_3PO_4, Li_2CO_3. The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.
3. Complex formation: Lithium forms more stable covalent bonds than the other alkali metals and therefore forms more stable complex compounds (Section 20.4) not only with oxygen donor ligands, but also with nitrogen donors. For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of $Li(NH_3)_4$.
4. Lithium reacts only very slowly with water.
5. Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air lithium forms the normal oxide, whereas the others form higher oxides such as peroxides and superoxides. Lithium reacts with nitrogen to form the nitride, Li_3N; the others do not react. Lithium hydride is more stable than the other hydrides, and lithium carbide forms more easily (with acetylene).
6. Lithium compounds are more covalent. Thus the halides are more soluble in organic solvent and the alkyls and aryls are more stable than those of the other alkali metals.

   The so-called “anomalous” properties of lithium occur because lithium is “unexpectedly” much less electropositive than sodium.

17.3.1.7 Sodium Hydroxide

Manufacture of sodium hydroxide by the Castner-Kellner process

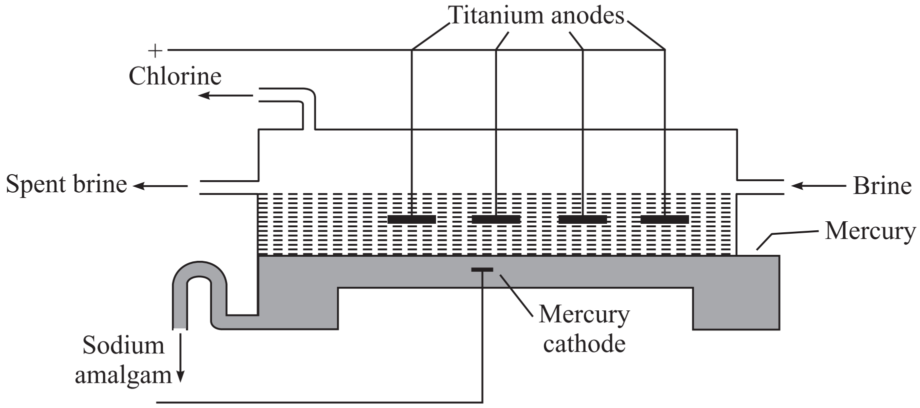


Fig. 17.3 The Castner-Kellner cell

In this process a saturated solution of sodium chloride (brine) flows through the cell (Fig. 17.3) in the same direction as a shallow stream of mercury which constitutes the cathode; the anode consists of a number of titanium blocks. On electrolysis chlorine is discharged at the anode and sodium at the cathode, where it dissolves in the mercury and is removed from the cell. The sodium amalgam is passed through water where the sodium reacts to form 50 per cent sodium hydroxide solution of high purity, the reaction being catalysed by the presence of iron grids. The mercury is then returned to the cell. The products are thus sodium hydroxide, chlorine and hydrogen.

Cathode **Anode**

Na^+ discharged $\longleftarrow$ Na^+Cl^- $\longrightarrow$ Cl^- discharged

$2Na^+ + 2e^- \rightarrow 2Na$ $\quad H_2O \rightleftharpoons H^+ + OH^-$ $\quad 2Cl^- \rightarrow 2Cl\bullet + 2e^-$

$Na + Hg \rightarrow Na/Hg$ $\quad 2Cl\bullet \rightarrow Cl_2$

$2Na/Hg + 2H_2O \longrightarrow 2Na^+OH^- + H_2 + 2Hg$

Sodium is discharged in preference to hydrogen in the cell, since hydrogen has a high overvoltage at a mercury electrode. This amounts to saying that the discharge of hydrogen ions or the combination of hydrogen atoms to give molecules is difficult to achieve at a mercury surface, i.e. mercury is a poor catalyst for either or both of these processes. Since sodium dissolves in mercury which is circulated through the cell, the formation of sodium hydroxide and hydrogen in the electrolytic cell itself is prevented.

Reactions of sodium hydroxide

Sodium hydroxide is a white deliquescent solid which is caustic and slimy to touch: it dissolves readily in water with vigorous evolution of heat. In aqueous solution this is completely dissociated and its reactions are essentially those of the hydroxide ion which is a strong base, i.e. it will neutralise acids and displace ammonia from ammonium salts when heated :

$$Na^+OH^-(aq) + H^+CI^-(aq) \longrightarrow Na^+CI^-(aq) + H_2O(1)$$

or $$OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$$

$$Na^+OH^-(aq) + NH_4{}^+CI^-(aq) \longrightarrow Na^+CI^-(aq) + H_2O(l) + NH_3(g)$$

or $$OH^-(aq) + NH_4{}^+(aq) \longrightarrow H_2O + NH_3(g)$$

In aqueous solution it reacts with many salts and precipitates the corresponding basic hydroxide, e.g.

$$Cu^{2+}SO_4{}^{2-}(aq) + 2Na^+OH^-(aq) \longrightarrow Cu(OH)_2(s) + (Na^+)_2SO_4{}^{2-}(aq)$$

or $$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$$

The hydroxides of the less electropositive metals are amphoteric and dissolve in an excess of alkali, e.g. the hydroxides of aluminium (III), lead (II), tin (11) and zinc(II):

$$A1^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)^-{}_4(aq)$$

aluminate ion

$$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$$

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow Zn(OH)_4{}^{2-}(aq)$$

zincate ion

Sodium reacts with a variety of non-metals, e.g. the halogens, silicon, sulphur, white phosphorus; sodium salts are formed in which the non-metal is incorporated into the anion.

Uses of Sodium hydroxide

Sodium hydroxide is used in the laboratory for absorbing carbon dioxide and other acidic gases, in a number of organic reactions involving hydrolysis and in volumetric analysis. Industrially it is used in the manufacture of soap (essentially sodium stearate) and sodium formate (obtained by heating sodium hydroxide with carbon monoxide under pressure).

17.3.1.8 Sodium Carbonate

The manufacture of sodium carbonate – the Solvay process

It is manufactured by the ammonia-soda or Solvay process. In theory the process involves the reaction between sodium chloride and calcium carbonate to produce sodium carbonate and calcium chloride, but in practice other chemicals are required, since the reaction as given below does not take place:

$$CaCO_3(s) + 2NaCl(s) \longrightarrow Na_2CO_3(s) + Ca(Cl)_2(s)$$

The raw materials are sodium chloride. calcium carbonate, a fuel and ammonia. The calcium carbonate is strongly heated to give quicklime and carbon dioxide:

$$Ca^{2+}CO_3^{2-}(s) \longrightarrow Ca^{2+}O^{2-}(s) + CO_2\ (g) \qquad (1)$$

The carbon dioxide is now passed up a large tower, fitted with perforated plates, down which a concentrated aqueous solution of sodium chloride saturated with ammonia trickles. The reactions taking place in the tower can be represented by the equations:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_3.H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad (2)$$

$$Na^+(aq) + Cl^-(aq) + NH_4^+(aq) + OH^-(aq) + CO_2(g) \longrightarrow$$
$$Na^+(aq) + HCO_3^-(aq) + NH_4^+(aq) + Cl^-(aq) \qquad (3)$$

$$Na^+(aq) + HCO_3^-(aq) \longrightarrow Na^+HCO_3^-(s) \qquad (4)$$

Sodium hydrogen carbonate, which is not very soluble in sodium chloride solution, due to the common ion effect is filtered and heated to produce sodium carbonate:

$$2Na^+HCO_3^-(s) \longrightarrow (Na^+)_2CO_3^{2-}(s) + H_2O(1) + CO_2(g) \qquad (5)$$

The sodium carbonate at this stage is contaminated with ammonium salts. If required pure, it is dissolved in water and carbon dioxide is blown through the solution. The precipitate of sodium hydrogen carbonate is filtered and heated to produce pure sodium carbonate; recrystallisation from water produces washing soda, $(Na^+)_2CO_3^-.10H_2O$.

$$(Na)_2CO_3^2(aq) + H_2O(1) + CO_2(g) \longrightarrow 2NaHCO_3(s) \qquad (6)$$

precipitated leaving ammonium salts in solution

The Solvay process is a very economical process since:

(a) sodium chloride and calcium carbonate are cheap;

(b) quicklime and ammonium chloride formed in reactions (1) and (3) respectively are reacted together to produce ammonia so that, apart from making up small losses, no additional ammonia is required;

(c) carbon dioxide formed in reactions (5) is reintroduced into the Solvay tower.

Properties and uses of sodium carbonate

Sodium carbonate is freely soluble in water and gives an alkaline reaction. It reacts with some salts in solution and precipitate the corresponding carbonates, e.g.

$$Ca^{2+}(Cl^-)_2(aq) + (Na^+)_2CO_3{}^{2-}(aq) \longrightarrow Ca^{2+}CO_3{}^{2-}(s) + 2Na^+Cl^-(aq)$$

Because of its alkaline reaction in solution, sodium carbonate frequently precipitate basic carbonates, e.g.

$$3Zn^{2+}(aq) + CO_3{}^{2-}(aq) + 4OH^-(aq) + 2H_2O(1) \longrightarrow ZnCO_3.2Zn(OH)_2.2H_2O(s)$$

In these instances the normal carbonate can usually be obtained by using sodium hydrogen carbonate solution.

Sodium carbonate is often used in the laboratory as a volumetric reagent. Industrially it is used in a wide variety of ways, including the manufacture of glass, in the preparation of sodium salts, in the treatment of hard water, for the manufacture of soap, and in paper making.

17.3.1.9 Sodium hydrogen carbonate

This can be obtained by passing carbon dioxide through a cold concentrated solution of the corresponding carbonate, e.g.

$$(Na^+)_2CO_3{}^{2-}(aq) + CO_2(g) + H_2O(1) \longrightarrow 2Na^+HCO_3{}^-(s)$$

Because sodium hydrogen carbonate solution is less alkaline than sodium carbonate solution, the former is often used to precipitate normal carbonates which would otherwise be formed as basic carbonates, e.g.

$$Cu^{2+}(aq) + 2HCO_3{}^-(aq) \longrightarrow CuCO_3(s) + H_2O(s) + CO_2(g)$$

17.3.1.10 Biological Importance of Sodium and Potassium

1. To keep normal osmotic pressure of body matter and to save many matter from loss
2. To increase nanomuscular
3. Sodium and potassium salt combine weak acid to give respective extracellular and intracellular matter. They form buffer.

17.3.1.11 Stability and Solubility of Carbonates and Sulphates:

The carbonates and sulphates of alkali metals are generally soluble in water and thermally stable. The carbonates are highly stable to heat and melt without decomposing. As the electropositive character increases down the group, the stability of the carbonates increases. Carbonate of lithium is not so stable to heat due to the small size of lithium.

INTEXT QUESTIONS 17.3

1. Name the important ores of sodium.
2. Arrange the alkali metals in order of increasing ionization enthalpy.
3. Which of the alkali metals forms only monoxide?
4. Write down the chemical equation for the reaction of sodium with water.
5. What type of bond exists in the hydrides of alkali metals?
6. Name the element which forms (i) peroxide, (ii) superoxide.
7. Write chemical equation when $NaHCO_3$ is heated.
8. Li^+ resembles Mg^{2+}. Why?
9. Name the common ore of Mg.
10. Arrange the alkaline earth metals in order of increasing reactivity.
11. Name an amphoteric oxide of alkaline earth metals.
12. Arrange the carbonates of alkaline earth metals in order of thermal stability.
13. What is the biological role of Ca^{2+}.

17.3.2 The Alkaline Earth Metals

You have seen a gradual increase in the size of the alkali metals as we move down the group 1 of the periodic table. Identical observations may be made in the case of alkaline earth metals placed in group 2 of the periodic table. Some physical properties of the alkaline earth metals are given in Table 17.4.

Table 17.4: Physical properties of the alkaline earth metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (g cm^{-3})	M.P. K	Electrode Potential (E°) volts
Be	89	899	1.5	1.85	1562	–1.70
Mg	136	737	1.2	1.74	924	–2.38
Ca	174	590	1.0	1.55	1124	–2.76
Sr	191	549	1.0	2.63	1062	–2.89
Ba	198	503	0.9	3.59	1002	–2.90

An alkaline earth metal atom is smaller in size compared to its adjacent alkali metal. This is due to the added proton in the nucleus, which exerts a pull on the electrons in an atom resulting in squeezing of the atom. This reduction in size shows higher control of the nucleus on the electrons in the shells.

The ease of losing electrons makes the alkaline earth metals good reducing agents. But this property is less prominent as compared to the corresponding alkali metals.

Notes

17.3.2.1 Occurrence

The alkaline earth metals are too reactive to occur native. Magnesium is the second most abundant metallic element in the sea, and it also occurs as carnallite ($KCl.MgCl_2.6H_2O$) in earth crust. Calcium occurs as calcium carbonate (marble, chalk etc) and with magnesium as dolomite ($CaCO_3.MgCO_3$). Other ores of calcium are anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$). Strontium and barium are rare and are found as carbonates and sulphates. Beryllium too is rare and is found as beryl ($Be_3Al_2(SiO_3)_6$).

17.3.2.2 Electronic Configuration

The electronic configurations of the alkaline earth metals are listed in Table 17.5.

Table 17.5: Electronic configuration

Element	Symbol	Atomic number	Electronic configuration
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^2$

17.3.2.3 Physical properties of alkaline earth metals

Alkaline earth metals are less electropositive than alkali metals. The electropositive character of alkaline earth metals increases down the group. They achieve an inert gas configuration by the loss of two electrons. Some physical properties and their trends are given in Table 17.6.

Table 17.6: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +2 oxidation state
2.	Atomic/ionic radii	$Be < Mg < Ca < Sr < Ba$ Size of alkaline earth metals increases from top to bottom due to increase in the number of shells.
3.	Ionization enthalpy	$Be > Mg > Ca > Sr > Ba$ As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	$Be > Mg > Ca > Sr > Ba$ As the electropositive character increases from top to bottom due to decrease in ionization energy, electronegativity decreases from top to bottom.

Notes

5.	Metallic character	$Be < Mg < Ca < Sr < Ba$ Metallic character increases as we go down the group due to increase in electropositive character.
6.	Density	Generally density increases from top to bottom as the atomic mass increases.
7.	Melting point & boiling point	They show higher values of melting and boiling points as compared to alkali metals because of the smaller size and stronger metallic bonds. There is no regular trend down the group. It depends upon packing.
8.	Flame coloration	Except Be and Mg (due to small size and higher ionization enthalpy) all other alkaline earth metals impart characteristic colours to the Bunsen flame. Ca: Brick red Sr: Crimson red Ba: Sea green

17.3.2.4 Chemical Properties of Alkaline Earth Metals

The alkaline earth metals are reactive metals, though less reactive than alkali metals. The reactivity increases from top to bottom in a group due to increase in electropositive character.

(i) **Reactivity and E° values:** The near constancy of the E° (M^{2+}/M) values for group 2 metals (Table 17.4) is somewhat similar to that for group 1 metals. Therefore, these metals are electropositive and are strong reducing agents. The less negative value for Be arises from, the large hydration energy associated with the small size of Be^{2+} being countered by relatively large value of the enthalpy of atomization of beryllium

(ii) **Oxides:** The alkaline earth metals burn in oxygen forming the ionic oxides of the type MO where M stands for alkaline earth metals except Sr, Ba, and Ra which form peroxides. Peroxides are formed with increasing ease and increasing stability as the metal ions become larger.

$$2Mg + O_2 \rightarrow 2MgO$$

$$2Be + O_2 \rightarrow 2BeO$$

$$2Ca + O_2 \rightarrow 2CaO$$

$$Ba + O_2 \rightarrow 2BaO$$

Basic character of the oxides increases gradually from BeO to BaO. Beryllium oxide is amphoteric, MgO is weakly basic while CaO is more basic.

Notes

(iii) Hydrides: The alkaline earth metals combine with hydrogen to form hydrides of general formula MH_2

$M + H_2 \rightarrow MH_2 (M = Mg, Ca, Sr, Ba)$

(iv) Reaction with water: Usually the alkaline earth metals react with water to liberate hydrogen. Be does not react with water or steam even at red heat and does not get oxidized in air below 837K.

$Mg + H_2O \rightarrow MgO + H_2$

Ca, Sr, and Ba react with cold water with increasing vigour.

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

(v) Halides: All the alkaline earth metals combine directly with the halogens at appropriate temperature forming halides, MX_2 where M stands for alkaline earth metals.

$M + X_2 \rightarrow MX_2$

(vi) Solubility and stability of carbonates and sulphates:

Carbonates: The carbonates of alkaline earth metals are sparingly soluble in water. They decompose if heated strongly. Their thermal stability increases with increase in the size of the cation. Decomposition temperatures of carbonates are given below:

$BeCO_3$	**$MgCO_3$**	**$CaCO_3$**	**$SrCO_3$**	**$BaCO_3$**
<373K	813K	1173K	1563K	1633K

Sulphates: The sulphates of alkaline earth metals are white solids, stable to heat. The sulphates, $BeSO_4$ and $MgSO_4$ are readily soluble and the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration energies of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore, their sulphates are soluble.

The sulphates decompose on heating, giving the oxides.

$MSO_4 \rightarrow MO + SO_3$

The thermal stability of sulphates increases with the increase in the size of cation.

This is shown by the temperature at which decomposition occurs:

$BeSO_4$	**$MgSO_4$**	**$CaSO_4$**	**$SrSO_4$**
773K	1168K	1422K	1647K

(vii) Complex compounds: Smaller ions of the group 2 elements form complexes. For example chlorophyll is a complex compound of magnesium. Beryllium forms complexes like $[BeF_4]^{2-}$.

17.3.2.5 Anomalous Nature of Beryllium: Diagonal Relationship to Aluminium

Beryllium, the first member of the group, appears to be very different from the other members, in the same way as lithium differs from the other alkali metals, and for the same reasons. In fact, the anomalous nature of the first member of the s- and p-block groups becomes more pronounced towards the middle of the table: beryllium differs more from magnesium than lithium does from sodium. Also, beryllium shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium; and the properties in which beryllium differs from magnesium, it shares with aluminium (in general). The cohesive properties of beryllium are much greater than those of magnesium: beryllium has higher melting and boiling points, enthalpy of fusion, etc., and density, and it is much harder. Similarly its attraction for outer electrons is greater than that of magnesium, leading to much lower atomic radii, higher electron affinity and ionization energy, etc. Its higher polarizing power leads to all its compounds being largely covalent, with lower melting and boiling points, enthalpies of formation etc., and with greater solubility in organic solvents than the corresponding magnesium compounds. The hydration enthalpy of the small Be^{2+} ion is very high and its salts are among the most soluble known. Despite this, its electrode potential is not high, because of its very high second ionization enthalpy. Nevertheless, it would be expected to react with water, and react vigorously with acids ($E^{\phi} = -1.70$). In fact, it does not react with water, and is resistant to acid. This must be a kinetic effect: perhaps an oxide film protects the metal. Certainly this is one of the metals rendered passive by concentrated nitric acid. The halides are hygroscopic and fume in air, and alll soluble salts are largely hydrolysed and polymerized in water except in strong acid or strong alkali solutions (beryllium is amphoteric, unlike magnesium, etc.):

$$2[Be(H_2O)_4]^{2+} \underset{H_3O^+}{\overset{H_2O}{\rightleftharpoons}} 2H_3O^+ + [(H_2O)_3BeOBe(H_2O)_3]^{2+} \xrightarrow{OH^-}$$

$$Be(OH)_2(s) \xrightarrow{OH^-} [Be(OH)_4]^{2-}\,(aq).$$

Beryllium is a poor reducing agent, and does not dissolve in ammonia to give blue reducing solutions.

17.3.2.6 Calcium oxide (CaO)

Manufacture of CaO

CaO (quick lime) is manufactured in enormous quantities (126 million tonnes in 1988) by roasting $CaCO_3$ in lime Kiln.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

CaO reacts exothermally with water, forming hydroxide

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$Ca(OH)_2$ is called slaked lime

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3$$

17.3.2.7 $CaCO_3$ Calcium Carbonate

$CaCO_3$ occurs in two different crystalline forms, calcite and aragonite. Both forms occur naturally as minerals. Calcite is the more stable: each Ca^{2+} is surrounded by six oxygen atoms from $CO_3{}^{2-}$ ions. Aragonite is a metastable form, and its standard enthalpy of formation is about 5 kJ mol^{-r} higher than that of calcite. In principle aragonite should decompose to calcite, but a high energy of activation prevents this happening. Aragonite can be made in the laboratory by precipitating from a hot solution. Its crystal structure has Ca^{2+} surrounded by nine oxygen atoms. This is a rather unusual coordination number.

Uses of Lime:

1. In steel making to remove phosphates and silicates as slag.
2. By mixing with SiO_2 and alumina or clay to make cement.
3. For making glass.
4. In the lime-soda process, which is part of the chlor-alkali industry, converting Na_2CO_3 to NaOH or vice versa.
5. For 'softening' water.
6. To make CaC_2.
7. To make slaked lime $Ca(OH)_2$ by treatment with water.

17.3.2.8 Biological Role of Mg^{2+} and Ca^{2+}

Mg^{2+} ions are concentrated in animal cells, and Ca^{2+} are concentrated in the body fluids outside the cell. They are also essential for the transmission of impulses along nerve fibres. Mg^{2+} is important in chlorophyll, in the green parts of plants. Ca^{2+} is important in bones and teeth as apatite $Ca_3(PO_4)_2$, and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2) \bullet CaF_2]$. Ca^{2+} ions are important in blood clotting, and to maintain the regular beating of the heart.

WHAT YOU HAVE LEARNT

- Hydrogen can either be placed with alkali metals or with halogens.
- Hydrogen exists in three isotopic forms namely hydrogen, deuterium and tritium.

- Hydrogen is a combustible gas and has reducing property.
- There are two important oxides of hydrogen: water and hydrogen peroxide.
- Cage-like structure of ice makes it float on water.
- Water containing deuterium in place of ordinary hydrogen is known as heavy water.
- Heavy water can be separated from ordinary water by electrolysis or distillation.
- Heavy water is used as moderator in nuclear reactors.
- Hydrogen peroxide acts both as oxidizing and reducing agent.
- Different types of hydrides i.e. ionic, covalent etc.
- Hydrogen as fuel.
- The alkali and alkaline earth metals show regular variation in various properties along a group and period.
- Alkali metals react with hydrogen, water and halogens to form hydrides, hydroxides and halides respectively.
- Diagonal relationship betrween Li^+ Mg^{2+}
- Manufacture of NaOH, Na_2 CO_3, $NaHCO_3$
- Biological role of alkali metals.
- Basic nature of oxides and hydroxides of group 1 and group 2 elements.
- Thermal stability and solubility of carbonates and sulphates.
- Manufacture of CaO and $CaCO_3$
- Biological role o alkaline earth metals.

TERMINAL EXERCISE

1. Write three general characteristics of the s-block elements which distinguish them from the elements of other blocks.
2. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
3. What happens when?

   (a) sodium metal is dropped in water.

   (b) sodium metal is heated in free supply of air.

   (c) sodium peroxide dissolves in water.

4. Explain why hydrogen is best placed separately in the periodic table of elements.
5. Describe the industrial applications of hydrogen.
6. Discuss the importance of heavy water in nuclear reactor and how is it prepared from normal water?
7. Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen?
8. Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice?
9. Show by proper chemical reactions how hydrogen peroxide can function both as an oxidizing and a reducing agent?
10. Compare the properties of alkali metals and alkaline earth metals with respect to:
    (a) atomic radii
    (b) ionization energy
    (c) melting points
    (d) reducing behavior
11. Explain the trends of solubility and stability of the carbonates and sulphates of alkaline earth metals.
12. Explain the process involved in the manufacture of NaOH, Na_2CO_3 and $NaHCO_3$ (Give Chemical equations only)
13. Explain the biological role of Ca^{2+} and Mg^{2+}.

ANSWERS TO INTEXT QUESTIONS

17.1

1. Three isotopes of hydrogen are (a) protium $^{1}_{1}H$, deuterium D or $^{2}_{1}H$ and (c) tritium T or $^{3}_{1}H$.
2. Tritium.
3. It is lightest of all the gases known.
4. Methane (CH_4).
5. Ammonia (NH_3).
6. Vegetable oils $+H_2 \xrightarrow[Ni]{443K}$ Vegetable ghee.

17.2

1. Ice is less dense as compared to water. It has open spaces in the hydrogen bonded structure.
2. D_2O; Moderator is nuclear reactors.
3. $BaO_2.8H_2O + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 + 8H_2O$
4. (a) as a bleaching agent.

   (b) germicide and disinfectant.
5. H_2O_2 reduces $KMnO_4$

   $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

   Mn(+7) is reduced to Mn(+2)
6. Three types of hydrides : ionic, covalent and interstitial
7. Ionic hydride

17.3

1. NaCl and $NaNO_3$.
2. $Cs < Rb < K < Na < Li$
3. Lithium
4. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
5. Ionic.
6. (i) Sodium (ii) potassium
7. $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
8. Same polarising power.
9. Carnallite ($KCl.MgCl_2.6H_2O$).
10. $Be < Mg < Ca < Sr < Ba$
11. BeO
12. $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
13. Teeth enamal

18

GENERAL CHARACTERISTICS OF THE P-BLOCK ELEMENTS

The *p*-block of the periodic table consists of the elements of groups 13,14, 15, 16, 17 and 18. These elements are characterised by the filling up of electrons in the outermost *p*-orbitals of their atoms. Some of these elements and their compounds play an important role in our daily life. For example:

- Nitrogen is used in the manufacture of ammonia, nitric acid and fertilizers. Trinitrotoluene (TNT), nitroglycrine, etc., are compounds of nitrogen, which are used as explosives.
- Oxygen present in air is essential for life and combustion processes.
- Carbohydrates, proteins, vitamins, enzymes, etc., which contain chain of carbon atoms, are responsible for the growth and development of living organism.

The usual trends (vertical as well as horizontal) in various properties observed in the *s*-block are observed in this block, too. As we move from top to bottom through a vertical column (group) some similarities are observed in the properties. However, this vertical similarity is less marked in the *p*-block than that observed in the *s*-block, especially in groups 13 and 15; vertical similarity is increasingly shown by the later groups. As far as the horizontal trend is concerned, the properties vary in a regular fashion as we move from left to right across a row (period).

In this lesson we shall study some important physical properties w.r.t. the of electronic configuration of the atom. Finally, we shall relate the periodicity in atomic properties to the observed chemical behaviour of their compounds, with special reference to their oxides, hydrides and halides.

OBJECTIVES

After reading this lesson you will be able to:

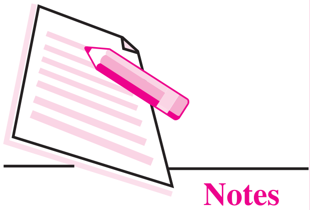
- describe the general mode of occurrence of these elements in nature;
- recall the electronic configurations of the p-block elements;
- explain the variations in atomic and physical properties such as
  - (i) atomic and ionic sizes;
  - (ii) ionization enhalpy;
  - (iii) electronegativity;
  - (iv) electron-gain enthalpy;
  - (v) metallic and non-metallic behaviours along the period and in a group of the periodic table;
- correlate the properties of the elements and their compounds with their positions in the periodic table;
- explain the anomalous properties of the first element in each group of this block and
- explain inert pair effect.

18.1 OCCURRENCE OF THE *P*-BLOCK ELEMENTS IN NATURE

The *p*-block elements do not follow any set pattern of mode of occurrence in nature. Some of them occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the forms. Noble gases occur in free state only. All other elements usually occur in the combined state. The distribution of these elements in nature is also far from any uniform pattern. Some of them are quite abundant, *e.g.*, oxygen, silicon, aluminium, nitrogen etc. On the other hand the heavier members in each group of the block are generally much less abundant. The important minerals associated with elements will be considered whenever it is necessary at the appropriate places in the text.

18.2 ELECTRONIC CONFIGURATION

Among the elements of *p*-block, the *p*-orbitals are successively filled in a systematic manner in each row. Corresponding to the filling up of 2*p*, 3*p*, 4*p*, 5*p* and 6*p* orbitals five rows of *p*-block elements are there. The outer electronic configuration of the atoms of these elements is ns^2np^{1-6}.



Notes

18.3 ATOMIC SIZE

The atomic radius of the of *p*-block elements generally decreases on moving across a period from left to right in the periodic table. It is because the addition of electrons takes place in the same valence shell and are subjected to an increased pull of the nuclear charge at each step. The variation in atomic size along a period is shown in Table 18.1.

Table 18.1 : Variation in Atomic Size in a row from boron to fluorine

Element	**Boron**	**Carbon**	**Nitrogen**	**Oxygen**	**Fluorine**
Outer electronic configuration	$2s^2\ 2p^1$	$2s^2\ 2p^2$	$2s^2\ 2p^3$	$2s^2\ 2p^4$	$2s^2\ 2p^5$
Nuclear charge	+5	+6	+7	+8	+9
Effective nuclear charge	+ 2.60	+ 3.25	+ 3.90	+ 4.55	+ 5.20
Atomic size (pm)	88	77	70	66	64

On moving down a group, the atomic radius of the elements increases as the atomic number increases. This is due to the increase in the number of shells as we move from one element to the next down the group. The increase in nuclear charge is more than compensated by the additional shell. The variation in atomic size on moving down a group is shown in Table 18.2.

Table 18.2 : Variation in atomic size down a group

Elements of Group 13	**Outer electron configuration**	**Nuclear charge**	**Effective nuclear charge**	**Atomic size (pm)**
Boron	$2s^2\ 2p^1$	+ 5	+ 2.60	88
Aluminium	$3s^2\ 3p^1$	+ 13	+ 11.60	118
Gallium	$4s^2\ 4p^1$	+ 31	+ 29.60	124
Indium	$5s^2\ 5p^1$	+ 49	+ 47.60	152
Thallium	$6s^2\ 6p^1$	+ 81	+ 79.60	178

18.4 IONIZATION ENTHALPY

It is the amount of energy required to remove the most loosely bound electron from the outermost shell of a neutral gaseous atom. It is measured in kJ mol^{-1} and is known as first ionization enthalpy.

The first ionization enthalpy of the *p*-block elements generally increases on moving from left to right along a period. It is because as we move from left to right along a period, the atomic size decreases. In a small atom, the electrons are held tightly. The larger the atom, the less strongly the electrons are held by the nucleus. The ionization enthalpy, therefore, increases with decrease in atomic size. However, there are certain exceptions, e.g., the first ionization enthalpy of a group 16 element is lower than that of a group 15 element. It is because in case of a group 15 element, the electron is to be removed from the half-filled *p*-orbitals. A comparison of first ionization energies of some elements is given in Table 18.3.

Table 18.3 : Comparison of first ionization enthalpies (kJ mol^{-1})

B	C	N	O	F	Ne
801	1086	1403	1310	1681	2080
AI	Si	P	S	CI	Ar
577	796	1062	999	1255	1521

In general the first ionization enthalpy decreases in a regular way on descending a group. It is because on descending a group, the atomic size increases. As a result the electrons are less tightly held by the nucleus and therefore, first ionization enthalpy decreases.

INTEXT QUESTIONS 18.1

1. Which of the following atoms is expected to have smaller size?
   (i) $_9$F and $_{17}$CI (ii) $_6$C and $_{14}$Si (iii) $_5$B and $_6$C (iv) $_6$C and $_7$N
2. Which atom in the following pairs of atoms is expected to have higher ionization enthalpy?
   (i) $_4$Be and $_5$B (ii) $_{16}$S and $_{17}$CI (iii) $_2$He and $_{10}$Ne (iv) $_8$O and $_{16}$S
3. Arrange the following atoms in order of increasing ionization enthalpy: $_2$He, $_4$Be, $_7$N, $_{11}$Na.
4. How does the ionization enthalpy vary in general in a group and in a period of the *p*-block elemetns?

18.5 ELECTRON GAIN ENTHALPY

When an electron is added to a neutral gaseous atom, heat enegy is either released or absorbed. The amount of heat energy released or absorbed when an extra electron is added to a neutral gaseous atom is termed as electron gain enthalpy, i.e., energy change for the process :

$$X(g) + e^- \longrightarrow X^-(g)$$

Generally for most of the atoms, the electron gain enthalpy is negative, *i.e.*, energy is released when an electron is added to a neutral gaseous atom. But for some atoms, the electron gain enthalpy is a positive quantity, *i.e.*, energy is absorbed during the addition of an electron.

Electron affinity generally becomes more negative on moving from left to right along a period. It is because on moving across a period, the atomic size decreases. As a result the force of attraction exerted by the nucleus on the electron increases.

Consequently the atom has a greater tendency to gain an electron. Hence, electron gain enthalpy becomes more negative.

On moving down a group, the electron gain enthalpy becomes less negative. This is due to the increase in atomic size and thus, less attraction for the electrons; the atom will have less tendency to gain an electron. Hence, electron gain enthalpy becomes less negative. But in the halogen group, the electron gain enthalpy of chlorine is more negative than that of fluorine. It is because the size of the F atom is very small which makes the addition of electron less favourable due to inter electronic repulsion. Similar situation exists for the first element of each group.

Table 18.4 : Electron gain enthalpies of some p-block elements in kJ mol^{-1}

B	**C**	**N**	**O**	**F**
– 0.30	– 1.25	+ 0.20	– 1.48	– 3.6
AI	Si	P	S	CI
– 0.52	– 1.90	– 0.80	– 2.0	– 3.8

18.6 ELECTRONEGATIVITY

Electronegativity is defined as a measure of the ability of an atom to attract the shared electron pair in a covalent bond to itself.

Electronegativity increases along the period and decreases down the group.

Fluorine is the most electronegative of all the elements. The second most electronegative element is *oxygen* followed by *nitrogen* in the third position.

18.7 METALLIC AND NON-METALLIC BEHAVIOUR

The elements can be broadly classified into metals and non-metals. Metals are electropositive in character i.e., they readily form positive ions by the loss of electrons, whereas non-metals are electronegative in character i.e., they readily form negative ions by the gain of electrons. The metallic and non-metallic character of *p*-block elements varies as follows:

Along the period the metallic character decreases, whereas non-metallic character increases. It is because on moving across the period, the atomic size decreases due to the increased nuclear charge and hence, ionization energy increases.

On moving down the group the metallic character increases, whereas non-metallic character, decreases. It is because on moving down a group, the atomic size increases. As a result the ionization energy decreases and tendency to lose electrons increases. Therefore, metallic character increases and non-metallic character decreases.

18.8 ANOMALOUS BEHAVIOUR OF THE FIRST ELEMENT IN EACH GROUP OF THE *p*-BLOCK

The elements comprising *s*-block and *p*-block are called main groups or representative elements.

Since the atomic radii decrease across a period, the *p*-block atoms are smaller than their nearest *s* or *d* block atoms; thus F atom has the smallest radius. Associated with small atom the 2*p* orbitals are very compact and influence the bonds formed. Interelectronic repulsions are thus more significant in 2*p* than in *np* orbitals (where $n > 2$). This results in the N–N, O–O and F–F bonds being comparatively weaker than the P–P, S–S and CI–CI bonds, respectively.

The small size of the atoms of N, O and F results in their high electonegativity values. This is reflected in the formation of relatively strong hydrogen bonds in X – H....Y, where X and Y may be N, O or F.

Carbon, nitrogen and oxygen differ from other elements of their respective groups due to their unique ability to form $p\pi$–$p\pi$ multiple bonds. For example C=C, C≡C, N=N, O=O, etc. The later members such as Si, P, S, etc., do not form $p\pi$–$p\pi$ bonds because the atomic orbitals (3p) are too large to achieve effective overlapping.

The valence shell capacity of the *p*-block elements in the second period limits the coordination number to a maximum of 4. However, in compounds of the heavier members the higher coordination numbers are attainable. Thus BH_4^- and BF_4^- contrast with $[AlF_6]^{3-}$; CF_4 contrasts with $[Si\,F_6]^{2-}$ and NH_4^+ contrasts with $[PCl_6]^-$. In the heavier members of each group *d*-orbitals are available for bonding and their participation may be envisaged in the attainment of the higher coordination number.

18.9 INERT PAIR EFFECT

Among the elements of *p*-block, in groups 13,14 and 15, there is a general trend that the higher oxidation states become less stable in going down the group. Thus although boron and aluminium are universally trivalent, gallium, indium and thallium exhibit +1 state as well. In fact +1 state of thallium is very stable. Similar situations are noticed in groups 14 and 15. Though carbon is universally tetravalent, it is possible to prepare divalent germanium, tin and lead compounds. The stable state of +3 in antimony and bismuth in group 15 is another example.

Outer electron configurations of group 13, 14 and 15 elements are ns^2np^1, ns^2np^2 and ns^2np^3, respectively. They are thus expected to show the higher oxidation state of +3, +4 and +5 respectively. But the preference of heavier elements of these groups to show +1, +2 and +3 states, respectively indicate that two electrons do not participate in bonding. The reluctance of *s*-electrons to take part in chemical bonding is known as *inert pair effect*.

The so called "inert pair effect" is therefore, ascribed to two factors.

1. The increase in the promotion energy from the ground state ($ns^2 np^1$) to the valence state ($ns^1 np^2$)
2. Poorer overlap of the orbitals of the large atoms and hence poorer bond energy.

The net result is the lesser stability of higher oxidation state with the increasing atomic number in these groups. Once the involved energies are taken into consideration, the so called "inert pair effect" term loses its significance.

INTEXT QUESTIONS 18.2

1. Why does fluorine have electron gain enthalpy lower than chlorine?
2. Which atom in the following pair of atoms has greater electron gain enthalpy?

   (i) F, Cl (ii) Br, I (iii)I, Xe (iv) O, F (v) O,S
3. Give two reasons for the fact that the first element in each group of *p*-block exhibits unique behaviour.
4. Explain why oxygen exists as a gas whereas sulphur exists as a solid.
5. Mention two reasons which are responsible for the so called "inert pair effect".
6. What is the consequence of "inert pair effect" on the oxidation states of Tl and Pb?

18.10 GENERAL TRENDS IN THE CHEMISTRY OF THE P-BLOCK ELEMENTS

The *p*-block elements except noble gases react with hydrogen, oxygen and halogens to form various hydrides, oxides and halides respectively. A more or less regular trend is observed in the properties of these compounds on moving down any particular group. The noble gases have almost zero electron afinity and have very high ionization enthalpies. Therefore, under normal conditions, the atoms of noble gases have little tendency to gain or lose electrons.

18.10.1 Hydrides

The hydrides of the *p*-block elements are listed in table 18.5. They are covalent molecules and their bond angles are consistent with VSEPR theory. The angles decrease from 109.5^0 in CH_4 to 107^0 in NH_3 and 104^0 in H_2O.

These hydrides are volatile in nature. Generally their acid strength increases from left to right and from top to bottom.

Table 18.5 : Hydrides of p-block elements

		Group		
13	14	15	16	17
B_2H_6	CH_4	NH_3	H_2O	HF
$(AIH_3)x$	SiH_4	PH_3	H_2S	HCI
Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr
InH_3	SnH_4	SbH_3	H_2Te	HI
TIH_3	PbH_4	BiH_3	H_2Po	–

18.10.2 Oxides

p-Block elements form a number of oxides on reacting with oxygen. The oxides E_2O_n ($n = 3$, 5 or 7) are the highest oxides formed by the elements in the groups 13, 15 or 17 respectively. The oxides EO_n ($n = 2$, 3 or 4) are formed by the elements in groups 14, 16 or 18 respectively. Thus, nitrogen forms NO, NO_2, N_2O_3, and N_2O_5; phosphorus forms P_4O_6 and P_4O_{10}, xenon forms XeO_3 and XeO_4.

- In any particular group, the basic nature of the oxides (oxidation state of the element remaining same) increases with increase in atomic number.
- In a particular period the acidity increases with increase in the oxidation state of the element.

18.10.3 Halides

A review of the properties of halides of *p*-block elements reveals that most of them are covalent halides. In a group the covalent character of halides decreases down the group. Where an element exhibits more than one oxidation state, the covalent character of a halide increases with the increase in the oxidation state of the element forming halides. For example, whereas $PbCl_2$ is an ionic halide, $PbCl_4$ is covalent. Similarly the covalent character of halides of a particular element increases from fluoride to chloride to bromide.

Covalent halides are generally gases, liquids or solids with low melting points. These halides usually hydrolyse to give the oxoacid of the element. For example $SiCl_4$ reacts vigorously with water

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

In general the chlorides, bromides and iodides are found to be more stable with lower oxidation state of the element, whereas fluorides are formed in the higher oxidation states. The halides are usually formed by the direct union of the element with the halogen. For example

$$C_{(s)} + Cl_2(g) \longrightarrow CCl_4(l)$$

$$2As_{(s)} + Cl_2(g) \longrightarrow AsCl_3(s)$$

INTEXT QUESTION 18.3

1. Which of the following oxides is the most acidic?

   (i) Al_2O_3 (ii) CO_2 (iii) SO_2

2. Which of the following hydrides of main group elements is the most acidic?

   (i) H_2Se (ii) H_2O (iii) HCI (iv) HI

3. Arrange the following in the increasing order of covalent character.

   $SiCl_4$, CCl_4, $SnCl_4$, $GeCl_4$

4. What happens when $SiCl_4$ reacts with water. Write complete chemical equation for the reaction.

5. How do the bond angles vary among the following hydrides NH_3, PH_3, AsH_3, SbH_3

6. Give equations for the formation of the following from the elements:

   (i) Al_2O_3 (ii) $SiCl_4$ (iii) CCl_4

7. Which is more covalent in each of the following pairs?

   (i) $AlCl_3$ and BCl_3 (ii) $PbCl_2$ and $PbCl_4$

WHAT YOU HAVE LEARNT

- The elements of groups 13, 14, 15, 16, 17 and 18 constitute the *p*-block of the periodic table.
- Some of the elements of the *p*-block are widely and abundantly found in nature, viz., oxygen, silicon, aluminium, etc.
- Many physical and chemical properties of the *p*-block main group elements show periodic variation with atomic number.

- The *ionization enthalpy* is the energy required to remove the outermost electron from a neutral gaseous atom.
- The electron *gain enthalpy* is the energy change when a neutral atom in a gaseous state accepts an electron.
- *Electronegativity* is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself.
- The top element in each group shows a unique behaviour.
- The reluctance of *s*-electrons to take part in bond formation is known as “inert pair effect”.
- *p*-Block elements form a number of oxides on reacting with oxygen.
- Most of the elements of the *p*-block form covalent halides.
- General characteristies of the *p*-block hydrides, halides and oxides.

TERMINAL EXERCISE

1. Which groups of the ‘periodic table’ constitute *p*-block?
2. How does the magnitude of ionization energy of an atom vary along the group in the periodic table?
3. How does electronegativity change along a row of elements in the periodic table?
4. Explain ‘Metallic character decreases along a period but increases on moving down a group’.
5. Discuss the trends in the chemistry of *p*-block elements with respect to:

   (i) acidic and basic nature of the oxides;

   (ii) ionic and covalent nature of the hydrides.
6. What is the cause of anomalous behaviour of the top element in each group of the *p*-block elements.
7. What is ‘inert pair effect’? Is there any inert pair present or is it a misnomer?
8. Comment on the nature (ionic/covalent) of the hydrides of the *p*-block elements
9. How does the covalent character of halides of an element change with oxidation state of the element?
10. Which is likely to form higher halides with an element exhibiting variable oxidation state, F_2 or Cl_2?

ANSWERS TO INTEXT QUESTIONS

18.1

1. (i) $_{9}F$ (ii) $_{6}C$ (iii) $_{6}C$ (iv) $_{7}N$
2. $_{4}Be$ (ii) $_{17}Cl$ (iii) $_{2}He$ (iv) $_{8}O$
3. Na < Be < N < He
4. In a group, it decreases down the group and it usually increases along a period.

18.2

1. The unexpectedly low value of electron gain enthalpy for F as compared to that of Cl atom may be attributed to the extremely small size of F atom vis-a-vis Cl atom. The addition of an electron produces a negative ion which has a high electron density and leads to increased interelectronic repulsions.
2. (i) Cl (ii) Br (iii) I (iv) F (v) S
3. (i) Small size (ii) absence of *d*-orbitals
4. Because oxygen can form multiple bonds (O = O).
5. (i) Lower bond energy in the compounds of heavier atoms and (ii) the higher energy involved in promotion from the ground state (s^2p^1) to the valence state (s^1p^2).
6. Lower oxidation states become more stable.

   For Tl, +1 and for Pb, +2.

18.3

1. SO_2
2. HI
3. $SnCl_4 < Ge\,Cl_4 < SiCl_4 < CCl_4$
4. $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$
5. The bond angle decreases from 107° to almost 90°.
6. (i) $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3\,(s)$

   (ii) $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$

   (iii) $C(s) + 2Cl_2(g) \rightarrow CCl_4(l)$
7. (i) BCl_3 (ii) $PbCl_4$

19

p-BLOCK ELEMENTS AND THEIR COMPOUNDS – I

You have already studied the general characteristics of the p-block elements in the previous lesson. Now, we shall discuss some of the important elements and their compounds. Groups 13, 14 and 15 of the periodic table will be considered in this lesson and groups 16, 17 and 18 in the next lesson.

OBJECTIVES

After reading this lesson, you will be able to

- describe some general characteristics of Group 13, 14 and 15;
- describe the methods of preparation of boric acid, borax, diborane and boron trifluoride;
- explain the structure of diborane,boric acid and boron trifluoride;
- list the uses of borax, boric acid and boron trifluoride;
- list examples of double salts;
- describe the preparation and uses of aluminium trichloride and potash alum;
- explain the structure of aluminium trichloride;
- list the allotropes of crystalline carbon;
- compare the structures of diamond and graphite;
- explain the structure and properties uses of carbon monoxide, carbon dioxide and silicon dioxide;
- compare hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride;
- describe preparation and uses of silicon carbide;

- describe silicones, silicates and zeolite;
- explain the preparation properties and uses of nitrogen;
- explain the processes for manufacture of ammonia and nitric acid;
- explain allotropic forms of phosphorons;
- list the properties and uses of ammonia and nitric acid;
- explain nitrogen fixation: natural and industrial and
- list a few nitrogenous, phosphatic and mixed fertilizers with their importance.

19.1 SOME GENERAL CHARACTERISATICS OF ELEMENTS OF GROUP 13

This group consists of B, Al, Ga, In and Tl.

All these elements exhibit a group valency of three, but because of the very large input of energy that is necessary to form the 3-valent ions–the sum of the first three ionisation energies–their compounds when anhydrous are either essentially covalent or contain an appreciable amount of covalent character. Boron never forms a B^{3+} ion since the enormous amount of energy required to remove three electrons from a small atom.

The electronic configurations of the boron and aluminium atoms are similar in as much as the penultimate shell has a noble gas configuration. whereas the penultimate shell of the gallium, indium and thallium atoms contains eighteen electrons. (Table 19.1)

Boron, which is non-metallic, and aluminium, which is clearly metallic, are best considered separately. Gallium, indium and thallium are weakly metallic.

Table 19.1: Physical properties of Group 13 elements

	Atomic Number	Electronic Configuration	Ionisation Energy/ kJmol^{-1}			Standard Electrode Potential/V	Atomic Radius/nm	Ionic Radius/nm	M.P. /°C	B.P. /°C
			First	Second	Third					
B	5	2.3 $1s^2 2s^2 2p^1$	800	2427	3650		0.080 Estimated value	0.020	2300	3930
Al	13	2.8.3 $\ldots 2s^2 2p^6 3s^2 3p^1$	578	1816	2744	–1.66	0.125	0.050	660	2470
Ga	31	2.8.18.3 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^1$	579	1979	2962	–0.52	0.125	0.062	29.8	2400
In	49	2.8.18.18.3 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^1$	558	1820	2705	–0.34	0.150	0.081	157	2000
T1	81	2.8.18.32.18.3 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^1$	589	1970	2880	+0.72	0.155	0.095	304	1460

Occurrence and Abundance

Boron is a fairly rare element, but it is well known because it occurs as concentrated deposits of borax $Na_2B_4O_7.10H_2O$ and kernite $Na_2B_4O_7.4H_2O$.

Aluminium is the most abundant metal, and the third most abundant element (after oxygen and silicon) by weight in the earth's crust (Table 19.2). It is well known and is commercially important. Aluminium metal is produced on a vast scale. Primary production was 17.6 million tonnes, and an additional 4 million tonnes is recycled. The most important ore of aluminium is bauxite. This is a generic name for several minerals with formulae varying between $A1_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3H_2O$.

Table 19.2: Abundance of the elements in the earth's crust by weight

	ppm	Relative abundance
B	9	38
Al	83000	3
Ga	19	33
In	0.24	63
Tl	0.5	60

Gallium is twice as abundant as boron, but indium and thallium are much less common. All three elements, Ga, In and Tl, occur as sulphides. Ga. In and Tl are not very well known.

18.1.1 Boron

Boron can be obtained as an amorphous brown powder by treating borax with hydrochloric acid, igniting the boric acid, H_3BO_3 obtained, to give the oxide, B_2O_3, and finally reducing the latter with magnesium at a high temperature:

$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3Mg\ O(s)$$

It is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

A crystalline form of boron can be obtained by thermal decomposition of boron tri-iodide on a tantalum filament:

$$2BI_3(s) \longrightarrow 2B(s) + 31_2(s)$$

Properties of boron

Amorphous boron is a very reactive element combining directly with oxygen, sulphur, nitrogen and the halogens to give respectively, an oxide, sulphide, nitride and a halide.

Reactions of Boron

Pure crystalline boron is very unreactive. However, it is attacked at high temperatures by strong oxidizing agents such as a mixture of hot concentrated H_2SO_4 and HNO_3, or by sodium peroxide. In contrast, finely divided amorphous boron (which contains between 2% and 5% of impurities) is more reactive. It burns in air or oxygen, forming the oxide. It also burns at white heat in nitrogen, forming the nitride BN. This is a slippery white solid with a layer structure similar to graphite. Boron also burns in the halogens, forming trihalides. It reacts directly with many metals, forming borides, which are hard and refractory. It reduces strong HNO_3 and H_2SO_4 slowly, and also liberates H_2 from fused NaOH. At red heat it will reduce steam to hydrogen:

$$2B(s) + 3H_2O(l) \longrightarrow B_2O_3(s) + 3H_2(g)$$

Some reactions of amorphous boron

Reaction	Comment
$4B + 3O_2 \rightarrow 2B_2O_3$	At high temperature
$4B + 3S \rightarrow B_2S_3$	At 1200°C
$2B + N_2 \rightarrow 2BN$	At very high temperature
$2B + 3F_2 \rightarrow 2BF_3$	At high temperature
$2B + 3Cl_2 \rightarrow 2BC1_3$	
$2B + 3Br_2 \rightarrow 2BBr_3$	
$2B + 3I_2 \rightarrow 2BI_3$	
$2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$	When fused with alkali
$2B + 2NH_3 \rightarrow 2BN + 3H_2$	At very high temperature
$B + M \rightarrow M_x.B_Y$	Many metals form borides (not group I) often nonstoichiometric

Notes

Reactions of Aluminium

Reaction with water and air

Thermodynamically Al should react with water and with air, but in fact, it is stable in both. The reason is that a very thin oxide film forms on the surface which protects the metal from further attack. This layer is only 10^{-4} to 10^{-6} mm thick. If the protective oxide covering is removed, for example by amalgamating with mercury, then the metal readily decomposes cold water, forming Al_2O_3 and liberating hydrogen.

Aluminium articles are often 'anodized' to give a decorative finish. This is done by electrolysing dilute H_2SO_4 with the aluminium as the anode. This produces a much thicker layer of oxide on the surface (10^{-2} mm). This layer can take up pigments, thus colouring the aluminium.

Aluminium burns in nitrogen at high temperatures, forming AlN.

Reaction with acids and alkalis

Aluminium dissolves in dilute mineral acids liberating hydrogen.

$$2Al + 6HCl \rightarrow 2Al^{3+} + 6Cl^- + 3H_2$$

However, concentrated HNO_3 renders the metal passive because it is an oxidizing agent, and produces a protective layer of oxide on the surface. Aluminium also dissolves in aqueous NaOH (and is therefore amphoteric), liberating hydrogen and forming aluminates.

$$2Al + 2NaOH + 6H_2O \rightarrow NaAl(OH)_4 \text{ or } \underset{\text{Sodium aluminate}}{NaAlO_2{\cdot}2H_2O} + 3H_2$$

Uses of aluminium

1. As structural metals in aircraft, ships, cars, and heat exchangers.
2. In buildings (doors, windows, cladding panels and mobile homes).
3. Container such as cans for drinks, tubes for toothpaste etc. and metal foil.
4. For cooking utensils.
5. To make electric power cables (on a weight for weight basis they conduct twice as well as copper).
6. Finely divided aluminium powder is called 'aluminium bronze', and is used in preparing aluminium paint.

19.2 COMPOUND BORON AND ALUMINIUM

Boron and aluminium are the first two members of Group 13 of the periodic table. Though the outermost electronic configurations of boron and aluminium are similar yet there is a big difference between the properties of their compounds. This will become clear when we study the compounds of boron and aluminium.

19.2.1 Boric Acid

Preparation : Boric acid (also called orthoboric acid) H_3BO_3, $[B(OH)_3]$ is prepared by the action of sulphuric acid on concentrated solution of borax ($Na_2B_4O_7 . 10H_2O$). Boric acid separates as white flaky crystals.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

Properties and Structure : Boric acid is a white crystalline solid. It is soluble in water. It behaves as a weak Lewis acid rather than a protonic acid because it combines with hydroxyl ions (OH^-) of water to liberate hydronium ions (H_3O^+). Thus

$$B(OH)_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$$

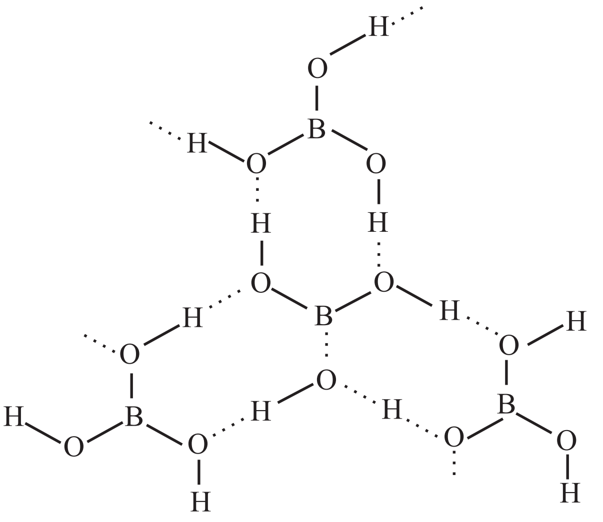


Fig. 19.1: *Structure of boric acid; the dotted lines represent hydrogen bonds*

When heated, it decomposes to metaboric acid and finally to boric anhydride (or boric oxide) at red heat

$$2B(OH)_3 \xrightarrow[H_2O]{375K} 2BO(OH) \xrightarrow[-H_2O]{\text{Red heat}} B_2O_3(\uparrow) \text{ (Boric oxide)}$$

In boric acid, $B(OH)_3$ units are linked by hydrogen bonds to give two dimensional sheets (Fig. 19.1). The sheets are held together by weak van der Waals forces which are responsible for the cleavage of solid structure into flakes.

Uses: Boric acid is used:

(i) as an antiseptic,

(ii) as a food preservative, and

(iii) in making enamels, pottery glazes and glass.

19.2.2 Borax, $Na_2B_4O_7.10H_2O$

In crude form borax occurs as *tincal* in dried up lakes of India. It is also prepared from the mineral colemanite, $Ca_2B_6O_{11}$ by the action of concentrated solution of sodium carbonate

$$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow 2CaCO_3 + Na_2B_4O_7 + 2Na\,BO_2$$

Borax is crystallised from the filtrate. Borax is a white crystalline solid of the formula $Na_2B_4O_7$. $10H_2O$. On heating it loses water of crystallisation.

It is used:

(i) as an alkaline buffer in dyeing and bleaching processes

(ii) as a preservative

(iii) in the manufacture of optical and borosilicate glasses

(iv) as a flux, and

(v) in making glazes for pottery and tiles.

19.2.3 Diborane, B_2H_6

Diborane is the most important hydride of boron.

Preparation:

It is prepared by the following methods:

(i) By the action of lithium aluminium hydride on boron trichloride

$$4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(ii) By the action of lithium hydride on boron trifluoride

$$8BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4$$

Properties:

- Diborane is a toxic gas and has a foul smell.
- It burns in oxygen to give enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O; \ \Delta H = -1976 \text{kJ mol}^{-1}$$

- It is readily hydrolysed by water

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

Structure : The molecular structure of diborane is shown below. The two boron atoms and the four terminal hydrogen atoms lie in one plane, the two bridging hydrogen atoms lie symmetrically above and below the plane. If we consider the bonding situation in B_2H_6, there are eight B–H bonds but only twelve valence electrons. Obviously there are not enough electrons to fill all the available orbitals to form eight normal covalent (two-centre) bonds. Thus bonding in diborane is described in terms of two multi centre bonds, i.e., 3c–2e or three centre two electron B–H–B bonds and four normal B–H bonds.

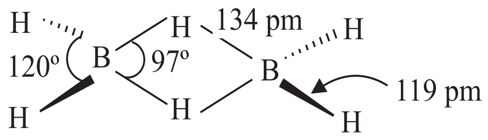


Fig. 19.2 : *Structure of diborane, B_2H_6*

19.2.4 Boron Trifluoride

Boron forms halides BX_3 (X = F, Cl, Br, I). All these halides with exception of fluoride, are formed by the action of appropriate halogen on boric oxide at high temperature. Boron trifluoride is formed by the action of hydrofluoric acid on boron oxide. Thus

$$B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$$

BF_3 hydrolyses according to the following equation

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4$$

BF_3 acts as an electron acceptor (Lewis acid) since B does not have an octet of electrons in its valence shell; infact it has a sextet. It forms complexes with nitrogen and oxygen donors, e.g. NH_3 and ether, thus completing the octet of boron.

$$F_3B \leftarrow NH_3 \quad \text{and} \quad F_3B \leftarrow OEt_2$$

Boron trifluoride is used as a catalyst in Friedel-Crafts reaction such as alkylation and acylation and in polymerization reactions.

The structure of boron trifluoride is shown in Fig 19.3:

B–F bond in BF_3 has a multiple bond character since its structure is a resonance hybrid of three resonating structures.

Note that in the resonating structures boron completes its octet.

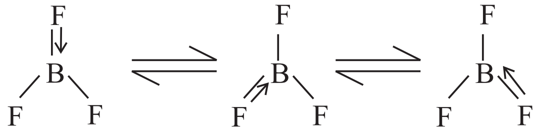


Fig 19.3 : *Resonatimg structures of boron trifluoride*

19.2.5 Aluminium trichloride

Aluminium trichloride exists as a dimer as Al_2Cl_6 at room temperature and as a monomer at high temperatures and is made by passing hydrogen chloride or chlorine over heated aluminium under anhydrous condition.

$$2Al + 6HCl \rightarrow Al_2Cl_6 + 3H_2$$

$$2Al + 3Cl_2 \rightarrow Al_2Cl_6$$

When pure, it is a white solid which sublimes at 453K. Aluminium has only three valence electrons. When these are used to form three covalent bonds, the atom has only six electrons in its valence shell. Since it is electron deficient it, therefore, exists as a dimer. The aluminium atoms complete their octets by dative bonding from two chlorine atoms. The arrangement of chlorine atoms about each aluminium atom is roughly tetrahedral. The structure of the dimer is shown in Fig. 19.4.

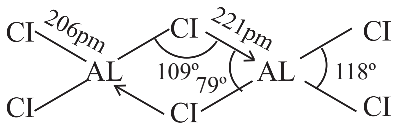


Fig.19.4 : *Structure of $AlCl_3$*

When treated with water it gives hydrated aluminium ions and Cl^- ions:

$$Al_2\,Cl_6 + 6H_2O \rightarrow 2[Al\,(H_2O)_6]^{3+} + 6Cl^-$$

Anhydrous aluminium chloride is used as a catalyst in Friedel-Crafts reaction because of its Lewis acid character.

19.2.6 Double Salts: Alums and Potash Alum

When two salts capable of indendent existence are mixed and the solution of the mixture is allowed to crystallise, crystals comprising both the salts are characteristically formed. However, in solution all the ions exist freely. Such substances are called double salts. For example, when a solution containing potassium sulphate and aluminium sulphate is allowed to crystallise, transparent octahedral crystals of potash alum, $K^+ Al^{3+} (SO^{2-}{}_4)_2 . 12\, H_2O$ are obtained. The solid contains $[K(H_2O)_6]^+$, $[Al\,(H_2O)_6]^{3+}$ and SO_4^{2-} ions and it is a double salt since it gives the tests of its constituent ions in solutions. The double sulphate with similar composition and properties are called alums.

It is possible to replace the trivalent aluminium cation by trivalent metal ion of the similar ionic size, e.g. Ti^{3+}, Cr^{3+}, Fe^{3+} and Co^{3+}. It is also possible to prepare a series of alums in which potassium ion is replaced by ammonium ion, NH_4^+.

The alums are isomorphous, a few typical ones are given below:

Ammonium alum	$(NH_4)\,Al\,(SO_4)_2.12H_2O$
Chrome alum	$KCr\,(SO_4)_2.12H_2O$
Ammonium chrome alum	$(NH_4)Cr\,(SO_4)_2.12H_2O$
Ferric alum	$K\,Fe\,(SO_4)_2.12H_2O$

Potash alum, $K\,Al\,(SO_4)_2.12H_2O$, is by far the most important of all the alums. It is used as a mordant in dyeing industry and also in purifying water. (Often it is formulated as $K_2SO_4.Al_2\,(SO_4)_3 \,.\, 24\,H_2O$).

INTEXT QUESTIONS 19.1

1. Write the formula of the following:
   (i) Boric acid (ii) Borax
2. Write one reaction for the preparation of diborane.
3. What is the general formula of alums?
4. Write the formula of anhydrous solid aluminium trichloride and its structure.
5. Mention one use each of
   (i) borax (ii) boric acid (iii) boron trifluoride
5. Why aluminium become non-reactive after reacting with HNO_3.
6. Orthoboric acid is monoprotonic or triprotonic.

19.3 SOME GENERAL REMARKS ABOUT GROUP 14

All these elements exhibit a group valency of four, but because an enormous amount of energy is needed to remove four electrons from their atoms, they form compounds which are predominantly covalent. Similarly the gain of four electrons to give the 4-valent anion is energetically impossible.

Germanium, tin and lead form 2-valent compounds in which the two s electrons are inert (inert pair effect). The stability of this state relative to the 4-valent state increases steadily from germanium to lead, i.e. 2-valent germanium compounds tend to be strongly reducing and revert to the 4-valent state, while for lead this is the predominant valency state. 2-valent compounds of tin and lead are often predominantly ionic.

Carbon is non-metallic and so too is silicon; germanium has properties of both metals and non-metals (it is a metalloid), while the elements tin and lead are definitely metallic. There is a smooth transition from non-metallic to metallic properties on passing down the series silicon, germanium, tin and lead, but the first member carbon differs considerably from silicon. The chemistry of silicon is very similar to that of boron, its diagonal neighbour in the Periodic Table.

Table 19.3: Physical properties of Group-14 elements

	Atomic Number	**Electronic Configuration**	**Atomic Radius/nm**	**Ionic Radius/nm**		**M.P. /°C**	**B.P. /°C**
				M^{2+}	**M^{4+}**		
C	6	2.4 $1s^2 2s^2 2p^2$	0.077				3580 (subl.)
Si	14	2.8.4 $\ldots 2s^2 2p^6 3s^2 3p^2$	0.117		0.041	1410	2360
Ge	32	2.8.18.4 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^2$	0.122	0.093	0.053	937	2830
Sn	50	2.8.18.18.4 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^2$	0.140	0.112	0.071	232	2270
Pb	82	2.8.18.18.8.4 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^2$	0.154	0.120	0.084	237	1744

The chemistry of carbon is dominated by its tendency to form chains and rings of carbon atoms in which other atoms, particularly hydrogen. play an important part. The chemistry of silicon is completely different.

Chemical properties of carbon

Carbon in any form will react with oxygen at a sufficiently high temperature to give carbon dioxide; in a deficiency of oxygen, carbon monoxide is formed as well. Charcoal will combine directly with sulphur, some metals and fluorine.

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

$$Ca(s) + 2C(s) \longrightarrow Ca^{2+}(C{\equiv}C)^{2-}(s)$$

$$C(s) + 2F_2(g) \longrightarrow CF_4(g)$$

It will reduce steam, forming water gas and many oxides of metals; these reductions are of industrial importance.

It is not attacked by dilute acids, but concentrated nitric acid and sulphuric acid are reduced if warmed with carbon according to the equations

$$C(s) + 4HNO_3(aq) \longrightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g)$$

$$C(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + 2SO_2(g) + CO_2(g)$$

19.4 CARBON AND SILICON

Carbon and silicon belong to Group 14 of the periodic table. Both elements show significant differences in their chemistry. There are thousands of hydrocarbons (alkanes and other compounds of carbon and hydrogen) but only a few silanes (compounds of silicon and hydrogen are known). It is because carbon has the unique ability to form compounds in which the carbon atoms are bonded to each other in chains or rings. This property is called *catenation* which is due to the fact that C–C bond is much stronger than Si- Si bond.

19.4.1 Allotropic Forms of Carbon

Diamond and Graphite : Structures and Properties

Diamond and graphite, both are crystalline forms of carbon. But they are structurally different. Due to the difference in the arrangement of carbon atoms, they show different properties. In diamond, each carbon atom is sp^3 hybridized and is linked to four other carbon atoms by strong covalent bonds in a tetrahedral fashion. It gives rise to a three-dimensional arrangement (Fig.19.5). On the other hand, in graphite, the carbon atoms are arranged in layers. In each layer a particular carbon atom is sp^2 hybdridized and is linked to three other carbon atoms in a hexagonal arrangement. The fourth electron is free and does not participate in bonding. The different layers are held together by weak van der Waals forces (Fig 19.6).

Chemically speaking diamond is unreactive and burns in oxygen only if heated above 800^0C, forming carbon dioxide. It reacts with fluorine (but not with chlorine) at 973 K giving carbon tetrafluoride. Alkalies and acids have no action on diamond. It is the hardest natural substance.

Graphite, on the other hand, is reactive. It burns in air at 873 K to form CO_2. It is not attacked by dilute acids but concentrated sulphuric acid reacts with graphite to give graphite bisulphate in solution. It does not react with chlorine also.

Diamond is used for cutting and grinding hard substances such as rocks, glass, etc., and in die for drawing wire for watch springs and lamp filaments. Beside all these, diamond is widely used in jewellery.

Notes

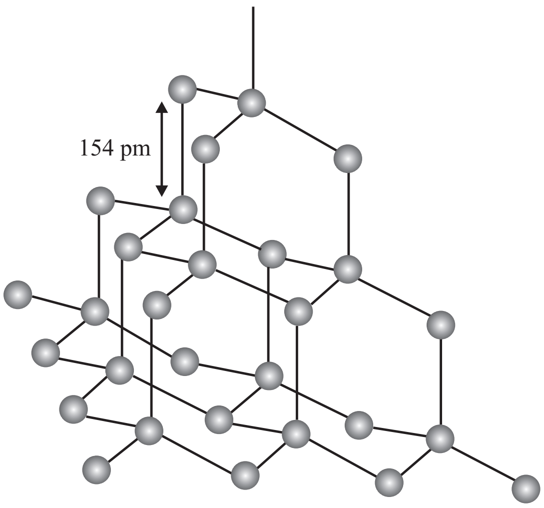


Fig. 19.5 : *Structure of diamond*

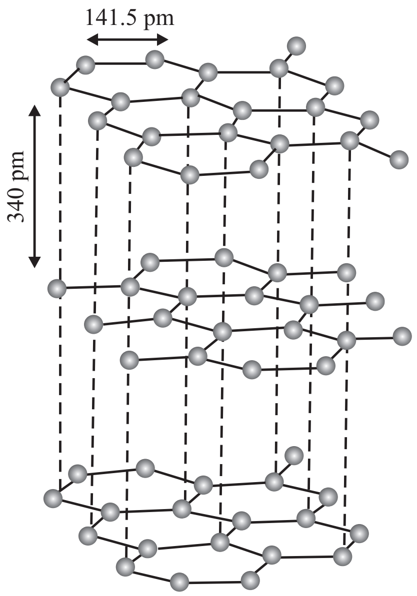


Fig. 19.6 : *Structure of graphite*

Graphite is used as electrodes,as lubricant, for making crucibles, for casting of metals, for lead pencils and as a constituent of heat resistant paints.

Fullerenes

Fullerene, a newly discovered allotrope of carbon is called "Buckminster Fullerene" after the name of American architect Buckminster Fuller. The most common Fullerene molecule has 60 carbon atoms and the carbon atoms are linked to create the shape of a hollow soccer ball. The outer surface of fullerenes can be altered by chemical reactions.

19.4.2 Oxides of Carbon and Silicon

Structure

Carbon forms two oxides, viz., carbon monoxide and carbon dioxide. The bonding in carbon monoxide may be represented as, three electron pairs shared between the two atoms. The three electron pairs consist of one sp hybridized σ bond and two π bonds.

$$:\mathrm{C}\ \vdots\vdots\ \mathrm{O}: \qquad \text{or} \qquad :\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}:$$

The structure of carbon dioxide on the other hand is linear O=C=O. There are two σ bonds and two π bonds in the molecule CO_2. The carbon atom uses sp hybrid orbitals to form σ bonds with oxygen atoms. The remaining two 2p orbitals of carbon overlap with 2p orbitals one each from the two O atoms to form the π bonds

$$O = C = O$$

Silicon also forms two oxides : SiO and SiO_2. Not much is known about silicon monoxide as its existence is only known at high temperatures. Silica (SiO_2) is widely found as sand and quartz.

Properties

Carbon monoxide is a neutral oxide. It is a colourless, odourless and a poisonous gas and burns with a blue flame. It is toxic because it forms a complex with the haemoglobin in the blood which prevents the haemoglobin from carrying oxygen around the body. This leads to oxygen deficiency resulting in unconsciousness or death. Carbon monoxide is an important industrial fuel and is also a strong reducing agent.

Carbon dioxide is an acidic oxide. It is a colourless and odourless gas and can be liquified under pressure at low temperature. Solid carbon dioxide is called dry ice.

SiO_2 is an acidic oxide and is unreactive in all its forms. It shows very limited reactions. It dissolves slowly in aqueous alkalies and more rapidly in fused alkalies or fused carbonates forming silicates. Silica also reacts with fluorine and HF to form silicon tetrafluoride

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

Uses of oxides of carbon

Carbon monoxide

(i) It is used as a reducing agent in metallurgical processes to reduce metal oxides. For example, in the blast furnace, it is used to reduce iron oxide to iron.

$$Fe_2O_3\ (s) + 3CO\ (g) \longrightarrow 2Fe\ (s) + 3CO_2(g)$$

(ii) In the presence of a catalyst, it can combine with hydrogen to give methanol (CH_3OH).

(iii) It forms carbonyl compounds. The nickel carbonyl $Ni(CO)_4$ is involved in the refinement of nickel.

(iv) It is used as a fuel.

(v) It is used in the synthesis of several organic compounds.

The main uses of carbon dioxide are as follows:

(i) Solid carbon dioxide also called *dry ice* is used as a refrigerant because when it is cooled at atmospheric pressure, it condenses into a solid rather than as a liquid. This solid sublime at –78°C

Notes

(ii) It is used in the production of *carbonated drinks.*

(iii) It is used in the production of washing soda ($Na_2CO_3.10H_2O$) and baking soda ($NaHCO_3$).

SiO_2 is a high melting solid and it exists in twelve different forms, each of which, has different structure. The main forms are quartz and cristobalite, each of which has a different structure at different temperatures. In all these forms silicon is tetrahedrally surrounded by four oxygen atoms and each oxygen is attached to two silicon atoms. The sp^3 orbitals of Si overlap with 2p orbitals of O atoms. Each corner of tetrahedron is shared by other tetrahedra. This gives an infinite structure – a macromolecule.

19.4.3 Halides of Carbon and Silicon

Carbon and silicon form tetrahalides like CCl_4 and $SiCl_4$, respectively. In the tetrahalides of these elements there are four covalent bonds, with a tetrahedral arrangement; the central atom is sp^3 hybridized. Carbon tetrachloride can be rightly called as tetrachloromethane and silicon tetrachloride as tetrachlorosilane.

- Carbon tetrachloride is prepared by the action of chlorine on carbon disulphide in the presence of a catalyst (usually $MnCl_2$)

$$CS_2 + 3Cl_2 \xrightarrow{MnCl_2} CCl_4 + S_2Cl_2$$

Silicon tetrachloride, $SiCl_4$, is formed by heating amorphous silicon in a current of dry chlorine.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

It can also be obtained by passing dry chlorine over an intimate mixture of silica and carbon strongly heated in a crucible. Thus

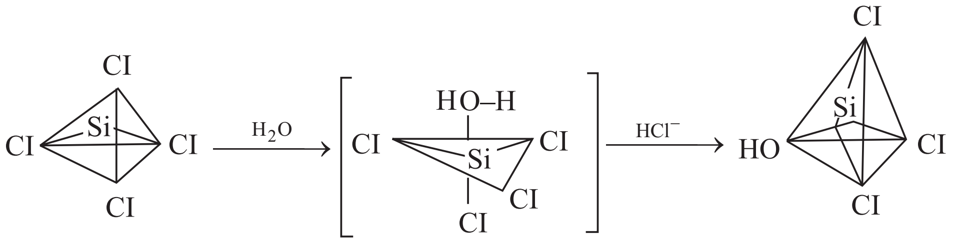
$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

Carbon tetrachloride is not hydrolysed by water whereas silicon tetrachloride is readily hydrolysed.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

The difference in the behaviour of CCl_4 and $SiCl_4$ towards water can be explained as follows.

A lone pair of electrons from the O atom of H_2O molecule is donated to the empty 3*d* orbital on Si. Subsequently one of the hydrogen atoms of water molecule combines with a chlorine atom of $SiCI_4$. This process goes on till all the chlorine atoms are replaced by –OH groups.



Since, there is no *d*-orbital in carbon in CCl_4 does not hydrolyse.

Silicon forms complex ion like SiF_6^{2-} but carbon does not form similer ions like CF_6^{2-}. It is because unlike carbon there are empty 3*d* orbitals in silicon. The availability of *d* orbitals is responsible for the ability of silicon and not carbon to form complex ion SiF_6^{2-}

19.4.4 Silicon Carbide, SiC

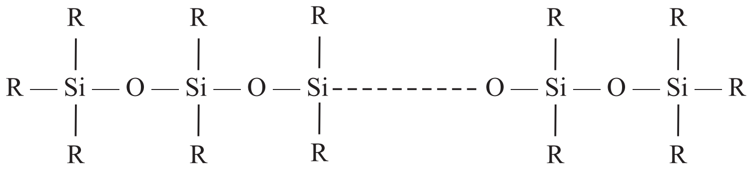
Silicon carbide (SiC) is commonly known as *carborundum*. It is extremely hard and chemically a very stable material. It is made by heating silica with excess of carbon in an electric furnace

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

In silicon carbide, there are three dimensional arrays of Si and C atoms, each atom of Si or C is tetrahedrally surrounded by four of the other type. Thus, this structure is very much similar to that of diamond. Silicon carbide or carborundum is widely used as an abrasive.

19.4.5 Silicones

These compounds are polymeric, the polymer chain containing alternately linked silicon and oxygen atoms. Alkyl or aryl groups, e.g. CH_3 or C_6H_5, are attached to the polymer backbone by means of covalent bonds to the silicon atoms. A typical silicone has the formula:



$$R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}\text{----------}O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-O-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}-R$$

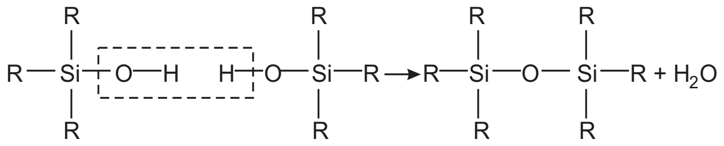
where R is an alkyl or aryl group.

Silicones are obtained by reacting a chloroalkane or a chlorobenzene with silicon in the presence of a copper catalyst and at a temperature of about 300°C. A mixture of alkyl or aryl chlorosilanes results:

$$RCl + Si \xrightarrow{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$$

After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:

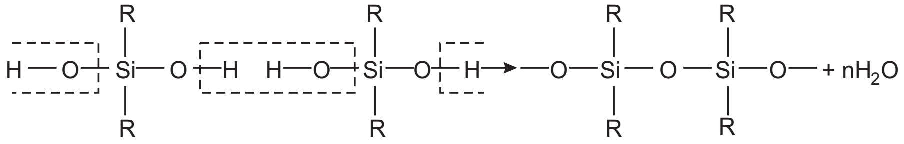
$$R_3SiCl + H_2O \longrightarrow R_3SiOH + HCl$$



$$R_3Si{-}O{-}H + H{-}O{-}SiR_3 \longrightarrow R_3Si{-}O{-}SiR_3 + H_2O$$

a dimer

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$



$$H{-}O{-}SiR_2{-}O{-}H + H{-}O{-}SiR_2{-}O{-}H \longrightarrow {-}O{-}SiR_2{-}O{-}SiR_2{-}O{-} + nH_2O$$

a polymer chain

The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

Hydrolysis of the trichlorosilane derivative gives a two-dimensional structure. By blending a mixture of chlorosilanes before hydrolysis, it is possible to produce polymers of varying chain length, R_3SiOH acting as a chain stopper and $RSi(OH)_3$ as a cross-linking agent.

The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent. Silicone fluids are thermally stable and their viscosity alters very little with temperature, and silicone rubbers retain their elasticity at much lower temperatures than ordinary rubber.

19.4.6 Silicates

The tendency of silicon to form single covalent bonds with oxygen atoms has been observed in the structures of silica and polysilicic acid. These structures and also those of a bewildering variety of silicates arc now readily understood in terms of the linking together of tetrahedral SiO_4 units. Paining considers the silicon-oxygen bond to be about 50 per cent ionic, and it is sometimes convenient to discuss the structures of silicates in terms of Si^{4+} ions tetrahedrally surrounded by four much larger oxygen atoms. Examples of some typical silicates are given below (Fig. 19.7).

Silicates containing discrete SiO_4^{4-} anions

Orthosilicates contain the simple SiO_4^{4-} ion, one example being beryllium orthosilicate, $(Be^{2+})_2SiO_4^{4-}$. As mentioned above, the SiO_4^{4-} group is tetrahedral, as would be expected.

19.4.6.1 Silicates containing $Si_2O_7^{6-}$ anions (one oxygen atom shared)

When one oxygen atom is shared between two tetrahedra, the pyrosilicate anion, $Si_2O_7^{6-}$ is the result. A typical pyrosilicate is $(Sc^{3+})_2Si_2O_7^{6-}$.

19.4.6.2 Silicates containing extended anions (two oxygen atoms shared) and (d))

When each tetrahedron shares two oxygen atoms, it is possible to have closed ring anions such as $Si_3O_9^{6-}$. Another possibility is the formation of infinite chains, the formula of these anions approximating to $(SiO_3)n^{2n-}$ Examples of silicates containing these anions are $Be^2Ti^4Si_3O_9^{6-}$ and $Ca^{2+}Mg^2(SiO_3^{2-})_2$.

When each tetrahedron shares three oxygen atoms, silicates in the form of extended sheets result. The empirical formula of these polysilicate anions is $SiO^-_{2\frac{1}{2}}$ or $Si_4O_{10}^{4-}$ Anions of this type are found in micas and clays and account for their ready cleavage into thin slices.

(a) The structure of the orthosilicate anion	(a)	$SiO4^4$
(b) The structure of the pyrosilicate anion (one oxygen anion shared)	(b)	$Si_2O_7^{6-}$
(c) The structure of a ring silicate anion (two oxygen atoms shared)	(c)	$Si_3O_9^{6-}$
(d) The structure of an extended silicate anion (two oxygen atoms shared)	(d)	$(SiO_3)_n^{2n-}$
(e) The structure of an extended silicate anion (three oxygen atoms shared). In this structure the silicate atoms are joined to four oxygen atoms. The fourth oxygen atom carries a single negative charge and is above the plane.	(e)	$Si_4O_{10}^{4-}$ or $SiO_{2\frac{1}{2}}$

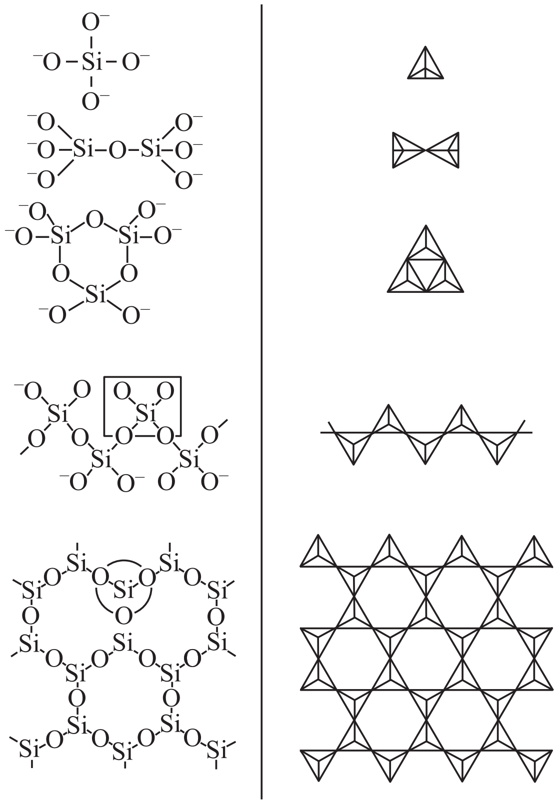


Fig. 19.7: Structure of Silicates

19.4.6.3 Zeolites

Zeolites have a much more open structure than the feldspars. The anion skeleton is penetrated by channels, giving a honeycomb-like structures These channels are large enough to allow them to exchange certain ions. They can also absorb or lose water and other small molecules without the structure breaking down. Zeolites are often used as ion-exchange materials, and as molecular sieves. Natrolite $Na_2[A1_2Si_3O_{10}]2H_2O$ is a natural ion exchanger. Permutit water softeners use sodium zeolites. Zeolites take Ca^{2+} ions from hard water and replace them by Na^+, thereby softening the water. The sodium zeolite (natrolite) gradually becomes a calcium zeolite, and eventually has to be regenerated by treatment with a strong solution of NaCl, when the reverse process takes place. In addition to naturally occurring minerals, many synthetic zeolites have been made. Zeolites also act as molecular sieves by absorbing molecules which are small enough to enter the cavities, but not those which are too big to enter. They can absorb water, CO_2, NH_3 and EtOH, and they are useful for separating straight chain hydrocarbons from branched chain compounds. Some other zeolites are healandite $Ca[A1_2Si_7O_{18}]6H_2O$, chabazite $Ca[A1_2Si_4O_{12}]6H_2O$, and analcite $Na[AISi_2O_6]H_2O$. Molecular sieves can be made with pores of appropriate size to remove small molecules selectively.

INTEXT QUESTIONS 19.2

1. Write two properties of diamond which are not exhibited by graphite.
2. What is the state of hybridization of carbon in (i) diamond (ii) graphite?
3. What is the nature of bond in carborundum?
4. Write the state of hybridization of carbon in CCl_4
5. Which one is affected by water and why; CCl_4 or $SiCl_4$?
6. Which is an acidic oxide, CO or CO_2?
7. What happens when SiO_2 is attacked by F_2?

19.5 SOME GENERAL CHARACTERISTICS OF ELEMENTS OF GROUP 15

This group consists of N, P, As, Sb and Bi.

Group 15 elements can complete the octet in chemical combination by gaining three electrons to form the 3-valent anion, by forming three covalent bonds, or by losing five electrons; the last possibility is ruled out on energetic grounds. Only nitrogen (and possibly phosphorus to a slight extent) forms the 3-valent ion and reactive metals are required for it to be possible; the N^{3-} ion is present in ionic nitrides, e.g. $(Li^+)_3N^{3-}$ and $(Ca^2+)_3(N^{3-})_2$. The majority of compounds formed by this group of elements are covalent.

Antimony and bismuth can form the 3-valent cation X^{3+} (the inert-pair effect), the Sb^3+ ion being present in $(Sb^{3+})_2(SO_4{}^{2-})_3$ and the Bi^{3+} ion in $Bi^{3+}(F^-)_3$ and $Bi^{3+}(N0_3{}^-)_3$. $5H_2O$.

Because phosphorus, arsenic, antimony and bismuth have vacant *d* orbitals they are able to form 5-covalent compounds which are not possible for nitrogen, e.g. in the formation of PCl_5, one of the 3*p* electrons of the phosphorus atom is promoted to the 3*d* level. giving five unpaired electrons for valency purposes.

Nitrogen and phosphorus are non-metallic; metallic properties first become apparent with arsenic and become progressively more important for antimony and bismuth. Of these elements only nitrogen is able to multiple bond with itself, the triple bond being present in the nitrogen molecule, $N\equiv N$.

Tabe 19.4: Physical properties of Group 15 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
N	7	2.5 $1s^22s^22p^3$	0.074		–210	–196
P	15	2.8.5 $\ldots 2s^22p^63s^23p^3$	0.110		44.1 (white)	280 (white)
As	33	2.8.18.5 $\ldots 3s^23p^63d^{10}4s^24p^3$	0.121	0.069		613 (sublimation)
Sb	51	2.8.18.18.5 $\ldots 4s^24p^64d^{10}5s^25p^3$	0.141	0.090	630	1380
Bi	83	2.8.18.18.8.5 $\ldots 5s^25p^65d^{10}6s^26p^3$	0.152	0.120	271	1560

Occurrence

Nitrogen occurs as an inert diatomic gas, 78 percent by volume in the atmosphere. Inorganic nitrogen compounds are usually soluble and are rarely found in nature except Chile saltpetre. Both nitrogen and phosphorus are essential constituents of all plant and animal tissue: nitrogen is present in proteins; and phosphorus is present as calcium phosphate in bones and teeth.

Dinitrogen

Preparation of dinitrogen

Nitrogen can be obtained :

(A) From air by the removal of oxygen etc., by physical or chemical means.

(B) By the decomposition of nitrogen compounds.

(A) *From air* : (a) The gas left after the removal of oxygen and carbon dioxide from air is almost nitrogen. Air is passed through two wash bottles one containing a solution of sodium hydroxide and the other sulphuric acid which remove carbon dioxide and moisture respectively. The dry air is now passed over heated iron or copper to remove oxygen.

$$2Cu + O_2 \rightarrow 2CuO$$

Nitrogen so collected in gas jars or holders contains about 1 per cent of noble gases.

(b) *By fractional evaporation of liquid air* : Nitrogen for industrial requirements is manufactured by this method. The boiling point of liquid nitrogen is –195.8°C, and of liquid oxygen is –183°C. Thus, the difference of 12.8°C in their boiling points, is sufficient to allow their separation from liquid air. T

(B) *From nitrogen compounds* : Nitrogen prepared from chemical compounds is usually called "*chemical nitrogen*". It is conveniently prepared in the laboratory by the following methods :

(i) When a solution of ammonium nitrite is heated in a flask, nitrogen is obtained.

$$NH_4NO_2 \rightarrow 2H_2O + N_2$$

(ii) *By the oxidation of* ammonia : When chlorine is passed into an excess of concentrated ammonia solution, nitrogen is evolved which is bubbled through water to remove ammonia and ammonium chloride.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

$$6NH_3 + 6HCl \rightarrow 6NH_4Cl$$

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

If ammonia is not present in excess or the action is prolonged, nitrogen trichloride is also formed which is highly explosive.

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

(iii) Very pure nitrogen is evolved by heating sodium or barium azide in vacuum.

$$Ba(N_3)_2 \rightarrow Ba+3N_2$$

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Properties

Physical: Nitrogen is a colourless, odourless and tasteless diatomic gas. Its specific gravity in the gaseous state is 0’96737, in the liquid state 0.804, and in the solid state 1.0265. It is slightly soluble in water, 100 volumes of water at 20°C dissolve only 1·64 volumes of gas. At –1955°C it is condensed to a colourless liquid which freezes to a white snow-like mass at –210°C. The gas is non-poisonous, but simply dilutes the oxygen of the air. Animals die in nitrogen for want of oxygen only. The gas is neither combustible nor a supporter of combustion,

It has been noted that at 3500°C about 5 per cent of nitrogen is dissociated into atoms.

$$N_2(95\%) \rightleftharpoons 2N\ (5\%)$$

Chemical : It is inert at room temperature because a large amount of energy is required to break N ≡ N bond. However, the compounds of nitrogen show great chemical activity.

(i) When nitrogen is passed over heated metals like lithium, calcium, magnesium and aluminium, it forms nitrides.

$$2Al + N_2 \rightarrow 2AlN$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

These nitrides are readily decomposed by water.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

(ii) At 200 atmospheres and in presence of a catalyst, finely divided iron and molybdenum as promotor at 450°-500°C, nitrogen combines with hydrogen. This reaction is utilized for the manufacture of ammonia by the Haber process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24000\ \text{cals.}$$

(iii) It combines with carbides to form cyanamides which react with superheated steam to evolve ammonia.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

(iv) In presence of lightning discharge or an electric spark, nitrogen combines with oxygen to form nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO - 43.2\ \text{Cals.}$$

This reaction is utilized for the manufacture of nitric acid.

Uses

(i) Nitrogen is used on a large scale for the manufacture of ammonia, nitric acid and other important nitrogen compounds.

(ii) It is used for filling electric bulbs,

(iii) In the manufacture of high temperature thermometers.

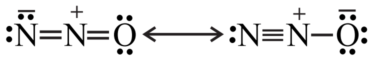
(iv) It is also used for providing an inert atmosphere in metallurgy and other industrial processes.

(v) It is the basis of two important activities of man *(a) agriculture* and (b) explosive.

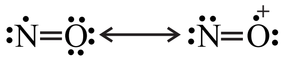
(vi) It is used as a source of cold when liquefied.

Structure of the Oxides of Nitrogen

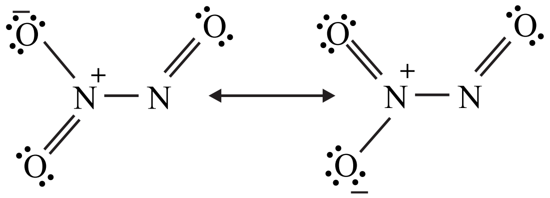
Dinitrogen Oxide, N_2O



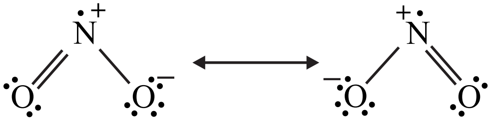
Nitrogen Oxide, NO



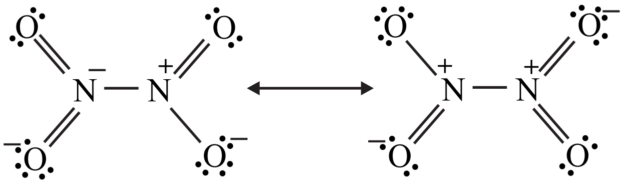
Dinitrogen trioxide, N_2O_3



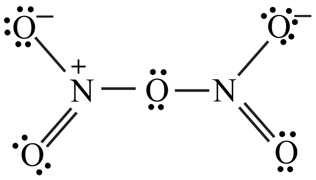
Nitrogen dioxide, NO_2



Dimer of NO_2 (N_2O_4)



Dinitrogen Pentaoxide



19.6 NITROGEN AND PHOSPHORUS

Nitrogen and phosphorus belong to Group 15 of the periodic table. They form a number of industrially important compounds like ammonia, nitric acid and fertilizers. Let us study about them.

19.6.1 Ammonia

Ammonia is prepared in the laboratory by heating an ammonium salt with a base:

$$2NH_4^+ + OH^- \rightarrow 2NH_3 + H_2O$$

or

$$2NH_4^+ + CaO \rightarrow Ca^{2+} + 2NH_3 + H_2O$$

It may also be prepared by treating a nitride with water.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

It is manufactured industrially by passing nitrogen and hydrogen over an iron catalyst at 750 K and under a pressure of about 200 atmospheres (Haber's process).

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H = -46 \text{ kJ mol}^{-1}$$

In the actual process the hydrogen required is obtained from water gas and the nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (1 : 3 by volume) is compressed to 200-300 atm and then passed into the catalytic tubes packed with the catalyst. The catalyst in made by fusing Fe_3O_4 with KOH and Al_2O_3. The temperature of the catalytic tubes is maintained at 673 –773K by heating them electrically. The issuing gas containing about 10 per cent ammonia is cooled and the liquid ammonia condenses. The unconverted mixture of hydrogen and nitrogen is returned to the inlet and passed again over the catalyst. A typical plant might be arranged as shown in Fig.19.7

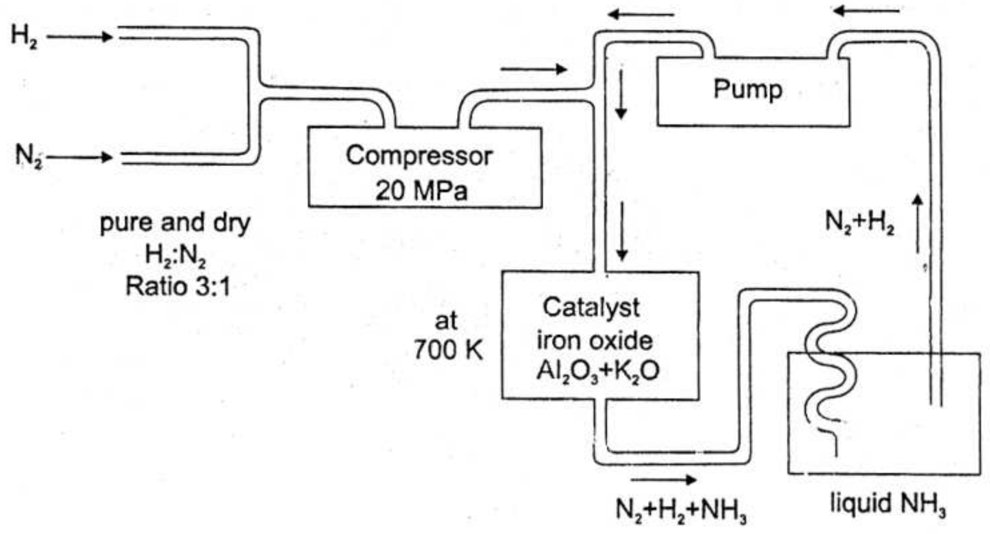


Fig. 19.7 : *The Haber process for the manufacture of ammonia*

Notes

Properties

Ammonia is a colourless and pungent smelling gas. It is readily liquified at a pressure of about nine atmospheres at ordinary temperatures. The liquid boils at –239.6K and freezes at –96K. Liquid ammonia resembles water in being highly associated because of its polar nature and strong hydrogen bonding.

Ammonia is extremely soluble in water. The hydrated ammonia molecule, $NH_3.H_2O$, is loosely called ammonium hydroxide, NH_4OH, which is a weak base, the ionization reaction being

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

The undissociated molecule, NH_4OH, is essentially a non-existent entity. It can only exist as NH_4^+ and OH^- ions.

Chemical reactions

(i) **Action of heat:** When heated above 500^0C it begins to decompose into its elements. The decomposition is accelerated by metallic catalysts

$$2NH_3 \rightarrow N_2 + 3H_2$$

(ii) **With oxygen :** Ammonia does not burn in air but freely burns in pure oxygen with a yellowish flame giving nitrogen and steam

$$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$$

In the presence of a catalyst, e.g. hot platinum, ammonia burns in air to give nitric oxide

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

(iii) **As a reducing agent.** If ammonia is passed over those heated metallic oxides which are reducible by hydrogen, e.g. CuO, PbO, etc, it is oxidised to nitrogen and water :

$$3PbO + 2NH_3 \rightarrow 3Pb + N_2 + 3H_2O$$

(iv) **With acids.** It is easily absorbed by acids to form ammonium salts, e.g.:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The reaction can occur even if the acid is a gas, e.g.:

$NH_3 + HCl \rightarrow NH_4Cl$ (i.e. $NH_4^+Cl^-$)

(v) **With chlorine.** Ammonia reacts with chlorine, the products varying according to conditions :

$$\left.\begin{array}{l}2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl \\ 6HCl + 6NH_3 \rightarrow 6NH_4Cl\end{array}\right\} \text{(with excess of ammonia)} \qquad ...(1)$$

$$\left.\begin{array}{l} NH_3 + 3Cl_2 \rightarrow \underset{\text{nitrogen trichloride}}{NCl_3} + 3HCl \\ HCl + NH_3 \rightarrow NH_4Cl \end{array}\right\} \begin{array}{l}\text{(when chlorine is in} \\ \text{large excess)}\end{array} \qquad ...(2)$$

(vi) **With metal salts**. With some metal salts, aqueous ammonia reacts to form metal hydroxides which are precipitated.

For example, ammonia solution precipitates copper(II) hydroxide when treated with a copper salt,

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

In excess of ammonia, the precipitate of $Cu(OH)_2$ dissolves to form tetraammine complex

$$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_3$$

$$\rightarrow \underset{\textbf{tetraamminecopper(II) sulphate}}{[Cu(NH_3)_4]^{2+}SO_4^{2-}} + 2H_2O$$

Similar complexes are formed with many metallic salts and complex ions such as $[Ag(NH_3)_2]^+$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$ are well known.

Uses :

Ammonia is used for a number of purposes, some important uses are :

(i) In the manufacture of ammonium sulphate for use as a fertilizer.

(ii) In the manufacture of nitric acid (Ostwald process)

(iii) In the manufacture of sodium carbonate by Solvay process.

(iv) Liquid ammonia is used in refrigerators.

(v) Ammonia solution is used as a domestic cleaner : as a grease remover and in laundry.

Structure : Ammonia molecule is trigonal pyramid with the nitrogen at the apex. The nitrogen atom is sp^3 hybridized in which a lone pair of electrons occupies one of the tetrahedral positions. The angle $H\hat{N}H$ becomes 107^0 instead of 109^0 (in CH_4) due to lone pair-bond pair repulsion (Fig. 19.8).

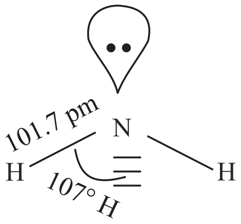
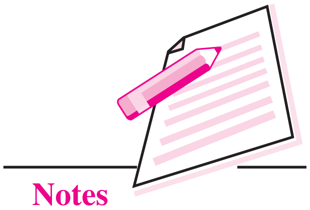


Fig. 19.8 : *Structure of ammonia*



19.6.2 Oxoacids of Nitrogen

There are several oxoacids of nitrogen such as nitrous acid, HNO_2, hyponitrous acid, $H_2N_2O_2$ and nitric acid, HNO_3. Of these nitric acid is the most important and will be considered here in detail.

Nitric Acid, HNO_3

Preparation

In the laboratory, nitric acid can be prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort and condensing the vapours coming out of the retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

In industry it is manufactured by the catalytic oxidation of ammonia which involves the following reactions (Ostwald process) :

$$4NH_3 + 5O_2 \xrightarrow[\text{Pt}]{1173\text{ K}} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The aqueous nitric acid can be concentrated by distillation followed by dehydration with conc. H_2SO_4.

Properties

Physical : It is a colourless liquid of density 1.50 g cm^{-3} at 248 K. The acid is freely miscible with water forming a constant boiling mixture containing 98% of acid, b.p.393K.

Chemical : (a) In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions.

$$H_2O + HNO_3 \longrightarrow H_3O^+ + NO_3^-$$

(b) It is neutralised by appropriate alkalies to yield nitrates.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

(c) On heating it gives NO_2

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

(d) It is a good oxidizing agent and oxidizes non metals, metals and organic compounds, some examples of which are given below :

(i) $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

(ii) $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

(iii) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(v) $Cu + \underset{\textbf{conc.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$3Cu + \underset{\textbf{dil.}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

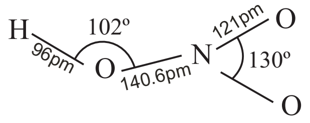
(vi) $4Zn + \underset{\textbf{dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

(vii) $Mg + \underset{\textbf{dil.}}{2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2$

(viii) Aluminium loses its normal reactivity i.e. becomes passive after being dipped in conc. HNO_3. This is due to the formation of a thin protective layer of aluminium oxide on its surface which prevents further action.

(ix) $\underset{\textbf{glycerine}}{C_3H_5(OH)_3} + 3HNO_3 \xrightarrow{\text{conc. } H_2SO_4} \underset{\textbf{trinitroglycerine (explosive)}}{C_3H_5(NO_2)_3} + 3H_2O$

Structure : In the gaseous state HNO_3 exists as a planar molecule with the structure: (Fig. 19.9):



Fig, 19.9 : *Structure of nitric acid molecule*

Uses : Nitric acid is used in the manufacture of nitrates which are used as fertilizers, and explosives, trinitroglycerine and trinitrotoluene (TNT)

- It is used as an oxidizing agent in labortory, e.g. Fe(II) gets oxidized to Fe(III)
- Conc. HNO_3 is a constituent of aqua regia ($HNO_3 : HCl = 1 : 3$)
- HNO_3 (100%) is a constituent of rocket propellant.

19.6.3 Allotropic forms of Phosphorus

The allotropy of phosphorus is rather complex but, essentially, there are three allotropic forms known as white, red and black phosphorus.

White phosphorus is formed as a soft, waxy solid whenever phosphorus vapour is condensed; structurally it contains tetrahedral P_4 units held together by van der Waals' forces. Since the P–P–P bond angles are 60° in each of these P_4 units there is a considerable amount of strain, and this makes itself felt in the high chemical reactivity of this allotrope.

White phosphorus very slowly changes into the red variety in the course of many years; this change can be accelerated by raising the temperature, and commercially this allotrope is made from white phosphorus by heating in the absence of air to 270°C for several days. Its structure is not known with certainty but it is certainly macromolecular; it is denser than white phosphorus.

The third allotrope, black phosphorus, can be obtained by subjecting white phosphorus to high pressures at 200°C in the absence of air. It too is macromolecular, with each phosphorus atom surrounded by three more atoms. It is an electrical conductor resembling graphite in this respect and also in its flakiness. Its density is higher than that of red phosphorus.

Only white and red phosphorus are normally encountered in the laboratory.

19.6.4 Phosphorus Halides

Phosphorus trichloride, PCl_3

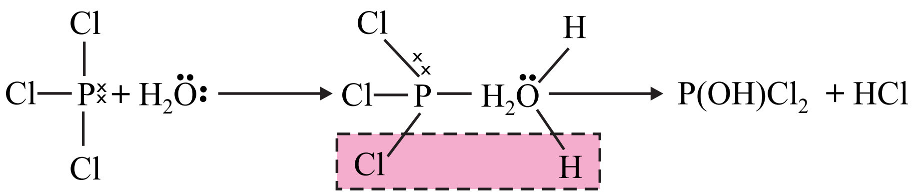
The trichloride, is obtained by passing chlorine over white phosphorus. The phosphorus burns with a pale green flame and phosphorus trichloride distils and is condensed as a colourless liquid. Since it is attacked by air and water, it is necessary to displace the air from the apparatus with a stream of carbon dioxide and to include a soda-lime drying tube.

$$P_4(s) + 6C1_2(g) \longrightarrow 4PC1_3(l)$$

Phosphorus trichloride is readily hydrolysed by water to phosphonic acid, H_3PO_3, and hydrogen chloride:

$$PCl_3(1) + 3H_2O(1) \longrightarrow H_3PO_3(aq) + 3HCl(g)$$

It is thought that the reaction takes place in stages, with the formation of complexes in which the oxygen atom of a water molecule is attached to the phosphorus atom (expansion of the octet can occur since the phosphorus atom has *d* orbitals available):



$$P(OH)C1_2 + H_2O \longrightarrow P(OH)_2Cl + HCl$$

$$P(OH)_2Cl + H_2O \longrightarrow P(OH)_3 + HCl$$

Phosphorus trichloride reacts with many compounds containing the –OH group, and it is used in organic chemistry for the preparation of acid chlorides and alkyl chlorides, e.g.

$$3CH_3COOH(l) + PCI_3(1) \longrightarrow 3CH_3COC1 + H_3PO_3$$

$$3C_2H_5OH(1) + PC1_3(1) \longrightarrow 3C_2H_5C1 + H_3PO_3$$

It readily combines with oxygen and chlorine (reversibly), the phosphorus atom increasing its covalency from three to five:

$$2PC1_3(1) + O_2(g) \longrightarrow \underset{\text{phosphorus trichloride oxide}}{2POCl_3(l)}$$

$$PC1_3(1) + Cl_2(g) \rightleftharpoons PCl_5(s)$$

Phosphorous pentachloride, PCl_5

Phosphorus pentachloride is prepared by passing chlorine through a flask into which phosphorus trichloride is dripping. Since it dissociates into the trichloride and chlorine very readily, the experiment is conducted in an ice-cooled apparatus.

$$PCl_3(l) + Cl_2(g) \rightleftharpoons PC1_5(s)$$

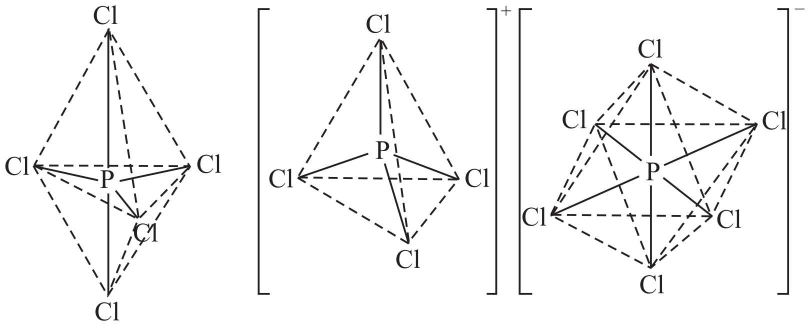
Like the trichloride it is attacked by compounds containing the hydroxyl group, e.g.

$$PCl_5(s) + H_2O(l) \longrightarrow POCl_3(1) + 2HCl(g)$$

$$POCl_3(1) + 3H_2O(l) \longrightarrow H_3PO_4(aq) + 3HCl(g)$$

$$CH_3COOH(l) + PCl_5(s) \longrightarrow CH_3COCl(1) + POC1_3(1) + HCl(g)$$

In the vapour state the phosphorus pentachloride molecule has a trigonal bipyramidal structure (Fig. 18.10(a)); in the solid state it is ionic, having the structure $(PCl_4^+)(PCl_6^-)$ (Fig. 18.10(b)).



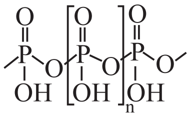
(a) (b)

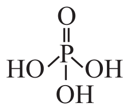
Table 19.10: The acids of phosphorus and their properties.

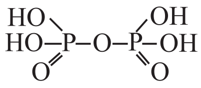
Acid	Nature	Preparation		Anion
H_3PO_2 or $H_2P(OH)O$	crystalline	white P_4 + alkali	$H_2PO_2^-$	strongly reducing
hypophosphorous	white solid	$H_2PO_2^-$ + H_2	hypophosphite	monobasic pK = 2
H_3PO_3 or $HPO(OH)_2$	deliquescent	P_2O_3 or PCl_3	H_2PO3^-, HPO_3^{2-}	reducing,but slow
orthophosphorous	colourless	+ H_2O	phosphite	dibasic pK_1 = 2
	solid			pK_2 = 6

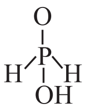
H_3PO_4	white solid	$P_2O_5 + H_2O$	$H_2PO_4^-$, HPO_4^{2-},	not oxidizing, tribasic
Orthophosphoric			PO_4^{3-} phosphate	
$H_2P_2O_4$	colourless	heat phosphates	$P_2O_7^{4-}$	tetrabasic $pK_{-1} = 2$
pyrophosphoric	solid	or phosphoric acid	pyrophosphate	
	linear and	heating	$[PO_3(PO_3)n{\bullet}OPO_3]^{(4+n)-}$	
	cyclic	phosphates	$[PO_3]_n^{n-}$	
	anions		polyphosphate	

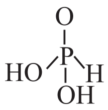
Structure of Oxyacids of Phosphorous


$[HPO_o]_n$
metaphosphoric acid


H_3PO_4
orthophosphoric acid


$H_1P_2O_7$
pyrophosphoric acid


H_3PO_2
hypophosphorous acid


H_3PO_3
orthophosphorous acid

INTEXT QUESTIONS 19.3

1. Does 'NH_4OH' exist as a molecule?
2. What is the bond angle in NH_3 molecule?
3. What is the state of hybridization of N in NH_3?
4. Draw the structure of pyrophosphoric acid.
5. What happen when PCl3 is treated with water.

WHAT YOU HAVE LEARNT

- General Characteristic of Group 13, 14, & 15.
- Method of preparation of boric acid. The acidic nature and structure of boric acid.
- Method of preparation and uses of borax.

- Methods of preparation and uses of boron trifluoride and diborane.
- The Lewis character and use of boron trifluoride.
- Preparation of aluminium trichloride and its structure
- Method of preparation of alums and uses
- The comparison of diamond and graphite.
- The structure and properties of carbon monoxide, carbon dioxide and silicon dioxide and their uses.
- Comparison of the hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride.
- Preparation and uses of silicon carbide (carborundum)
- Preparation and uses of silicons.
- Preparation and structure of silicates and zerolites.
- Preparation, properties and uses of nitrogen.
- Structure of oxides of nitrogen.
- The methods of preparation, properties and uses of ammonia and nitric acid.
- Structure of the oxides and oxoacids of nitrogen Halides of phosphorus Allotropic forms of phosphorus oxyacids of phosphorous.

TERMINAL QUESTIONS

1. Why is boric acid not a protonic acid?
2. Discuss the structure of boric acid.
3. Draw the Lewis structure of CO and CO_2 molecules.
4. Why does BF_3 act as a Lewis acid?
5. What is catenation ? Why does carbon show catenation but silicon does not?
6. Compare the structure of CO_2 and SiO_2.
7. Describe briefly the Haber process for the manufacture of ammonia.
8. Why is graphite a conductor of electricity but diamond is not?
9. Explain different types of silicones.
10. Explain ortho and pro silicates.

ANSWERS TO INTEXT QUESTIONS

19.1

1. (i) $B(OH)_3$ (ii) $Na_2B_4O_7.10H_2O$
2. $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$
3. $NM(SO_4)_2 .12H_2O$

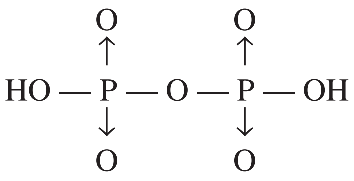
   Where N = monovalent large cation like K^+ or NH_4^+ and M = trivalent cation like Al^{3+}, Fe^{3+}, Cr^{3+}
4. Al_2Cl_6
5. (i) as a flux, for glazing pottery and tiles : in the manufacture of optical and borosilicate glasses.
   (ii) as an antiseptic, as a food preservative, for making enamels
   (iii) as a catalyst in Friedel-Crafts reaction.
6. Monoprotonic
7. Due to the formation of oxide layer

19.2

1. Hardness and conducting nature. Diamond : hard, non conducting; graphite: soft, conducting.
2. sp^3 in diamond and sp^2 in graphite.
3. Covalent
4. sp^3
5. $SiCl_4$, as silicon can accept electron pair in its d-orbitals from water molecule.
6. CO_2
7. $SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$

19.3

1. No. Nitrogen cannot increase its covalency beyond 4.
2. 107^0.
3. sp^3
4.



$$HO - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{P}} - O - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{P}} - OH$$

5. $PCl_3 + 3H_2O \longrightarrow H3PO_3 + 3HCl$

20

p-BLOCK ELEMENTS AND THEIR COMPOUNDS - II

You have already studied the chemistry of the elements of Groups 13, 14 and 15. In this lesson we shall deal with the chemistry of the elements of Groups 16, 17 and 18.

OBJECTIVES

After reading this lesson you will be able to:

- explain general characteristics of group 16, 17 and 18 elements;
- classify oxides into acidic, basic and amphoteric types;
- recall the preparation, properties and uses of ozone;
- explain the allotripic forms of sulphur;
- describe the manufacture of sulphuric acid;
- proporation properties and uses of SO_2;
- structure oxoacids of sulphur;
- recall the characteristics of hydrogen halides (HF, HCl);
- list the oxides and oxoacids of chlorine;
- compare the acidic behaviour of oxoacids of chlorine;
- write the general molecular formulae of interhalogen compounds;
- discuss the structures of interhalogen compounds;
- list a few chloro fluoro carbons and explain their uses and their effect on environment;
- explain the unreactive nature of noble gases;
- explain occurance of noble gases;
- recall the preparation of xenon fluorides and oxides, and
- illustrate the structures of XeF_2, XeF_4, XeF_6, XeO_3 and XeO_4.

20.1 SOME CHARACTERISTIC PROPERTIES OF THE ELEMENTS OF GROUP 16

The Group 16 elements show the usual gradation from non metallic to metallic properties with increasing atomic number that occurs in any periodic group. Oxygen and sulphur are non-metals, selenium and tellurium are semiconductors and polonium is metallic.

These elements can enter into chemical combination and complete their octets by gaining two electrons to form the 2 di-valent ions, e.g. O^{2-}, S^{2-}, except for polonium which is too metallic, or by forming two covalent bonds, e.g. the hydrides H_2O, H_2S, H_2Se, H_2Te and H_2Po.

The two heavier members of this group can form the 4-valent cation X^{4+} e.g. there is evidence of the presence of Te^{4+} ions in the dioxide TeO_2 and of Po^{4+} ions in the dioxide, PoO_2, and sulphate, $Po(SO_4)_2$.

Because sulphur, selenium, tellurium and polonium have vacant *d* orbitals that can be utilised without too great an energy change, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, the valencies of sulphur in H_2S, SCl_4 and SF_6 are two, four and six, respectively. Oxygen, in common with other first row members of the Periodic Table, cannot expand its octet.

Oxygen exists in the form of discrete molecules, a double bond uniting two oxygen atoms together, $O = O$. The atoms of the other Group elements do not form multiple bond to themselves and sulphur, in particular, shows a strong tendency to catenate, puckered S_8 rings being present in rhombic and monoclinic sulphur. There are two forms of selenium corresponding in structure to rhombic and monoclinic sulphur in which Se_8 rings, are present. These forms, however, are readily converted into a 'metallic' form of the element called grey selenium. As far as is known, there is only one form of tellurium which has the same structure as grey selenium. Polonium is truly metallic.

Table 20.1: Properties of Group 16 elements

	Atomic Number.	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm	M.P. /°C	B.P. /°C
O	8	2.6 $Ls^2 2s^2 2p^4$	0·074	0.140	–218	–183
S	16	2.8.6 $....2s^2 2p^6 3s^2 3p^4$	0.104	0.184	119^*	445
Se	34	2.8.18.6 $....3s^2 3p^6 3d^{10} 4s^2 4p^4$	0·117	0.198	217^{**}	685

Te	52	2.8.18.18.6 ....$4s^2 4p^6 4d^{10} 5s^2 5p^4$	0.137	0·221	450	990
Po	84	2.8.18.32.18.6 .... $5s^2 5p^6 5d^{10} 6s^2 6p4$	0.140		254	960

* For monoclinic sulphur

** For grey selenium

Occurrance

Oxygen occurs in the atmosphere to the extent of about 21 per cent by volume (23 per cent by weight). This percentage remains constant by the operation of the highly complex process termed photosynthesis, The element is present in the earth's crust and in water to the extent of about 50 per cent and 89 per cent by weight, respectively. It is an essential ingredient in all living matter and is of prime importance in respiration and combustion processes. Although only slightly soluble in water, enough oxygen dissolves to support marine life.

Preparation of dioxygen

1. By heating chlorates, nitrates and permanganates :

$$2KC1O_3 + (MnO_2) \rightarrow 2KC1 + 3O_2 + (MnO_2)$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

2. By heating metallic oxides :

$$2HgO \rightarrow 2Hg + O_2$$

$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

$$2Ag_2O \rightarrow 4Ag + O_2$$

3. By the action of bleaching powder on hydrogen peroxide solution.

$$Ca(OCl)_2 \rightarrow 2H_2O_2 \rightarrow CaCl_2 + 2H_2O + 2O_2$$

4. By the action of hot and concentrated sulphuric acid on potassium dichromate or potassium permanganate.

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

5. By the action of sodium peroxide on water.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

Manufacture of oxygen :

(1) By the electrolysis of water : Where ever electricity is cheap, oxygen can be conveniently manufactured by the electrolysis of water. The electrolysis is carried out in iron tanks containing a solution of caustic soda or acidified water. The electrodes used are of iron or nickel and a current of 1000 amperes is used. Oxygen is evolved at the anode and hydrogen at the cathode. A porous diaphragm is used to prevent the mixing of hydrogen and oxygen.

2. From air : When barium oxide is heated in air to about 500°C it combines with oxygen to form barium peroxide, BaO_2. On raising the temperature to about 800°C, the peroxide decomposes to give barium oxide and oxygen.

$2BaO + O_2 \rightarrow 2BaO_2$ (at about 500°C)

$2BaO_2 \rightarrow 2BaO + O_2$ (at about 800°C)

It can be prepared from liquified air. There is a difference of 12·5°C in the boiling points of oxygen and nitrogen ; oxygen boils at –182.5°C while nitrogen at –195°C. This difference is sufficient to enable a separation of the two by fractional distillation.

PROPERTIES

Physical

Oxygen is colourless, tasteless and odourless gas and slightly heavier than air. Liquid oxygen is pale blue with boiling point–182·5°C and specific gravity 1·2386 at –210°C. The liquid solidifies on cooling at –218·4°C to a light blue solid. It is somewhat soluble in water (about 3%), a fact responsible for aquatic life. Liquid oxygen is paramagnetic and is strongly attracted by magnet.

Chemical

Oxygen is essentially required for the burning or combustion of substances in air. Combustion is much more brilliant in pure oxygen. Molecular oxygen combines directly with most of the elements, exceptions being the inert gases, the halogens, gold and platinum. It is a fairly good oxidising agent in aqueous solution and directly oxidises Cr^{2+}, Fe^{2+}, SO_3^{2-}, V^{2+}, and Ti^{3+} ions. The gas oxidises some substances at ordinary temperature, some at higher temperatures, and some in presence of suitable catalysts.

(i) *At ordinary temperatures* : Phosphorus is slowly oxidised in oxygen to form its pentoxide at room temperature. The oxidation of alkali and alkaline earth metals and the rusting of iron take place at ordinary temperatures. Nitric oxide quickly combines with oxygen to give brown fumes of dioxide, NO_2

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$4Na + O_2 \rightarrow 2Na_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

One of the most important reactions of molecular oxygen is the one that takes place between the inspired oxygen and the protein haemoglobin at the body temperature.

(ii) *At higher temperatures* : At higher temperatures it combines with almost all the elements to form compounds with the evolution of much energy. The binary compounds so obtained are known as oxides.

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

$$C + O_2 \rightarrow CO_2$$

$$2Mg + O_2 \rightarrow 2MgO$$

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

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

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Uses : Apart from it being an absolute necessity for terrestrial life, oxygen is used for many industrial purposes.

(i) *For the production of high temperature flames* :

Oxy-hydrogen flame = 2400°—2800°C

Oxy-coal gas flame = 2200°—2400°C

Oxy-acetylene flame = 3100°—3300°C

Oxy-acetylene flame produces hydrogen which prevents the oxidation of metals during welding or cutting.

$$C_2H_2 + O_2 \rightarrow 2CO + H_2$$

(ii) *For medical purposes* : When even a patient is unable to breath sufficient air, oxygen is given for artificial respiration.

(iii) *In iron and steel industry* : Addition of oxygen to the air blast in blast furnace raises the temperature required for the manufacture of iron and steel.

(iv) *In rocket fuels* : Liquid oxygen is an important constituent of the fuels used in rockets.

(v) It is also used for bleaching purposes.

(vi) Oxygen is used as an oxidizing agent in laboratories and in many industries.

20.2 OXYGEN AND SULPHUR

Oxygen and sulphur are the first two members of the 16th group of the periodic table.

In this section you will learn about some compounds of oxygen and sulphur including environmentally important ozone and industrially important sulphuric acid.

20.2.1 Classification of Oxides

The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. An understanding of the nature of an oxide provides a clue to the nature of the element which forms the oxide. Depending upon the acid-base behaviour of the oxides, they can be classified into the following categories.

(1) Acidic oxides

(2) Basic oxides

(3) Amphoteric oxides

(4) Neutral oxides

(1) Acidic Oxides : Acidic oxides are generally formed by non-metallic elements and some metals in higher oxidation states. Examples of some acidic oxides are CO_2, SO_2, N_2O_5, P_4O_{10}, Cl_2O_7, Mn_2O_7, etc. These oxides combine with water to form acids whereas with alkalies they form salt and water.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

However, certain acidic oxides do not form acids on reacting with water. But they react with alkalies to form salt and water, e.g., SiO_2

$$SiO_2 + 2\,NaOH \longrightarrow \underset{\textbf{Sodium silicate}}{Na_2SiO_3} + H_2O$$

(2) Basic oxides : Metals combine with oxygen to form basic oxides. The basic oxides react with acids to form salt and water.

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

The oxides of the metals of Groups 1 and 2 react with water to form hydroxides known as **alkalies**.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

(3) Amphoteric oxides : Almost all metallic oxides are basic oxides. But some metallic oxides show the characteristics of both acidic as well as basic oxides, i.e., they react with both acids as well as bases to form salt and water. Such oxides are called *amphoteric oxides*. The oxides of zinc, aluminium, lead and tin are amphoteric in nature.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2NaOH \longrightarrow \underset{\textbf{Sodium zincate}}{Na_2ZnO_2} + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\textbf{Sodium aluminate}}{2NaAlO_2} + H_2O$$

(4) Neutral oxides : These oxides are neither acidic nor basic. Examples are carbon monoxide, (CO), nitric oxide (NO), nitrous oxide (N_2O) , etc.

INTEXT QUESTIONS 20.1

1. Give one example each of basic oxide, acidic oxide and amphoteric oxide.
2. Classify the following oxides into acidic, basic or amphoteric oxides : K_2O, SiO_2, SO_2, FeO, Al_2O_3, ZnO, CrO_3.
3. Give chemical equations to illustrate the amphoteric behaviour of ZnO.
4. Name the compound formed when the oxide of an element of Group 1 or 2 reacts with acid?
5. Oxygen is a gas but Sulphur is solid why?

20.3 OZONE

Ozone is an allotrope of oxygen. You must have learnt through the media that ozone layer depletion in the upper atmosphere is causing a great environmental concern. We will now study the preparation, properties, importance and uses of ozone.

Ozone is formed around high voltage electrical installations. Traces of ozone are formed in forests by decay of organic matter. Ozone is prepared industrially by Siemen's ozonizer.

Siemens ozonizer : In this apparatus metal electrodes are used to produce an electric field. Two coaxial glass tubes are fused together at one end. The outer tube has an inlet for oxygen or air and an outlet for ozone (with oxygen or air). The inner side of the inner tube and the outer side of the outer tube are coated with tinfoil (T). These are connected to the terminals of an induction coil or high voltage transformer.

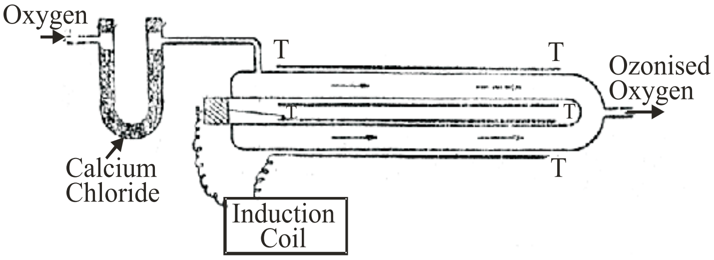
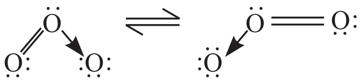


Fig. 20.1 : *Siemen's Ozonizer*

Pure, dry and cold oxygen or air is passed through the inlet in a slow current. Electrical energy is absorbed and about 5 to 10 percent of oxygen is converted into ozone.

All rubber and cork fittings are avoided because of the corrosive action of ozone on these materials.

Structure of Ozone : Ozone forms a V-shaped molecule. The central O atom uses sp^2 hybrid orbitals for bonding. The structure of ozone can be explained as a resonance hybrid of the following two structures, (oxygen – oxygen bond length 128 pm and bond angle 117º)



Properties of Ozone

(a) **Physical :** Ozone is a pale blue gas which turns into blue liquid at 161K. At 80K it freezes to a violet black solid. It is ten times as soluble in water as oxygen.

(b) **Chemical :** The chief characteristic of ozone is that it is unstable and that it gives energy loaded nascent oxygen. Its reactions are closely paralleled to the reactions of hydrogen peroxide.

1. *Catalytic decomposition :* Ozone in aqueous solution decomposes on standing. Above 373K ozone decomposes very rapidly. Even at ordinary temperature it decomposes in the presence of chlorine, bromine, nitrogen pentoxide and other acidic oxides and oxides of transition metals.

$$2O_3 \rightarrow 3O_2.$$

2. *Oxidizing properties :* In the presence of reducing agents ozone furnishes active atom of oxygen according to the equation.

$$O_3 \rightarrow O_2 + O$$

In most of the reactions, oxygen gas is liberated as the reduction product from ozone.

(i) It oxidizes black lead sulphide to white lead sulphate

$$4O_3 + PbS \rightarrow PbSO_4 + 4O_2$$

(ii) Ozone oxidizes acidified ferrous sulphate to ferric sulphate

$$O_3 + 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

(iii) Ozone oxidizes moist sulphur to sulphuric acid and phosphorus to phosphoric acid.

$$3O_3 + S + H_2O \rightarrow H_2SO_4 + 3O_2$$

$$5O_3 + 2P + 3H_2O \rightarrow 2H_3PO_4 + 5O_2$$

(iv) *Ozone tails mercury.* Normally mercury does not stick to glass but if exposed to ozone it loses its convex meniscus and leaves a ‘tail’ or trail of minute droplets on a glass surface. This is supposed to be due to the formation of stray molecules of mercurous oxide which affect the surface only.

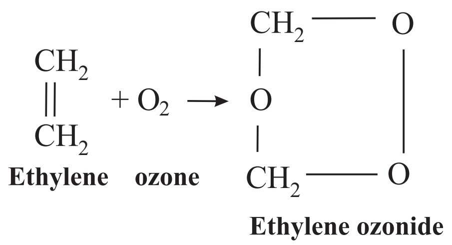
$$O_3 + 2Hg \rightarrow Hg_2O + O_2$$

The ‘tailing’ effect can be removed by washing with dilute acid.

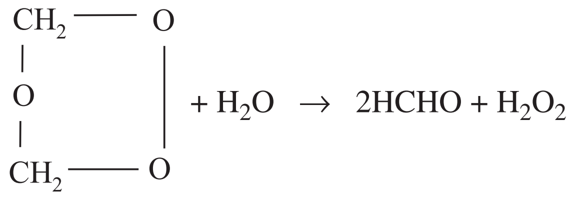
(v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.

$$O_3 + 3SnCl_2 + 6HCl \rightarrow 3SnCl_4 + 3H_2O$$

3. *Ozonides :* All unsaturated organic compounds combine with ozone to form unstable compounds called ozonides, e.g.



The ozonides are hydrolysed by water to give aldehydes or ketones or both.



This technique is called *ozonolysis* and is widely used to locate the position of double bond in organic compounds.

Uses of Ozone

Some of its applications are given below :

1. ***Water purification :*** Small ozone-air plants function as part of the water purification set up. Ozone is a powerful germicide and it can purify a water spray effectively; it does not produce the unwanted by-products that other sterilizing agents do.
2. ***Air purification :*** Ozone is also used to purify air in tunnels, wells and crowded subways and cinema halls.
3. ***Refining oils :*** Vegetable oil and ghee go rancid when stored for a long time. This is caused by bacterial growth in the small water content present in them. If ozone is bubbled through oil, all such growing organisms are destroyed and we get purified oil.
4. ***Dry bleach*** **:** Ozone is also used to bleach waxes, flour, sugar and starch. Hydrogen peroxide, which produces water and other agents which act only in solution, cannot be used in these cases.
5. ***In Industry and in the Laboratory*** **:** It is widely used in certain organic preparation. Its use in ozonolyses has already been mentioned.

INTEXT QUESTIONS 20.2

1. What are ozonides? What happens when an ozonide is hydrolysed?
2. Write the reactions which occur when ozone reacts with (i) ferrous sulphate (ii) stannous chloride
3. Which is more soluble in water, oxygen or ozone?
4. Draw the structure of ozone molecule, O_3.
5. What is meant by “tailing of mercury”? How is it removed?

20.4 ALLOTROPIC FORMS OF SULPHUR

Rhombic sulphur

This is the form of sulphur normally encountered and consists of S_8 structural units packed together to give crystals whose shape is shown in Fig. Fairly large crystals can be obtained by allowing a solution of powdered sulphur in carbon disulphide to evaporate slowly; they are yellow, transparent and have a density of 2.06 g cm^{-3}.

Notes

Monoclinic sulphur

This form of sulphur is formed when molten sulphur is allowed to crystallise above 95.6°C. Like rhombic sulphur it consists of S_8 structural units, but these are arranged differently in the crystal lattice. The temperature of 95.6°C is the transition temperature for sulphur; below temperature, 95.6°C rhombic sulphur is the more stable allotrope and above it, the monoclinic sulphur is the more stable of the two forms.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.6°C} \text{Monoclinic sulphur}$$

Crystals of monoclinic sulphur are amber-yellow in colour and have a density of 1.96 g cm^{-3}.

Amorphous sulphur

A number of forms of sulphur which possess no regular crystalline form can be obtained when sulphur is liberated in chemical reactions, e.g. by the action of dilute hydrochloric acid on a solution of sodium thio-sulphate:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g) + S(s)$$

Plastic sulphur

This is obtained, by pouring nearly boiling sulphur into cold water. It consists of a completely random arrangement of chains of sulphur atoms which, when stretched, align themselves parallel to each other. On standing, it slowly changes over into rhombic sulphur, as the chains of sulphur atoms break and reform the S_8 cyclic units.

The action of heat on sulphur

Both rhombic and monoclinic sulphur melt to a yellow liquid. Owing to the conversion of rhombic to monoclinic sulphur, and also to possible variations in the percentage of allotropes of liquid sulphur formed, the melting points are not sharp: rhombic sulphur melts at approximately 113°C and monoclinic sulphur at approximately 119°C. As the temperature rises the colour of the liquid darkens until it is nearly black, and it becomes viscous. At about 200°C the viscosity begins to fall and at its boiling point of 445°C the liquid is again mobile.

There is still some doubt concerning a complete explanation of these observations, but a recent theory runs as follows: as the sulphur melts the S_8 rings begin to open and it is possible that other ring systems containing possibly six and four sulphur atoms form. It is known, however, that sulphur chains begin to form and reach their maximum chain length at 200°C, corresponding to the maximum viscosity of liquid sulphur. The decrease in viscosity of liquid sulphur that occurs above 200°C is explained as being due to the breakdown of these long chains and the re-formation of S_8 rings. Sulphur vapour contains S_8 rings, together

Notes

with smaller fragments such as S_8, S_4 and S_2. At very high temperatures atomic sulphur is formed.

Sulphur Dioxide, SO_2

Priestley (1774) obtained this gas by heating mercury with concentrated sulphuric acid and called it *vitriolic acid air.* Lavoisier in 1777 determined its composition.

It is found in volcanic gases and in traces in the air of towns; being derived from the burning of iron pyrites present as impurity in coal.

Preparation : *By the reduction of sulphuric acid ' It is* prepared in the *laboratory* by reducing hot concentrated sulphuric acid with copper turnings.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

The gas is dried by concentrated sulphuric acid, calcium chloride or phosphorus pentoxide and is collected by upward displacement of air or over mercury.

The reduction of concentrated sulphuric acid may also be brought about by heating with mercury, silver, sulphur or charcoal.

$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + 2H_2O + SO_2$$

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$$

$$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

$$C + 2H_2SO_4 \longrightarrow 2H_2O + CO_2 + 2SO_2$$

(ii) By the action of aliab on sulphites or bisulphites :

$$NaHSO_3 + 2H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$$

(iii) By burning sulphur or sulphide ores :

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

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

(iv) Now-a-days, it is commercially prepared by heating *anhydrite* ($CaSO_4$) with clay and coke at 1200°C.

$$2CaSO_4 + C \longrightarrow 2CaO + 2SO_2 + CO_2$$

Properties : It is a colourless gas with an odour well known as that of burning sulphur. It is $2\frac{1}{4}$ times as heavy as air. It is easily liquified by compression (2.5 atm at 15°C) or by cooling in a freezing mixture. Its critical temperature is 157.15°C and critical pressure 77.65 atm. The liquid is colourless, boils at —10°C and freezes at –75'5°C. Liquid sulphur dioxide is a good solvent for iodine, sulphur, phosphorus etc.

(i) Incombustible and non-supporter of combustion : It is incombustible and does not support combustion in the ordinary sense, but heated potassium, magnesium, tin and iron burn in the gas.

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

(ii) Decomposition : When heated to 1200°C it decomposes to an appreciable extent giving sulphur trioxide and sulphur.

$$3SO_2 \longrightarrow 2SO_2 + S$$

It is also decomposed in a strong beam of light.

(iii) Acidic nature : It is highly soluble in water forming unstable sulphurous acid.

$$HO_2 + SO_2 \rightleftharpoons H_2SO_3$$

Being an acidic oxide, it combines with basic oxides forming sulphites, e.g.,

$$CaO + SO_2 \longrightarrow CaSO_3$$

(*iv*) It combines with certain metallic dioxides yielding metallic sulphates, e.g.,

$$PbO_2 + SO_2 \longrightarrow PbSO_4$$

(*v*) It combines with oxygen and with chlorine

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(vi) Reducing properties : In presence of moisture, it acts as a fairly strong reducing agent. For example

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 2H_2$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + H_2SO_4$$

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + 2HCl + H_2SO_4$$

$$2KIO_3 + 5SO_2 + 2H_2O \longrightarrow 2I_2 + 2KHSO_4 + 3H_2SO_4$$

$$Hg_2(NO_3)_2 + SO_2 + 2H_2O \longrightarrow 2Hg + 2HNO_3 + 3H_2SO_4$$

(vii) Oxidising properties : It also acts as an oxidising agent. Such as

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

$$C + SO_2 \longrightarrow CO_2 + S$$

(viii) Bleaching properties : In presence of moisture it acts as a mild bleaching agent;

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

the nascent hydrogen bleaches the colour of the substance. Thus sulphur dioxide bleaches by *reduction*

Uses:

It is used

(i) in the manufacture of sulphuric acid.

(ii) in the refining of sugar and kerosene oil.

(iii) in fumigation and in preserving fruits since it has antiseptic properties.

(iv) As a refrigerant in the liquid state.

(v) For bleaching delicate articles such as wool, silk and straw.

(vi) In the preparation of sodium and calcium bisulphites which are used in paper industry.

(viii) As an *antichlor* in removing excess chlorine from bleached materails.

20.5 SULPHURIC ACID

The most important compound of sulphur is sulphuric acid. Sulphuric acid or the 'oil of Vitriol' was known to the alchemists and their predecessors. Before the coming of Chamber process in the last century, it was obtained by heating hydrated sulphates.

Manufacture : The two main processes used for the manufacture of sulphuric acid are (1) Lead Chamber process and (2) the Contact process. Nowadays sulphuric acid is mostly manufactured by Contact process.

Manufacture of sulphuric acid by Contact Process involves the following steps:

(i) Sulphur dioxide gas is produced by burning sulphur in air or by roasting of pyrites.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(ii) Sulphur dioxide produced is then freed from dust and other impurities such as arsenic compounds.

(iii) The purified sulphur dioxide in then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to 720K.

$$2SO_2 + O_2 \xrightarrow[720K]{V_2O_5} 2SO_3$$

The plant is operated at a pressure of 2 atmosphere and temperature of 720K.

(iv) The sulphur trioxide gas in then absorbed in conc. H_2SO_4 to form *oleum* ($H_2S_2O_7$). If SO_3 is directly dissolved in water, a highly corrosive mist of sulphuric acid is formed.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

(v) Oleum is then diluted with water to obtain sulphuric acid of desired strength.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulphuric acid obtained from the contact process is about 96-98% pure.

Properties of Sulphuric acid

(i) Physical properties : Pure sulphuric acid is a thick colourless oily liquid. Its melting point is 283.5K. Concentrated sulphuric acid dissolves in water with the liberation of a large amount of heat. While preparing dilute H_2SO_4, water must not be added to conc. H_2SO_4. Dilute sulphuric acid is prepared by adding conc. H_2SO_4 slowly and with constant stirring to water. If water is added to the acid, the heat produced is so large that it could throw out drops of sulphuric acid and burn you.

Chemical properties : The most important properties of sulphuric acid are its oxidizing and dehydrating properties.

(i) **Oxidizing properties :** Hot concentrated sulphuric acid acts as an oxidizing agent and oxidizes metals, non-metals and compounds.

Oxidation of metals.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2$$

Oxidation of non-metals

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

Oxidation of compounds

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

$$8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$

$$3H_2S + H_2SO_4 \longrightarrow 4S + 4H_2O$$

Dehydrating properties : Conc. H_2SO_4 is a strong dehydrating agent. It removes water of crystallization from copper sulphate (which is blue in colour) and turns it to white colour.

$$\underset{\textbf{blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\text{conc. } H_2SO_4} \underset{\textbf{white}}{CuSO_4}$$

It also removes water from carbohydrates leaving behind, black mass of carbon.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

Uses of Sulphuric Acid

Sulphuric acid is known as the king of chemicals. It is practically used in every industry. It is used in the manufacture of fertilizers, paints and pigments, detergents, plastics and fibres, etc.

Notes

Structures of Oxyacids of Sulphur

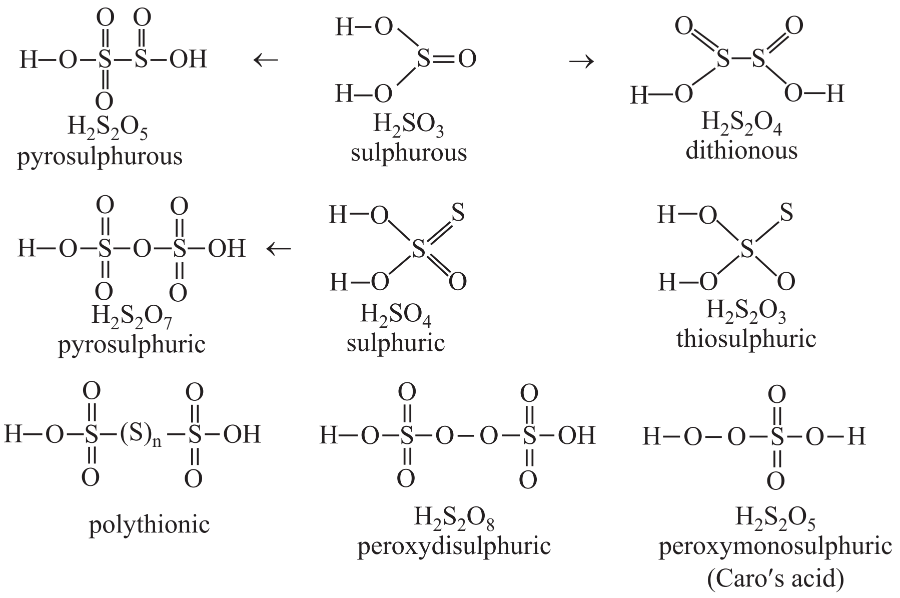


Fig. 20.2: *Some oxyacids of sulphur.*

INTEXT QUESTIONS 20.3

1. Write a reaction to show the

   (i) oxidizing property of sulphuric acid

   (ii) dehydrating property of sulphuric acid

2. In the manufacture of sulphuric acid by Contact process, SO_3 is dissolved in conc. H_2SO_4 and not in water. Why?

3. Write the reaction that takes place in the presence of a catalyst in the contact process.

20.6 SOME GENERAL CHARACTERISTICS PROPERTIES OF ELEMENTS OF GROUP 17

All members of Group 17 are non-metallic, although there is the usual increase in ‘metallic’ character with increasing atomic number, e.g. dipyridine iodine nitrate can be written as $[1(\text{pyridine})_2]^+NO_3^-$, containing the 1^+ ion as part of a complex. Fluorine and chlorine are gases, bromine is a volatile liquid, and iodine is a dark shiny coloured solid. Astatine is radioactive and very short-lived; what little chemistry that has been carried out with this element has employed tracer techniques.

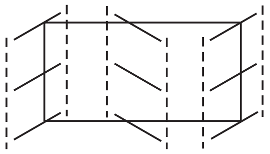
These elements can enter into chemical combination and complete their octets by gaining one electron to form the 1-valent ion, e.g. F^-, Cl^-, etc., and by forming one covalent bond, e.g. the elements themselves F_2, Cl_2, Br_2, I_2 and their hydrides HF, HCl, HBr and HI.

Because chlorine, bromine and iodine have easily accessible *d* orbitals available, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, iodine shows valencies of 1, 3, 5 and 7 respectively in the compounds ICI, ICI_3, IF_5 and IF_7. Like nitrogen and oxygen (the first members of Group 15 and 16, respectively), fluorine cannot expand its octet and is thus restricted to a covalency of 1.

The molecules of the halogens are diatomic with only weak van der Waals' forces operating between the individual molecules; however, in the case of iodine these forces are sufficiently strong to bind the iodine molecules into a three dimensional lattice (fig.). This structure is easily broken down on heating, and in fact, iodine sublimes at one atmosphere pressure if warmed gently.

The Structure of iodine

There is sufficient difference between fluorine and chlorine in chemical behavior to warrant a separate treatment of the former element. Chlorine, bromine and iodine are treated as a group.



|—| Molecules in plane of paper
|- -| Molecules below and above the plane of the paper

Table 20.2: Physical properties of Group 17 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
F	9	2.7 $\ldots 1s^2 2s^2 2p^5$	0.072	0.136	–220	–188
Cl	17	2.8.7 $\ldots 2s^2 2p^6 3s^2 3p^5$	0.099	0.181	–101	–34.7
Br	35	2.8.18.7 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^5$	0.114	0.195	–7.2	58.8
I	53	2.8.18.18.7 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^5$	0.133	0.216	114	184
At	85	2.8.18.32.18.5 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^5$				

Occurrence

Fluorine and chlorine are fairly abundant, bromine and iodine less so,. Fluorine is present mainly in the insoluble fluorides of calcium: calcium fluoride; cryolite, Na_3AlF_6; and fluoroapatite, $3Ca_3(PO_4)_2$. CaF_2. Sea-water contains the chlorides, bromides, and iodides, of sodium, potassium, magnesium, and calcium. The deposits of dried-up seas contain these compounds, mainly the chlorides, for example sodium chloride and carnallite, $KCl{\cdot}MgCl_2$. Certain forms of marine life concentrate iodine in their systems.

20.7 FLUORINE AND CHLORINE

Fluorine and chlorine are the first two members of Group17. Fluorine is the most electronegative element. In this section we shall briefly learn about fluorine and chlorine and study in some detail about the hydrogen halides, oxides and oxoacids of chlorine and interhalogen compounds.

Fluorine is extremely difficult to prepare owing to its highly reactive nature. It is the strongest chemical oxidizing agent hence cannot be prepared by oxidation of fluoride ions. It is prepared by the electrolysis of potassium hydrogen fluoride (KHF_2) in anhydrous hydrogen fluoride. Hydrogen fluoride undergoes electrolytic dissociation.

$$2HF \rightarrow F_2 + H_2$$

The fluorine obtained is contaminated with hydrogen fluoride which may be removed by passing the gas over solid NaF.

Fluorine is a pale yellow gas which fumes in air.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2.$$

Fluorine is highly reactive. It combines with various metals and non-metals to form fluorides. With hydrogen halides it acts as an oxidizing agent, e.g.

$$2HX + F_2 \rightarrow 2HF + X_2 \text{ (X = Cl, Br or I)}$$

Fluorine is widely used in the preparation of fluorinated hydrocarbons which in turn find various uses in industry.

Chlorine is usually prepared by the oxidation of chlorides by strong oxidizing agents, such as MnO_2, $KMnO_4$.

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

On a large scale chlorine is obtained as a by product in the electrolysis of sodium chloride.

Chlorine is a greenish yellow gas and can be liquified by pressure alone at room temperature, It is quite reactive and forms chlorides of metals and nonmetals when reacted with them. It also oxidizes ammonia to nitrogen

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

Large quantities of chlorine are used in bleaching industry and in the manufacture of plastics, synthetic rubbers, antiseptics and insecticides.

20.7.1 Hydrogen Halides and Hydrohalic Acids

The hydrogen halides under consideration are HF, HCl, HBr and HI. The bond distance H–X increases with the size of halogen atom. The bond also becomes more covalent and less ionic. Since the bond length increases, the hydrogen halide in aqueous solution loses hydrogen ion more easily with increasing size of halogen, and the acid strength increases in the order $HF < HCl < HBr < HI$

The aqueous solutions of hydrogen halides are, in general, known as hydrohalic acids or simply halogen acids (hydrofluoric, hydrochloric hydrobromic, and hydroiodic acids)

Preparation of Hydrogen Halides

Industrially HF is made by heating CaF_2 with strong H_2SO_4.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Hydrogen chloride is made by heating a mixture of NaCl and conc. H_2SO_4 at 423 K.

$$NaCl + H_2SO_4 \xrightarrow{423\ K} HCl + NaHSO_4$$

$$NaCl + NaHSO_4 \xrightarrow{823\ K} HCl + Na_2SO_4$$

High purity HCl is made by the direct combination of the elements (H_2 and Cl_2)

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Phosphoric acid is used to make HI

$$H_3PO_4 + NaI \longrightarrow HI + NaH_2PO_4$$

HBr is made by a similar method. Also we use red phosphorus for making HBr and HI

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

$$PBr_3 + 6H_2O \longrightarrow 6HBr + 2H_3PO_3$$

$$2P + 3I_2 \longrightarrow 2PI_3$$

$$2PI_3 + 6H_2O \longrightarrow 6HI + 2H_3PO_3$$

Properties of the Halogen Halides

- HF is a liquid at room temperature (b.p. 293 K), whereas HCl, HBr and HI are gases.
- The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds between the F atom of one molecule and the H atom of another molecule (Fig. 20.2).

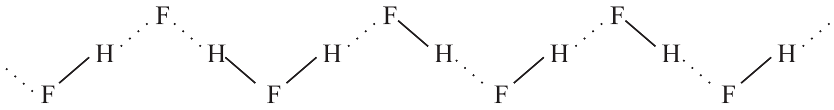


Fig. 20.2 : *Hydrogen bonded chain in HF*

In the gaseous state, the hydrogen halides are essentially covalent. In the aqueous solutions they ionize to form ions but HF ionizes to a very small extent

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

The bond dissociation energy of the hydrogen halides follow the order HF>HCl>HBr>HI.

The stability of hydrogen halides to thermal decomposition therefore decreases in the order HF > HCl > HBr > HI. The acid strength of the acids increases in the order HF < HCl < HBr < HI. The aqueous solution known as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid possess the usual property of acids, e.g. they react with bases to form salts and water and with metals to form salts and hydrogen.

Uses of Hydrogen Halides

Hydrogen fluoride is used to prepare certain fluorides mainly fluorocarbons or freons. It is also used in etching glass and in removing sand from casting. Hydrogen chloride is primarily used for preparing chlorides. Large quantities of hydrochloric acid are used in the manufacture of aniline dyes and for cleaning iron before galvanization. Hydrogen bromide and hydrogen iodide are used to prepare bromide and iodide salts. Hydrogen iodide is also used as a reducing agent in organic chemistry.

20.7.2 Oxides and Oxoacids of Halogens

There are several compounds containing halogen and oxygen. Oxygen is less electronegative than fluorine, hence the compounds of oxygen with fluorine are known as oxygen fluorides (e.g. OF_2). Other halogens are less electronegative than oxygen. Thus they are known as halogen oxides. Only the oxides of chlorine are important and they are described here.

Oxides of chlorine The main oxides are listed below :

Chlorine monoxide, Cl_2O

Chlorine dioxide, ClO_2

Chlorine hexoxide, Cl_2O_6

Chlorine heptoxide, Cl_2O_7

Chlorine monoxide, Cl_2O, is prepared by passing chlorine over freshly prepared mercury (II) oxide

$$2\,Cl_2 + 2\,HgO \longrightarrow Cl_2O + HgO.\,HgCl_2$$

It is a pale yellow gas which decomposes violently on heating and dissolves in water forming hypochlorous acid. $Cl_2O + H_2O \longrightarrow 2HOCl$

It is a powerful oxidizing agent.

Chlorine dioxide, ClO_2, is prepared by the action of concentrated sulphuric acid on potassium chlorate

$$KClO_3 + H_2SO_4 \longrightarrow \underset{\textbf{chloric acid}}{HClO_3} + KHSO_4.$$

$$3HClO_3 \longrightarrow \underset{\textbf{perchloric acid}}{HClO_4} + 2ClO_2 + H_2O$$

It is an orange gas and explosive in nature.

Chlorine hexoxide, Cl_2O_6, is prepared by the action of ozone on chlorine at low temperature. It is a red liquid and dissolves in alkalies producing chlorate and perchlorate

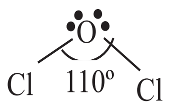
$$Cl_2O_6 + 2OH^- \longrightarrow ClO_3^- + ClO_4^- + H_2O$$

Chlorine heptoxide, Cl_2O_7, is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263 K.

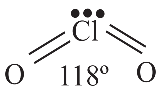
$$P_4O_{10} + 4HClO_4 \longrightarrow 4\,HPO_3 + 2Cl_2O_7$$

It is a colourless oil which explodes on heating or striking.

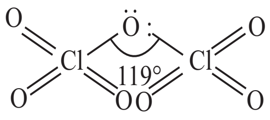
The structures of chlorine oxides are as follows :



Cl_2O



ClO_2



Cl_2O_7

Notes

Oxoacids of chlorine

Chlorine forms four oxoacids, HOCl, HOClO, $HOClO_2$ and $HOClO_3$

Hypochlorous acid, HOCl is known only in solution - It is prepared by shaking chlorine water.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

Its salt NaOCl is used as a bleaching agent.

Chlorous acid, HOClO is also known in solution, certain chlorite salts of alkali and alkaline earth metals are known in solid state, e.g., $NaClO_2, 3H_2O$. The acid is prepared by the action of barium chlorite with sulphuric acid.

$$\underset{\textbf{barium chlorite}}{Ba\,(ClO_2)_2} + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$$

Chloric acid, $HOClO_2$ is prepared by the action of barium chlorate with sulphuric acid.

$$\underset{\textbf{barium chlorate}}{Ba\,(ClO_3)_2} + H_2SO_4 \longrightarrow HClO_2 + BaSO_4$$

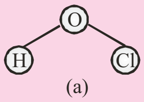
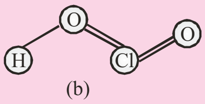
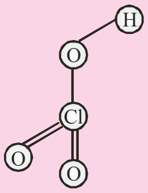
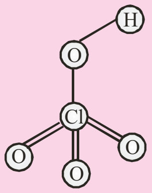
Perchloric acid, $HOClO_3$, is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure

$$\underset{\textbf{potassium perchlorate}}{2KClO_4} + H_2SO_4 \longrightarrow 2HClO_4 + K_2SO_4$$

It is a colourless oily liquid and combines vigonously with water forming hydronium perchlorate ($H_3O^+ ClO_4^-$). It is one of the strong acids. It is also an oxidizing agent.

The oxoacids of chlorine are listed in the following table showing their structures.

Table 20.3 : Oxoacids of chlorine

Name	Hypochlorous acid (a)	Chlorous acid (b)	Chloric acid (c)	Perchloric acid (d)
Formula of oxoacid	HOCl	HOClO	$HOClO_2$	$HOCl\ O_3$
Oxidation state of chlorine	+1	+3	+5	+7
Structure	 (a)	 (b)	 (c)	 (d)

Notes

The acid strength of the oxoacids of chlorine increases as the number of O-atoms present in the acid increases.It is because oxygen is more electronegative then chlorine. As the number of O atoms bonded to the Cl atom increases, more electrons will be pulled away more strongly from the O–H bond. As a result the O–H bond will be weakened. Thus $HOClO_3$ require the least energy to break the O–H bond and form H^+. Thus, HOCl is a very weak acid whereas $HOClO_3$ is the strongest acid, thus the acid strength increases in the order.

$$HOCl < HOClO < HOClO_2 < HOClO_3$$

20.7.3 Chlorofluorocarbons (CFC)

Chlorofluorocarbons are the compounds of carbon where chlorine and fluorine are substituted for hydrogen in saturated hydrocarbons e.g. CCl_2F_2, $CFCl_3$, $C_2F_4Cl_2$ etc. These compounds have very high capacity to retain heat. It is believed that the capacity to retain heat is about 10,000 times more than that of carbon-dioxide. Thus these molecules are capable of cooling other systems by taking away their heat.

Chlorofluorocarbons are also termed as **freons**. About 5 thousand metric tonnes of CFC's are still being produced in our country annually. In addition to their usage as aerosols, solvents, foam blowing agents and refrigerants, they are also known to cause environmental hazard. CFCs react with protective ozone layer in the stratosphere, thus causing perforation through which radiations from outer sphere enter our atmosphere and cause damage to our life systems. The destruction of ozone layer is termed as *ozone depletion* and it is creating a ozone hole.

20.7.4 Interhalogen Compounds

The halogens form a series of mixed binary compounds called the interhalogens. These compounds are of the type XX', XX_3', XX_5', and XX_7'. The compounds of the type XX' are known for all combinations. Compounds of XX_3', and XX_5' types are known for some, and of XX_7' type only IF_7 is known.

Preparation

The interhalogen compounds can be prepared by direct reaction between the halogens. They can also be prepared by the action of a halogen on a lower interhalogen.

$$Cl_2 + F_2 \text{ (equal volumes)} \xrightarrow{473K} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess } F_2) \xrightarrow{573K} 2ClF_3$$

$$I_2 + 5F_2 \xrightarrow{293K} 2IF_5$$

$$I_2 + 7F_2 \xrightarrow{523-573K} 2IF_7$$

INTEXT QUESTIONS 20.4

1. Name the most electronegative halogen.
2. Name the halogen that can react with an inert gas.
3. Write a chemical reaction used for the laboratory preparation of chlorine.
4. Arrange the hydroacids of halogens in the decreasing order of their strength.
5. What group of carbon compounds is supposed to cause ozone depletion.

20.8 THE NOBLE GASES

The gaseous elements helium, neon, argon, krypton, xenon and radon constitute the 18 group of the periodic table. Because of their low, abundance on the earth, they have been called *rare gases*, and due to their chemical inertness, they have been called inert or noble gases. With the discovery that some of them can form compounds under suitable conditions, we no longer refer to them as inert gases. All of them, except helium, have the closed shell, np^6, configurations Helium has the ls2 configuration. The electronic configuration accounts for their high degree of chemical inertness in ordinary chemical reactions.

Occurrence

All the noble gases, except radon, are present in atmosphere. The relative percentages of the noble gases in dry air are given in the following table.

Table 20.4: Relative Abundance of 18 Group Elements in Dry Air

Element	Percentage
Helium (He)	5.2×10^{-4}
Neon (Ne)	1.8×10^{-3}
Argon (Ar)	9.3×10^{-1}
Krypton (Kr)	1.1×10^{-4}
Xenon (Xe)	8.7×10^{-6}
Radon (Rn)	–

In addition helium is present up to l0 per cent in natural gas. It also results from the decay of certain radioactive elements and is found in some uranium minerals. Radon is produced in the radioactive decay of radium.

Properties

The outer electronic configuration and the general trends in properties of the noble gases are summarised in Table

Table 20.5: Relative Abundance of 18 Group Elements in Dry Air

***	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	[He] $2s^22p^6$	[Ne] $3s^33p^6$	[Ar] $3d^{10}4s^24p^6$	[Kr] $4d^{10}5s^25p^6$	[Xe] $4f^{14}5d^{10}6s^26p^6$
Atomic radii	**120**	**160**	**190**	**200**	**220**	**-**
Ionic radii/kJmol^{-1}	2372	2080	1520	1351	1170	1037
Election gain enthalpy/kJmol^{-1}	48	116	96	96	77	68
Den (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
M.P.	-	24.6	83.8	115.9	161.3	202
B.P.	4.2	27.1	87.2	119.7	165.0	211
Fraction in Air (% volume) radiactive	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

20.9 COMPOUNDS OF NOBLE GASES

The group 18 of the periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon. These elements are termed as **'noble gases'**. The name noble gases implies that they tend to be unreactive and are reluctant to react just like noble metals. Except helium which has 2 electrons and forms a complete shell $1s^2$, the other elements of the group have a closed octet of electrons in their outer shell $ns^2\ np^6$. This electronic configuration is very stable and the ionization energies of the atoms of these elements are very high. Therefore, the atoms of noble gases have a little tendency to gain or lose electrons. Hence these elements exhibit lack of chemical reactivity.

The first compound of noble gases was made by Neil Bartlett in 1962 by the reaction of xenon with PtF_6. Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar do not form any compounds whereas Kr does form KrF_2. Radon is a radioactive element and all its isotopes have very short half lives.

Xenon Compounds

Xenon reacts with fluorine to form binary fluorides, XeF_2, XeF_4 and XeF_6. The product formed depends on the temperature and xenon-fluorine ratio. Thus

$$\underset{(2:1\ \text{ratio})}{Xe + F_2} \xrightarrow{873\ \text{K},\ 1\ \text{bar}} XeF_2(s)$$

$$\underset{(1:5\ \text{ratio})}{Xe + 2F_2} \xrightarrow{873\ \text{K},\ 7\ \text{bar}} XeF_4(s)$$

$$\underset{(1:20\ \text{ratio})}{Xe + 3F_2} \xrightarrow{573\ \text{K},\ 60\ \text{bar}} XeF_6\ (s)$$

XeF_2, XeF_4 and XeF_6 are all white solids. They readily sublime at 298 K. They differ in their reactions with water

XeF_2 dissolves in water and undergoes slow hydrolysis in water.

$$2\ XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

XeF_4 and XeF_6 react with water violently to give xenon trioxide and hydrogen fluoride.

$$6\ XeF_4 + 12H_2O \longrightarrow 4\ Xe + 2XeO_3 + 24\ HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeF_6 on partial hydrolysis gives, xenon oxofluorides.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

The xenon fluorides react with strong Lewis acids to form complexes.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+\ [PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+\ [SbF_6]^-$$

XeF_6 may also act as a fluoride accepter from fluoride ion donors to form fluoroxenate anions.

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^-\ (M = Na, K, Rb, Cs)$$

XeO_3 can be prepared by hydrolysis of XeF_6

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeO_4 can be prepared by the reaction of barium peroxenate with conc. sulphuric acid

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

Structure of Xenon compounds

The structures and shapes of the common xenon fluorides and oxides are shown below. The shapes of these molecules can be explained in terms of VSEPR theory which you have already learnt in chemical bonding.

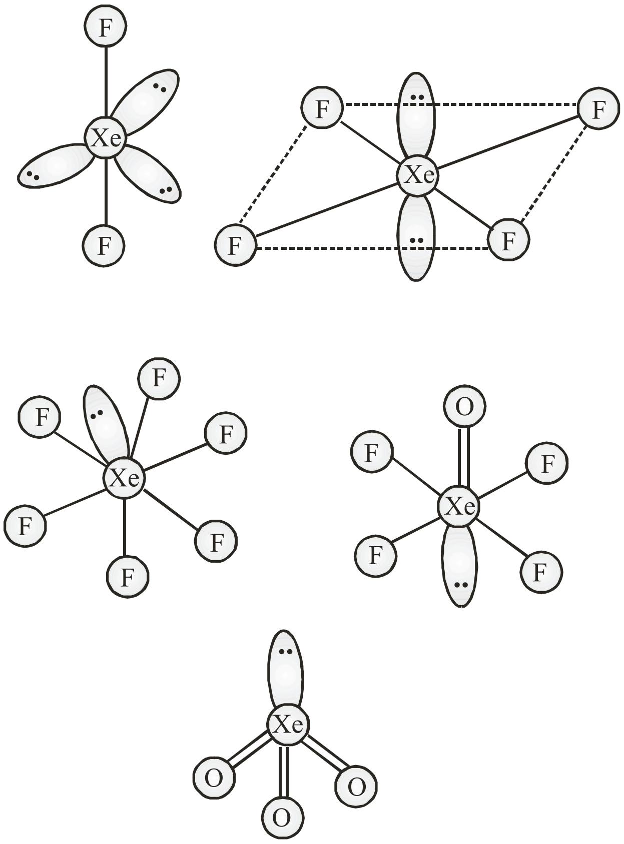


Fig. 20.3 : *The structures of* XeF_2, XeF_4, XeF_6, XeO_3 *and* $XeOF_4$

WHAT YOU HAVE LEARNT

- General characterics of the elements o Group 16, 17 & 18.
- While sulphur exists as S_8 molecules oxygen exists as O_2 molecules. Both these elements form divalent anions however sulphur also shows +4 and +6 oxidation state. Oxygen and sulphur are non-metals of group number 16.
- The binary compounds of oxygen with other elements are known as oxides. The oxides can be classified as : acidic oxides, basic oxides and amphoteric oxides.
- Ozone, an allotrope of oxygen is prepared by Siemen's ozonizer.
- Allotropic forms of Sulphur preparation properties and uses of SO_2.

Notes

- Sulphuric acid displays strong acid character and possesses oxidizing and dehydrating properties.
- Structure of oxoacids of Sulphur.
- Chlorine forms a number of oxoacids : HOCl, $HClO_2$, $HClO_3$ and $HClO_4$.
- The binary compounds of halogens with one another are called inter halogen compounds.
- Halogens are placed in group number 17 of the periodic table. All members of the group are very reactive. They show variable oxidation states. Halogens react with other halogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids.
- Fluorochlorocarbons are called freons which decompose ozone and are therefore environmentally hazardous.
- Occurance of noble gases.
- Helium, neon, argon, krypton, xenon and radon are the members of Group number 18 and are collectively called noble gases.
- Xenon is known to react with fluorine to form XeF_2, XeF_4 and XeF_6.

TERMINAL EXERCISES

1. Which one of the following oxides can react with an acid as well as with an alkali : SO_2, CaO, ZnO, MgO?
2. Write two oxides which do not react with either acids or alkalies. Which type of oxides are they?
3. Is ozone an allotrope of oxygen? Which is more soluble in water oxygen or ozone?
4. What is the state of hybridization of the central oxygen atom in O_3 molecule?
5. Why does ozone tail mercury?
6. Which property of ozone makes it useful for bleaching?
7. Write the conditions which are required to convert SO_2 to SO_3 in the manufacture of sulphuric acid by contact process.
8. What is oleum?
9. Why is sulphuric acid known as king of chemicals?
10. Write down the structure of oxo acids of sulphur.

11. Fluorine never acts as a central atom in any interhalogen compounds. Why?
12. Draw the structure of BrF_4^- .
13. Arrange the hydrogen halides in order of their acid strength in aqueous solution.
14. Why is F_2O not known as fluorine oxide? Instead it is known as oxygen fluoride, OF_2.
15. Which is the strongest acid among the oxoacids of chlorine and why?
16. What happens when XeF_4 reacts with SbF_5? Write the complete equation for the reaction.

ANSWERS TO INTEXT QUESTIONS

20.1

1. Basic oxide : CaO; acidic oxide : SO_2 ; amphoteric oxide : ZnO.
2. Acidic oxide : SiO_2, SO_2, CrO_3

   Basic oxide : K_2O, FeO

   Amphoteric oxide : Al_2O_3, ZnO

3. $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

   $ZnO + 2NaOH \longrightarrow Na_2Zn\,O_2 + H_2O$

4. An oxide of group 1, K_2O and of Gr 2 BaO

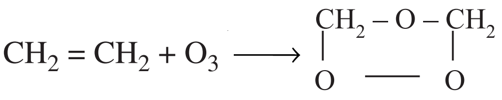
   $K_2O + 2HCl \longrightarrow 2KCl + H_2O$

   $BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$

   Oxygen has multiple bonds but sulphur has single bond.

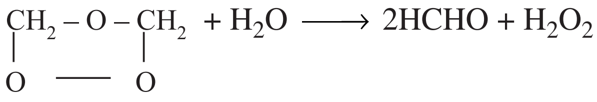
20.2

When ethene combines with O_3, an ozonide is formed, thus



$$CH_2 = CH_2 + O_3 \longrightarrow \begin{array}{ccccc} CH_2 & - & O & - & CH_2 \\ | & & & & | \\ O & & \text{——} & & O \end{array}$$

On hydrolysis it gives HCHO,

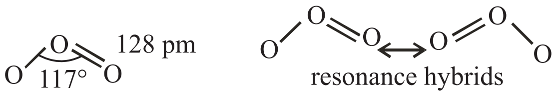


$$\begin{array}{ccccc} CH_2 & - & O & - & CH_2 \\ | & & & & | \\ O & & \text{——} & & O \end{array} + H_2O \longrightarrow 2HCHO + H_2O_2$$

2. (i) $2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$

   (ii) $3SnCl_2 + O_3 + 6HCl \longrightarrow 3\,SnCl_4 + 3H_2O$

3. Ozone is 10 times more soluble than O_2.

4. 

5. Mercury loses its convex meniscus and leaves a "tail" or a trail of minute droplets on a glass surface when exposed to ozone. This is due to the formation of mercurous oxide. The tailing effect can be removed by washing the mercury with a dilute acid.

20.3

1 (i) Oxidizing property of conc. H_2SO_4

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(ii) Dehydrating property : It removes water from sugar

$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11\,H_2O$

2. A corrosive mist of sulphuric acid is formed.

3. $2SO_2 + O_2 \xrightarrow[720\text{ K}]{V_2O_5} 2SO_3$

20.4

1. Fluorine
2. Fluorine
3. $2\,NaCl + 3H_2SO_4 + MnO_2 \longrightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2$
4. HI > HBr > HCl > HF
5. Chlorofluorocarbons (or freons)

21

d-BLOCK AND f-BLOCK ELEMENTS

You have already learnt in lesson 3 on periodic classification, that each period (except the first period) of the periodic table starts with the filling of *ns* subshell and ends with the filling of *np* subshell (*n* is the principal quantum number and also the number of the period). The long form of the periodic table is based on the filling of electrons in various levels in order of increasing energy as given by Aufbau principle. In the fourth period, filling of the 4th shell commences with the filling of 4*s* subshell followed by 3*d* and 4*p* subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number (3*d*) starts getting filled instead of the expected subshell 4*p*. This group of elements that occurs in between the *4s* and *4p* elements is referred to as *3d* elements or elements of first transition series (see periodic table). *4f* Series consist of 14 members from Ce to Lu (At. No. 58-71), where the penultimate subshell, *4f* subshell is filled up. They have general electronic configuration [Xe] $4f^{1\text{-}14}\,5d^{1,2}\,6s^2$. La is also included in this series: it is the prototype for the succeeding 14 elements. In this lesson you will study more about these elements and also about the preparation, properties and uses of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$).

OBJECTIVES

After reading this lesson, you will be able to:

- define transition metals and write their electronic configuration;
- list the general and characteristic properties of the transition elements;
- explain the properties of 3d transition series: metallic character, variable oxidation state, variation in atomic and ionic radii, catalytic properties,

coloured ions, complex formation, magnetic properties, interstitial compounds and alloy formation;

- recall the preparation of potassium permanganate from pyrolusite ore;
- write the chemical equations illustrating the oxidizing properties of $KMnO_4$ in acidic, alkaline and neutral media (acidic: $FeSO_4$, SO_2, alkaline: KI and ethene, neutral: H_2S and $MnSO_4$);
- recall the preparation of potassium dichromate from chromite ore;
- write the oxidation reactions of potassium dichromate with SO_2 and ferrous sulphate in acidic medium;
- write electronic configuration of lanthanoides (4f-elements) and actinoids (5f-elements);
- explain oxidation states of lanthanoids and actinoids;
- explain the comparison between lanthanoids and actinoids;
- explain lanthanoide contraction.

21.1 OCCURRENCE OF THE FIRST-ROW TRANSITION METAL ELEMENTS

Only a few of the transition elements occur in free state e.g. Au and Pt. Most of the these elements occur as oxides, sulphides and carbonates in nature. (See module 6, lesson 18)

21.2 *d*-BLOCK ELEMENTS

d-Block elements occupy the middle portion of the periodic table i.e. between *s*- and *p*- block elements. They include elements from groups 3 to 12. In these elements the outermost shell contains one or two electrons in their outer most i.e, ns orbital but the last electron enters into the inner d-subshell i.e. (*n*-1) *d* orbital. The elements of the *d-block* are metallic in nature. Their general characteristic properties are intermediate between those of the s-block elements, on one hand and of the p-block elements on the other. We can say that *d*-block elements represent a change (or transition) from the most electropositive *s*-block elements to the least electropositive *p*-block elements and are, therefore, also named as transition elements.

Transition elements are elements in which the *d* subshell is partially filled either in atomic state or in ionic state.

There are four series of transition elements in the periodic table. The first transition series begins with scandium (At. No. 21) and ends at copper (At. No. 29) whereas the second, third and fourth series begin with yttrium (At. No. 39), lanthanum (At. No. 57) and actinium (At. No. 89) and end at silver (At. No. 47), gold (At. No. 79) and at the element having atomic number 112 (a synthetic element), respectively. These series are also referred to as *3d, 4d, 5d* and *6d* series, respectively. It may be noted that although elemental copper, silver and gold as well as Cu^{1+}, Ag^{1+} and Au^{1+} have a d^{10} configuration but Cu^{2+} has a $3d^9$, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration and that is why these elements are classified as transition elements. On the other hand, zinc, cadmium and mercury do not have partially filled *d* subshell either in the elemental state or in any of their common ions. These elements, therefore, are not transition elements. However, zinc, cadmium and mercury are often considered along with *d*- block elements.

INTEXT QUESTIONS 21.1

1. What are transition elements?
2. How many elements comprise the first transition series? Give names of all these elements.
3. Whereas copper is a transition element, zinc is not included amongst transition elements. Explain.
4. Although Cu^+, Ag^+ and Au^+ have d^{10} configuration but Cu, Ag and Au are transition elements, why?

21.2 ELECTRONIC CONFIGURATION

The general electronic configuration of transition elements is $(n-1)\ d^{1-10}\ ns^{1-2}$. The (n-1) stands for inner shell and the *d*-orbitals may have one to ten electrons and the *s*-orbital of the outermost shell (n) may have one or two electrons. It is observed from the Fig. 21.1 that 4*s* orbital ($l = 0$ and $n = 4$) is of lower energy than 3*d* orbitals ($l = 2$ and $n = 3$) upto potassium (At. No.19). The energy of both these orbitals is almost same in case of calcium (At. No. 20), but the energy of 3*d* orbitals decreases with further increase of nuclear charge and becomes lower than *4s,* and 4*p,* (in case of scandium At. No.21). Thus after filling of 4*s* orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to 3*d* orbital instead of 4*p,* as the former is of lower energy than the latter. This means that 21st electron enters the underlying principal quantum level with n = 3 rather than the outermost level with n = 4 which started filling at potassium (At. No.19), the first element of the fourth period. In the case of next nine elements following calcium, the incoming electron is filled in the *d*- subshell. Since half filled and completely filled subshells are stabler than the one in which one electron is short, an electron gets transferred from 4*s* to 3*d* in case of the elements with atomic number 24 and 29. Consequently, configuration of chromium and copper have only one 4*s* electron (Table 21.1).

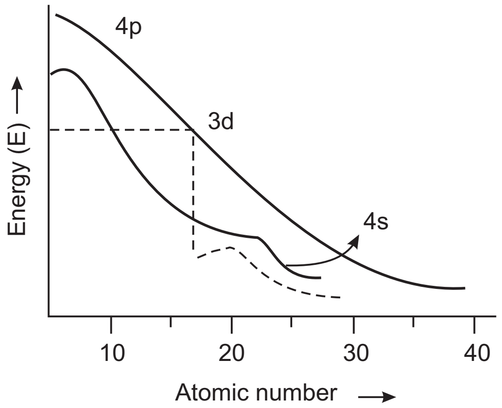


Fig. 21.1 : *Variation of energy of orbitals vs atomic number*

Table 21.1: Electronic configuration of first series(or 3*d*) transition elements

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
Titanium	Ti	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
Vanadium	V	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Manganese	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

As can be seen, in case of zinc, the 30th electron goes to 4*s* level and not 3*d* level which is already full. Thus by definition, zinc cannot be called a member of *d*block elements. Besides, no compound of zinc is known to have a partially filled 3*d* subshell. Thus it does not fit into the definition of a transition element either. Hence zinc cannot be rightly called either a *d*-block element or transition element. However, zinc and other members of group 12, viz., cadmium and mercury are discussed along with 3*d,* 4*d* and 5*d* transition elements for the sake of convenience.

It is important to understand at this point, the process of ionization (i.e. oxidation) of transition elements. From what has been said above regarding filling of the orbitals, it is logical to conclude that during ionization electrons should be lost first from the (n-1) *d* subshells and then from the 4*s* level. This, however, is not the case. The reason for the deviation from the expected behavior is that once the filling of the *3d* subshell commences at scandium (At. No.21) energy of 3*d* subshell decreases and becomes lower than that of 4*s* subshell. Consequently, on ionization, the first row transition elements lose electrons from the 4*s* subshell followed by the loss from 3*d* level. For example vanadium (Z = 23) has electronic configuration V= $[Ar]3d^3\,4s^2$ and the electronic configuration of V^{2+} is $[Ar]3d^3$, Similarly electronic configuration of V^{3+} and V^{4+} are $[Ar]3d^2$ and $[Ar]3d^1$, respectively. In some cases, however, for example scandium, all the electrons beyond the core of 18 electrons are lost in single step. It is important to note that though 3*d* orbitals are of higher energy than 4*s* orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of same energy.

INTEXT QUESTIONS 21.2

1. Write the general electronic configuration of transition elements.
2. Write down the electronic configuration of the following elements in ground state: Sc, Cr, Cu and Zn.
3. Write down the electronic configuration of the following ions: Cr^{3+}, Ti^{4+}, Ni^{3+} and Cu^{2+}.
4. Why the electronic configuration of Mn^{2+} is $3d^5$ and not $3d^2\,4s^2$?

21.3 PHYSICAL PROPERTIES

Some important physical properties of *d*-block elements are listed in Table 21.2. Like *s*-block elements, *d*-block elements are also metals. But properties of these elements are markedly different from those of *s*-block elements. The interesting feature of the chemistry of transition elements is that similarities in the properties of transition elements are much more marked as compared to those in *s*-block. Almost all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture. All the transition elements have typical metallic structure except mercury, which is liquid at room temperature.

Transition elements show high melting and boiling points. They typically melt above 1356 K. It is due to the small atomic size and strong interatomic bonding. All the transition elements are hard except zinc, cadmium and mercury. They show high enthalpy of atomization (Table 21.2). Densities of transition elements are very high as compared to those of s-block elements. The density of the elements in a given transition series increases across a period and reaches a maximum value at groups 8,9 and 10. This trend can be explained on the basis of small radii and close packed structure of the elements.

Atomic radii

The radii of the elements decrease from left to right across a row in the transition series until near the end, then the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra electrons are added. The

Table 21.2: Some important physical properties of 1st transition series

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$	$3d^{10} 4s^2$
Atomic radius (pm)	160	146	131	125	129	126	125	124	128	133
Ionic radius M^{2+} (pm)	–	90	88	84	80	76	74	72	69	79
Ionic radius M^{3+} (pm)	81	76	74	69	66	64	63	63	–	–
Crystal structure	fcc	hcp	bcc	bcc	bcc	bcc,fcc	hcp,fcc	fcc	fcc	hcp
Density (g ml^{-1})	3.1	4.5	6.1	7.2	7.6	7.9	8.7	8.9	8.9	7.1
Melting point (K)	1817	1998	2173	2148	1518	1809	1768	1726	1356	693
Boiling point (K)	3003	3533	3723	2138	2423	3273	3173	3003	2868	1179
Stable oxidation states	+3	+4	+3,+4,+5	+2,+3,+6	+2,+3,+4,+7	+2,+3	+2,+3	+2	+1,+2	+2
Ist ionization enthalpy (kJ mol^{-1})	632	659	650	652	717	762	758	736	745	906
Electronegatively	1.3	1.5	1.05	1.6	1.05	1.8	1.8	1.8	1.8	1.6
Heat of fusion (kJ mol^{-1})	15.9	15.5	17.6	13.8	14.6	15.3	15.2	17.6	13.0	7.4
Heat of vaporization (kJ mol^{-1})	338.9	445.6	443.6	305.4	224.7	353.9	389.1	380.7	338.9	114.6
Reduction potential $(E^0)M^{2+}/M(V)$	–	–1.63	–1.20	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76

d-orbital electrons shield the nuclear charge poorly. Thus the effective nuclear charge increases and, therefore, electrons are attracted more strongly, hence contraction in size occurs. There is an increase in atomic radii with increase in atomic number in a given group, for example Ti (146 pm), Zr (157 pm) and Hf (157 pm). The very close similarity between the radii of elements of second and third transition series is a consequence of the filling of the 4*f*- subshell (causing lanthanide contraction which you will study later in this lesson).

INTEXT QUESTIONS 21.3

1. Why do transition elements show higher melting and boiling points?
2. Why do the radii of transition elements decrease along a period?
3. Why do transition elements show higher density as compared to *s*-block elements?

21.4 CHARACTERISTIC PROPERTIES

These are the properties shown only by transition elements. On the basis of these properties transition elements can be distinguished from *s* and *p*-block elements.

21.4.1 Variable Oxidation States

s-block, *d*-block and *f*-block elements show positive oxidation states (except H which shows –1 oxidation state also) whereas, most of the *p*-block elements show both positive and negative states. The number of electrons used for bonding by an electropositive element is equal to its positive oxidation state. A characteristic property of *d*-block elements is their ability to exhibit a variety of oxidation states in their compounds. This is due to the fact that for bonding, in addition to ns electrons, these elements can use inner (n-1)d electrons as well because of very small difference in their energies. Thus, depending upon the number of d electrons involved in bonding, different oxidation states arise. The lowest oxidation state is usually equal to the number of *s*-electrons present (except Sc). For example, copper has an electronic configuration of $3d^{10}4s^1$ and shows oxidation state of + 1 besides the usual oxidation state of +2. The highest oxidation states are observed in compounds with fluorine and oxygen, which are the two most electronegative elements. The different oxidation states of elements of the first transition series are given below:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*
+3	(+2)	+2	+2	+2	(+1)	(+1)	(+1)	+1	(+1)
	+3	+3	+3	(+3)	+2	+2	+2	+2	+2
	+4	+4	+4	+4	+3	+3	(+3)	(+3)	
		+5	(+5)	(+6)	+6	(+4)	(+4)		
			+6	+7					

(* Given for comparison only.) Here the rare oxidation states are given in parentheses.

An examination of the common oxidation states given above, reveals the following:

Except for scandium, the most common oxidation state of 3*d* elements is +2 which arises from the loss of two 4*s* electrons. This means that after scandium, *d* orbitals become more stable than *s* orbital. Compounds having oxidation states +2 and +3 of these elements have ionic bonds whereas bonds are essentially covalent in higher oxidation states. For example, in case of permanganate ion, MnO_4^-, bonds formed between manganese and oxygen are covalent. Considering the acid base character of the oxides, it can be inferred that increase in oxidation state leads to decrease in basic character of the oxide and vice-versa. For example, MnO is a basic oxide whereas Mn_2O_7 is an acidic oxide.

Since transition metals exhibit multiple oxidation states, their compounds in the higher oxidation states are strong oxidizing agents as they tend to accept electrons and come to stable lower oxidation states.

21.4.2 Magnetic Properties

Substances possess two types of magnetic behaviour, either diamagnetism or paramagnetism. Diamagnetic substances are either repelled or remain unaffected by an applied magnetic field whereas, paramagnetic substances are attracted towards the applied field.

There is a strong co-relation between the magnetic behaviour, electronic configuration and oxidation state. Paramagnetism arises due to the presence of unpaired electrons (Table 21.3). Since transition metal ions generally contain unpaired electrons a large number of transition metal ions exhibit paramagnetic behavior.

Magnetic moment (μ) of paramagnetic material can be calculated (in B.M., Bohr Magneton) by using the expression: $\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

For example, Ni^{2+} ion has two unpaired electrons (i.e. n = 2). The magnetic moment can be calculated as $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ B.M The mangentic moments of some 3*d* metals ions are listed in Table 21.3 which shows that greater the number of unpaired electrons, greater is the magnetic moment.

Table 21.3 : Magnetic moments of some ions of the transition elements:

Ion	Electronic configuration	Number of unpaired electrons	Calculated magnetic moments (B.M.)
Sc^{3+}	$3d^0$	0	0
Ti^{3+}	$3d^1$	1	1.73

Ti^{2+}	$3d^2$	2	2.83
V^{2+}	$3d^3$	3	3.87
Cr^{2+}	$3d^4$	4	4.90
Mn^{2+}	$3d^5$	5	5.92
Fe^{2+}	$3d^6$	4	4.90
Co^{2+}	$3d^7$	3	3.87
Ni^{2+}	$3d^8$	2	2.83
Cu^{2+}	$3d^9$	1	1.73

Compounds containing Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+} and Cu^{+} ions are diamagnetic since these ions do not contain any unpaired electron.

21.4.3. Colour of Ions and Compounds

Most of the compounds of *d*-block elements are coloured or they give coloured solution when dissolved in water (Table 21.4). This property of transition elements is in marked contrast to that of the *s*- and *p*-block elements, which often yield white compounds. In transition metal compounds colour is generally associated with incomplete (n-1) *d* subshell of the transition metal. When white light, which has colored constituents, interacts with a substance, a part of it is absorbed by the substance. For example, if red portion of white light is absorbed by a substance, it would appear blue (the complementary colour of red). This is observed in case of copper sulphate solution. Since most compounds of transition elements are coloured, there must be energy transition, which can absorb some of the energy of the visible light. The colour of transition metal ions containing unpaired electrons is attributed to electronic transitions from one energy level to another in the *d*-subshell. In these metals the energy difference between the various *d*-orbitals is in the same order of magnitude as the energies of the radiation of white light (A. = 4000 to 8000 A).

Table 21.4 : Colours of hydrated ions of some transition elements

Hexahydrated ion of	Number of d electrons	Color of solid/solution
Ti^{3+}	1	Violet
V^{3+}	2	Blue
V^{2+}	3	Violet
Cr^{3+}	3	Green
Mn^{3+}	4	Violet
Fe^{3+}	5	Yellow/colorless
Mn^{2+}	5	Yellow/colorless
Fe^{2+}	6	Pale green

Co^{2+}	7	Pink
Ni^{2+}	8	Green
Cu^{2+}	9	Blue

21.4.4 Alloy and Interstitial Compound Formation

In the Table 21.2 it may be observed that the atomic size of the elements of first transition series is quite close to each other. Thus, in the crystal lattice, anyone of these elements can easily replace another element of similar size forming solid solutions and smooth alloys. Transition elements, therefore, form a number of alloys. Cr, V and Mn are used to produce alloy steel and stainless steel, copper forms brass, bronze etc. Besides, transition metals also form a number of interstitial compounds in which they take up atoms of small size, like hydrogen, carbon and nitrogen etc. These are located in the vacant spaces of metal lattices and are bound firmly there in. The products thus obtained are hard and rigid. For example, steel and cast iron become hard due to formation of an interstitial compound with carbon. In such compounds, malleability and ductility may marginally decrease but tenacity is considerably enhanced. Some examples of alloys are given in Table 21.5.

Table 21.5 : Examples of some alloys

Alloy	Composition
Brass	Cu (50%-80%) and Zn (50%-20%)
Bronze	Cu (90%-93%) and Sn (10%-7%)
Gun metal	Cu (88%), Sn (10%) and Zn (2%)
Bell metal	Cu (80%) and Sn (20%)

21.4.5 Complex Formation

Transition metals exhibit a strong tendency to form complexes with different ligands due to the following reasons:

1. Small size and high charge density.
2. Variable oxidation states.
3. Availability of vacant d-orbitals to accept electron pairs from ligands.

You will learn more about complexes in the next lesson

21.4.6 Catalytic Properties

The catalytic activity of transition metals and their compounds is associated with their variable oxidation states. Typical catalysts are vanadium(V) oxide (contact process for sulphuric acid), finely divided iron (Haber's process), nickel (catalytic hydrogenation) and palladium(II) chloride and a copper(II) salt for the production of ethanol from ethane and water (Wacker's process). Haemoglobin, a large molecule containing Fe(II), acts as a catalyst for the respiration process.

Catalysis at a solid surface involves the formation of bonds between reactant molecules and the catalyst surface atoms, this has the effect of increasing the concentration of the reactants at the catalyst surface and also of weakening the bonds in the reactant molecules (the activation energy is lowered).

Transition metal ions function as catalysts by changing their oxidation states, e.g., Fe(III) cations catalyse the reaction between iodide and peroxodisulphate ions:

$$2I^-(aq) + S_2O_8^{2-}(aq) \xrightarrow{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

An oversimplified, explanation of this catalysis reaction might be:

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$

It is known that both the above reactions can take place, and it would be expected that two reactions between ions of opposite charge would be faster than one reaction between ions of the same type of charge.

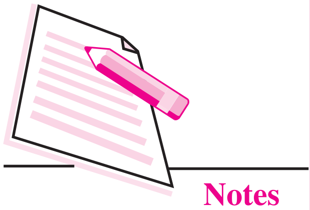
INTEXT QUESTIONS 21.4

1. Why do transition elements act as good catalysts?
2. Name some of the common catalysts you have studied.
3. Which of the following compounds are expected to be diamagnetic: $CrCl_3$, $ScCl_3$, $CuSO_4$, $CoCl_2$, $TiCl_4$ and $ZnCl_2$?
4. Which of the following do you expect to be colored and why, Cr^+ and Cu^+?
5. Name any two alloys of transition elements.
6. Calculate in B.M., magnetic moments expected for the following ions:

   V^{4+}, Ni^{3+}, V^{4+}, Ni^{3+}, Cr^{3+} and Ti^{4+}.

21.5 IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

The preparation, properties and applications of two important compounds of transition elements viz. $K_2Cr_2O_7$ and $KMnO_4$ which are widely used in industry and laboratory are discussed below:



Notes

21.5.1 Potassium Dichromate ($K_2Cr_2O_7$)

Mineral chromite ($FeO.Cr_2O_3$) is the starting material for the manufacture of all chromates and dichromates. Soluble chromates are prepared using alkali metal oxides, hydroxides or carbonates whereas insoluble chromates are made by double decomposition of soluble chromates.

Large Scale Production of Potassium Dichromate from Chromite ore

A mixture of finely powdered chromite, sodium carbonate and quick lime is heated in a reverberatory furnace in free supply of air. Carbon dioxide is evolved and sodium chromate is formed. The function of quick lime is to keep the mass porous and prevent fusion.

$$\underset{\textbf{Chromite}}{4FeO.Cr_2O_3} + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

The mass after roasting is extracted with water, which dissolves soluble sodium chromate leaving behind insoluble ferric oxide. After concentrating the solution containing sodium chromate, concentrated sulphuric acid is added.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium sulphate produced, crystallizes out and is removed. On further concentrating the solution, deliquescent red crystals of sodium dichromate separate out slowly on cooling. When a hot saturated solution of sodium dichromate is mixed with a saturated solution of potassium chloride, sodium chloride separates out, followed by separation of garnet red triclinic crystals of potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Since potassium dichromate is moderately soluble in cold water (100 gL^{-1} at 298 K) but easily soluble in hot water (1000 g L^{-1}) at 373 K, it is readily purified by recrystallization from water.

Physical Properties

$K_2Cr_2O_7$ forms orange red prismatic crystals. Its specific gravity is 2.676 and its melting point is 696 K. It is moderately soluble in cold water but highly soluble in hot water and insoluble in alcohol.

Chemical Properties

1. Since chromium forms stable compounds in low oxidation states as well, potassium dichromate in which oxidation number of chromium is +6, acts as a powerful oxidizing agent. For this reason, it is used as a primary standard in volumetric analyses. In acidic solutions, one molecule of potassium dichromate furnishes three atoms (i.e. six equivalents) of available oxygen as follows:

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$

The available oxygen then oxidizes ferrous, iodide ions and sulphur dioxide as follows:

$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

$2HI + [O] \rightarrow H_2O + I_2$

$SO_2 + [O] + H_2O \rightarrow H_2SO_4$

These reactions can also be shown as ionic equations.

In acidic solution, the oxidizing action of $K_2Cr_2O_7$ can be represented as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

The ionic equation for the reducing action of Fe(II) can be represented as:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

The complete ionic equation may be obtained by adding the half reaction of dichromate ion to the half reaction of Fe(II):

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3-} + 7H_2O$

$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 6$

$Cr_2O_7^{2-}.+ 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Similarly the reactions of dichromate with iodide ion and sulphur dioxide can be written as given below:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$(2I^- \rightarrow I_2 + 2e^-) \times 3$

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$(SO_2 + 2H_2O \rightarrow SO_4^{2+} + 2e^-) \times 3$

$Cr_2O_7^{2-} + 3SO_2 + 14H^+ \sim 2Cr^{3+} + 3SO_4^{2-} + H_2O$

2. Potassium dichromate when heated with concentrated sulphuric acid with an ionic chloride (such as NaCl, KCl etc.) forms red vapours of chromyl chloride, (CrO_2Cl_2) as follows:

$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$[NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4$

$[CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O] \times 2$

$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

Red vapours of chromyl chloride, a derivative of chromic acid is absorbed in dilute solution of NaOH . A yellow solution of sodium chromate is formed. On acidifying this solution with acetic acid and adding lead acetate, a yellow precipitate of lead chromate, is formed which is soluble on heating and reappears on cooling. This is used as a confirmatory test to detect the presence of chloride ions in qualitative analysis.

3. When concentrated sulphuric acid is added to a solution of chromate or dichromate, a red coloured solution of chromic trioxide often called "chromic acid", is obtained. In the acidic solution it exists as dichromic acid ($H_2Cr_2O_7$). Chromium trioxide is a very powerful oxidizing agent.
4. Oxidation number of chromium is +6 in both chromates and dichromates. However, *in* neutral aqueous solution, dichromate ions exist in equilibrium with chromate ions as:

$$\underset{\textbf{Orange}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\textbf{Yellow}}{2CrO_4^{2-}} + 2H^+$$

Thus in an acidic medium, equilibrium shifts to the left and dichromate ions exist whereas in alkaline medium, only monomeric chromate ions exist.

Uses:

1. Potassium dichromate is used as an important volumetric reagent for the estimation of Fe^{2+}, I^-, SO_3^{2-} etc.
2. It is used in the manufacture of chrome alum, which is an important compound used for tanning of leather and dyeing of fabrics.

INTEXT QUESTIONS 21.5

1. Name the starting materials used in preparation of soluble chromate and dichromates.
2. Write down the formula of chromite ore.
3. How is sodium dichromate converted into potassium dichromate?
4. What happens when potassium dichromate is heated with an alkali metal chloride and concentrated sulphuric acid?
5. Give the molecular formula of chrome alum. What are its uses?
6. Why does dichromate act as an oxidizing agent?
7. What happens when a base is added to dichromate?
8. What is the oxidation state of chromium in (i) K_2CrO_4 and (ii) $K_2Cr_2O_7$?

21.5.2 Potassium Permanganate ($KMnO_4$)

Pyrolusite ore (MnO_2) is the starting material for the manufacture of potassium permanganate. Pyrolusite is first converted into potassium manganate which is then oxidized to potassium permanganate.

Conversion of pyrolusite into potassium manganate

When pyrolusite is fused with hydroxide of sodium or potassium in the presence of air manganite first formed is converted into a dark green mass of corresponding manganate as follows :

$$MnO_2 + 2KOH \rightarrow \underset{\textbf{Potassium manganite}}{K_2MnO_3} + H_2O$$

$$2K_2MnO_3 + O_2 \rightarrow \underset{\textbf{Potassium manganate}}{2K_2MnO_4}$$

The dark green mass of potassium manganate is dissolved in a small quantity of cold water to form a dark green solution from which dark green crystals of potassium manganate may be obtained on concentraion.

Conversion of potassium manganate to potassium permanganate :

Any of the following methods can be used for preparing potassium permanganate.

1. When green concentrated solution of potassium manganate is gently warmed, or largely diluted with water, the green color changes to pink owing to the formation of potassium permanganate. Potassium manganate is stable in alkaline solutions or in pure water. But even a trace of acid, like carbonic acid, is enough to bring about its disproportionation :

   $$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

2. Potassium manganate may also be converted into potassium permanganate by oxidation either chemically with chlorine or ozone or electrolytically at the anode.

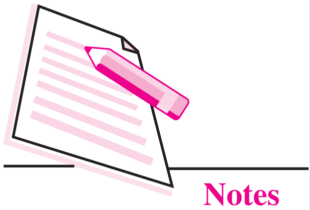
Chemical oxidation:

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2.$$

Anodic oxidation:

$$\underset{\text{green}}{MnO_4^{2-}} \rightarrow \underset{\text{purple}}{MnO_4^-} + e^- \text{ (at anode)}$$



Physical properties

Potassium permanganate forms dark purple red rhombic prisms. It is sparingly soluble in water (5.31 g in 100 mL at 298K) giving a deep purple colored solution which is opaque until very dilute. The crystals on heating evolve oxygen and form a black powder of potassium manganate and manganese dioxide.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Chemical properties

Potassium permanganate is a powerful oxidizing agent. The action is different in acidic, neutral and alkaline solutions.

(i) In acidic solution, two molecules of permanganate furnish five atoms of oxygen as follows :

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

In ionic form the equation is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Ferrous sulphate is oxidized to ferric sulphate by acidified potassium permanganate.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

or

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Sulphur dioxide is oxidized to sulphuric acid:

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

or

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

(ii) In neutral solution the main reaction is:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$KMnO_4$ oxidises Mn^{2+} salts to MnO_2 and H_2S to S and SO_4^{2-} as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

$$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$$

(ii) In alkaline solutions the main reaction is:

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$$

In ionic form the equation is:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

However, MnO_4^{2-} is further reduced to MnO_2 hence the complete equation representing the oxidizing behaviour of $KMnO_4$ in alkaline solution is same as in neutral medium

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2^- + 4OH^-$$

Alkaline permanganate oxidizes iodides to iodates and ethene to ethylene glycol:

$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

$$2KMnO_4 + 3CH_2 = CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2 - CH_2OH + 2KOH$$

Uses:

1. Potassium permanganate is used as an oxidizing agent in the laboratory and in industry.
2. Because of its oxidizing properties, it is used for disinfecting wells and lake water, as mouthwash, for washing wounds and gargling during throat infections.
3. It is used as a reagent in volumetric analyses for estimating Fe(II) ion, oxalic acid, oxalate ion, sulphites and hydrogen peroxide.

INTEXT QUESTIONS 21.6

1. How is potassium manganate converted into potassium permanganate?
2. Give reactions of $KMnO_4$ to show that it acts as an oxidizing agent in neutral, alkaline and acidic medium.
3. Why is $KMnO_4$ added to wells and lakes from where water is drawn for drinking?
4. Write down the chemical formulae of pyrolusite ore, potassium permanganate and potassium manganate.
5. In which medium (acidic, basic or neutral), $KMnO_4$ acts as better oxidizing agent?
6. What is the color of K_2MnO_4 and of $KMnO_4$?
7. What are the oxidation states of Mn in MnO_2, K_2MnO_4 and $KMnO_4$?

21.6 *f*-BLOCK ELEMENTS (LANTHANOIDES)

In addition to *d*-block elements, there are two rows of elements shown separately at the bottom of the periodic table. The elements from La to Lu (14 elements) are called lanthanoides. They are characterised by the filling up of the anti penultimate 4*f* orbitals. They are extremely similar to each other in properties. Earlier these were called the rare earths. This name is not appropriate because many of these elements are not particularly rare. Now these elements are known as inner transition elements (because they form transition series within the *d*-block transition elements) or lanthanoids.

21.6.1 Electronic Configuration

Lanthanum is the first member of the third transition series, and it has one 5*d* and two 6*s* electrons. The next element is cerium, which while still retaining two 6*s* electrons, has two electrons in the 4*f* orbitals and none in the 5*d* orbitals. There are 7 separate 4*f* orbitals, each of which can accommodate two electrons with opposite spins. The atoms of the elements from cerium to lutetium have two to fourteen electrons in 4*f*- orbitals, respectively. These elements constitute the first inner transition series known as lanthanides and, although lanthanum itself does not possess any 4*f* electrons, it is customary to include this element in this series.

The filling up of the 4*f* orbitals is regular with some exceptions (Table 21.6); the element europium has the outer electronic configuration $4f^7 5s^2 5p^6 5d^0 6s^2$ and the next element gadolinium has the extra electron in the 5*d* orbital. The element ytterbium has a full compliment of 4*f* electrons ($4f^{14} 5s^2 5p^6 5d^0 6s^2$) and the extra electron in the lutetium atom enters the 5d orbitals ($4f^{14} 5s^2 5p^6 5d^1 6s^2$). Except for lanthanum, gadolinium and lutetium, which have a single 5d electron, the lanthanoides do not have electrons in the 5*d* orbitals.

Table 21.6: Electronic configuration of lanthanides

Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	$[Xe]4f^0 5d^1 6s^2$
Cerium	Ce	58	$[Xe]4f^2 6s^2$
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$
Neodymium	Nd	60	$[Xe]4f^4 6s^2$
Promethium	Pm	61	$[Xe]4f^5 6s^2$
Samarium	Sm	62	$[Xe]4f^6 6s^2$
Europium	Eu	63	$[Xe]4f^7 6s^2$
Gadolinium	Gd	64	$[Xe]4f^7 5d^1 6s^2$
Terbium	Tb	65	$[Xe]4f^9 6s^2$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$
Erbium	Er	68	$[Xe]4f^{12} 6s^2$
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$
Lutetium	Lu	71	$[Xe]4f^{14} 5d^1 6s^2$

21.6.2 The lanthanoide contraction

Each succeeding lanthanoide differs from its immediate predecessor in having one more electron in the 4*f* orbitals (except for some exceptions as discussed above) and one extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus; thus there is a gradual increase in the attraction of the nucleus for the peripheral electrons as the nuclear charge increases, and a consequent contraction in atomic radius is observed. For example, the ionic radii of the +3 cations decrease steadily from a value of 115 pm for La^{3+} to a value of 93 pm for Lu^{3+}. The regular decrease in atomic radii with increase in atomic number is known as lanthanoide contraction.

The lanthanoide contraction considerably influences the chemistry of the elements, which succeed the lanthanides in the periodic table; for instance the atomic radii of zirconium (At. No. 40) and hafnium (At. No. 72) are almost identical and the chemistry of these two elements is strikingly similar. Incidentally, the density of hafnium (which immediately follows the lanthanides) is almost twice the density of zirconium (which is in the same group).

21.6.3 Oxidation states of lanthanIODS

Table 21.7: Electronic configuration and oxidation states

Element	**Electronic configuration of atoms**				**Oxidation states**		
Lanthanum	La	[Xe]	$5d^1$	$6s^2$	+ III		
Cerium	Ce	[Xe] $4f^1$	$5d^1$	$6s^2$		+ III	+ IV
Praseodymium	Pr	[Xe] $4f^3$		$6s^2$		+ III	(+ IV)
Neodymium	Nd	[Xe] $4f^4$		$6s^2$	(+II)	+ III	
Promethiurm	Pm	[Xe] $4f^5$		$6s^2$	(+II)	+ III	
Samarium	Sm	[Xe] $4f^6$		$6s^2$	(+II)	+ III	
Europium	Eu	[Xe] $4f^7$		$6s^2$	+ II	+ III	
Gadolinium	Gd	[Xe] $4f^8$	$5d^1$	$6s^2$		+ III	
Terbium	Th	[Xe] $4f^9$		$6s^2$		+ III	(+ IV)
Dysprosium	Dy	[Xe] $4f^{10}$		$6s^2$		+ III	(+ IV)
Holmium	Ho	*[Xe]* $4j^{11}$		$6s^2$		+ III	
Erbium	Er	[Xe] $4f^{12}$		$6s^2$		+ *III*	
Thulium	Tm	[Xe] $4f^{13}$		$6s^2$	(+ II)	+ III	
Ytterbium	Yb	[Xe] $4f^{14}$		$6s^2$	+ II	+ III	
Lutetium	Lu	[Xe] 4f14 $5d^1$		$6s^2$	+ III		

The sum of first three ionization enthalpies of the lanthanoids are comparatively low so these elements are highly electropositive and the compounds of these elements are essentially all ionic in nature.The characteristic oxidation state of these elements is +3, however some of them also show +2 and +4 oxidation states which are less stable as compared to +3.. Like transition elements, fluorides and oxides stabilize higher oxidation states whereas bromides and iodides stabilize lower oxidation states. The elements show (+ II) and (+ IV) oxidation states, particularly when they lead to:

(a) Noble gas electronic configuration, *e.g.,* Ce^{4+} ($4f^0$).

(b) Half filled *f*-orbital, *e.g.,* Eu^{2+} and Tb^{4+} ($4f^7$).

(c) Completely filled *f*-orbital, *e.g.,* Yb^{2+} ($4f^{14}$).

Due to only one stable oxidation states, *i.e.,* + III, lanthanoid elements resemble each other much more than the transition elements.

21.7 ACTINOIDS

Electronic Configuration

The electronic configuration of actinoids do not follow the simple patternn found in the lanthanoids. It might have been expected that after Ac the 5*f* orbitals would become lower in energy than the 6*d* orbitals. However, for the first four actinide elements Th, Pa, U and Np the difference in energy between 5*f* and 6*d* orbitals is small. Thus in these elements electrons may occupy the 5*f* or the 6*d* orbitals or sometimes both. Later in the actinide series the 5*f* orbital becomes appreciably lower in energy, thus from Pu onwards the 5*f* orbital fills in a regular way.

Oxidation states of actinoids are given in the Table below.

Table 21.8: The elements and their oxidation states

Atomic Number	Element	Symbol	Outer electronic structure			Oxidation states*					
89	Actinium	Ac		$6d^1$	$7s^2$		III				
90	Thorium	Th		$6d^2$	$7s^2$		III	IV			
91	Protactinium	Pa	$5f^2$	$6d^1$	$7s^2$		III	IV	V		
92	Uranium	U	$5f^3$	$6d^1$	$7s^2$		III	IV	V	VI	
93	Neptunium	Np	$5f^4$	$6d^1$	$7s^2$		III	IV	V	VI	VII
94	Plutonium	Pu	$5f^6$		$7s^2$		III	IV	V	VI	VII
95	Americium	Am	$5f^7$		$7s^2$	II	III	IV	V	VI	

96	Curium	Cm	$5f^7$	$6d^1$	$7s^2$		III	IV
97	Berkelium	Bk	$5f^9$		$7s^2$		III	IV
98	Californium	Cf	$5f^{10}$		$7s^2$		III	IV
99	Einsteinium	Es	$5f^{11}$		$7s^2$	II	III	
100	Fermium	Fm	$5f^{12}$		$7s^2$	II	III	
101	Mendelevium	Md	$5f^{13}$		$7s^2$	II	III	
102	Nobelium	No	$5f^{14}$		$7s^2$	II	III	
103	Lawrencium	Lr	$5f^{14}$	$6d^1$	$7s^2$	II		

21.7.1 Oxidation States

As seen in the table +2 oxidation state is quite rare. Am^{2+} has $5f^7$ electronic configuration.

Like lanthanoids all the actinoids show +3 oxidation state. This +3 oxidation state is not the most stable oxidation state for Th, Pu, U and Np. For example, U^{3+} is readily oxidized in air, and in solution. +III is the most stable oxidation state for higher actinoids *i.e., from* $_{95}$Am to $_{103}$Lw (except$_{102}$ No]. They show similar properties to that of lanthanoids. The higher oxidation states involve all the outer electrons for bonding (including $5f$ electrons). Oxidation states other than +3 are also exhibited by some of these elements e.g. Np and Pu show as high as +VII oxidation state and Am and heavy actinoids show +II oxidation state. Np in + VII oxidation state acts as an oxidizing agent.

21.7.2 Comparison between lanthanoids and actinoids

Similarlity

1. Orbitals are filled progressively in both the series.
2. +III is the prominent oxidation state for both the series.
3. In both the series, $4f$ and $5f$ electrons imperfectly shield, therefore both show contraction in size.
4. They show line like spectra.
5. Both $4f$ and $5f$ block elements show ion exchange behavior.
6. Hydroxides, carbonates and fluorides of bivalent actinoids as well as lanthanoids are soluble whereas nitrates, perchlorates and sulphates are insoluble.

Differences

1. There is large energy gap between $4f$ and $5d$ sub-shells, the energy gap between $5f$ and $6d$ is small so the chemistry of actionoids is not similar to that of lanthanoids.

2. Pm is the only radioactive elements among the lanthanoids, whereas almost all the actinoids are radioactive elements.
3. The maximum oxidation shown by the lanthanoids +IV, whereas antioids show upto +VII oxidation state.
4. Lathanoids do not form complexes easily but actinoids form complexes.
5. 4*f* electrons have greater screening effect as compared to 5*f* electrons.
6. Lanthanoids do not from oxocations but auinoids form oxocations such as UO^{2+}, UO_2^+, NPO_2^+ and PuO_2^+.
7. The compounds of lanthanoids are less basic as compared to the compounds of actinoids.

INTEXT QUESTIONS 21.7

1. How many elements constitute lanthanoide series?
2. Why Zr and Hf show almost same properties?
3. Write down the electronic configuration of the following in the ground state: Gd, Lu, Ho, Er.
4. Write down the electronic configuration of the following ions: Eu^{3+}, Yb^{3+}, Ce^{4+}.
5. Which is characteristic oxidation state of Lanthanoids?
6. Actinoids show variable oxidation state why?
7. Are actinoids form oxocation?

WHAT YOU HAVE LEARNT

- Transition elements have partially filled *d*-orbitals either in atomic or ionic state.
- They show general electronic configuration $(n\text{-}1)d^{1-10}ns^{1,2}$.
- They show high M.P. and B.P. due to strong inter-atomic bonding.
- They show variable oxidation states.
- They form colored ions and compounds.
- They show paramagnetic behaviour.
- They form complexes.
- They form alloy and interstitial compounds.

- Manufacture of $K_2Cr_2O_7$ and $KMnO_4$.
- $K_2Cr_2O_7$ and $KMnO_4$ act as oxidizing agents.

  These compounds are used in volumetric analysis.
- Electronic configuration of lanthanoids and actinoids.
- Lanthanoid contraction oxidation states of lanthanoids and actinoids.
- Comparison between lanthanoids and actinoids.

TERMINAL EXERCISES

1. What distinguishes a transition metal from a representative metal?
2. Why is zinc not considered a transition metal?
3. Explain why atomic radii decrease very gradually from Sc to Cu.
4. Write down the ground state electronic configuration of the first row transition elements. Explain the irregularities.
5. Write down the electronic configuration of the following ions:

   V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, Sc^{3+} and Ti^{4+}
6. Why do transition elements have more oxidation states than other elements?
7. Give the highest oxidation states for the elements from Sc to Cu.
8. How would you define transition elements? List the properties associated with transition elements.
9. How do the following properties vary in transition elements?

   (a) Stability of the various oxidation states.

   (b) Ability to form complexes.
10. What do you understand by the terms paramagnetism and diamagnetism? Predict the magnetic moments for Fe^{2+}, Co^{3+}, Ni^{3+} and Cu^{+} ions.
11. 4*s* sub-shell is filled prior to 3*d*- sub-shell but on ionization 4*s* electrons are removed first. Explain.
12. Why does Mn(II) show maximum paramagnetic character amongst the bivalent ions of first transition series?
13. Why is Cu^{2+} ion colored and paramagnetic while Zn^{2+} ion is colorless and diamagnetic.
14. Why do transition elements.

    (a) show variable oxidation states?

    (b) form a large number of coordination compounds?

    (c) give colored and paramagnetic ions?

    (d) exhibit good catalytic properties?

15. Discuss the main characteristic features of the transition elements with special reference to their atomic size, variable oxidation states, magnetic and catalytic properties.

16. Explain the trends of variations of:

    (a) melting and boiling points.

    (b) atomic radius in the first transition series.

17. A solution of $KMnO_4$ on reduction yields either a colorless solution or a brown precipitate or a green solution depending on the pH of the solution. What different stages of the reduction do these represent and how are they carried out?

18. A black color compound [X] of manganese when fused with KOH under atmospheric oxygen gave a green colored compound [Y]. When the compound [Y] was treated with an oxidizing agent (chlorine or ozone), it gave a purple colored solution [Z]. Identify X, Y, Z and write the chemical equation.

19. Compound [A] of chromium when treated with sodium carbonate in the presence of atmospheric oxygen gave a yellow colored compound [B]. Compound [B] on treatment with acid gave an orange colored compound [C]. [B] can also be obtained by treatment of [C] with alkali. Identify the compound A, B, C and write the chemical equations.

20. Why do transition elements form a large number of alloys and interstitial compounds?

21. What are lanthanides? Why are they called inner transition elements?

22. What is lanthanide contraction and what are its consequences?

23. Write the electronic configurations of the following in ground state:

    Eu, Ho and Gd.

24. Describe two oxidizing properties of potassium dichromate.

25. Describe two oxidizing properties of potassium permanganate.

26. Compare between the properties of lanthanoids and actinoids.

ANSWERS TO INTEXT QUESTIONS

21.1

1. Transition elements are defined as "Elements whose atoms have partially filled *d*-orbitals either in the atomic or in ionic state (common oxidation state).

2. 10 elements constitute the first transition series. These are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn.

3. Since zinc does not have partially filled *d*-orbitals either in atomic or in ionic state.

4. Because there are partially filled *d*-orbitals in Cu^{2+}, Ag^{2+} and Au^{3+}.

21.2

1. General electronic configuration of transition elements is: $(n{-}1)d^{1-10}\,ns^{1\text{ or }2}$.

2. $Sc = [Ar]3d^1 4s^2$, $Cr = [Ar]3d^5 4s^1$, $Zn = [Ar]3d^{10} 4s^2$, $Cu = [Ar]\ 3d^{10}\ 4s^1$

3. $Cr^{3+} = [Ar]3d^3$, $Ti^{4+} = [Ar]3d^0$, $Ni^{3+} = [Ar]3d^7$ and $Cu^{2+} = [Ar]3d^9$

4. Because less amount of energy is required to remove an electron from 4*s* instead of 3*d* orbital. It is due to the fact that after Sc, 3*d*, becomes lower in energy than 4*s*.

21.3

1. due to strong interatomic bonding.

2. due to increase in effective nuclear charge.

3. due to small size. Size does not increase in the same proportion as the atomic mass.

21.4

1. due to variable oxidation states.

2. V_2O_5 (contact process for H_2SO_4) and iron (Haber's process)

3. $ScCl_3(3d^0)$, $TiCl_4(3d^0)$ and $ZnCl_2(3d^{10})$.

4. Cr^+ because it has partially filled *d*-orbital i.e. $3d^5$.

5. Nichrome and brass.

6. $V^{4+}3d^1\ \sqrt{n(n+2)} = \sqrt{n(1+2)} = \sqrt{3} =$ 1.73 B.M., $Ni^{3+}3d^7 n = 3$, $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M

21.5

1. Chromite ore, Na_2CO_3 and O_2
2. $FeO.Cr_2O_3$.
3. $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$
4. $K_2Cr_2O_7 + 4NaCl = 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

5. $KCr(SO_4)_2.12H_2O$ or $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, tanning of leather and dyeing fabrics.
6. For Cr, +3 is the stable oxidation state but in $K_2Cr_2O_7$ the oxidation state of Cr is +6.
7. $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$. Dichromate changes to chromate.
8. (i) +6 (ii) +6.

21.6

1. By oxidation with ozone or chlorine

   $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$

   $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$
2. Alkaline:

   $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

   Neutral:

   $2MnO_4^- + 2H_2O + 3Mn^{2+} \rightarrow 5MnO_2 + 4H^+$

   Acidic:

   $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2 = O$
3. Because it is used as disinfectant (kill microorganisms)
4. Pyrolusite MnO_2, potassium permanganate $KMnO_4$, potassium manganate K_2MnO_4.
5. In acidic medium, because it liberates 5O atoms or change in oxidation state of Mn is from +7 to +2.
6. K_2MnO_4, green and $KMnO_4$, purple.
7. $MnO_2 = +4$, $K_2MnO_4 = +6$ and $KMnO_4 = +7$.

21.7

1. 14.
2. Due to lanthanide contraction. (Due to same size)
3. Gd$[Xe]5f^7 5d^1 6s^2$, Lu$[Xe]4f^{14} 5d^1 6s^2$, Ho $[Xe]4f^{11} 6s^2$ and Er $[Xe]4f^{12} 6s^2$
4. $Eu^{3+} = [Xe]4f^6$, $Yb^{3+} = [Xe]4f^{13}$ and $Ce^{4+} = [Xe]4f^0$
5. +3
6. Difference in the energy of (n-2)f and ns is negligible. So more elements are available for chemical bonding.
7. Yes

22

COORDINATION COMPOUNDS

You have come across compounds like $Na[Ag(CN)_2]$ and $Na_2[Zn(CN)_4]$. Such compounds are referred to as coordination compounds or complex compounds. Coordination compounds play an important role in the chemical industry and in life itself. For example, the Ziegler-Natta catalyst which is used for polymerization of ethylene, is a complex containing the metals aluminum and titanium. Metal complexes play important role in biological systems. For example, chlorophyll, which is vital for photosynthesis in plants, is a magnesium complex and heamoglobin, which carries oxygen to animal cells, is an iron complex. These are the compounds that contain a central atom or ion, usually a metal, surrounded by a number of ions or molecules. The complexes tend to retain their identity even in solution, although partial dissociation may occur. Complex ion may be cationic, anionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

In this lesson you will study about the complexes including their nomenclature and nature of bonding in them.

OBJECTIVES

After reading this lesson, the learner will be able to,

- state the postulates of Werner's theory;
- define ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valance bond theory;
- apply VB theory to explain hybridization, shape and magnetic behavior of the following complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ and

- explain Crystal Field Theory (CFT);
- explain the colour and magnetic behaviour of coordination compounds on the basis of CFT.
- explain the isomerism in coordination compounds;
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.

22.1 WERNERS' COORDINATION THEORY

Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like $CoCl_3$ reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds: $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound are different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner's coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The important postulates of **Werner's theory** are:

1. Metals exhibit two types of valence:
   (a) Primary valence (ionizable)
   (b) Secondary valence (non-ionizable).

Primary or ionizable valence is satisfied by negative ions and corresponds to oxidation state of the metal. The secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

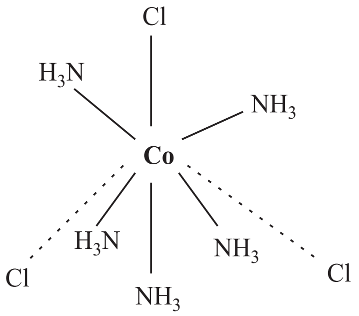
Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence is directed toward fixed positions in space i.e. this has spatial arrangement corresponding to different coordination number.

For the complexes $CoCl_3.6NH_3$ $CoCl_3.5NH_3$ and $CoCl_3.4NH_{3,}$ the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner's postulate these compounds are formulated as:

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions.

On the basis of Werner's theory the structure of $[Co(NH_3)_5Cl]\ Cl_2$ is:



Primary valance (ionizable)(--------)
Secondary valance (non-ionizable) (———)

One of the three chloride ions satisfy both primary and secondary valence.

He also postulated that octahedral, tetrahedral and square planar shapes are more common for coordination compounds of transition elements. Six coordinated complexes such as $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are octahedral whereas four coordinated such as $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are tetrahedral and square planar, respectively.

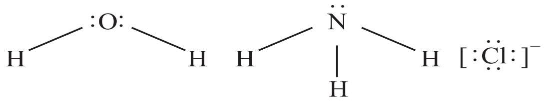
INTEXT QUESTIONS 22.1

1. Explain primary valence.
2. Explain secondary valence.
3. What is the number of the secondary valence in the following: $[Cr(H_2O)_6]\ Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$?
4. What is shape associated with a six-coordinated complex?
5. How many types of shapes are possible for four-coordinate complexes?

22.2 DEFINITION OF SOME IMPORTANT TERMS

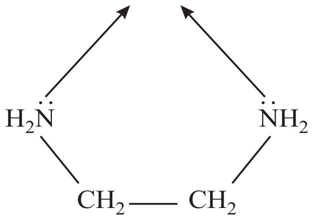
There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

Ligand: the molecules or ions that are attached to the metal in a complex ion are called ligands. The interaction between a metal atom and the ligands can be thought of as Lewis acid-base reaction. As you know a Lewis base is a substance capable of donating one or more electron pairs, every ligand has at least one unshared pair of valence electron. Few examples are shown below:



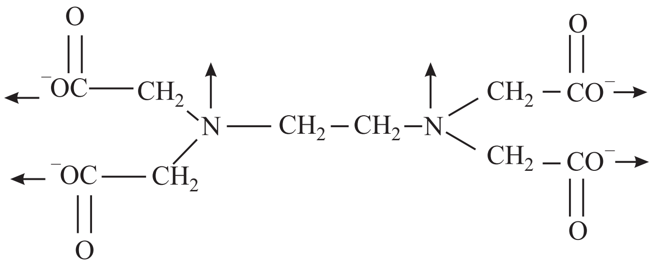
The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu^{2+} is the acceptor atom in the $[Cu(NH_3)_4]^{2+}$ complex ion.

Depending on the number of the donor atoms present, ligands are defined as monodentate, bidentate or polydentate. H_2O and NH_3 are monodentate ligands with only one donor atom in each. Ethylenediamine (en) is a bidentate ligand.



Ethylenediamine

The two nitrogen atoms can coordinate with a metal atom. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw (from the Greek Chele, meaning "claw") one example is ethylenediaminetetraacetate ion (EDTA), a polydentate (hexadentate) ligand.



Ethylenediaminetetraccetate ion

Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in $[Co(NH_3)_6]^{3+}$ is six. Similarly the coordination number of Ag^+ in $[Ag(NH_3)_2]^+$ is 2, that of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[Fe(CN)_6]^{3-}$ is 6.

Coordination sphere: The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere. The ligands and the metal atom inside the square brackets behave as single constituent unit.

$$\underset{\textbf{Coordination sphere}}{\overbrace{[Cr(NH_3)_4Cl_2]}}\ Cl$$

Oxidation number: Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the $[PtCl_6]^{2-}$ ion for example, each chloride ion has an oxidation number of –1, so the oxidation number of Pt must be +4. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in $[Cu(NH_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of copper is +2.

INTEXT QUESTIONS 22.2

1. What is the coordination number of the metal ion in the following?
   (i) $[Co(NH_3)_5Cl]^+$
   (ii) $[Cr(en)_2Cl_2]^+$
   (iii) $[NiCl_4]^{2-}$
2. What is the oxidation state of the metal ion in the following?
   (i) $[MnCl_6]^{4-}$
   (ii) $[Fe(CN)_6]^{3-}$
   (iii) $[Cr(NH_3)_6]^{3+}$
   (iv) $[Ni(en)_3]^{2+}$
3. Give an example of a chelate ligand.
4. Give one example of each monodentate, bidentate and polydenatate ligand.
5. What is the oxidation and coordination number of Co in this $[Co(en)_2(H_2O)CN]^{2+}$ complex ion Which ligand is bidentate in the above complex?

22.3 RULES OF NOMENCLATURE OF COORDINATION COMPOUNDS

We have already discussed about the ligands and oxidation number of metal, our next step is, to learn how to name these coordination compounds. The rules for naming coordination compounds as recommended by IUPAC are as follows:

1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compound, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ first, respectively.

2. Within a complex ligands are named first, in alphabetical order, and the metal ion is named last.

3. The name of anionic ligand ends with the letter 'O', whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H_2O (aqua), CO (carbonyl) and NH_3 (ammine). The table given below lists some common ligands:

Table 22.1: Some Common Ligands

Ligand	Name of the ligand in coordination compounds
Fluoride (F^-)	Fluro
Chloride (Cl^-)	Chloro
Bromide (Br^-)	Bromo
Hydroxide (OH^-)	Hydroxo
Sulphate (SO_4^{2-})	Sulphato
Oxide (O^{2-})	Oxo
Carbonate (CO_3^{2-})	Carbonato
Oxalate ($C_2O_4^{2-}$)	Oxalato
Thiocyanate (SCN^-)	Thiocyanato
Cyanide (CN^-)	Cyano
Isothiocyanate (NCS^-)	Isothiocyanato
Ethylenediamine ($NH_2CH_2CH_2NH_2$)	Etylenediamine
Ammonia (NH_3)	Ammine
Water (H_2O)	Aqua
Carbon monoxide (CO)	Carbonyl
EDTA	Ethylenediamineteracetato

4. When several ligands of a particular kind are present, we use the Greek prefix di, tri- tetra etc to name them. Thus the ligands in cation $[Co(NH_3)_4Cl_2]^+$ are named as "tetraammine dichloro" (note that prefixes are ignored when alphabetizing ligands). If the ligand itself contains a Greek prefix, we use the prefixes *bis,tris and tetrakis* etc to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di, therefore, if two such ligands are present the name is *bis*(ethylenediamine).

5. The oxidation number of the metal is written in roman numerals following the name of the metal. For example, the roman numeral III is used to indicate the +3 oxidation state of chromium in $[Cr(NH_3)_4Cl_2]^+$, which is named as tetraamminedichlorochromium (III) ion.

6. If the complex is an anion, its name ends in –ate. For example, in $K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the numeral (II) indicate the oxidation state of iron. Table given below gives tha name of anions containing metal atoms (Table 22.2).

7. If the complex is either a cation or is neutral, no change is required in the name of the central metal ion. For example $[Co(NH_3)_6]^{3+}$ and $[Ni(CO)_4]$ are named as hexaamminecobalt(III)ion and tetracarbonyl nickel(0), respectively.

Table 22.2: Some anions containing metal atoms

Metal	Name of metal in anionic state
Copper	Cuperate
Zinc	Zincate
Aluminum	Aluminate
Chromium	Chromate
Tin	Stannate
Cobalt	Cobaltate
Nickel	Nickelate
Gold	Aurate
Silver	Argentate
Lead	Plumbate
Rhodium	Rhodate
Iron	Ferrate
Manganese	Manganate

A. few examples are given below:

$[Co(H_2O)_6]Cl_3$	hexaaquacobalt(III) chloride
$K_2[PtCl_6]$	potassium hexachloroplatinate(IV)
$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Co(en)_2Cl_2]Cl$	dichlorobis (ethylenediamine)cobalt(III) chloride.

INTEXT QUESTIONS 22.3

1. Write down the name of the following complexes:
   - (a) $[Co(NH_3)_4Cl_2]^+$
   - (b) $(NH_4)_3[Cr(NCS)_6]$
   - (c) $Ni(CO)_4$
   - (d) $K_4[Fe(CN)_6]$
   - (e) $[Cr(en)_3]Cl_3$
2. Write down the formula of the following:
   - (a) Tetrachloronickelate(II)
   - (b) Pentaamminenitrocobalt(III) ion
   - (c) Potassium hexacyanoferrate(III)
   - (d) Dichlorobis(ethylenediammine) chromium(III) ion

22.4 VALENCE BOND THEORY

Linus Pauling of the California Institute of Technology developed the valance bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling's ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and magnetic properties of metal complexes.

The basic principles, which are involved in the valence bond treatment of coordination compounds are:

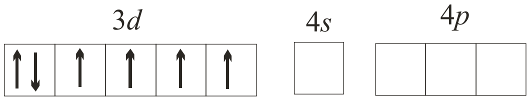
(a) Hybridization of valance orbitals of the central metal/ ion

(b) Bonding between ligand and the metal ion/atom.

(c) Relation between the type of bond and the observed magnetic behaviour.

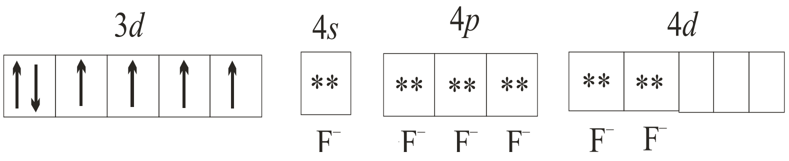
Six Coordinate Complexes

Let us explain by taking simple examples such as $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$. Although in both the complexes, the oxidation state of cobalt is +3, but $[CoF_6]^{3-}$ is paramagnetic and $[Co(NH_3)_6]^{3+}$ is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g. Co^{3+}. Cobalt atom has the outer electronic configuration $3d^7 4s^2$. Thus Co^{3+} ion will have the configuration $3d^6$ and the electrons will be arranged as:



Co^{+3} ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

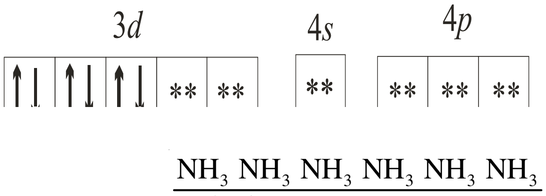
As Co^{3+} ion combines with six fluoride ligands in $[CoF_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one 4*s*, three 4*p* and two 4*d*. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The *d*-orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. It is shown below:



sp^3d^2, outer orbital complex

Since the outer 4d orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex will be high-spin paramagnetic, because it has four unpaired electrons.

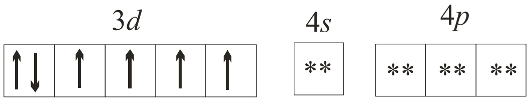
An alternative octahedral arrangement in $[Co(NH_3)_6]^{3+}$ is possible when the electrons on metal ion are rearranged as shown below:



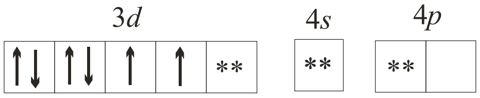
d^2sp^3, inner orbital complex

Since inner *d*-orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral (sp^3) and square planar (dsp^2):



tetrahedral sp^3



square planar dsp^2

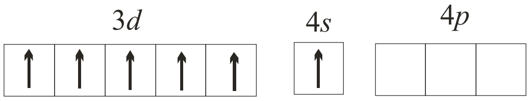
About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:

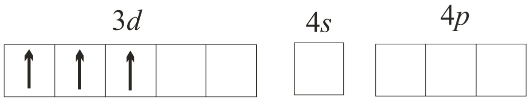
1. $Cr(NH_3)_6]^{3+}$

The electronic configuration of only 3d, 4s and 4p orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr^{3+} ion are given in (i) and (ii) below:

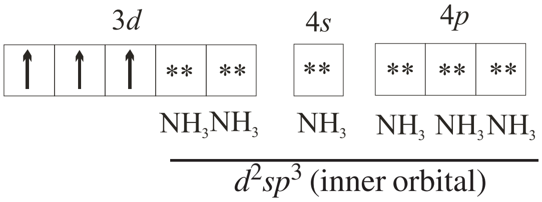
(i) Cr ground state:



(ii) Cr^{3+}



(iii) $[Cr(NH_3)_6]^{3+}$

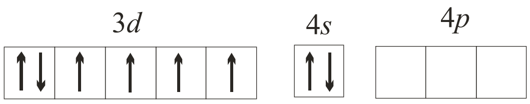


The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

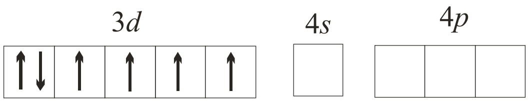
$$\sqrt{n}(n+2) = \sqrt{3}(\sqrt{3+2}) = \sqrt{15} = 3.87\text{B.M}$$

2. $[Fe(CN)_6]^{4-}$

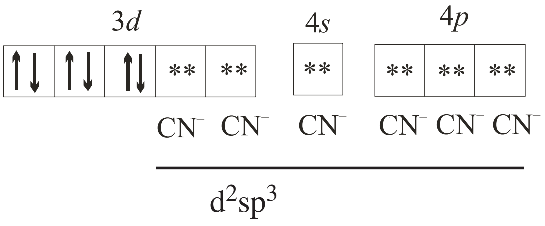
(i) Fe



(ii) Fe^{2+}



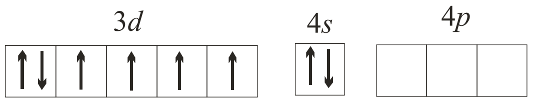
(iii) $[Fe(CN)_6]^{4-}$



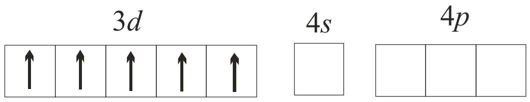
The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diamagnetic.

3. $[Fe(CN)_6]^{3-}$

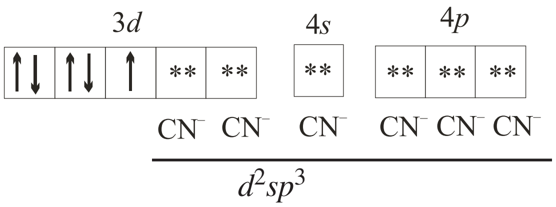
(i) Fe



(ii) Fe^{3+}



(iii) $[Fe(CN)_6]^{3-}$

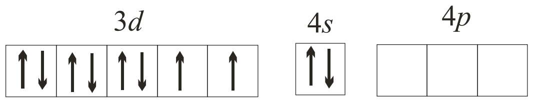


The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

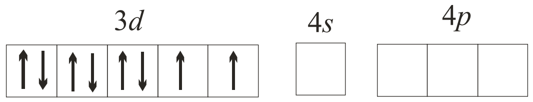
Four coordinate complexes:

1. $[NiCl_4]^{2-}$

(i) Ni

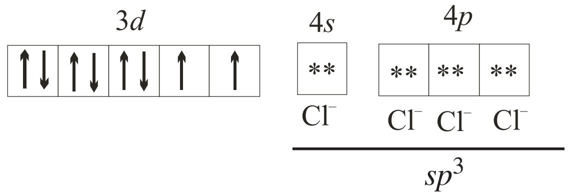


(ii) Ni^{2+}



Notes

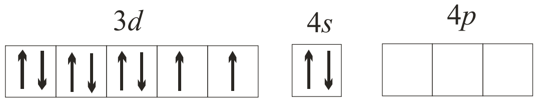
(iii) $[NiCl_4]^{2-}$



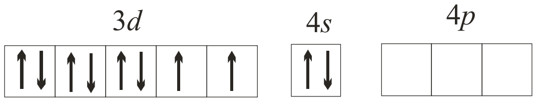
The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. $Ni(CO)_4$

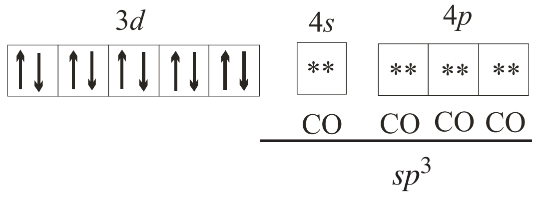
(i) Ni



(ii) Ni(O)



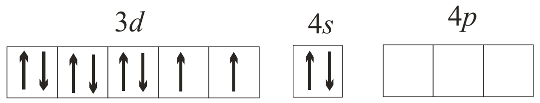
(iii) $Ni(CO)_4$



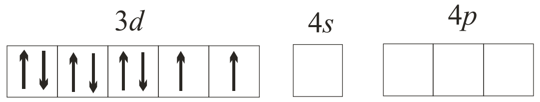
The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

3. $[Ni(CN)_4]^{2-}$

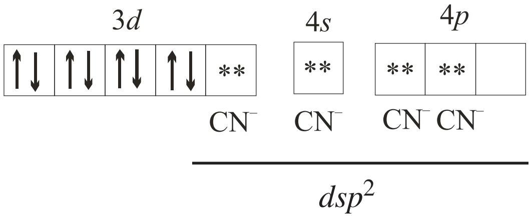
(i) Ni



(ii) Ni^{2+}



(iii) $[Ni(CN)_4]^{2-}$



The resulting complex is square planar and diamagnetic.

22.5 CRYSTAL FIELD THEORY

Although valence bond theory explains the bonding and magnetic properties of complexes, it is limited in two important ways. First, the theory cannot easily explain the color of complexes. Second, the theory is difficult to extend quantitatively. Consequently, another theory—crystal field theory—has emerged as the prevailing view of transition-metal complexes. This theory has been given by Bethe and van Vlack.

Crystal field theory is *a model of the electronic structure of transition-metal complexes that considers how the energies of the d orbitals of a metal ion are affected by the electric field of the ligands.* According to this theory, the ligands in a transition-metal complex are treated as point charges. So a ligand anion becomes simply a point of negative charge. A neutral ligand, with its electron pair that it donates to the metal atom, is replaced by a partial negative charge, representing the negative end of the molecular dipole. In an electric field of these negative charges, the five *d* orbtails of the metal atom no longer have exactly the same energy. The result, as you will see, explains both the paramagnetism and the color observed in certain complexes.

Effect of an Octahedral Field on the *d* Orbitals

All five *d* orbtails of an isolated metal atom have the same energy. But if the atom is brought into the electric field of several point charges, these *d* orbitals may be affected in different ways and therefore may have different energies. To understand how this can happen, you must first see what these *d* orbitals look like. You will then be able to picture what happens to them in the crystal field theory of an octahedral complex.

Figure 22.1 shows the shapes of the five *d* orbitals. The orbital labeled dz^2 has a dumbbell shape along the *z*-axis, with a collar in the *x–y* plane surrounding this dumbbell. Remember that this shape represents the volume most likely to be occupied by an electron in this orbital. The other four *d* orbitals have "cloverleaf" shapes, each differing from one another only in the orientation of the lobes in space. The “cloverleaf” orbital $dx^2 - y^2$ has its lobes along the *x*-axis and the *y*-axis. Orbitals *dxy*, *dxz*, and *dyz* have their lobes directed between the two sets of axes desinated in the orbital label. Orbital *dxy*, for example, has its lobes lying between the *x*- and *y*-axes.

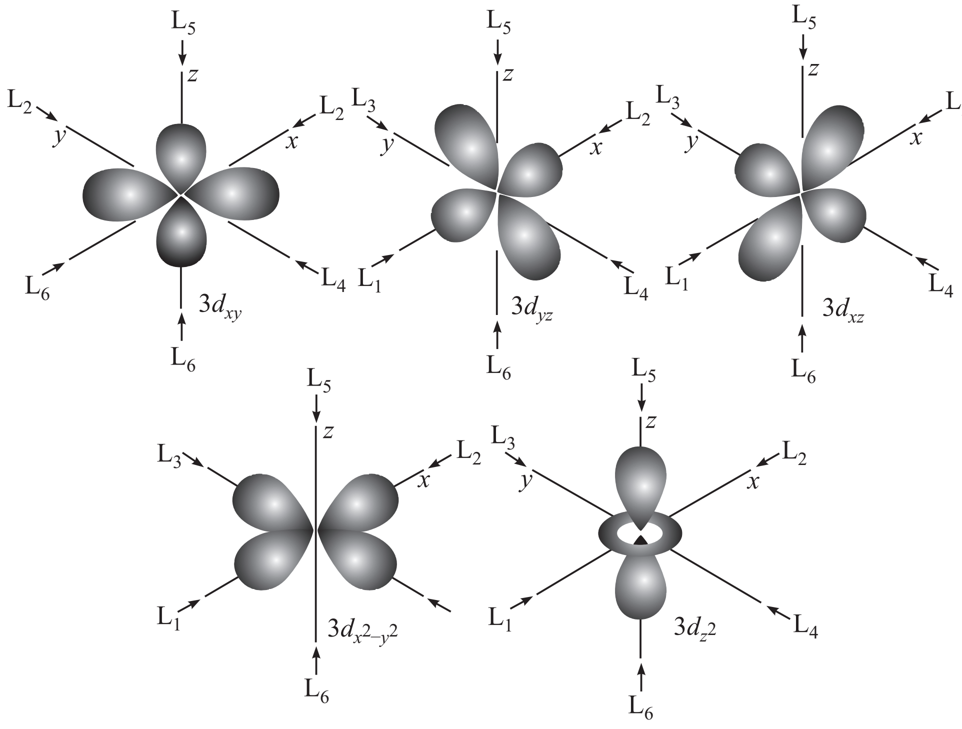


Fig. 22.1: *Shapes of d orbitals*

A complex ion with six ligands will have the ligands arranged octahedrally about the metal atom to reduce mutual repulsion. Imagine that the anionic ligands are replaced by point negative charges and the neutral legands are replaced by the partial negative charge from the molecuar dipoles. The six charges are placed at equal distances from the metal atom, one charge on each of the positive and negative sides of the *x*-, *y*-, and *z*-axes.

Fundamentally, the bonding in this model of a complex is due to the attraction of the positive metal ion for the negative charges of the ligands. However, an electron in a *d*-orbital of the metal atom is repelled by the negative charge of the ligands.

When ligands approach along the *x*, *y*, and *z* axes, electrons in the 3*d* orbital will be repelled but as can be seen from above diagrams the effect will be greater for the $3dz^2$ and $3dx^2 - y^2$ orbitals since these two orbitals have lobes lying along the line of approaching ligands. The net result is that the energy of the $3dz^2$ and $3dx^2 - y^2$ orbitals is raised relative to the energy of the 3*dxy*, 3*dxz*, and 3*dyz* orbitals i.e. the degeneracy of the 3d orbitals is now destroyed.

The 3*d* levels are split into an upper group of two (doubly degenerate and labeled eg) and a lower group of three (trebly degenerate and labeled t_{2g}), the spilliting of the levels is represented by the symbol Δ. If we reckon the zero of energy as the state of affairs that would obtain if each of the fire 3*d* orbitals had interacted equally with the six ligands, then each of the upper two orbitls is raised by 3/5 Δ while each of the three lower oubitals is lowered by 2/5 Δ (Δ collecdtively). As shown in diagram.

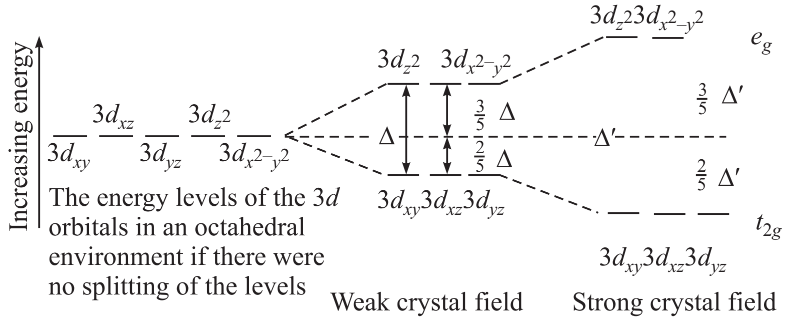


Fig. 22.2: *The splitting of the 3d levels in an octahedral environment of ligands.*

If we now consider the example of a transition metal ion with only one 3d electron surrounded octahedrally by six ligands, e.g. $[Ti\ (H_2O)_6]^{3+}$, then this single 3d electron will normally occupy one of the three degenerate lower levels (t_{2g}). In order to transfer this electron into an upper level (eg) radiation of the appropriate frequency must be supplied. Transition metal ions are coloured because radiation in the visible spectrum is of the right frequency to promote this electronic transition, and in particular $[Ti\ (H_2O)_6]^{3+}$ ions are purple because green light (wavelength about 500 nm) is absorbed, i.e. white light minus green light gives purple light. The relationship between Δ and the frequency of light absorbed is given by the usual expressions-

$$\Delta = h\nu$$

Where h is Planck's constant and ν is the frequency absorbed.

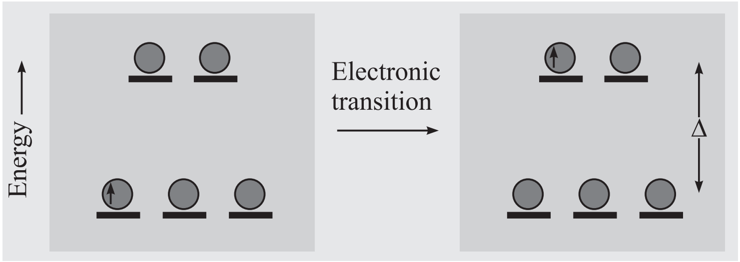


Fig. 22.3: *The electronic tranistion responsible for the visible absorption in $Ti(H_2O)_6^{3+}$. An electron undergoes a transition from a lower-enrgy d orbital to a higher-nergy d orbital. The energy change equals the crystal field splitting Δ.*

Similar considerations apply to complexes in which the central transition metal ion has more than one 3d electrons although needless to say the presence of more than one electron in the 3d orbitals leads to slight complications.

It is found experimentally that for a given transition series (in the case of first transition series) the value of Δ depends upon (a) the charge carried by the central transition metal ion, (b) the nature of the ligand and, (c) the transition metal ion itself. In general, for a given ligand, the crystal field spilitting is greater for M^{3+} octahedral complexes compared to that in Mn^{2+} octahedral complexes, while for transition metal ions carrying the same charge, the value of Δ increase in the order,

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 <$ ethylenediamine $< NO_2^- < CN^-$,

where the above ions and neutral molecules are the ligands which may surround the transition metal ion. This order is known as the spectro chemical series.

Since small changes in the values of Δ can significantly affect the colour of the light absorbed by transition metal ions, it is not surprising that transition metal ions can show a wide range of colour in different environment.

Magnetic Properties

In order to explain why the same transition metal ion can often display two widely different degrees of paramagnetism in different environments. It is necessary to consider the spectrochemical series. For instance, the CN^- ion produces a greater crystal field spilitting than other ligands.

Consider, for example, the octahderal complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ (Figure). The electron configuration of Fe^{3+} is $[Ar]3d^5$, and there are two possible ways to distribute the five d electrons among the d orbitals.

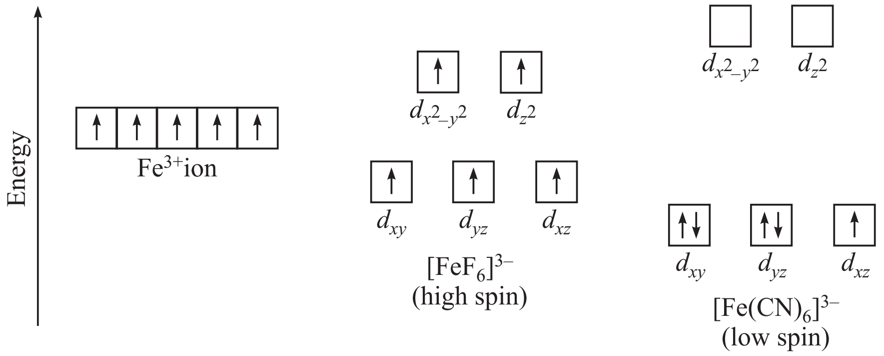


Fig. 22.4: *Energy-level digrams for the Fe^{3+} ion and for the $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$*

As discussed earlier the d orbitals are split into two groups i.e. t_{2g} and e_g. If the value of Δ is small then high-spin complex is formed but if value of Δ is large then complex will be of low spin type.

High-spin complexes are more paramegnetic than low-spin complexes. d^4, d^5, d^6 and d^7 electronic configuration form low and high spin complexes. It is not possible to differenciate d^1 d^2 d^3 d^8 and d^9 systems on the basis of magnetic moments.

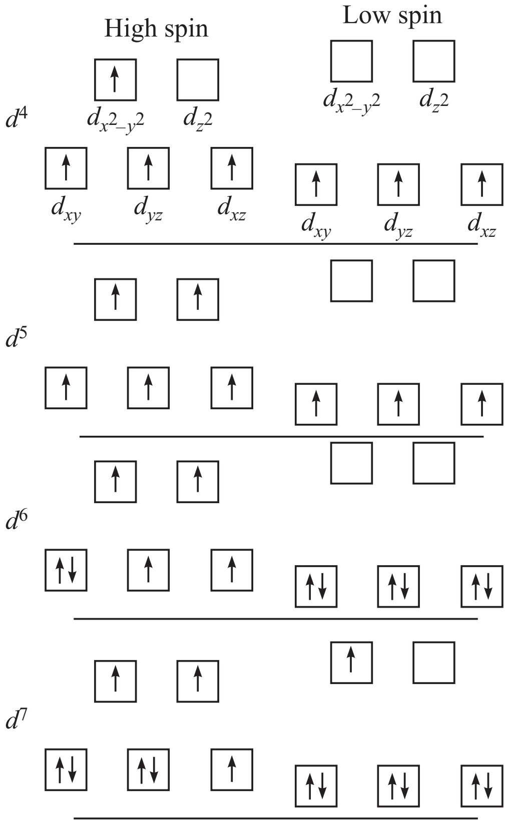


Fig. 22.5: *Orbital diagrams for the high spin and low spin octahedral complexes corresponding to the electron configuration d^4, d^5, d^6, and d^7.*

INTEXT QUESTIONS 22.4

1. Name the type of hybridization present in: $[Co(NH_3)_6]^{3+\cdot}$.
2. $[Fe(CN)_6]^{3-}$ is diamagnetic or paramagnetic?
3. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ have sp^3 or dsp^2 hybridization?
4. Which one is diamagnetic: $[Ni(CN)_4]^{2-}$ or $[NiCl_4]^{2-}$?
5. What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?
6. $[FeF_6]^4$ is paramagnetic but $[Fe(CN)_6]^{4-}$ is diamagnetic. explain by CFT.
7. Which is strong field ligand F^- or CN^-.

22.6 ISOMERISM

Compounds which have the same molecular formula, but different structural formulae are said to be isomers. There are many types of isomerism possible The isomerism can be classified as:

Isomerism

Structural isomerism	Stereo isomerism
(a) Ionisation (b) Hydrate (c) Coordination (d) Linkage	(a) Geometrical (b) Optical

1) **Structural isomerism.** This may be subdivided into sub-classes; for example:

   (a) Ionization isomerism, when the compounds yield different ions in solution, e.g. $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^+ Br^-$.

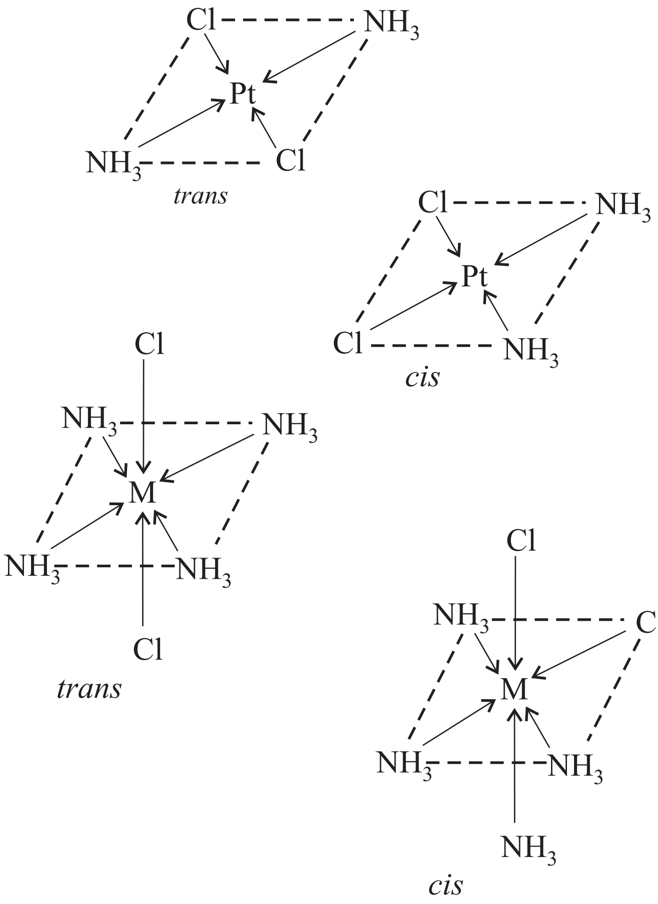
   (b) Hydration isomerism. These compounds show different conductivities in solution, and they precipitate different amounts of silver chloride from cold silver nitrate solution. e.g. $[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5CI]Cl_2.H_2O$ (light green), and $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ (dark green).

   (c) Coordination isomerism, when cation and anion both are complexes. e.g. $[Co(NH_3)_6]^{3+}$ $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ $[Co(C_2O_4)_3]^{3-}$.

   (d) Linkage Isomerism: Complexes in which linkages of ligand is different for example $[Co(NH_3)_5\ SCN]]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$.

2) **Geometrical isomerism.** These are isomers in which the composition of the first coordination sphere is the same, but the geometrical arrangement of the ligands varies. This is often called *cis-trans* isomerism, referring to the relative positions of two selected ligands. This isomerism is only possible for coordination numbers greater than or equal to four, e.g. *cis* and *trans* $PtCl_2(NH_3)_2$.

3) **Optical isomerism**. Any molecule which contains no plane or centre of symmetry may exist in two forms which are non-superiposable mirror images of one another. These have identical chemical and physical properties except that they rotate the plane of plane-polarized light equally but in opposite directions, and they react differently with other optically active compounds. Such compounds are normally obtained as a 50:50 mixture (called a racemic mixture) of the two optical isomers (called enantiomers, or enantiomorphs), which is therefore optically inactive, such as $[Co(en)_3]^{3+}3C1^-$.



Two examples of *cis-trans* isomers

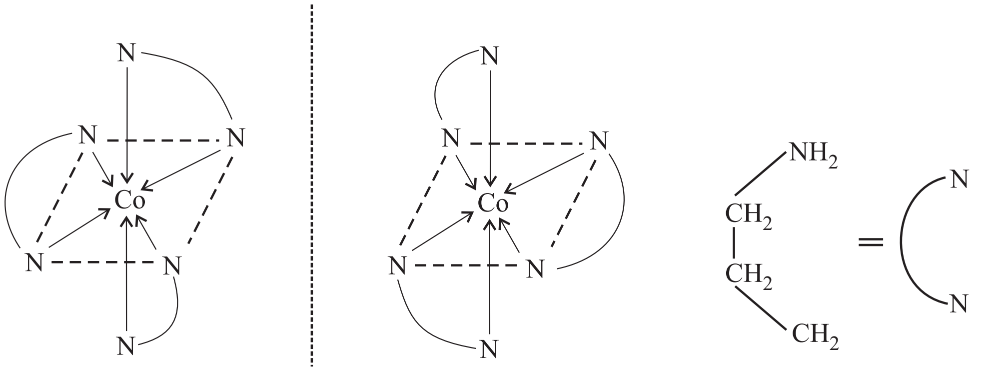


Fig. 22.6: *The enantiomers of* $[Co(en)_3]^{3+}$ *(en = ethylenediamine), also called 1,2-di-aminoethane.*

22.7 APPLICATIONS OF COORDINATION COMPOUNDS

Coordination compounds are found in living systems and have many uses in the home, in industry and in medicines. A few examples are given below:

Extraction of metals: cyanide ions are used for the for the extraction of gold and silver. The crushed ore is heated with an aq. cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion $[Au(CN)_2]^-$.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq) + 4\,OH^-(aq)$$

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound $Ni(CO)_4$ and then decomposing the latter to pure nickel.

Medicines: EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin cis $[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is used to lower blood pressure during surgery.

Qualitative Analyses: complex formation is useful for qualitative analyses.

(a) Separation of Ag^+ from Pb^{2+} & Hg^{2+}

$$Ag^+ + 2NH_{3(aq.)} \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]^+}$$

(b) Separation of IIA and IIB groups: The cations of IIB group form soluble complex with yellow ammonium sulphide.

(c) Cu^{2+} ion forms complex on addition of ammonia $[Cu(NH_3)_4]^{2+}$.

(d) Fe^{2+} forms a blue complex with $K_3Fe(CN)_6$, i.e. $K\,Fe^{II}[Fe^{III}(CN)_6]$.

(f) Cobalt(II) gives color with HCl due to the formation of complex $[CoCl_4]^{2-}$.

(g) Nickel forms a red complex $[Ni(DMG)_2]$ with dimethylglyoxime (H_2DMG).

INTEXT QUESTIONS 22.5

1. Name two elements which are extracted by complexation.
2. What is the use of EDTA in medicine?
3. Name the compound of platinum which is used as anticancer agent?
4. Give two uses of complexes in qualitative analyses
5. Write down geometrical isomers of $Pt(NH_3)Cl_2$.
6. $[Co(NH_3)_5SCN]^{2+}$ and $[Co(NH_3)_5NCS)^{2+}$ is the example of ....

WHAT YOU HAVE LEARNT

- Coordination compounds are compound in which a central metal ion is attached to a group of surrounding ligands by coordinate covalent bond. Ligands can be monodentate or polydentate, depending upon the number of donor atoms attached to the metal. Polydentate ligands are also called chelating agents. They form complexes that have rings of atoms known as chelate rings.
- The number of donor atoms bonded to a metal is called the coordination number of the metal. Common coordination number and geometries are 2 (linear), 4 (tetrahedral and square planar), and 6 (octahedral).
- Systematic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.
- Valance Bond Theory describes the bonding in complexes in terms of two-electron, coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands; sp (linear), sp^3 (tetrahedral), dsp^2 (square planar) and d^2sp^3 or sp^3d^2 (octahedral).
- Colour and magnetic behaviour of the complexes by using Crystal Field theory.
- Structural isomension i.e. ionisation, hydrate, coordination and Linkage Stereoisomerism, Geometrical and optical.
- Complexes are very useful in qualitative analyses and in medicine.

TERMINAL EXERCISE

1. Define the following:
   (i) Coordination number
   (ii) Coordination sphere
   (iii) Oxidation number
2. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.
3. Write the postulates of Werner's theory of coordination compounds.

4. Write down the name of the following complexes:
   (i) $K_3[Cr(C_2O_4)_3]$
   (ii) $[Co(NH_3)_2(H_2O)_2Cl_2]^+$
   (iii) $[Pt(en)_2]^{2+}$
   (iv) $[NiCl_4]^{2-}$
   (v) $[Fe(CN)_6]^{4-}$

5. Write down the formulae of the following complexes:
   (i) Tris(ethylenediamine)platinum(IV)
   (ii) Tetraaquadibromocobalt(III) ion
   (iii) Sodium tetraiodozincate(II)
   (iv) Tetracyanonickelate(II) ion
   (v) Dichlorotetrathiocyanatochromium(III) ion

6. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?

7. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are tetrahedral but differ in magnetic behaviour, explain.

8. $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic but have different geometry, explain.

9. $[NiCl_4]^{2-}$ is paramagnetic whereas $[Ni(CN)_4]^{2-}$ is diamagnetic, explain.

10. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:
    (i) $[Fe(CN)_6]^{4-}$
    (ii) $[Cr(NH_3)_6]^{2+}$
    (iii) $[Fe(CN)_6]^{3-}$
    (iv) $[NiCl_4]^{2-}$
    (v) $Ni(CO)_4$

11. Explain the application of complexes in extraction of elements, medicines and qualitative analyses.

12. Write down geometrical and optical isomeric of $[Co(Cu)_2Cl_2]^+$.

13. $[Co(NH_3)_6]^{3+}$ is yellow in colour but $[CoF_6]^{3-}$ is blue. Why?

14. $\{Fe(H_2O)_6]^{3+}$ shows magnetic moment is 5.9 BM but magnetic mement of $[Fe(CN)_6]^{3+}$ is 1.82 BM. Explain on the basis of CFT.

ANWERS TO INTEXT QUESTIONS

22.1

1. Primary valence corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions only.
2. Secondary valence of the metal corresponds to coordination number and is satisfied by negative ions or neutral molecules.
3. In both secondary valance is 6.
4. Octahedral.
5. Two i.e. Tetrahedral or square planar.

22.2

1. (i) 6
   (ii) 6
   (iii) 4
2. (i) +2
   (ii) +3
   (iii) +3
   (iv) +2
3. EDTA
4. NH_3, ethylenediammine and EDTA
5. +3, 6, Ethylenediammine.

22.3

1. (i) Tetraamminedichlorocobalt (III) ion
   (ii) Ammonium-hexaisothiocyanatochromate (III)
   (iii) Tetracarbonylnickel (0)
   (iv) Potassium-hexacyanoferrate (II)
   (v) Tris(ethylenediamine) chromium (III) chloride
2. (i) $[NiCl_4]^{2-}$
   (ii) $[Co(NH_3)_5NO_2]^{2+}$

(iii) $K_3[Fe(CN)_6]^-$

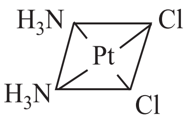
(iv) $[Cr(en)_2Cl_2]^+$

22.4

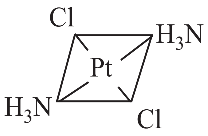
1. d^2sp^3
2. $[Fe(CN)_6]^{3-}$ is paramagnetic because it has one unpaired electron.
3. Both the complexes have sp^3 (tetrahedral) hybridization.
4. $[Ni(CN)_4]^{2-}$ is diamagnetic because it is square planar (dsp^2 hybridization). It has no unpaired electron.
5. Inner – d^2sp^3, outer – sp^3d^2
6. F^- is weak field ligand therefore electron will be filled $t_{2g}{}^4eg^{02}$ (i.e. four unpaired electron) therefore paramagnetic but CN^- is strong field ligand so electronic configuration will be $t_{2g}{}^6eg^0$ (no unpaired electron)
7. F^- weak field CN^- strong field ligand.

22.5

1. Gold and silver are extracted by cyanide process.
2. EDTA forms soluble complex with elements. It is used in the treatment of lead poisoning.
3. Cis-platin
4. $[Cu(NH_3)_4]^{2+}$ & $[Ni(DMG)_2]$
5.



(Cis)



(Trans)

6. Linkage isomerism

$Fe^{2+} = 3d^6$

MODULE - VII
CHEMISTRY OF ORGANIC COMPOUNDS

23. Nomenclature and General Principles
24. Hydrocarbons
25. Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)
26. Alcohols, Phenols and Ethers
27. Aldehydes, Ketones and Carboxylic Acids
28. Compounds of Carbon Containing Nitrogen
29. Biomolecules

23

NOMENCLATURE AND GENERAL PRINCIPLES

Organic compounds are all around us in several forms. They are present in a vast range of substances like fuels, foods, polymers and plastics, textiles, dyes, drugs, medicines, explosives, cosmetics, paints and pesticides. The word organic is derived from the word organism because the body of living things is composed mainly of organic compounds. In addition to the organic compounds of animals and plants origin, a large number of them have been synthesized in the laboratory. All organic compounds are known to contain carbon. The carbon atoms have a unique property called 'catenation' which is the ability to form long chains, rings and networks of carbon atoms resulting into the formation of large number of carbon compounds.

The basic organic compounds are *hydrocarbons* (compounds of carbon and hydrogen) which can be converted to different types of organic compounds by performing different reactions. The *organic chemistry* is the branch of chemistry which deals with the study of compounds of carbon. Some compounds containing carbon are not studied in this branch of chemistry such as oxides of carbon, metal carbides, metal cyanides, and metal carbonates and these come under 'Inorganic Chemistry'.

This lesson describes various rules for naming of organic compounds based upon IUPAC system. A distinction between different types of bond fission in organic compounds is also explained. Various types of reactions and electronic effects are discussed with examples. This lesson also covers different types of isomerism.

OBJECTIVES

After reading this lesson, you will be able to:

- name various types of organic compounds according to IUPAC system;
- distinguish between different types of bond fission;

- explain different types of reactions: substitution, addition, elimination and molecular rearrangements;
- identify nuclophiles and electrophiles;
- explain electronic effects in a covalent bond such as inductive effect; electromeric effect, resonance, hyperconjugation and steric hindrance;
- explain structural isomerism and stereoisomerism.
- define absolute configuration;
- assign absolute configuration (R-S and D-L) to a chiral centre; and
- qualitative and quantitative analysis of organic compound.

23.1 CLASSIFICATION OF HYDROCARBONS

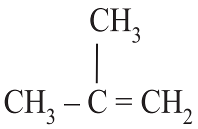
All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

1. **Open-chain or Aliphatic compounds:** This class includes all hydrocarbons (saturated and unsaturated) and their derivatives which have open-chain structures. Saturated hydrocarbons are those which contain single bonds between all carbon atoms such as

$CH_3 - CH_3$ and $CH_3 - CH_2 - CH_3$

On the other hand, unsaturated compounds contain a double (–C = C–) or a triple (–C ≡ C–) bond between two carbon atoms.

For example :



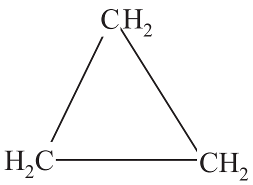
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$

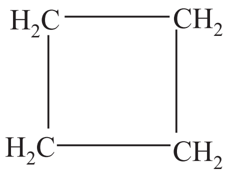
$CH_3 - CH = CH_2$ $CH_3 - C{\equiv}CH$

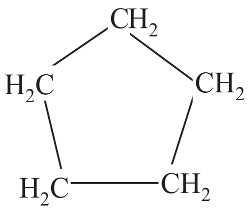
2. **Closed-chain or cyclic compounds:** These compounds have atleast one ring (cyclic) system. These are further divided into two sub-classes: **homocyclic** and **heterocyclic** based on the atoms present in the ring. They are called **homocyclic** or **carbocyclic** when the ring is formed by carbon atoms only.

Homocyclic (carbocyclic) compounds may again be divided into two groups namely **alicyclic** and **aromatic** compounds.

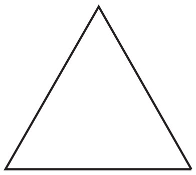
(i) **Alicyclic compounds:** This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:

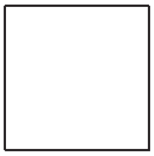


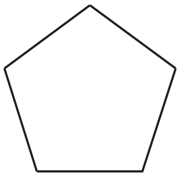




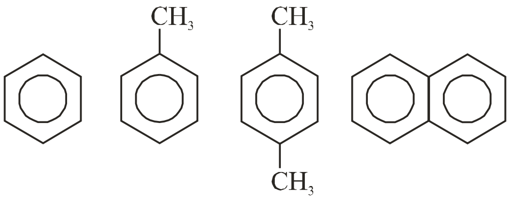
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a –CH_2–group.



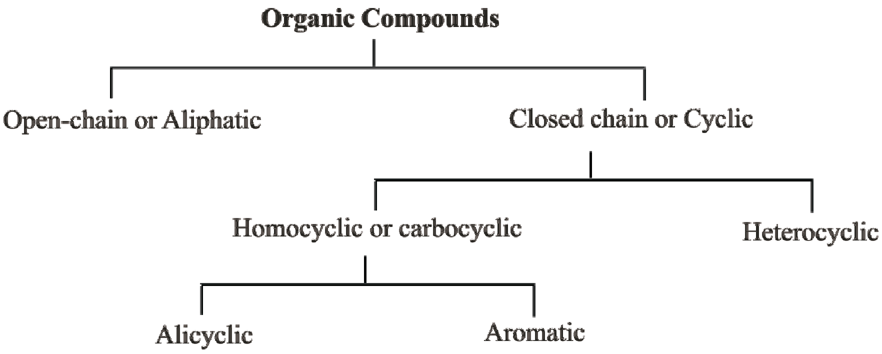




(ii) Aromatic compounds: The group of homocyclic compounds having special set of properties are called aromatic compounds which will be discussed in Lesson 24. They also have characteristic smell or *aroma* and hence called *aromatic*. These include aromatic hydrocarbons and their derivatives are examples of such compounds are as follows :

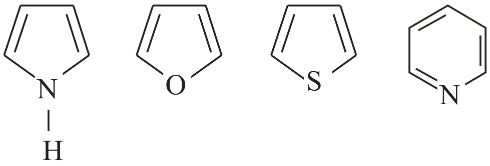


The above classification of the organic compounds can be summarised as below:



On the other hand, **heterocyclic compounds** contain one or more atom (usually O, N or S atom) other than the carbon atoms.

Some examples of heterocyclic compounds are as follows:



23.2 NOMENCLATURE OF ORGANIC COMPOUNDS

In the beginning, the organic compounds were named after the source from which they were obtained e.g. methane was named as marsh gas as well as damp fire because it was obtained from marshy places. Similarly, formic was named so because it was obtained from red ants (Latin name *formica*). These names of organic compounds are called common names or trivial names. There was no systematic basis for naming them and it was very difficult task to remember the names of so many organic compounds. Even the same compound was known by different names. In order to bring uniformity and rationality in naming the organic compounds throughout the world, International Union of Chemistry (in 1958) came out with a system of nomenclature later known as IUPAC (International Union of Pure and Applied Chemistry) system. Before explaining IUPAC system of nomenclature, we shall discuss about homologous series.

Homologous Series: A series of compounds in which the molecular formula of a compound differs from those of its neighbouring compounds by the CH_2 group, is known as a **homologous series**. Each of such homologous series is given a general name. For example, homologous series of open chain saturated hydrocarbons is known as **alkanes** and open chain unsaturated hydrocarbons form *two* series of compounds namely **alkenes** and **alkynes,** which contain carbon - carbon double bond and triple bond, respectively. Some members of homologous series of aliphatic hydrocarbons are listed in the Table 23.1.

Table 23.1: Homologous series of hydrocarbons

Satuarated		**Unsaturated**			
General Name : *Alkanes* **General Formula : C_nH_{2n+2}**		***Alkenes*** **C_nH_{2n}**			***Alkynes*** **C_nH_{2n-2}**
CH_4	Methane				
C_2H_6	Ethane	C_2H_4	Ethene	C_2H_2	Ethyne
C_3H_8	Propane	C_3H_6	Propene	C_3H_4	Propyne
C_4H_{10}	Butane	C_4H_8	Butene	C_4H_6	Butyne
C_5H_{12}	Pentane	C_5H_{10}	Pentene	C_5H_8	Pentyne
C_6H_{14}	Hexane	C_6H_{12}	Hexene	C_6H_{10}	Hexyne
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...

23.2.1 IUPAC Nomenclature of Acyclic Hydrocarbons

Acyclic hydrocarbons include straight chain as well as branched chain compounds.

Notes

(a) Straight chain Hydrocarbons: The names of these hydrocarbons consist of two parts. The first one is word **root** and second one is **suffix**. The word root designates the number of carbon atoms in the chain. Special word roots (*Meth-, Eth-, Prop-, But-,* etc.) are used for chains containing *one to four carbon atoms* but for chains of *five and more carbon atoms,* Greek number roots such as Pent-, Hex - etc. are used the in IUPAC word roots for a few carbon chains are given below in Table 23.2.

Table 23.2 : Some Word Roots and corresponding number of carbon atoms

Number of C- Atoms	Word root	Number of C- Atoms	Word root
1	Meth -	6	Hex -
2	Eth -	7	Hept-
3	Prop -	8	Oct-
4	But -	9	Non-
5	Pent-	10	Dec-

The general word root for any carbon chain is **alk.**

In order to write the IUPAC name, a suffix is added to the word root to indicate saturation or unsaturation in the hydrocarbons. These suffixes are listed below in the Table 23.3.

Table 23.3 : Types of hydrocarbons and suffixes in their name

Class of compound	Suffix	General name
Saturated	-ane	Alkane
Unsaturated (>C=C<)	-ene	Alkene
Unsaturated (–C≡C–)	-yne	Alkyne

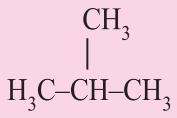
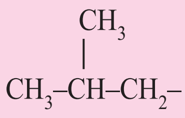
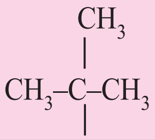
Let us consider some examples:

Compound	IUPAC Name	Word root	Suffix
$CH_3CH_2CH_3$	Propane	Prop-	ane
$CH_3CH_2CH_2CH_2CH_3$	Pentane	Pent-	ane
$CH_2 = CH_2$	Ethene	Eth-	ene
$CH_3-C \equiv CH$	Propyne	Prop-	yne

b) Branched chain Hydrocarbons

In branched chain hydrocarbons, one or more alkyl groups are present as side chain attached to the main straight chain of carbon atoms. The carbon atoms of the side chain constitute **alkyl groups.** These alkyl groups are written as prefixes in the IUPAC name. An alkyl group is obtained from an alkane by removing one hydrogen atom. Since the general formula of alkane is C_nH_{2n+2}, the general formula of alkyl group is C_nH_{2n+1}. The alkyl groups are generally represented by R– and named by replacing the suffix **ane** of the corresponding alkane by **yl**. Let us see some examples of the alkyl groups given in the Table 23.4.

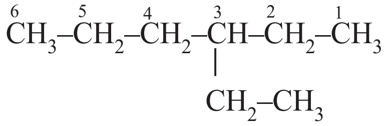
Table 23.4: Some alkyl groups

Parent Chain	Formula R-H	Alkyl group R-	Name
Methane	CH_4	CH_3-	Methyl
Ethane	CH_3CH_3	CH_3CH_2-	Ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2-$	Propyl
		$CH_3-\overset{\vert}{CH}-CH_3$	Isopropyl
Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$	Butyl
		$CH_3CH_2-\underset{\vert}{CH}-CH_3$	*sec*-butyl
Isobutane	 $H_3C-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-$	Isobutyl
		 $CH_3-\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$	*tert*-butyl

Branched chain hydrocarbons are named using the following rules in IUPAC system.

Rule 1. Longest chain Rule: According to this rule, the longest possible chain of carbon atoms is considered and the compound is named as the derivative of the corresponding alkane. *If some multiple bond is present, the selected chain must contain the carbon atoms of the multiple bond.* The number of carbon atoms in the selected chain determines the *word root* and the saturation or unsaturation will determine the *suffix.*

Let us consider the following example:

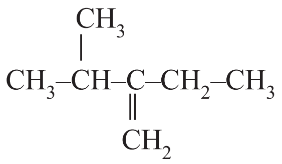


$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\underset{\underset{CH_2-CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

Word root **-Hex** + Suffix **-ane**

Since it has a main chain of *six* carbon atoms; hence, it will be named as a derivative of **hexane**.

Similarly,

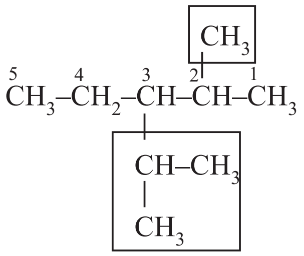


$CH_3-CH(CH_3)-C(=CH_2)-CH_2-CH_3$

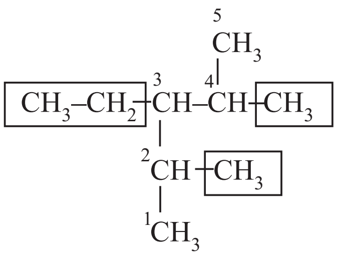
Wordroot - **But** + Suffix - **ene**

The main chain of carbon atoms containing double bond consists of *four* carbon atoms. Therefore, the compound will be a derivative of butene.

If two equally long chains are possible, the chain with maximum number of side chains is selected as the main chain.



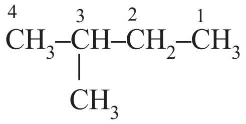
Main chain has 2 branches **(Wrong)**



Main chain has 3 branches **(Correct)**

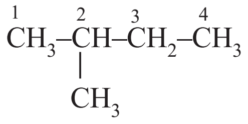
Rule 2: Lowest number or lowest sum rule: The longest carbon chain is numbered from one end to another and the positions of the side chain are indicated by the number of carbon atoms to which these are attached. The numbering is done in such a way that :

a) The substituted carbon atoms have the lowest possible numbers.



$\overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}H_3$

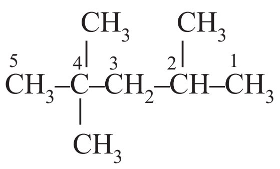
Wrong numbering



$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H_2-\overset{4}{C}H_3$

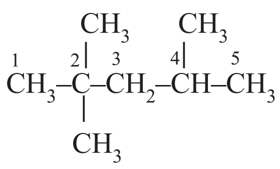
Correct numbering

b) The sum of numbers used to indicate the positions of various alkyl groups must be the lowest.



$\overset{5}{C}H_3-\overset{4}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{2}{C}H(CH_3)-\overset{1}{C}H_3$

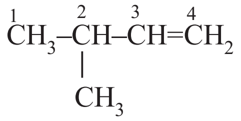
Sum of positions = 2+4+4 = 10
(Wrong)



$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H(CH_3)-\overset{5}{C}H_3$

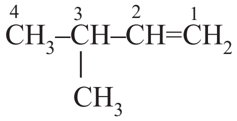
Sum of positions = 2+ 2+4 = 8
(Correct)

Rule 3 : If some multiple bond is present in the chain the carbon atoms involved in the multiple bond should get the lowest possible numbers. For example :



$\overset{1}{C}H_3-\underset{\displaystyle |\atop CH_3}{\overset{2}{C}H}-\overset{3}{C}H=\overset{4}{C}H_2$

Wrong numbering



$\overset{4}{C}H_3-\underset{\displaystyle |\atop CH_3}{\overset{3}{C}H}-\overset{2}{C}H=\overset{1}{C}H_2$

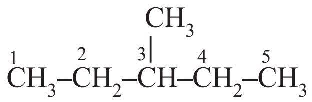
Correct numbering

Rule 4 : Naming of compounds with one alkyl group as the substituent (side chain)

The name of a substituted hydrocarbon consists of the following parts.

Position of substituent - Name of *substituent,* Word *root, Suffix.*

Let us consider a compound represented by the following structure:

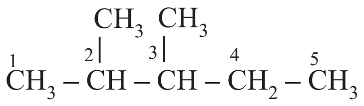


$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{\displaystyle CH_3 \atop 3|}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_3$

In the given structure, we find that the longest chain consists of *five* carbon atoms and the substituent is ***methyl*** group at position number 3. The word root is **Pent** and suffix is **ane.** Hence, the name is 3-methylpentane.

Rule 5 : Naming the same alkyl groups at different positions or more than one alkyl groups

If the compound contains more than one identical alkyl groups, their positions are indicated separately and the prefixes *di* (for two), *tri* (for three) etc. are attached to the name of the substituents. The positions of the substituents are separated by commas (,). In the following structure, two methyl groups are attached to the main chain of five carbon atoms.



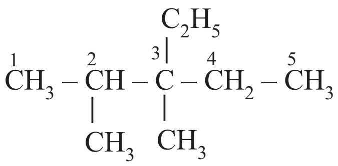
$\overset{1}{C}H_3-\overset{\displaystyle CH_3 \atop 2|}{C}H-\overset{\displaystyle CH_3 \atop 3|}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_3$

You can see that they are attached to the positions 2 and 3 of the main chain. Hence, the name of the compound is 2,3-dimethylpentane.

Rule 6: Naming different alkyl substituents

If there are different alkyl substituents present in the compound, their names are written in the alphabetical order. However, the prefixes *di, tri,* etc. are not considered in deciding the alphabetical order.

For example, in the compound shown below the longest chain consists of **five carbon atoms;** hence, the parent hydrocarbon is pentane. The main chain has two methyl groups at C_2 and C_3 and one ethyl group at C_3 as substituents. The names of these alkyl



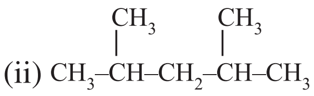
$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{C_2H_5}}{|}}{\overset{3}{\mathrm{C}}}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$$

groups are written before the name of parent alkane and their positions are indicated by number of carbon atom to which they are attached. Thus, the name of the compound will be 3-ethyl-2, 3-dimethylpentane.

INTEXT QUESTIONS 23.1

1. Identify word *root* and *suffix* for the following :
   (i) $CH_3CH_2CH_2CH_2CH_2CH_3$
   (ii) $CH_3CH_2CH = CHCH_2$
   (iii) $CH_3C \equiv CH$
2. Give IUPAC name to the following compounds

(i) $CH_3–CH=CH–CH_2–CH_2–CH_2–CH_2–CH_3$

(ii) 

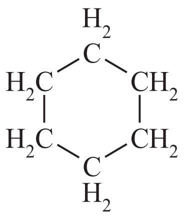
$$\mathrm{CH_3}-\underset{}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_3}$$

23.2.2 Nomenclature of Cyclic Hydrocarbons

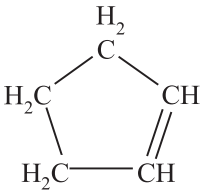
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) Alicyclic Compounds

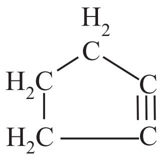
As we have already discussed (in Section 23.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix* **'cyclo'** before the *word root*. The suffix **ane, ene** or **yne** are written according to the saturation or unsaturation in the ring structure. Given below are some examples of alicyclic compounds.



Cyclohexane

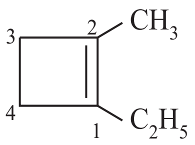


Cyclopentene

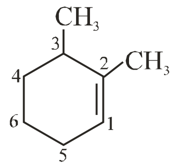


Cyclopentyne

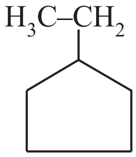
If an alkyl substituent is present, it is indicated by the appropriate *prefix* and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



1-Ethyl-2-methylcyclobutene



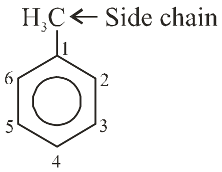
2,3-Dimethylcyclohexene



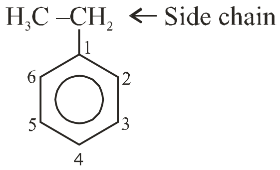
Ethylcyclopentane

b) Aromatic Compounds

The most important members of this class are benzene and its derivatives. For naming an alkyl substituted benzene, the carbon atoms of benzene are numbered from 1 to 6 by giving the lowest possible number to the position of the side chain or substituent. This is shown below.

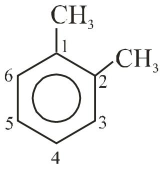


Methylbenzene
(Toluene)

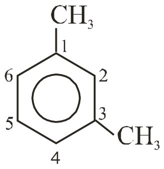


Ethylbenzene

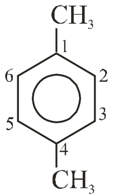
Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1,2; 1,3 and 1, 4 derivatives. These are also known as *ortho*- (or *o*–), *meta*- (or *m*-) and *para*- (or *p*-) substituted compounds, respectively.



1, 2-Dimethylbenzene
(*ortho*-Xylene)



1, 3-Dimethylbenzene
(*meta*-Xylene)



1, 4-Dimethylbenzene
(*para*-Xylene)

23.2.3 Writing Structure of Hydrocarbons from their IUPAC Names

Till now, we have named hydrocarbons from their structures using IUPAC nomenclature. Let us now do the reverse exercise i.e. writing structure of hydrocarbons when their IUPAC names are given. Let us take some examples to write structures for given IUPAC names.

Example 1. Writing the structure of **4-Ethyl-5-methylhex-2-ene**

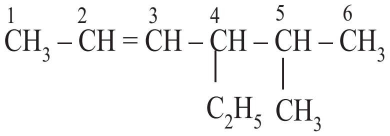
Step 1 The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C_2 is drawn.

$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

Step 2 Attach ethyl group at C_4 and methyl group at C_5.

Step 3 Attach H-atoms to the C-atoms of main chain to satisfy tetravalency of all the carbon atoms.

Thus, the correct structure of the compound is as given below:



$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{C_2H_5}{\overset{4}{CH}}-\underset{CH_3}{\overset{5}{CH}}-\overset{6}{CH_3}$$

Example 2. Writing the structure of **Octa-3,5-diene**

Step 1- The skeleton of parent hydrocarbon chain of **eight** carbon atoms is drawn.

Step 2- Make C=C at C_3 and at C_5.

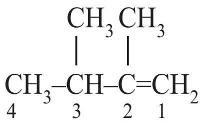
Step 3- Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms.

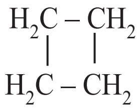
The correct structure of the compund is as follows :

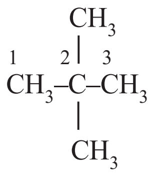
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH}=\overset{6}{CH}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

The following compounds illustrate some more examples:

(i) 2,3-Dimethylbut-1-ene (ii) Cyclobutane (iii) 2,2-Dimethylpropane





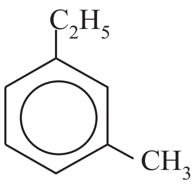


After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.

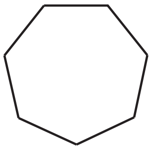
INTEXT QUESTIONS 23.2

1. Write IUPAC names for the following compounds :

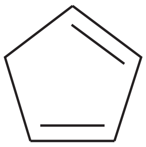
(i)



(ii)



(iii)



2. Write the structural formula for the following compounds:

(i) 1,3-Dimethylcyclohexane (ii) Ethylcyclobutane (iii) *n*-Propylbenzene

23.2.4 IUPAC Nomenclature of Aliphatic Organic Compounds Containing Functional Groups

A **functional group** is an atom or group of atoms which is responsible for characteristic properties of a compound. For example :

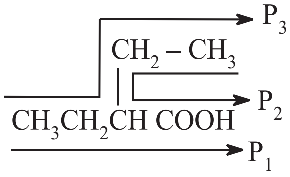
–Cl, –Br, –I, –COOH, –OH, $–NH_2$ etc.

a) Compounds with one functional group (monofunctional Derivatives): The derivatives of hydrocarbons containing only one functional group are called monofunctional derivatives.

Most of the IUPAC names of functional derivatives of hydrocarbons are derived by replacing the suffix **ane** of the parent alkane (corresponding to the number of carbon-atoms in the longest chain) by a specific *suffix* for the functional groups, (see Table 23.5). There are some derivatives in which a particular *prefix* is added to the parent alkane name as in *nitroalkanes, haloalkanes,* and *haloarenes etc*. Given below are some rules for the IUPAC nomenclature of organic compounds containing functional groups. In addition to the *rules listed below,* all the general rules discussed earlier for naming of hydrocarbons are also applicable to such compounds.

Rule1: First of all the longest chain of carbon atoms containing the functional group is identified. In case of carbon containing functional group, (–CHO, –COOH) the main chain must include the carbon atom of the group.

For Example :



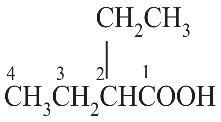
(Structure –I)

P_1 or P_2 are correct selections of chain of carbon atoms whereas P_3 is wrong selection as it does not include the carbon atom of the functional group.

Rule 2: The longest continuous carbon atom chain is numbered from that end which will give the lowest number to the carbon atom bearing the functional group.

Rule 3: There is a specific **suffix** for each functional group that replaces the ending **-e** in the name of the corresponding parent alkane.

Rule 4: If the carbon chain is branched, then the attached alkyl groups are named and numbered as in Structure I (rule 1) main chain contain a branch of two carbon atoms i.e., ethyl group at position 2.



$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H(CH_2CH_3)\overset{1}{C}OOH$$

(Structure I)

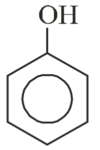
Rule 5: While writing the name of the compound, place the substituents in the alphabetical order.

Table 23.5 lists some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

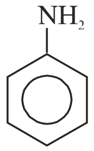
Table 23.5: Some Common Functional Groups and their Aliphatic Derivatives

Functional Group	Suffix/ Prefix	General name	Example (IUPAC name)
–OH (Hydroxy)	–ol	Alkanol (Alcohols)	CH_3CH_2OH (Ethanol)
–COOH (Carboxyl)	–oic acid	Alkanoic acid	CH_3COOH (Ethanoic acid)
$–SO_3H$ (Sulphonic)	–	Alkylsulphonic acid	$CH_3CH_2SO_3H$ (Ethyl sulphonic acid)
–CHO (Aldehydic)	–al	Alkanal	CH_3CHO (Ethanal)
>CO (Ketonic)	–one	Alkanone	CH_3COCH_3 (Propanone)
$–CONH_2$ (Amide)	–amide	Alkanamide	CH_3CONH_2 (Ethanamide)
–COX (Carboxyl halide)	–oyl halide	Alkanoyl halide	CH_3COCl (Ethanoyl chloride)
–COO– (Ester)	–oate	Alkyl alkanoate	CH_3COOCH_3 (Methyl ethanoate)
–CN(Cyano	–nitrile	Alkanenitrile	CH_3CH_2CN (Propanenitrile)
–SH (Thiol)	–thiol	Alkanethiols	CH_3CH_2SH (Ethanethiol)
$–NH_2$ (Amino)	–amine	Alkanamine	$CH_3CH_2NH_2$ (Ethanamine)
–O – (Ether)	–oxy	Alkoxyalkane	$CH_3–O–CH_3$ (Methoxymethane)
–C≡C– (Yne)	–yne	Alkyne	$CH_3C≡CCH_3$ (But-2-yne)
–C=C– (Ene)	–ene	Alkene	$CH_3CH=CHCH_3$ (But-2-ene)
–X = –F,–Cl, –Br, –I	–Halo **(Prefix)**	Haloalkane	$CH_3CH_2–X$ (Haloethane)
$–NO_2$ (Nitro)	–Nitro **(Prefix)**	Nitroalkane	$CH_3CH_2NO_2$ (Nitroethane)

Certain derivatives have some specific general names e.g. monohydroxybenzene is called **phenol** and monoaminobenzene as **aniline.**

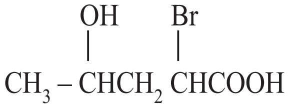


Phenol



Aniline

b) Naming of Organic compounds with more than one functional group: In case of organic compounds containing more than one functional group, one group is given preference over the other(s) in deciding the parent compound. The priority order of the various functional groups is as follows; –COOH, –COOR, $-SO_3H$, –COX, $-CONH_2$, –CHO, –CO–, –CN, –OH, –SH, –O–, $-NH_2$, –X (halogen), $-NO_2$, –C=C–, and –C≡C–. Let us try to name a polyfunctional compound by following the priority of the functional groups.



$$CH_3-\underset{}{\overset{\overset{OH}{|}}{C}}HCH_2\overset{\overset{Br}{|}}{C}HCOOH$$

2-Bromo-4-hydroxypentanoic acid

In the above example, –COOH group is given priority over the –OH and –Br (halo) groups.

23.3 TYPES OF REACTIONS IN ORGANIC COMPOUNDS

You are aware that a chemical reaction occurs when one substance is converted into another substance(s). A chemical reaction is accompained by breaking of some bonds and by making of some others. In organic chemistry, this can happen in more than one way involving a variety of reactions. The different types of reactions in organic compounds are: (i)Substitution (ii) Elimination (iii) Addition and (iv)Molecular Rearrangements.

These different ways of occurrence of organic reactions can be understood by the study of reaction mechanisms. A **reaction mechanism** is defined as the detailed knowledge of the steps involved in a process in which the reactant molecules change into products. Let us explain first some of the terms used in reaction mechanism.

23.3.1 Breaking of a Covalent Bond - Types of Bond Fission

Chemical reactions involve breaking of one or more of the existing chemical bonds in reactant molecule(s) and formation of new bonds leading to products. *The breaking of a covalent bond is known as bond fission.* We know that a covalent bond is formed by the sharing of two electrons from two atoms. During bond breaking or bond fission, the two shared electrons can be distributed equally or unequally between the two bonded atoms. There are **two types of bond fission.**

1. **Homolytic fission:** *The fission of a covalent bond with equal sharing of bonding electrons is known as homolytic fission.*
   Homolytic fission in a hypothetical molecule: $A—B \longrightarrow \underset{\text{(Free radicals)}}{A\bullet + B\bullet}$

   Now consider the following C-C bond fission:

$$H_3C - CH_3 \xrightarrow[\text{Light}]{\text{Heat}} \bullet CH_3 + \bullet CH_3$$

(Free radicals)

The neutral species so formed are known as **free radicals.**

Free radicals are neutral but reactive species having an unpaired electron and these can also initiate a chemical reactiion.

2. **Heterolytic fission :** *The fission of a covalent bond involving unequal sharing of bonding electrons is known as heterolytic fission.* The heterolytic fission of a hypothetical molecule is shown below.

$$A : B \rightarrow \underset{\textbf{Carbocation}}{A^+} \quad + \quad \underset{\textbf{Carbanion}}{B^-}$$

This type of bond fission results in the formation of *ions*. The ion which has a *positive charge on the carbon atom,* is known as the **carbonium ion** or a **carbocation.** For example,

$CH_3\overset{+}{C}H_2$ (Ethyl carbocation) and $CH_3\overset{+}{C}HCH_3$ (Isopropyl carbocation)

On the other hand, an ion with a *negative charge* on the carbon atom is known as the **carbanion.**

For example,

$CH_3\overset{-}{C}H_2$ (Ethyl carbanion), $\overset{-}{C}H_3$ (Methyl carbanion)

The charged species obtained by the heterolytic fission initiate chemical reactions and they are classified as electrophiles and nucleophiles.

Electrophiles: An electrophile is an electron deficient species and it may be positively charged or neutral. Examples are H^+, NO_2^+, Br^+, Cl^+, Ag^+, $CH_3\overset{+}{C}O$, BF_3 etc. Thus, an electrophile is an electron seeking species and hence, it attacks at a position of high electron density.

Nucleophiles : A nucleophile is negatively charged or electron rich neutral species. Examples of nucleophiles are OH^-, NO_2^-, H_2O, $:NH_3$ etc. Nucleophiles attacks a position of low electron density.

23.3.2 Electron Displacements in a Covalent Bond

For a reaction to take place by breaking of a covalent bond, with the attack of a nucleophile or electrophile, the molecule or bond under attack must develop polarity on some of its carbon atoms. This polarity can only be developed by the displacement (partial or complete) of bonding electrons due to certain effects. Some of these electronic effects are permanent (e.g. inductive) and others are temporary (e.g. electromeric) in nature. Such changes or effects involving displacement of electrons in the substrate molecules (molecule under attack of a reagent) are known as electron displacement or **electronic effects**. Some of these effects are discussed below.

(a) Inductive effect: In a covalent bond between the two dissimilar atoms, the shared electron pair is attracted more towards the atom having greater electronegativity. Let us consider the case of a haloalkane (higher than halomethane). The halogen atom (X) being more electronegative than carbon atom, pulls the bonded electrons of the C–X bond. Thus, the C–X bond is polarised as shown below.

$$C^{\delta+} \rightarrow C^{\delta-}$$

The carbon atom gets a partial + ve charge (δ +) and halogen atom a partial negative charge (δ–). This positively charged C_1 attracts bonded electrons of $C_1 - C_2$ bond, thus making C_2 atom a little less positive than C_1. Similarly, this +ve charge is shifted to C_3 but to a very less magnitude (nearly zero +ve charge is present after third atom)

$$\underset{3}{\overset{\delta\delta\delta+}{C}} \rightarrow \underset{2}{\overset{\delta\delta+}{C}} \rightarrow \underset{1}{\overset{\delta+}{C}} \rightarrow \overset{\delta-}{X} \text{ (where X = F, Cl, Br).}$$

This transmission of induced charges along a chain of σ bonded carbon atoms is known as ***inductive effect****.* The inductive effect is a permanent polarisation in the molecule and it decreases as we move along a chain of carbon atoms, away from the electronegative atom. Many of the properties of organic compounds such as acidic strength of carboxylic acids are explained on the basis of inductive effect.

Groups with – I Effect (Electron Withdrawing Groups) :

Any atom or group of atoms that withdraws electrons more strongly than the H-atom, is said to have – I effect. Following are various groups arranged in the decreasing order of their –I effect.

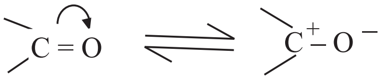
$$(CH_3)_3N^+ > -NO_2 > -CN > -F > -Cl > -Br > -I > -OH > -OCH_3 > -C_6H_5 > -H$$

Groups with + I Effect (Electron Releasing Groups) :

Any atom or group of atoms that repels electrons more strongly than hydrogen, is said to have +I effect.Following are the various groups in the decreasing order of +I effect.

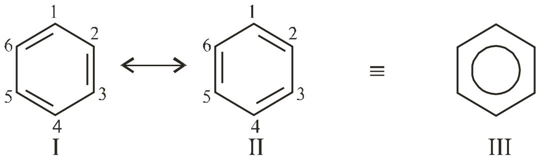
$$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > -CH_3 > -H$$

(b) Electromeric effect : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g. $>C=C<$, $>C=O$, $>C=N$ etc.). It involves the complete transfer of electrons resulting into the development of + ve and – ve charges within the molecule. The electromeric effect takes place in the direction of more electronegative atom and is generally shown by an arrow starting from the original position of the electron pair and ending at the new position of the electron pair. In a carbonyl group it operates as follows :



The electromeric effect is represented by the symbol **E**. It is known as **+E effect** when displacement of electron pair is away from the atom or group, or **– E effect** when the displacement is towards the atom or group. As in above example it is +E effect for C and –E effect for O.

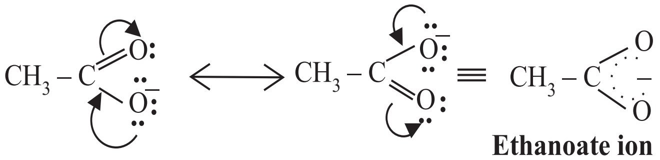
(c) Resonance : This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound are arrived at by the redistribution of valence electrons. The true structure of the compound is an intermediate of all the possible resonating structures or canonical structures and thus called *a resonance hybrid*. For example, the benzene molecule (C_6H_6) may be represented by the following two structures, I and II.



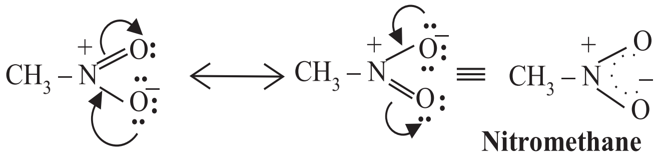
Resonating or canonical structures Resonance hybrid

The evidence in support of the hybrid structure (III) of 'benzene' is available from the bond length data. Equal bond lengths of all C–C bonds (139 pm), which is an intermediate value of C–C single bond (154 pm) and C=C double bond (130 pm) lengths, indicates that each C–C bond in benzene (structure III) has a partial double bond character. Hence, structure III, a resonance hybrid, represents the benzene molecule.

Some more examples of resonance structures are as follows:

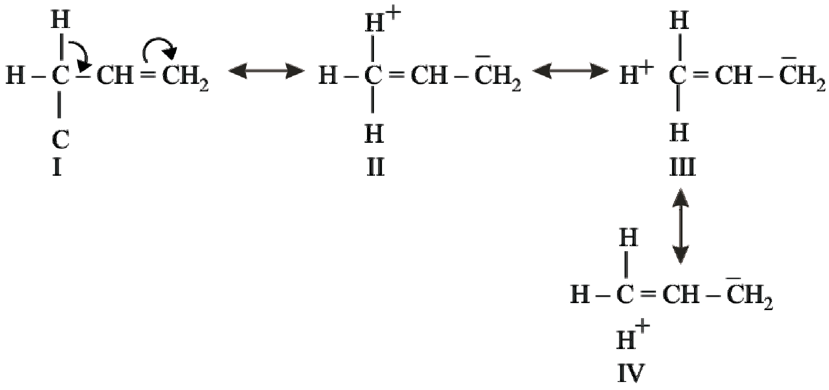


Ethanoate ion



Nitromethane

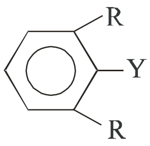
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance*. It involves the conjugation of σ (sigma) bond with π (pi) bond. For example, hyperconjugation in propene can be represented as follows.



The structures II to IV have no bond between one of the H-atom and the C-atom.

23.3.3 Steric Hinderance

The effect is caused by the large bulky groups present in the vicinity of the reaction centre. This effect was first observed by Hofmann (1872) and Meyer (1874). They regarded it as mechanical hinderance for the attacking species to approach the reaction site. Hofmann (1872) observed that when a compound of the type



(where, Y = $-COOH$, $-CONH_2$, $-CHO$, $-NH_2$ etc. and R = $-CH_3$, $-C_2H_5$ etc) is treated with the reagents such as Cl^-, Br^-, I^-, OH^-, etc., the reaction is hindered or retarded by the substituents at 'R'. The magnitude of hinderance is proportional to the size and number of substituents present in the vicinity of reaction site. Meyer (1874) observed that rate of esterification of aliphatic carboxylic acids and found that their activity was decreased by increasing the number of substituents at the carbon atom adjacent to the COOH group.

$$\underset{\text{decreasing order of reactivity with alcohols}}{\underline{CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCO}}$$

INTEXT QUESTIONS 23.3

1. What is the condition of polarity for a covalent bond?
2. Identify the groups with –I and +I effect from the following species :

   $-NO_2$, $-CH_3$, $-CN$, $-C_2H_5$, $-C_6H_5$ and $CH_3-\underset{|}{CH}-CH_3$

3. What is the difference between electromeric and inductive effects?
4. Classify the following species as electrophiles or nucleophiles :

   (i) H_3O^+ (ii) NO_2^+ (iii) Br^- (iv) $C_2H_5O^-$

   (v) CH_3COO^- (vi) SO_3 (vii) CN^- (viii) $^+CH_3$ (ix) $:NH_3$

With the above general background, let us study various types of reactions in a little more details.

23.3.5 Substitution Reactions

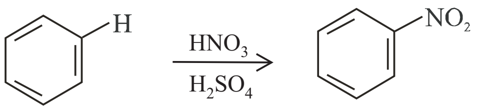
A substitution reaction involves the displacement of one atom or group in a molecule by another atom or group. Aliphatic compounds undergo **nucleophilic substitution** reactions. For example, a haloalkane can be converted to a wide variety of compounds by replacing halogen atom (X) with different nucleophiles as shown below.

$$\overset{\delta+}{R}-\overset{\delta-}{X}+Nu: \longrightarrow R-Nu+X^-$$

Haloalkane

(where R- is an alkyl group and $Nu:$= $-OH$, $-NH_2$, $-CN$, $-SH$, $-OR'$, $-NHR'$ etc.)

There is yet another type of substitution reaction which takes place in an aromatic hydrocarbons. In this case, an **electrophilic reagent** attacks the aromatic ring because the latter is electron rich. The leaving group, in this case, is always one of the hydrogen atom of the ring.

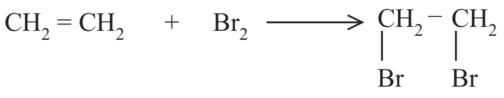


Nitrobenzene

For example, in case of nitration the $-NO_2$ group replaces one hydrogen atom of benzene.

23.3.6 Addition Reactions

Unsaturated hydrocarbons such as alkenes and alkynes are extremely reactive towards a wide variety of reagents. The carbon-carbon double bond (–C=C–) of an alkene contains two types of bonds; one σ (sigma) bond and another π (pi) bond. In alkynes, out of the three carbon-carbon bonds, one is σ (sigma) bond and the other two are π (pi) bonds. The π (pi) bond is weaker than the σ (sigma) bond and breaks easily. For example, the colour of bromine solution disappears when added to the unsaturated hydrocarbons. This is due to the following addition reaction.



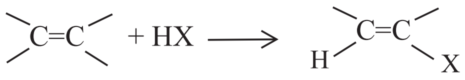
$$CH_2=CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

1, 2-Dibromoethane
(Colourless)

Similarly, hydrogen, halogen acids and chlorine add on to a –C=C– double bond, as shown below.

$$CH_3-CH=CH_2+H_2 \xrightarrow{(Ni/Pt\ as\ catalyst)} CH_3\,CH_2\,CH_3$$

The multiple bond of an alkene or alkyne is a region of high electron density. Therefore, it is easily attacked by the electrophilic reagents. One of the most thoroughly studied addition reactions is that of halogen acids.



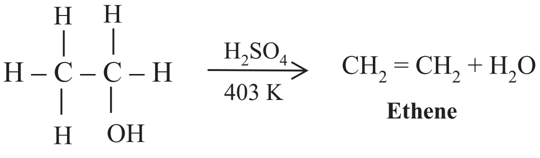
In alkynes (–C≡C–), two molecules of hydrogen add; first to give an alkene and finally the corresponding alkane, as shown below:

$$CH_3C\equiv CH \xrightarrow{+H_2/Ni-Pt} CH_2CH=CH_2 \xrightarrow{+H_2/Ni-Pt} CH_3CH$$

Propyne **Propene** **Propane**

23.3.7 Elimination Reactions

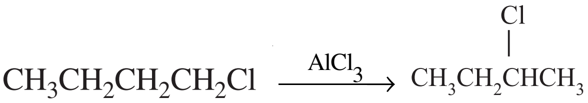
From the above discussion, you know that we get a saturated compound by the addition reaction of an alkene. The reverse reaction i.e. the formation of an alkene from a saturated compound, can also be carried out and is called an **elimination reaction.** An elimination reaction is characterized by the removal of a small molecule from adjacent carbon atoms and the formation of a double bond. For example, when alcohols are heated with a strong acid as the catalyst, a molecule of water is removed and a double bond is formed.



Ethanol **Ethene**

23.3.8 Molecular Rearrangements

A molecular rearrangement proceeds with a fundamental change in the hydrocarbon skeleton of the molecule. During this reaction, an atom or group migrates from one position to another. For instance, 1-chlorobutane in the presence of a Lewis acid ($AlCl_3$) rearranges to 2-chlorobutane.



$$CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3} CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_3$$

1- Chlorobutane **2 - Chlorobutane**

INTEXT QUESTIONS 23.4

1. Write the products of each of the following reactions:

   (i) $CH_3CH_2Br + CN^- \longrightarrow$

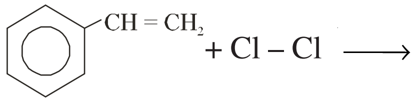
   (ii) $CH_3Cl + RNH_2 \longrightarrow$

2. Write the conditions for nitration of benzene.

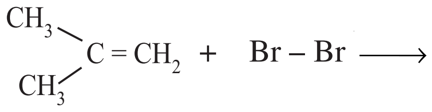
3. Predict the products of the following reactions :

   (i) $CH_2 = CH_2 \xrightarrow{+HBr}$

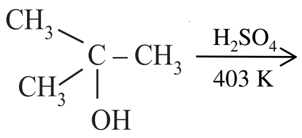
   (ii)



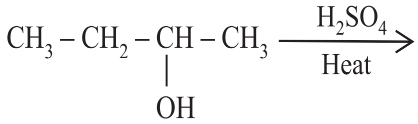
   (iii)



   (iv)



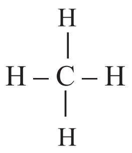
   (v)



$$CH_3 - CH_2 - \underset{OH}{\underset{|}{C}H} - CH_3 \xrightarrow[Heat]{H_2SO_4}$$

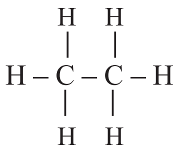
23.4 ISOMERISM

The simple alkanes containing upto three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below :



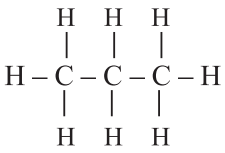
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methane



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

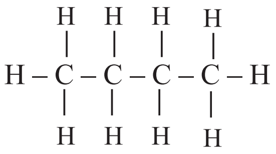
Ethane



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

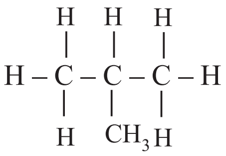
Propane

But for next higher hydrocarbon i.e. butane (C_4H_{10}), there are two possible ways in which the carbon atoms can be linked together. They may be linked to form a **straight chain** or a **branched chain.**



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

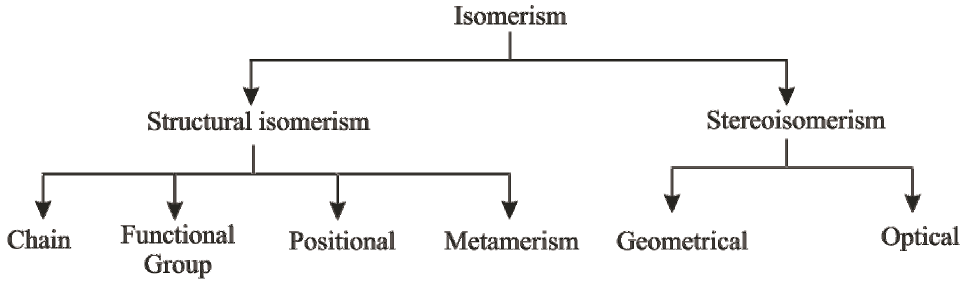
Butane (b.p.- –5 °C) 268 K



$$\begin{array}{c} H\ \ \ H\ \ \ H \\ |\ \ \ \ |\ \ \ \ | \\ H-C-C-C-H \\ |\ \ \ \ |\ \ \ \ | \\ H\ \ CH_3\ H \end{array}$$

(2-Methylpropane) (b.p.- 12 °C) 261 K

Thus, there are two types of butane which are different compounds and they show different properties. *Different substances which have the same molecular formula but differ in their structures, physical or chemical properties are called* ***isomers*** and this phenomenon is known as **isomerism.** The isomerism can be of various types as shown below :

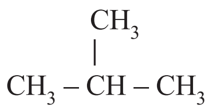


1. Structural Isomerism : Compounds which have the same molecular formula but differ in their structure are called **structural isomers** and the phenomenon is called **structural isomerism**. This is further subdivided into four types; **chain, functional, positional isomerism**, and **metamerism**.

(i) **Chain isomerism :** These isomers differ in the chain of the carbon atoms, for instance, *n*-butane and isobutane are two isomers of C_4H_{10}.

$CH_3-CH_2-CH_2-CH_3$

***n*-Butane**



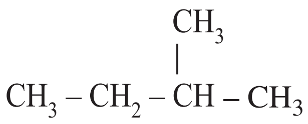
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$

Isobutane

Similarly, pentane (C_5H_{12}) has the following three isomers :

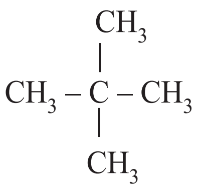
$CH_3-CH_2-CH_2-CH_2-CH_3$

***n*-Pentane**



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

2-Methylbutane
(*Iso*pentane)



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

2,2- Dimethylpropane
(*Neo*pentane)

Similarily, hexane (molecular formula C_6H_{14}) can have five chain isomers.

(ii) **Functional isomerism :** These isomers differ in the type of functional group. For example; *ethanol* and *ether* the two isomers having molecular formula C_2H_6O, belong to two different classes of organic compounds. Similarly, the two isomers corresponding to molecular formula $C_3H_6O_2$ are, an acid and an ester having quite distinct structures and properties.

(Molecular Formula: C_2H_6O) C_2H_5OH and $CH_3—O—CH_3$

Ethanol **(alcohol)** **Methoxymethane** **(ether)**

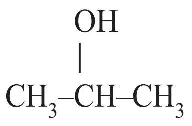
(Molecular Formula: $C_3H_6O_2$) CH_3CH_2COOH and $CH_3—COOCH_3$

Propanoic acid **Methyl ethanoate**

(iii) **Positional isomerism:** These isomers differ in the attachment of the functional group to the chain at different positions. Examples are as follows :

$CH_3CH_2CH_2OH$ and

Propan-1-ol

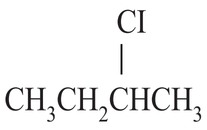


$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$

Propan-2-ol

$CH_3CH_2CH_2CH_2Cl$ and

1-Chlorobutane



$CH_3CH_2\overset{\overset{CI}{|}}{CH}CH_3$

2-Chlorobutane

(iv) **Metamerism** is exhibited by those compounds in which functional group comes in between the carbon chain and breaks the continuity of the chain. This breaking occurs at different positions and different isomers are formed which are called Metamers. For example, 1-methoxypropane and ethoxyethane are two metamers differing in chain length (size of alkyl groups) on the two sides of oxygen atom as shown below.

$CH_3 - O - CH_2CH_2CH_3$ and $CH_3\,CH_2 - O - CH_2CH_3$

1-Methoxypropane **Ethoxyethane**

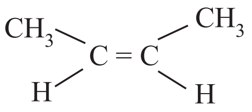
2. Stereoisomerism : Steroisomerism is exhibited by the compounds which have the same structural formula i.e. their atoms are connected in the same order, but they differ from each other in the way these atoms (or groups) are arranged in space.

Stereoisomerism can be further divided into **conformational isomerism** and **Configurational isomerism**.

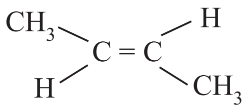
The **absolute configuration** of a compound *is the actual three dimensional arrangement of the groups or atoms in space*. Thus, *configurational isomers* have uique configuration. These isomers *cannot* be converted to each other *without breaking of bonds*. The configurational isomerism could be further sub-divided into **geometrical** and **optical isomerisms**. These are explained below.

Conformational isomerism is exhibited by those isomers which can be interconverted **without breaking of bonds**. Thus, conformational isomers are obtained by **rotation** about single bonds. The conformational isomerism is explained using ethane as the example, see section 24.13.

(i) **Geometrical Isomerism:** Consider two isomers of 2-butene as shown below.

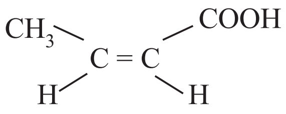


cis– **But-2-ene**

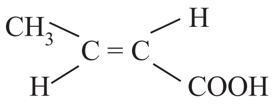


trans– **But-2-ene**

A *cis*- **isomer** is the one having identical groups on same side of double bond. On the other hand, a *trans*-**isomer** has identical groups on opposite side. In the above structures, *cis*-2- butene (two – CH_3 groups on the same side) and *trans*-2-butene (two – CH_3 groups on different sides) are two geometrical isomers (stereoisomers) as they differ in the geometries of the groups around the double bond. Another example of *cis*-and *trans*-isomerism is **2-butenoic acid** or **But-2-enoic acid.**



cis- **But-2-enoic acid**



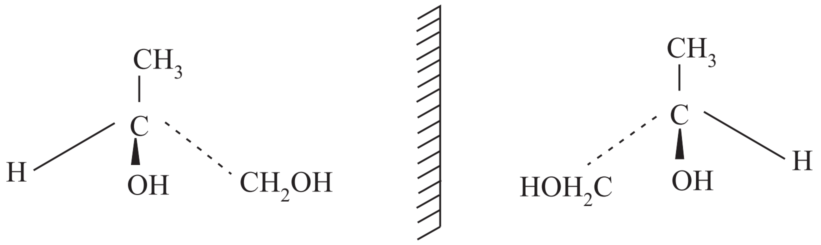
trans-**But-2-enoic acid**

Note that in the above examples, the two isomers exist because the rotation of groups across C=C bond is not possible (it is also called as restricted rotation).

Geometrical isomerisms is also shown by cyclic compounds and compounds containing –C=N– bond, about which you will study at higher level.

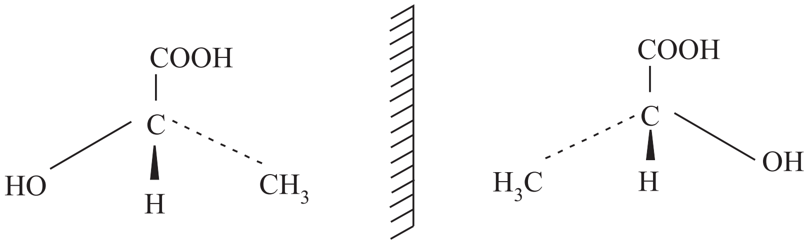
(ii) **Optical Isomerism:** The optical isomerism is shown by the compounds having at least one carbon atom joined to four different atoms or groups. Such a carbon atom is called **asymmetric** or **chiral** carbon atom; and those which are not chiral (do not have four different groups) are called **achiral.** A chiral compound can have two different arrangements of groups attached to the chiral carbon as shown below for 1,2-dihydroxypropane.

The wedge sign (▲) shows that the direction of the bonds is towards the viewer and dotted line (.....) indicates backward direction of the bonds.



Mirror

The resulting isomers are non-superimposable mirror images of each other and are called enantiomers. Thus, the enantiomers differ in the three-dimensional arrangement of atoms or groups. Another example of enantiomers is that of lactieacid as shown below:



Mirror

Enantiomers of Lactic acid

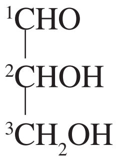
The optical isomers have idenical physical properties except optical activity. They rotate the plane of plain polarized light in opposite directions. The **plain polarized light** is defined as the light that vibrates in one plane only. *The rotation of the plane of polarized light is called* ***optical activity.*** Those substances that can rotate the plane of polarized light are said to be **optically active.** Compounds that rotate the plane of plane polarized light to the right (clockwise) are said to be **dextrorotatory.** The dextrorotatory is denoted by **'*d*' or (+)** before the name of the compound. Similarly, compounds that rotate the plane to the left (anticlockwise) are called **laevorotatory** and this is denoted by placing **'*l*'** or **(-)** before the name of the compound. A mixture containing equal amounts of ***d*- and *l*- isomers** is called a **recemic mixture** and is optically inactive denoted by ***dl*** or ±.

Assignment of Configuration

The nature of rotation whether *laevo* or *dextro*, i.e. *l*- or *d*- does not indicate the actual arrangement of atoms or groups of a molecule in space. In other words, by knowing the optical activity, one cannot tell about the *absolute configuration* of a compound. The absolute configuration in case of geometrical isomers is indicated by the designations *cis*- or *trans*- followed by the name of the compounds.

However, in case of optical isomers, the absolute configuration is given by D, L system and *R*, *S* system. For assiging the absolute configuration of a compound as *D* or *L* **or** *R* or *S*, the structure of a compound has to be written in a particular way.

One such way was given by Emil Fischer and the structure represented in such a way is called **Fischer projection**. For drawing such projections, a molecule is oriented vertically so that the carbon atom number 1 which is most highly oxidised is placed at the top in the chain. For example, in case of glyceraldehyde, the carbon atom carrying carbonyl group is placed at the top in the vertical chian as shown below:

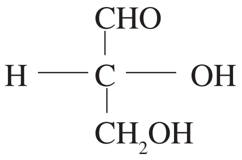


$$\begin{array}{l} {}^{1}CHO \\ \,| \\ {}^{2}CHOH \\ \,| \\ {}^{3}CH_2OH \end{array}$$

Glyceraldehyde

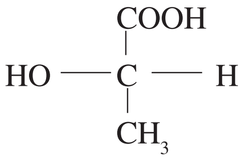
Then, the main substituent attached to the carbon, for the configuration to be arranged is looked for. Here, in case of glyceraldehyde, the configuration is to be assigned to C-2 atom and the main substituent attached to C-2 atoms is an –OH group. Please note that, here, C-2 atom is attached to 4 different substituents and such a centre (atom) in the molecule is called a **chiral centre.** It is also represented by an asterisk (*) mark in the structure.

If, in a Fischer projection, the main substituent appears on the *right*, then the particular molecule is said to have **D configuration.** In the other situation, if the main substituent in the molecule appears on the *left side* in the Fischer projection, then that compound said to have **L configuration**. The structures of D-glyceraldehyde and L-lactic acid are shown below:



$$\begin{array}{ccc} & CHO & \\ & | & \\ H — & C & — OH \\ & | & \\ & CH_2OH & \end{array}$$

D-(+)-Glyceraldehyde



$$\begin{array}{ccc} & COOH & \\ & | & \\ HO — & C & — H \\ & | & \\ & CH_3 & \end{array}$$

L(+)-Lactic acid

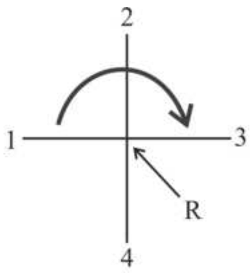
Note that in addition to configuration as D or L, the signs of rotation (i.e. + or –) are also given in the names of the compounds above. You can see that both the compounds are dextrorotatory though one is having D configuration while other has L configuration. Thus, the configurations are not related to the directions (or signs) of the rotation of plane polarized light. The D, L system of assigning configurations is widely used for carbohydrates and amino acids.

However, this system can not be applied equally well to all compounds because sometimes it is not easy to identify the main chain and the main substituent in the structure of the compound. In such situations, another system called, ***R*, *S* convention** is used to assign the absolute configuration of a chiral centre in a compound.

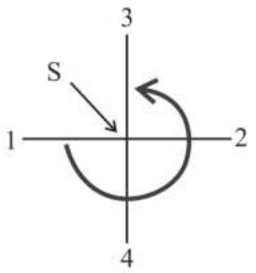
Assignment of Absolute Configuration as *R* or *S*

First of all, the Fischer projection of a particular given optical isomer is written. Then, the four substituents attached to the chiral carbon, for which the absolute configuration is to be assigned, are identified. These substituents are then assigned a priority order as 1, 2, 3 and 4 according to certain rules which were given by Cohn-Ingold and Prelog.

The Fischer projection of the molecule is then rearranged, if required, so as to place the substituent of lowest priority, *i.e.* substituent number 4, at the bottom of the Fischer projection. There are also certain rules to convert one fisher projection to another about which you will study in higher classes. When we place the substituent of lowest priority at the bottom in the Fischer projection, there are two ways in which the other substituents (1, 2 and 3) appear depending upon the actual position of these groups in the molecules. These are shown below.

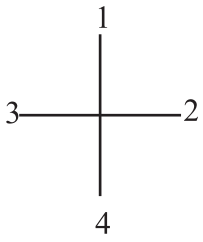


I

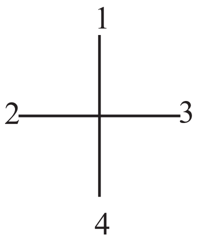


II

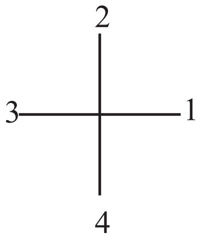
Now, it we ignore 4 and trace a path from 1 → 2 → 3, it will be *clockwise* in I while *anticlockwise* in II. The isomer I is said to have *R* configuration at chiral centre while in isomer II, the chiral centre is said to have *S* configuration.
You may also be thinking that the following arrangements of 1, 2, 3 are also possible.



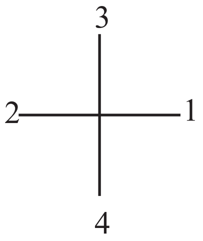
III



IV

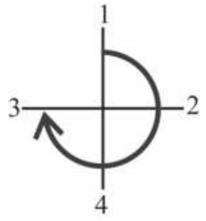


V



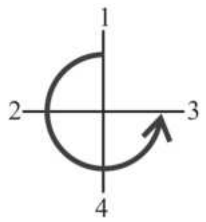
VI

But again, to assign the configuration we have to follow the same rules. *i.e.* trace the path from 1 → 2 → 3 and see it is *clockwise* or *anticlockwise*. Accordingly, the configuration is given as *R* or *S*. This is illustrated below for the representations II to VI alongiwth their absolute configurations R or S:



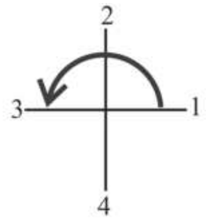
R

III



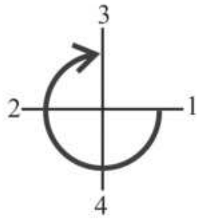
S

IV



S

V

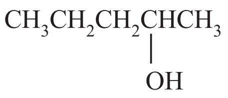
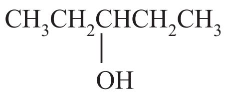


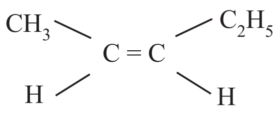
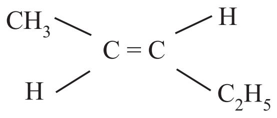
R

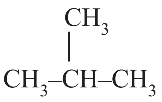
VI

INTEXT QUESTIONS 23.5

1. Is 1-butene a structural isomer of **cis-** or **trans**-2-butene?
2. Identify the type of isomerism exhibited by the following pairs of compounds:

(i) 
$CH_3CH_2CH_2\underset{OH}{CH}CH_3$ and 
$CH_3CH_2\underset{OH}{CH}CH_2CH_3$

(ii) 
and 

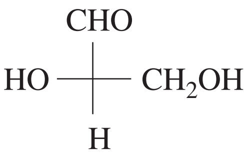
(iii) $CH_3CH_2CH_2CH_3$ and 
$CH_3{-}\overset{CH_3}{CH}{-}CH_3$

(iv) $CH_3CH_2CH_2OH$ and $CH_3CH_2 - O - CH_3$

3. Write the structures of all the isomers of hexane (C_6H_{14}).
4. Which one of the following compounds would show geometrical isomerism?

(i) $CH_3CH_2CH = CHCH_2CH_3$ (ii) $CHF = CHF$ (iii) $CH_2 = CHCH_2CH_3$

5. Assign the configuration as R or S to the following compound



23.5 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Organic compounds contain C and H; in addition to these, they may also contain O, N, S, halogens, and phosphorous.

23.5.1. Detection of C and H

Many organic compounds burn with a sooty flame or char when strongly heated. C and H are detected by heating the compound with CuO (copper oxide) in a dry test tube. They are oxidised to CO_2 and H_2O, respectively. CO_2 turns lime water milky and H_2O turns anhydrous $CuSO_4$ to hydrated $CuSO_4$ which is blue in colour.

(i) $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

(ii) $H + CuO \xrightarrow{\Delta} Cu + H_2O$

(iii) $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$

(iv) $\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$

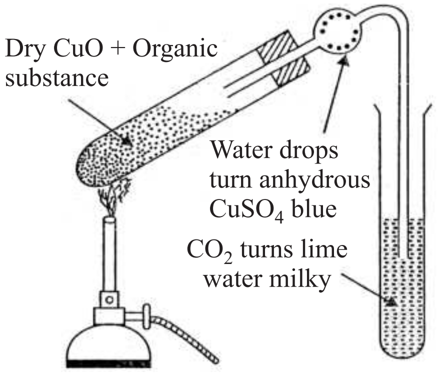


Fig. 23.1 *Detection of carbon and hydrogen*

23.5.2 Detection of Other Elements

N, S, halogens, and phosphorus present in an organic compound are detected by **Lassaigne's test**, by fusing the compound with sodium metal, which converts the elements present in the compound from covalent to ionic form. The following reactions occur:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX \ (X = Cl, Br, \text{or } I)$$

C, N, S, and X come from organic compound.

NaCN, Na_2S, and NaX so formed are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne's extract (L.E.).

(a) **Test for nitrogen:** The sodium fusion extract or L.E. is boiled with $FeSO_4$ and then acidified with conc. H_2SO_4. The appearance of Prussian blue colour confirms the presence of N. The following reactions occur:

(i) $$Fe^{2+} + 6CN \longrightarrow \underset{\textbf{Hexa cyanoferrate (II)}}{\left[Fe^{2+}(\overset{6-}{CN})_6\right]^{4-}}$$

(ii) $$Fe^{2+} \xrightarrow[H_2SO_4]{\text{Conc.}} Fe^{3+} + \bar{e}$$

(iii) $$\left[Fe^{2+}(\overset{6-}{CN})_6\right]^{4-} + 4Fe^{3+} \longrightarrow \underset{\substack{\textbf{Ferriferro cyanide}\\ \textbf{(Prussian blue)}}}{Fe_4^{3+}\left[Fe^{2+}(\overset{6-}{CN})_6\right]_3^{4-}} \cdot H_2O$$

(iv) This test is not given by compounds which do not contain C atoms but contain N atoms, for example, NH_2NH_2 (hydrazine), NH_2OH (hydroxylamine). Since these compounds do not contain C atoms, so in sodium fusion extract, CN ion is not formed and Prussian blue colour is not observed.

(v) This test is also not given by diazonium salts (e.g, Ph N≡N–X), although they contain both C and N elements, because they decompose and lose N_2 on heating much before they have a chance to react with the fused sodium metal.

(vi) If S is present along with N, the appearance of blood red colour confirms the presence of both.

$$Na + N + C + S \longrightarrow NaCNS \text{ (Sodium thiocyanate)}$$

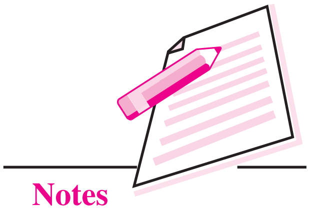
$$\underset{\textbf{Thiocyanatc ion}}{3\ CNS^{\ominus}} + Fe^{+3} \longrightarrow \underset{\substack{\textbf{Ferric thiocyanate}\\ \textbf{(Blood-red colour)}}}{Fe(CNS)_3}$$

(vii) If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to give cyanide and sulphide. These ions give usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

(b) **Test for sulphur:** The sodium fusion extract or L.E: is treated with sodium nitroprusside. The appearance of violet colour indicates the presence of S.

(i) $$\underset{\text{Sulphide ion}}{S^{2-}} + \left[Fe^{2+}\overset{5-}{(CN)_5}\,\overset{1+}{NO}\right]^{2-} \longrightarrow \underset{\text{Violet colour}}{\left[Fe^{2+}\overset{5-}{(CN)_5}\,\overset{1-}{NOS}\right]^{-4}}$$



Notes

(ii) The L.E. is acidified with acetic acid and lead acetate is added to it. The appearance of black precipitate of lead sulphide indicates the presence of S.

$$Pb^{2+} + S^{2-} \longrightarrow \underset{\text{black ppt.}}{PbS}$$

(c) Test for halogens

(i) L.E. is acidified with HNO_3 and then treated with $AgNO_3$. A white precipitate soluble in NH_4OH indicates the presence of Cl, a pale yellow precipitate partiatly soluble in NH_4OH indicates the presence of Br, and a yellow precipitate insoluble in NH_4OH shows the presence of I.

$$AgNO_3 + NaCl \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{soluble in } (NH_4OH)}}{AgCl\downarrow} + NaNO_3$$

$$AgNO_3 + NaBr \longrightarrow \underset{\substack{\text{Pale-yellow ppt.}\\ \text{partly soluble in } NH_4OH}}{AgBr\downarrow} + NaNO_3$$

$$AgNO_3 + NaI \longrightarrow \underset{\substack{\text{Dark-yellow ppt.}\\ \text{insoluble in } NH_4OH}}{AgI\downarrow} + NaNO_3$$

(ii) If N and S are also present in the compound, the L.E. is first boiled with conc. HNO_3 to decompose the NaCN or Na_2S formed during Lassaigne's test. These ions would otherwise interfere with the $AgNO_3$ test for halogens. If these ions are not removed, they would give a white precipitate of AgCN or Ag_2S with $AgNO_3$ and will confuse it for AgCl.

(iii) **Organic layer test:** Add CS_2 or $CC1_4$ to the L.E. and then add Cl_2 water or $KMnO_4$, shake, and keep it for some time. The appearance of orange colour in organic layer confirms the presence of Br, while violet colour confirms iodine.

$$2Br^{\ominus} + 2Cl_2 \longrightarrow \underset{\text{Orange colour}}{Br_2} + 2Cl^{\ominus}$$

$$2I^{\ominus} + 2Cl_2 \longrightarrow \underset{\text{Violet colour}}{I_2} + 2Cl^{\ominus}$$

$$16H^{\oplus} + 2MnO_4^{\ominus} + 10Br^{\ominus} \longrightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$$

$$16H^{\oplus} + 2MnO_4^{\ominus} + 10I^{\ominus} \longrightarrow 5I_2 + 2Mn^{2+} + 8H_2O$$

(iv) **Beilstein test:** The organic compound is heated on a clean copper wire in Bunsen flame. A green or blue colour due to the formation of volatile copper halides confirms the presence of halogens. This test is not satisfactory as some compounds which do not contain halogens also give this test, for example urea and thiourea. Moreover, this test does not tell which halogen is present in the compound.

(d) **Test for phosphorus:** The organic compound is heated with an oxidising agent (sodium peroxide). Phosphorus is oxidised to phosphate. The solution is then boiled with cone. HNO_3 and treated with ammonium molybdate. A yellow precipitate confirms the presence of phosphorous.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\text{Ammonium phosoph molybdate}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2$$

23.6 QUANTITATIVE ANALYSIS

(a) **Estimation of C and H:** The percentage composition of elements present in an organic compound is determined by the methods based on the following principle:

Liebig's combustion method: A known mass of compound is heated with CuO. The carbon present is oxidised to CO_2 and hydrogen to H_2O. The CO_2 is absorbed in KOH solution, while H_2O vapours are absorbed in anhydrous $CaC1_2$ and weighed (Fig. 23.2).

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound}} \times 100$$

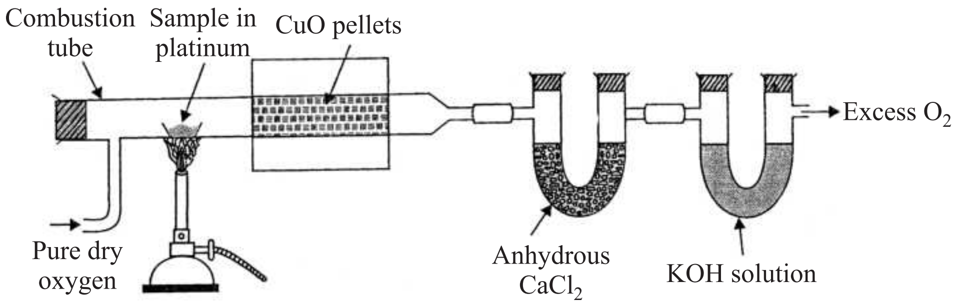


Fig. 23.2 *Estimation of carbon and hydrogen*

b. **Estimation of halogens:**

Carius method: A known mass of compound is heated with cone. HNO_3 in the presence of $AgNO_3$ contained in a hard glass tube known as Carius tube (Fig. 23.3 in a furnance. C and H are oxidised to CO_2 and H_2O. The halogen forms the corresponding AgX. It is filtered, dried, and weighed.

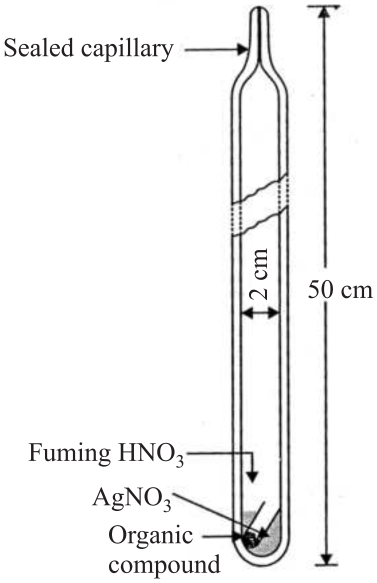


Fig. 23.3 *Carius method*

$$\text{i. Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$$

$$\text{ii. Percentage of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$$

$$\text{iii. Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$$

$$\text{iv. Percentage of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$$

(c) Estimation of sulphur: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in the presence of $BaC1_2$ solution in Carius tube. Sulphur is oxidised to H_2SO_4 and precipitated as $BaSO_4$. It is filtered, dried, and weighed.

$$\text{Percentage of S} = \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

$$= \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

(d) Estimation of phosphorus

First method: A known mass of compound is heated with fuming HNO_3 in Carius tube which converts phosphorus to H_3PO_4 (phosphoric acid). It is precipitated as ammonium phosphomolybdate $[(NH_4)_3PO_4.12MoO_3]$ by adding NH_3 and ammonium molybdate $(NH_4)_2MoO_4]$. It is filtered, dried, and weighed.

Percentage of P

$$= \frac{\text{Atomic mass of P}}{\text{Molecular mass of ammonium phospho molybdate}} \times \frac{\text{Mass of ammonium phospho molybdate} \times 100}{\text{Mass of compound}}$$

$$= \frac{31}{1877} \times \frac{\text{Mass of } (NH_4)_3 \cdot PO_4 \cdot 12MoO_3 \times 100}{\text{Mass of compound}}$$

Second method: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in Carius tube which converts phosphorous to H_3PO_4. Magnesia mixture ($MgC1_2$ + NH_4C1) is then added, which gives the precipitate of magnesium ammonium phosphate ($MgNH_4.PO_4$) which on heating gives magnesium pyrophosphate ($Mg_2P_2O_7$), which is weighed.

Percentage of P

$$= \frac{\text{Atomic mass of P}}{\text{Molecular mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$

$$= \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$

(e) **Estimation of nitrogen:** There are two methods for the estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) **Dumas method:** A known mass of compound is heated with copper oxide (CuO),in an atmosphere of CO_2, which gives free nitrogen along with CO_2 and H_2O.

$$C_xH_yN_z + (2x + y/2)CuO \longrightarrow xCO_2 + y/2(H_2O) + z/2(N_2) + (2x + y/2)Cu$$

The gaseous mixture is passed over a heated copper gauze which converts traces of nitrogen oxides formed to N_2. The gaseous mixture is collected over an aqueous solution of KOH which absorbs CO_2, and nitrogen is collected in the upper part of the graduated tube (Fig. 23.4).

Let the volume of N_2 collected be V_1 ml

Volume of N_2 at STP = $\frac{p_1V_1 \times 273}{760 \times T_1}$ = V ml

where p_1 and V_1 are the pressure and volume of N_2, and p_1 = atmospheric pressure – aqueous tension. 22400 ml of N_2 at STP weighs 28 g

V ml of N_2 at STP weighs = $\frac{28 \times V}{22400}$ g

Percentage of N is

$$\frac{\text{Molecular mass of } N_2}{22400 \text{ ml}} \times \frac{\text{Volume of } N_2 \text{ at STP} \times 100}{\text{Mass of compound}}$$

$$= \frac{28}{22400} \times \frac{\text{V ml} \times 100}{\text{Mass of compound}}$$

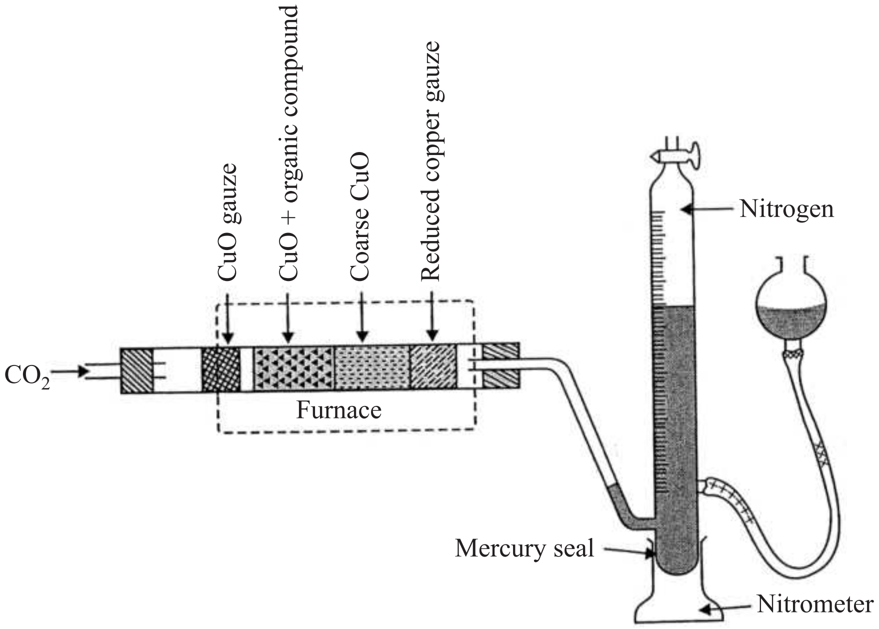


Fig. 23.4 *Dumas method*

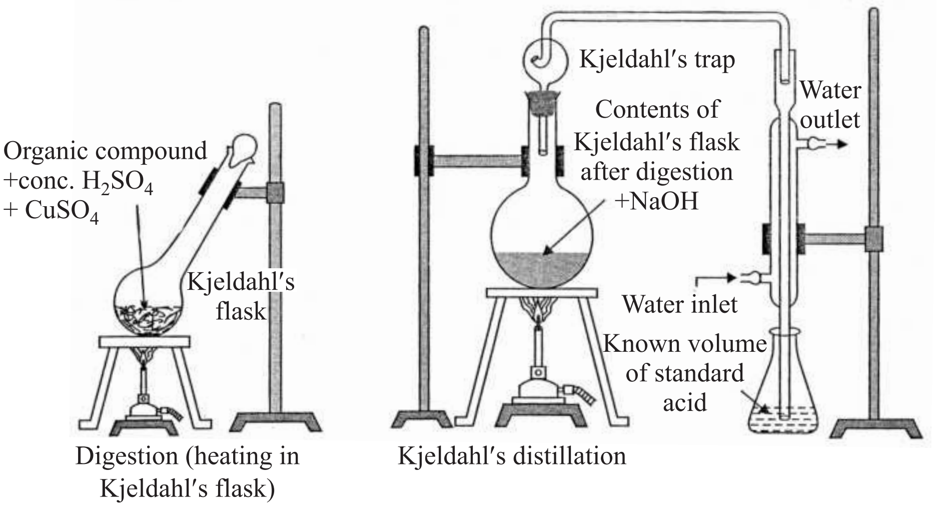


Fig. 23.5 *Kjeldahl's method*

(ii) Kjeldahl's method: A known mass of organic compound (0.5 g) is mixed with K_2SO_4 (10 g) and $CuSO_4$ (1.0 g) or a drop of mercury (Hg) and conc. H_2SO_4 (25 ml), and heated in Kjeldahl's flask. $CuSO_4$ or Hg acts as a catalyst, while K_2SO_4 raises the boiling point of H_2SO_4

(Fig. 23.5). The nitrogen in the organic compound is quantitatively converted to ammonium sulphate. The resulting mixture is then distilled with excess of NaOH solution and the NH_3 evolved is passed into a known but excess volume of standard HCl or H_2SO_4. The acid left unused is estimated by titration with some standard alkali. The amount of acid used against NH_3 can thus be known and from this the percentage of nitrogen is calculated.

1. $C + H + S \xrightarrow[H_2SO_4]{Conc.} CO_2 + H_2O + SO_2$

2. $N \xrightarrow[H_2SO_4]{Conc.} (NH_4)_2SO_4$

3. $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$

4. $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Calculation of percentage of N

Let the mass of organic compound *m* g.

Volume of H_2SO_4 of molarity M [or (2M) normality] taken = V ml

Volume of NaOH of molarity M (or M normality)

used for titration excess of H_2SO_4 = V_1 ml

mEq. of excess H_2SO_4 = mEq. of NaOH = M V_1 mEq.

Total mEq. of H_2SO_4 taken = 2 MV

mEq. of H_2SO_4 used for neutralisation of NH_3 = (2 MV – MV_1)

∴ mEq. of NH_3 = (2 MV – MV_1)

1000 mEq. or 1000 ml of *M* NH_3 solution contains = 17 g of NH_3 = 14 g of N

∴ (2 MV – MV_1) mEq. of NH_3 solution contains

$$= \frac{14 \times (2MV - MV_1)}{1000} \text{ g of N}$$

$$\text{Percentage of N} = \frac{14 \times (2MV - MV_1) \times 100}{1000 \times m}$$

$$= \frac{1.4 \times 2M(V - V_1/2)}{m}$$

$$\text{Percentage of N} = \frac{1.4 \times \text{ mEq. of } H_2SO_4 \text{ used to neutralise } NH_3}{\text{Mass of the compound}}$$

(iii) This method is not applicable to compounds containing N in nitro and azo groups, and N present in the ring (e.g., pyridine) as N of these compounds does not change to $(NH_4)_2SO_4$ (ammonium sulphate) under these reaction conditions.

(f) Estimation of oxygen

First method: It is usually found by the difference between the total percentage composition (100) and sum of the percentages of all the other elements, e.g.,

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N)

Second method (Aluise's method): A known mass of compound is decomposed by heating it in the presence of N_2 gas. The mixture of gaseous products containing O_2 is passed over red hot coke when all the O_2 is converted to CO. This mixture is heated with I_2O_5 (iodine pentaoxide) in which CO is oxidised to CO_2 liberating I_2. Organic compound $\xrightarrow{\Delta}$ Other gaseous product + O_2

$$2C + O_2 \xrightarrow{1373\text{ K}} 2CO$$

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + I_2$$

Percentage of O

$$= \frac{\text{Molecular mass of } O_2}{\text{Molecular mass of } CO_2} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compouund}}$$

$$= \frac{32}{44} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}}$$

(g) CHN elemental analyser: Nowadays, the estimation of elements in an organic compound is carried out with automatic experimental techniques using micro quantities of the compound. The elements C, H, and N present in an organic compound are determined by an automatic instrument called CHN elemental analyser using a very small amount of the compound (1-3 mg), which displays the result within a very short time.

WHAT YOU HAVE LEARNT

- Organic compounds are classified into **aliphatic** (open-chain), **homocyclic** (closed ring) or **carbocyclic (alicyclic and aromatic)** hydrocarbons and their derivatives, and **heterocyclic** compounds (contain at least one heteroatom i.e., N,S,O in the ring).

- **Homologous series** of organic copmounds and IUPAC naming of different classes.
- The substitution, elimination, additions reactions and molecular rearrangements.
- **Homolytic** fission of a covalent bond produces free radicals because each of the parting away atoms takes away its shared electron.
- **Heterolytic fission** of a covalent bond produces ions because one of the atoms takes away both the shared electrons.
- **Electrophiles** are positively charged or electron deficient species.
- **Nucleophiles** are negatively charged or electron rich species.
- Benzene ring undergoes aromatic substitution reactions.
- A **functional group** is an atom or group responsible for specific properties of a compound.
- The compounds which have the same molecular formula but different structure are called structural **isomers.**
- Isomerism is classified into **structural isomerism** and **stereoisomerism**.
- A carbon atom attached to four different groups is called **chiral** atom or **asymmetric** carbon atom.
- The non-superimposable mirror image isomers of a compound are called enantiomers. They are optically active and rotate the plain of plain polarized light in opposite directions.
- The absolute configuration of a chirol carbon can be specified as *R* or *S*.

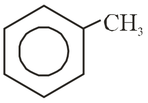
TERMINAL EXERCISE

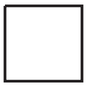
1. What are hydrocarbons? Explain giving two examples.
2. Give two examples of aromatic hydrocarbons.
3. Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names.

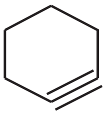
(i) $(CH_3)_3CH$ (ii) $CH_3CH = CH_2$

(iii) $(CH_3)_4C$ (iv) $CH_3\,C \equiv CH$

(v) $CH_3\,C \equiv CCH_3$ (vi) $CH_2 = CH_2$

(vii) 

(viii 

(ix) 

4. Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula:

   (i) C_5H_{10} and (ii) C_5H_8.

5. Write the structures of the following compounds :

   (i) Isobutylbenzene

   (ii) 4-Methyl-2-pentene

   (iii) Hepta-1,6-diene

   (iv) Cyclobutene

6. Write the structures for the following compounds:

   (i) 1-Bromo-3-methylhexane

   (ii) 3-Chloro-2,4-dimethylpentane

   (iii) 3-Methylbutanal

   (iv) Ethyl propanoate

   (v) 2-Methylbutanenitrile

   (vi) Cyclohexene

   (vii) 3-Methylhexan-2-one

7. What are electrophilic aromatic substitution reactions? How will you prepare nitrobenzene from benzene?

8. Draw all the possible structural isomers having the molecular formula C_4H_9Cl and give their IUPAC names.

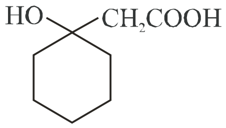
9. What is a nucleophilic aliphatic substitution reaction? Give one example.

10. Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.

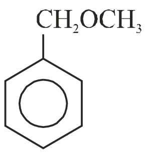
11. Write a short note on the following; (i) Structural isomerism (ii) Stereo-isomerism

12. Define a functional group. Identify the functional group(s) present in following compounds :

   (i)

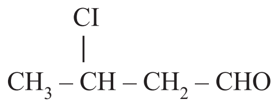


   (ii)



   (iii) $CH_3COCH_2C \equiv CH$

   (iv) $CH_3CH_2CH_2 - O–CH_3$

(v) 
$CH_3 - \underset{}{\overset{Cl}{\overset{|}{C}}}H - CH_2 - CHO$

(vi) CH_3CONH_2

15. Describe hyperconjugation in terms of resonance.

ANSWERS TO INTEXT QUESTIONS

23.1

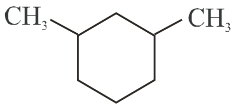
1.

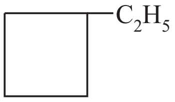
Word root	**Suffix**
(i) Hex	ane
(ii) Pent	2–ene
(iii) Prop	yne

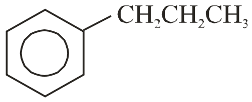
2. (i) Oct-2-ene (ii) 2, 4-Dimethylpentane

23.2

1. (i) 1-ethyl-3-methylbenzene
   (ii) Cycloheptane
   (iii) Cyclopenta-1,3-diene

2. (i) 

(ii) 

(iii) 

23.3

1. Covalent bond between two different atoms having large difference in their electronegativities.

2. **–I effect groups** $–NO_2$, $–CN$, $–C_6H_5$ **+**
   I effect groups $–CH_3$, $–C_2H_5$, $CH_3\underset{|}{C}HCH_3$.

3. Electromeric effect is temporary polarization, whereas inductive effect is permanent polarisation of a covalent bond.

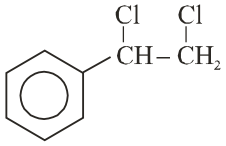
4. (i) Electrophile (ii) Electrophile
   (iii) Nucleophile (iv) Nucleophile
   (v) Nucleophile (vi) Nucleophile

(vii) Nucleophile (viii) electrophile

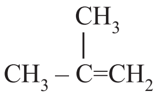
(ix) Nucleophile

23.4

1. (i) CH_3CH_2CN (ii) CH_3NHR
2. HNO_3 in presence of H_2SO_4.
3. (i) CH_3CH_2Br

   (ii) 

   (iii) $(CH_3)_2\ CBr - CH_2Br$ (major product)

   (iv) 
   $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$

   (v) $CH_3–CH=CHCH_3$ (major product)

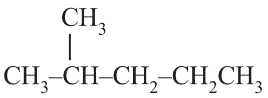
23.5

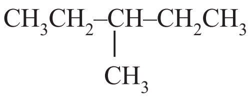
1. Yes
2. (i) Positional isomerism

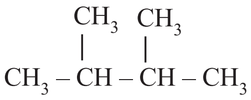
   (ii) Geometrical isomerism

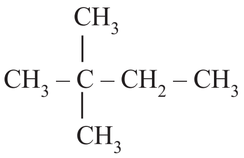
   (iii) Chain isomerism

   (iv) Functional group isomerism
3. (i) $CH_3CH_2CH_2CH_2CH_2CH_3$

   (ii) 
   $CH_3–\overset{\overset{\displaystyle CH_3}{|}}{CH}–CH_2–CH_2CH_3$

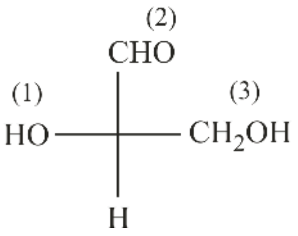
   (iii) 
   $CH_3CH_2–\underset{\underset{\displaystyle CH_3}{|}}{CH}–CH_2CH_3$

   (iv) 
   $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$

   (v) 
   $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_3$

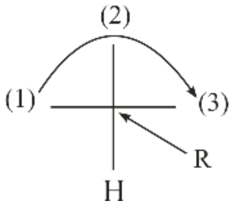
4. (i) Yes
   (ii) Yes
   (iii) No

5.



(i) Priority of groups is shwon as (1), (2) and (3)

(ii) path from (1) → 2 → 3 is clockwise, therefore, the absolute configuration of chiral chain is R.



24

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillation of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

OBJECTIVES

After reading this lesson, you will be able to :

- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- draw the conformations of ethane and compare their relative stability;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;

- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various aromatic compounds using resonance;
- state Huckel rule and its use;
- describe methods of preparation, physical properties and chemical properties of benzene;
- list various uses of hydrocarbons; and
- explain the term carcinogenicity and Toxicity.

24.1 ALKANES (PARAFFINS)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as *paraffins* (*parum* means little, *affins* means affinity).

24.1.1 Methods of Preparation

Some important methods of preparation of alkanes are as follows:

1. **From Haloalkanes (Alkyl Halides):** Monohaloalkanes can be converted to alkanes by following three methods :

   a) **By reduction of haloalkanes:** The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents :

   (i) Zinc and dilute HCl

$$\underset{\textbf{Bromomethane}}{CH_3Br} + Zn + 2\,HCl \longrightarrow \underset{\textbf{Methane}}{CH_4} + ZnCl_2 + HBr$$

   (ii) HI in the presence of red phosphorus

$$\underset{\textbf{Iodoethane}}{C_2H_5I} + HI \xrightarrow[423\text{ K}]{\text{red phosphorus}} \underset{\textbf{Methane}}{C_2H_6} + ZnCl_2 + HBr$$

   (iii) Catalytic reduction

$$\underset{\textbf{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow{\text{Pt (catalyst)}} \underset{\textbf{Methane}}{CH_4} + HCl$$

   b) **By using Grignard's Reagent :** A Grignard reagent is a compund of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br + Mg} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethyl Magnesium Bromide}}{C_2H_5MgBr}$$

The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called *active hydrogen*. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr + C_2H_5OH \rightarrow CH_4 + Mg(OC_2H_5)Br$$

$$C_2H_5MgBr + H_2O \rightarrow C_2H_6 + Mg(OH)Br$$

c) **By Wurtz Reaction :** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$\underset{\textbf{Bromoethane}}{CH_3 - Br} + 2\,Na + Br - CH_3 \xrightarrow{\text{dry ether}} \underset{\textbf{Ethane}}{CH_3 - CH_3} + 2\,NaBr$$

2. **From Unsaturated Hydrocarbons :** The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2 = CH_2 + H_2 \xrightarrow[573\text{ K}]{\text{Ni or Pt}} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow[573\text{ K}]{\text{Ni or Pt}} CH_3 - CH_3$$

This reaction is also called **hydrogenation** and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. **From Alcohols, Aldehydes and Ketones :** Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes.The general reactions are as shown below.

$$\underset{\textbf{Alcohol}}{ROH} + 2HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RH} + I_2 + H_2O$$

$$\underset{\textbf{Aldehyde}}{RCHO} + 4HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RCH_3} + 2\,I_2 + H_2O$$

$$\underset{\textbf{Ketone}}{RCOR'} + 4HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RCH_2R'} + 2\,I_2 + H_2O$$

4. **From Carboxylic Acids :** Carboxylic acids can produce alkanes in a number of ways as shown below :

i) Heating with soda lime : $RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$

In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

ii) By Reduction of carboxylic acid:

$$\mathrm{RCOOH} + 6\,\mathrm{HI} \xrightarrow{\text{red P}/423\text{ K}} \mathrm{RCH_3} + 3\,\mathrm{I_2} + 2\mathrm{H_2O}$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.

$$\underset{\textbf{Sodium salt of carboxylic acid}}{\mathrm{RCOONa}} \xrightarrow{\text{electrolysis}} \underset{\textbf{Anion}}{\mathrm{RCOO^-}} + \underset{\textbf{Cation}}{\mathrm{Na^+}}$$

At Anode :

$$\mathrm{RCOO^-} \longrightarrow \mathrm{RCOO^\bullet} + e^-$$

$$\mathrm{RCOO^\bullet} \longrightarrow \mathrm{R^\bullet} + \mathrm{CO_2}$$

$$\mathrm{R^\bullet} + \mathrm{R^\bullet} \longrightarrow \mathrm{R-R}$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\textbf{Sodium ethanote}}{2\,\mathrm{CH_3COONa}} \longrightarrow \underset{\textbf{Ethane (at anode)}}{\mathrm{CH_3-CH_3}}$$

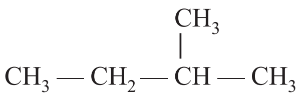
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

24.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid, and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area, and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

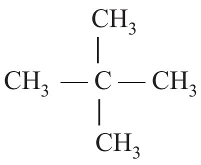
$$\mathrm{CH_3-CH_2-CH_2-CH_2-CH_3}$$

***n*-Pentane**



$$CH_3 - CH_2 - \overset{\overset{CH_3}{|}}{CH} - CH_3$$

2-Methylbutane (Isopentane)



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

2,2-Dimethylpropane (Neopentane)

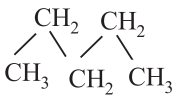
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms.* All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

Boiling Point: *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

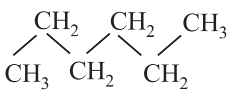
Melting Point: Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice.

In alkanes, each carbon atom is *sp*^{3} hybridized which results in a bond angle of 109°28′. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.



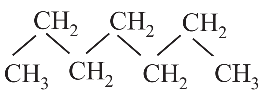
***n*-Pentane**

(Carbon atoms = 5, m.p.142 K)



***n*-Hexane**

(Carbon atoms =6, m.p. = 179 K)



***n*-Heptane**

(carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

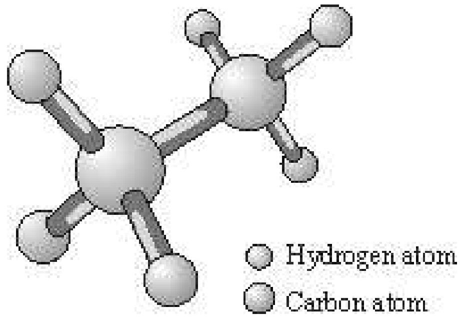
24.1.3 Conformations of Ethane

You have studied section 25.3.2 that electronic displacements affect the physical and chemical properties of organic compounds. You will now study how the forces present within the molecules affect their structures and stabilities. In fact, these interactions make some geometric arrangements of atoms energetically *more favorable* than others.

In ethane molecule, C_2H_6, the two carbon atoms are linked together by a single bond called *sigma* (σ) bond.

$$\begin{array}{c}\text{sigma } (\sigma) \text{ bond} \\ \downarrow \\ H_3C - CH_3 \\ \text{ethane}\end{array}$$

If we make a model of ethane molecule showing the C — C bond and the hydrogens attached to carbon atoms, it will look like as follows :



Model of ethane molecule

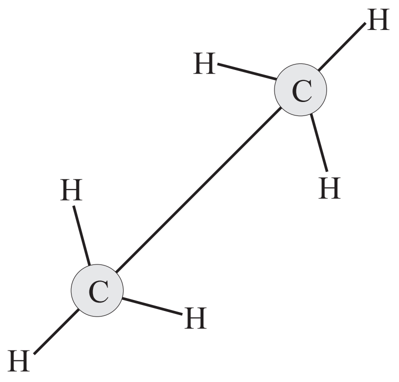
The groups bonded through a sigma bond can easily rotate with respect to each other. *i.e.* the two — CH_3 groups in ethane can rotate with respect to each other. The different arrangement of atoms resulting from such a rotation are called **conformations** and each such specific conformation is called a **conformer** (from *confor*mational iso*mer*).

The conformational isomers can be represented in the following two ways:

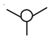
(i) Sawhorse representations

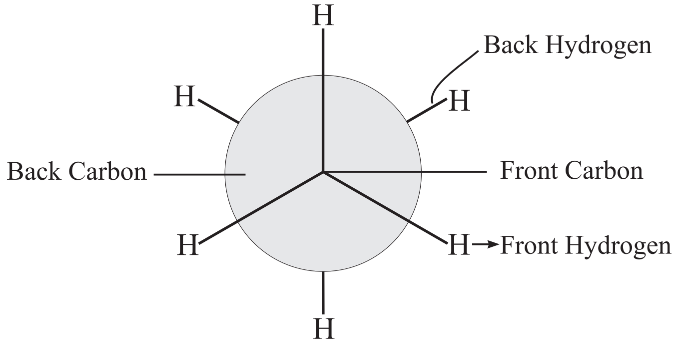
(ii) Newman projections

The **Sawhorse representations** show the carbon–carbon bond from an oblique angle and indicate the spatial arrangement of all C — H bonds.



Sawhorse Projections

In **Newman projections** the two carbon atoms are viewed along the C — C bond axis. The front carbon and its bonds are represented as  whereas the back carbon and its bonds are represented as .

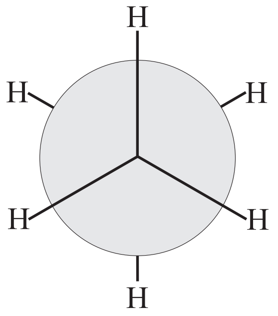


Newman Projection

The Newman projections are easier to draw and in such drawings, the relative positions of atoms are easily visualised. Therefore, we will use Newman projections to study the conformations of ethane.

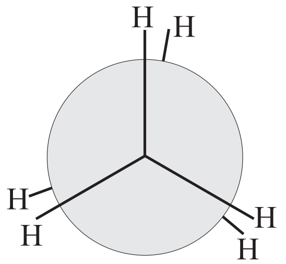
Several conformations of ethane are possible. But, there are two extreme possibilities. These are discussed below:

(i) In this conformation all the six C — H bonds are *as far away as possible*. This conformation is called **staggered conformation** and is shown below:



Staggered conformation of ethane

(ii) Another conformation in which all the six C — H bonds *are as close as possible is* shown below:



Eclipsed conformation of ethane

This is called **eclipsed conformation.** The three rear hydrogens are drawn little more rotated than the perfectly eclipsed positions to make them visible in the structure.

Remember that there are infinite number of possible conformations in between the staggered and the eclipsed conformations. All these conformations originate by the rotation of the C — C bond.

The *staggered conformation* is the **most slable** conformation whereas the *eclipsed conformation* is the **least stable** conformation of ethane. The eclipsed conformation has about 12 kJ mol^{-1} higher energy than the staggered conformation.

24.1.4 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$\underset{\textbf{Methane}}{CH_4} + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} \underset{\textbf{Chloromethane}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Tetrachloromethane}}{CCl_4}$$

Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals i.e. chlorine atoms with an unpaired electron $(\dot{C}l)$. The chlorine radicals then combine with methane and form methyl radical $[\dot{C}H_3]$. The methyl radical further reacts with chlorine molecule and produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) **Chain Initiation Step:** It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet} \qquad (h\nu = \text{energy of light})$$

(ii) **Chain Propagation Step :** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

(iii) **Chain Termination Step :** In this step, free radicals combine with one another and the further reaction stops.

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

2. **Oxidation:** Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature.For example :

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \; + \; 890 \text{ KJ mol}^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

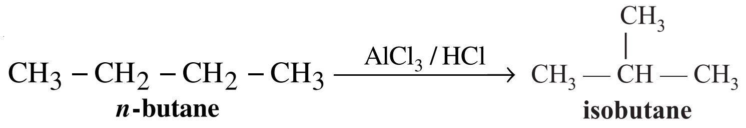
$$2C_2H_6 + 5O_2 \xrightarrow{\text{heat}} 4CO + 6H_2O$$

3. **Cracking or Pyrolysis:** At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\text{ K}} CH_3CH = CH_2 + H_2$$

or $$CH_2 = CH_2 + CH_4$$

4. **Isomerisation :** *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.



$$\underset{\textbf{\textit{n}-butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{AlCl_3\,/\,HCl} \underset{\textbf{isobutane}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3}$$

24.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer–isobutane, are the major constituents of LPG .

INTEXT QUESTIONS 24.1

1. List four important uses of hydrocarbons.
2. What is Grignard's reagent in a molecule?
3. What is an active hydrogen in a molecule?
4. What makes the physical properties of various hydrocarbons different?
5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.
6. Name three isomers of pentane.
7. Which one has higher b.p. *n*-butane or *n*-pentane? Explain.
8. Write the balanced chemical equation for the complete combustion of propane.

24.2 Alkenes

These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

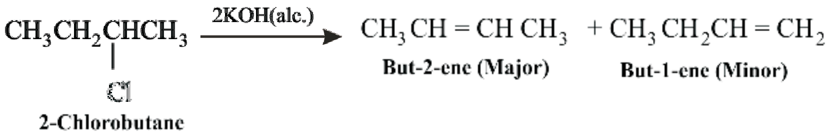
24.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes: Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$CH_3 - CH_2 - Cl + KOH(alc.) \rightarrow CH_2 = CH_2 + KCl + H_2O$$

Chloroethane **Ethene**



$$\underset{\textbf{2-Chlorobutane}}{CH_3CH_2\underset{|\atop Cl}{C}HCH_3} \xrightarrow{2KOH(alc.)} \underset{\textbf{But-2-ene (Major)}}{CH_3CH=CHCH_3} + \underset{\textbf{But-1-ene (Minor)}}{CH_3CH_2CH=CH_2}$$

The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : ***It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product.*** In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the –C=C– group.

2. From Alcohols : Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[623-633K]{Al_2O_3} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[433K]{conc.\ H_2SO_4} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

24.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State : Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points : The boiling points of alkenes increase with molecular mass as is shown in Table 24.1.

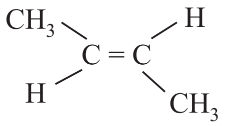
Table 24.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent-1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

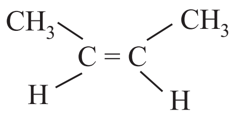
Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the ***cis*** and ***trans*** isomers have different melting points.

For example



***trans*-But-2-ene**

(m.p. 167 K)



***cis*-But-2-ene**

(m.p. = 134 K)

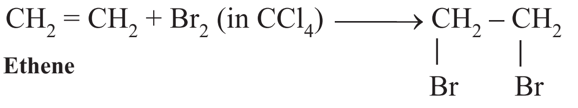
24.2.3 Chemical Properties of Alkenes

1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

(i) **Addition of Hydrogen :** Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{\text{Ni (Pt or Pd)}} \underset{\textbf{Ethane}}{CH_3 - CH_3}$$

(ii) **Addition of Halogens :** Halogens on addition to alkenes, form 1,2-dihaloalkanes.



$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + Br_2 \text{ (in } CCl_4) \longrightarrow \underset{\textbf{1, 2-Dibromoethane}}{\underset{\displaystyle Br}{\underset{|}{CH_2}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}}$$

As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

(iii) **Addition of Halogen Acids (HX) :** When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

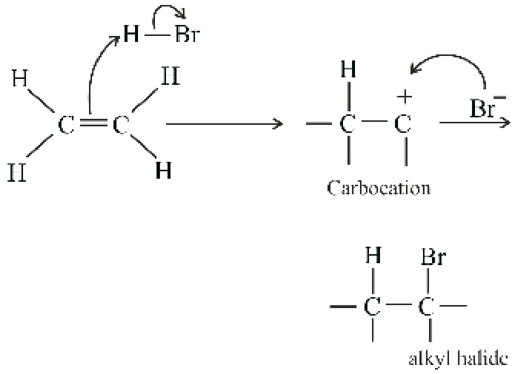
$$\underset{\textbf{Ethene}}{CH_2 = CH_2} \quad + \quad HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3 - CH_2 - Br}$$

In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the **Markownikoff's rule. This rule states that in the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.** In other words, hydrogen atom of HX goes to the carbon atom with more number of H-atoms attached to it.

$$CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBr\,CH_3$$

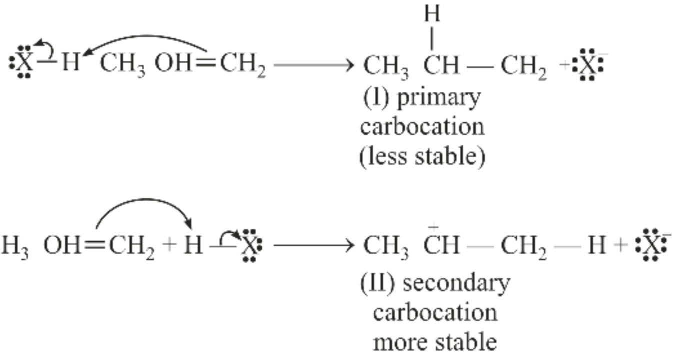
Propene **2-Bromopropane**

Mechanism of Electrophilic Addition: You have studied earlier that the electron cloud of the pi bond is present above and below the plane of the molecule in alkenes. Various electron seeking species and reagents thus react with the alkenes. For example, H^+ of HX(HBr) can add to the double bond to yield a carbocation.



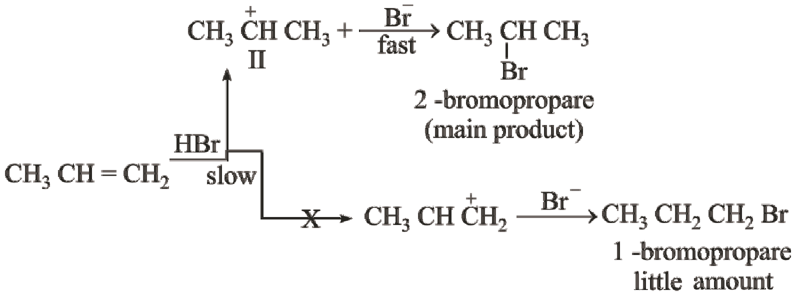
The carbocation being highly reactive reacts with the halide ion in the second step to yield an alkyl halide (alkyl bromide).

In case, the starting alkene is unsymmetrical *e.g.* propene, then in the first step of formation of a carbocation, there are two possibilities of attachment of H^+ of HX which are shown below:



This would lead to the formation of two carbocations as shown above.

The two possible carbocations have different stabilities *i.e.* the secondary carbocation (II) is more stable than the primary carbocation (I). Therefore, the secondary carbocation (II) is formed preferentially in the first step. Further reaction, *i.e.* attack of Br^- on the carbocation, thus yields 2-bromopropane as the major product.



Thus, the above explanation describes for the formation of 2-bromopropane as the major product as per the Markownikoff's rule.

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as **Anti-Markownikoff's addition** or **peroxide effect**.

$$CH_3CH = CH_2 + HBr \xrightarrow{\text{benzoyl peroxide}} CH_3CH_2 - CH_2 - Br$$

Propene **1 – Bromopropane**

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3 - CH_2 - OH$$

Ethene **Ethanol**

(v) Addition of H_2SO_4

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - HSO_4$$

Ethene **Ethyl hydrogen sulphate**

(vi) Addition Polymerization : The process in which many molecules of an alkene add together to form a larger molecule is called **addition polymerization.**

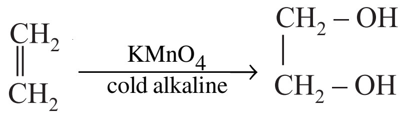
$$n\,(CH_2{=}CH_2) \xrightarrow[\text{heat, pressure}]{} \left(CH_2 - CH_2 \right)_n$$

Ethene **Polyethene**

2. **Oxidation :** The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$, oxygen and ozone.

(i) **Oxidation with $KMnO_4$**

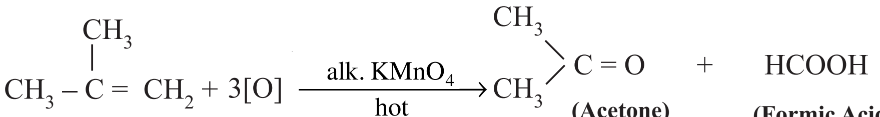
Alkenes are unsaturated hydrocarbons having Pi (π)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



$$CH_2{=}CH_2 \xrightarrow[\text{cold alkaline}]{KMnO_4} CH_2(OH){-}CH_2(OH)$$

Ethene **Ethanediol**

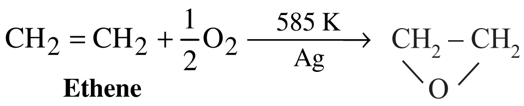
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH_2+3[O] \xrightarrow[\text{hot}]{\text{alk. } KMnO_4} (CH_3)_2C=O \quad + \quad HCOOH$$

2-Methylpropene **(Acetone) Propanone** **(Formic Acid) Methanoic acid**

(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



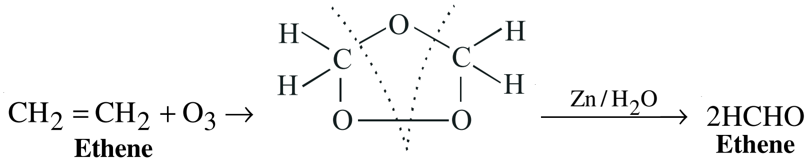
$$CH_2=CH_2+\frac{1}{2}O_2 \xrightarrow[Ag]{585\ K} CH_2-CH_2 \text{ (bridged by O)}$$

Ethene **Epoxyethane**

(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called **combustion.**

$$CH_2=CH_2+3\,O_2 \xrightarrow{\text{heat}} 2\,CO_2+2\,H_2O \quad \Delta H=-1411\text{ KJ mol}^{-1}$$

(iv) Oxidation with Ozone : Ozone adds to the alkene forming ozonide. The ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

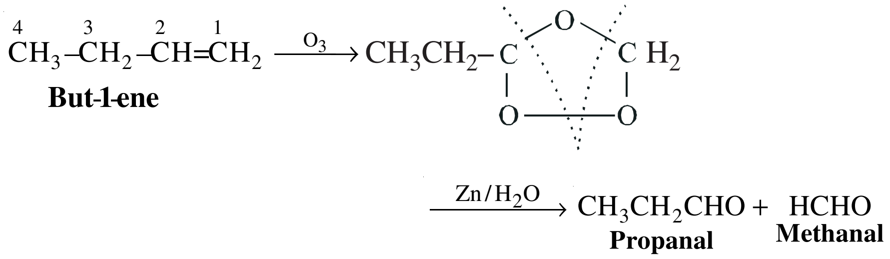


$$CH_2=CH_2+O_3 \rightarrow \text{Ozonide} \xrightarrow{Zn/H_2O} 2HCHO$$

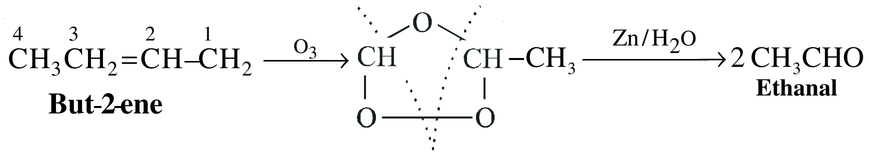
Ethene **Ozonide** **Ethene**

This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below.



When but-1-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.



24.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

INTEXT QUESTIONS 24.2

1. Which one has higher boiling point: *cis* but-2-ene or *trans* but-2-ene?
2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.
3. Write the conditions for hydrogenation of alkenes.
4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

24.3 ALKYNES

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH}, \quad \underset{\textbf{Propyne}}{CH_3 - C \equiv CH}, \quad \underset{\textbf{But-2-yne}}{CH_3 - C \equiv C - CH_3}$$

24.3.1 Preparation of Ethyne (Acetylene)

Some important methods for preparation of ethyne are explained below.

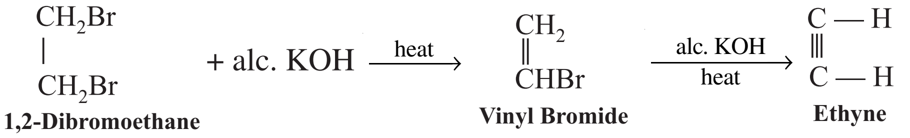
1. From Calcium Carbide: Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

$$\underset{\textbf{Calcium carbide}}{CaC_2} + \underset{\textbf{Water}}{2\,H_2O} \longrightarrow \underset{\textbf{Ethyne}}{H-C\equiv C-H} + Ca(OH)_2$$

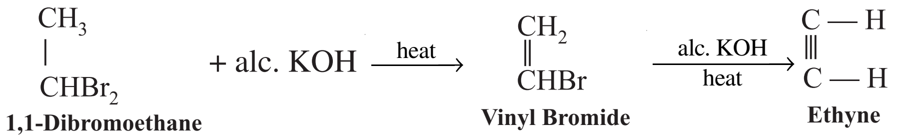
Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.



$$\underset{\textbf{1,2-Dibromoethane}}{\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{c}CH_2\\ \|\\ CHBr\end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{c}C-H\\ |||\\ C-H\end{array}}$$



$$\underset{\textbf{1,1-Dibromoethane}}{\begin{array}{c}CH_3\\ |\\ CHBr_2\end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{c}CH_2\\ \|\\ CHBr\end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{c}C-H\\ |||\\ C-H\end{array}}$$

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R-C\equiv CH + Na \xrightarrow{\text{liq. } NH_3} R-C\equiv C^-Na^+$$

$$R-C\equiv C^-Na^+ + CH_3I \longrightarrow R-C\equiv C-CH_3 + NaI$$

24.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.
2. They are colourless and odourless, except ethyne which has a garlic odour.
3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter

molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.

4. Alkynes are very slightly soluble in water and soluble in acetone.

24.3.3 Chemical Properties of Alkynes

1. **Addition Reactions** : Some of the addition reactions of alkynes are as follows.

   (i) **Addition of Hydrogen :** Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.

$$CH \equiv CH + H_2 \xrightarrow[573\ K]{Ni\ or\ Pt\ or\ Pd} CH_2 = CH_2 \xrightarrow{H_2\ +\ Ni\ or\ Pt\ or\ Pd} CH_3 - CH_3$$

   (ii) **Addition of Halogens :** When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

$$\underset{\textbf{Ethyne}}{CH \equiv CH} \xrightarrow{Br_2\ in\ CCl_4} \underset{\textbf{1,2-Dibromoethene}}{CHBr = CHBr} \xrightarrow{Br_2\ in\ CCl_4} \underset{\textbf{1,1,2,2-Tetrabromoethane}}{CHBr_2 - CHBr_2}$$

   (iii) **Addition of Halogen Acids (HX) :** Addition of HBr to ethyne is as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH} \xrightarrow{HBr} \underset{\textbf{Bromoethene}}{CH_2 = CHBr} \xrightarrow{HBr} \underset{\textbf{1,1–Dibromoethane}}{CH_3 - CHBr_2}$$

   (iv) **Addition of Water :** Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.

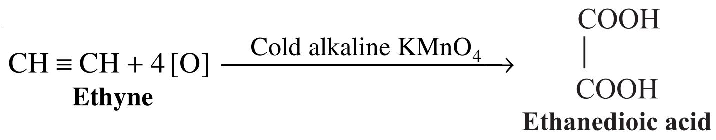
$$\underset{\textbf{Ethyne}}{CH \equiv CH + H_2O} \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\substack{\textbf{Vinyl Alcohol}\\ \textbf{(Unstable)}}}{[CH_2 = CHOH]} \xrightleftharpoons{Rearrangement} \underset{\textbf{Ethanal}}{CH_3CHO}$$

   (v) **Addition of H_2SO_4:** Conc. H_2SO_4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{conc.\ H_2SO_4} \underset{\textbf{Vinyl hydrogen sulphate}}{CH_2 = CHHSO_4} \xrightarrow{H_2SO_4} \underset{\textbf{Ethylidene hydrogen sulphate}}{CH_3 - CH\ (HSO_4)_2}$$

2. **Oxidation** : Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

   (i) **Oxidation with $KMnO_4$**



$$\underset{\textbf{Ethyne}}{CH \equiv CH + 4\,[O]} \xrightarrow{Cold\ alkaline\ KMnO_4} \underset{\textbf{Ethanedioic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}}$$

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$R-C\equiv C-R' \xrightarrow[\text{heat}]{KMnO_4 + KOH} RCOOH + R'COOH$$

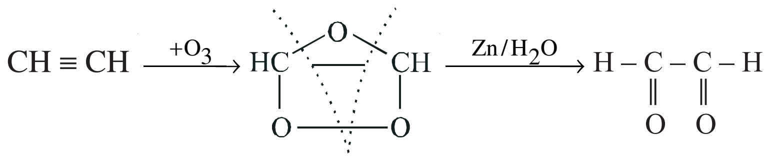
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH\equiv CH + 4\,[O] \xrightarrow[\text{heat}]{KMnO_4 + KOH} (COOH)_2 \xrightarrow[\text{Heat}]{[O]} 2\,CO_2 + H_2O$$

Combustion : Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\,C_2H_2 + 5\,O_2 \xrightarrow{\text{heat}} 4\,CO_2 + 2\,H_2O \quad \Delta H = -1300\ \text{KJ mol}^{-1}$$

Ozonolysis : On ozonolysis, alkynes give dicarbonyl compounds at the position of C≡C without breaking the chain of carbon atoms as shown below:



3. **Formation of Acetylides :** Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$CH\equiv CH + 2Cu(NH_3)_2 \longrightarrow \underset{\textbf{Cuprous acetylide (red)}}{CuC\equiv CCu} + 2\,NH^+_4 + 2\,NH_3$$

$$CH\equiv CH + 2Ag(NH_3)_2 \longrightarrow \underset{\textbf{Silver acetylide (white)}}{AgC\equiv CAg} + 2\,NH^+_4 + 2\,NH_3$$

24.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of *s*-character of the hydrocarbon. The greater the percentage of *s*-character of a hydrocarbon, the more will be its acidic nature.

Table 24.2 : % *s*-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	Type of hybridization	(%) s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*- character, they are the most acidic in nature. An *sp*-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of *sp* hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodamide. **The following reactions**

of ethyne with sodium and sodamide confirm its acidic nature. In these reactions, disodium acetylide is formed.

$$\underset{\textbf{Ethyne (Acetylene)}}{H-C\equiv C-H+2\,Na}\xrightarrow{\text{Heat}}\underset{\textbf{Disodium Acetylide}}{Na-C\equiv C-Na}+H_2$$

$$\underset{\textbf{Ethyne}}{H-C\equiv C-H}+\underset{\textbf{Sodamide}}{2\,NaNH_2}\xrightarrow{\text{Heat}}\underset{\textbf{Disodium Acetylide}}{Na-C\equiv C-Na}+2\,NH_3$$

24.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800ºC) which is used for for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

24.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The folloiwng table shows different tests for distinction between alkanes, alkenes and alkynes :

Table 24.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1.	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2.	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour of $KMnO_4$ is discharged
3.	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4.	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

INTEXT QUESTIONS 24.3

1. How is ethyne prepared from calcium carbide?
2. Give one reaction to confirm the acidic nature of ethyne.
3. What is the percentage of *s*-character in ethane, ethene and ethyne?

24.4 AROMATIC HYDROCARBONS

Till now, we have explained various methods of preparation of aliphatic hydrocarbons. Now, we shall deal with an aromatic hydrocarbon (benzene) in detail. It is one of the major components obtained by the destructive distillation of coal as shown in Fig. 24.1

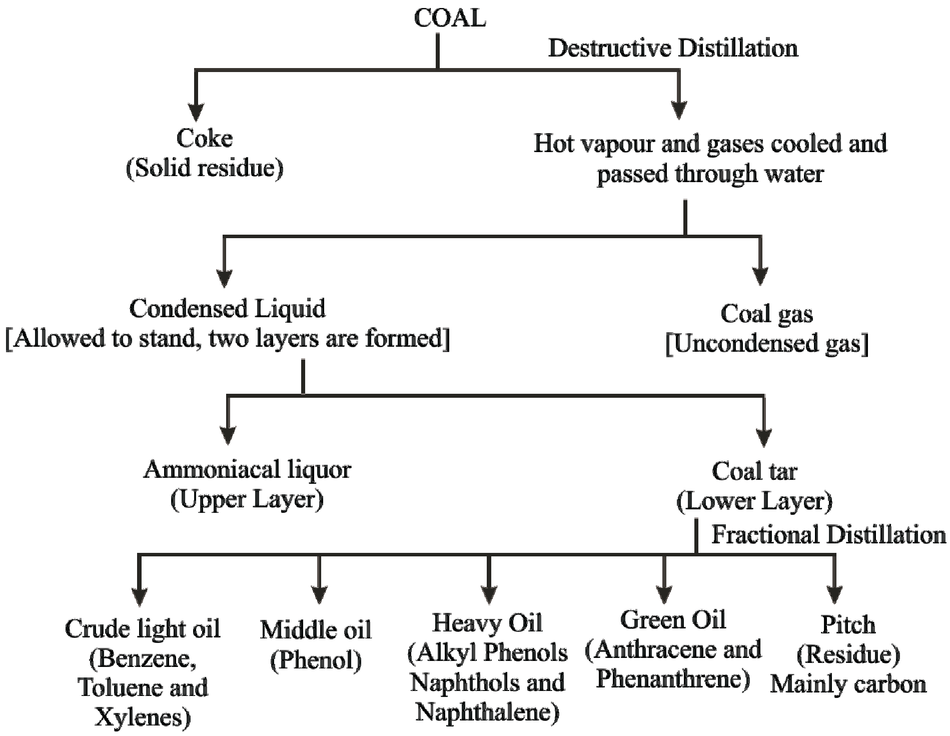


Fig. 24.1 : *Destructive Distillation of coal*

24.4.1 Structure of Benzene

The molecular formula of benzene is C_6H_6 which indicates that benzene is an unsaturated hydrocarbon. The unsaturation in benzene can be verified by the following reactions.

(i) Benzene undergoes the addition of H_2 in the presence of Ni or Pt as catalyst.

$$\underset{\textbf{Benzene}}{C_6H_6 + 3H_2} \xrightarrow{\text{Ni or Pt}} \underset{\textbf{Cyclohexane}}{C_6H_{12}}$$

(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

$$\underset{\textbf{Benzene}}{C_6H_6 + 3\,Cl_2} \xrightarrow{h\nu} \underset{\textbf{Benzene hexachloride (B.H.C.)}}{C_6H_6Cl_6}$$

Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes i.e., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions.

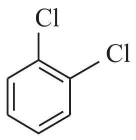
e.g. $$\underset{\textbf{Benzene}}{C_6H_6 + Br_2} \xrightarrow{\text{Fe or FeCl}_3} \underset{\textbf{Bromobenzene}}{C_6H_5Br + HBr}$$

Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.

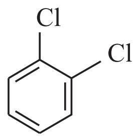
or

As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 and all the carbon-carbon bond lengths are equal i.e. 139 pm.

If Kekule's structure is to be taken as a true structure, then benzene should form only one monosubstitution product and two ortho distubstitution products, shown below as (a) and (b).



(a)



(b)

In structure (a), the two halogen atoms are on the doubly bonded carbon atoms, whereas in structure (b), the two halogen atoms are on singly bonded carbon atoms. As per the Kekule's structure these two isomers (a and b) should exist and show different properties. But, in reality, only one ortho disubstituted product exists. In order to explain this, Kekule proposed a dynamic equilibrium between the two structures.

Kekule's structure does not explain the stability of benzene and its some unusual reactions. Resonance can explain the unusual behaviour of benzene. Let us now study about resonance.

Resonance : ***The phenomenon by virtue of which a single molecule can be represented in two or more structures is called resonance.*** The actual structure is the resonance hybrid of all the canonical or resonating structure. (see lesson 25)

Heat of hydrogenation data provides proof for resonance stabalization in benzene. **The heat of hydrogenation is the amount of heat liberated when hydrogen is added to one mole of an unsaturated compound in the presence of a catalyst.**

$$\text{Cyclohexene} \quad + \quad H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5 \text{ KJ mol}^{-1}$$

(One – C = C– bond)

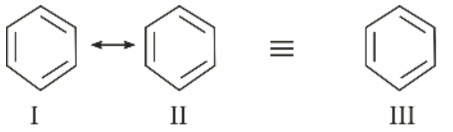
If the three double bonds in benzene do not interact, then it should behave like cyclohexatriene and the amount of heat liberated on adding there molecules of hydrogen should be 358.5 KJ mol^{-1}. But, the actual heat of hydrogenation of benzene is 208.2 kJ mol^{-1}.

$$\text{Benzene} \quad + \quad 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2 \text{ kJ mol}^{-1}$$

(Three – C = C– bond)

This difference of (358.5 – 208.2) 150.3 kJ mol^{-1} in the heat of hydrogenation is the measure of stability of benzene. Benzene acquires stability due to resonance and hence, this energy is called resonance energy of benzene.

Thus, the structure of benzene can be described as a resonance hybrid of two equivalent forms, (I) and (II). None of these two forms is correct by itself.



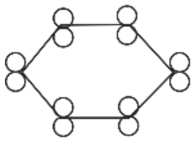
Resonance forms of benzene

Resonance hybrid structure showing delocalisation of electrons

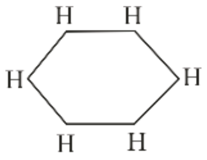
and the actual structure is intermediate of these two forms. This can be represented as III where the circle inside the ring indicates the equivalence of the carbon-carbon bonds. The carbon-carbon bond length has been found to be 139 pm. which is same for all the carbon-carbon bonds in benzene. Also, this value of bond length is intermediate between the typical C—C single (154 pm) and C=C double bond (134 pm) lengths.

Molecular Orbital Picture of Benzene

All the six carbon atoms of benzene are sp^2 hybridised. All C—C—C bond angles are 120° and there is a p orbital on each carbon atom. All the six p-orbitals are perpendicular to the plane of the six-membered carbon ring. The overlap of these p orbitals leads to a delocalised electron cloud above and below the place of the carbon ring. This is shown below in IV and V.



IV



V

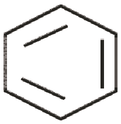
24.4.2 Aromaticity

So far you have studied that benzene

- is a cyclic conjugated molecule.
- is unusually stable.
- is planar in nature and its all C — C bond lengths are equal.
- can be represented as a resonance hybrid of two structures.
- undergoes substitution reactions rather than addition reactions.

Though the above properties indicate that benzene is *aromatic* in nature. But to complete the argument for its aromatic nature, we have to check whether it follows **Huckel's rule** or not. According to **Huckel rule** – a molecule is aromatic only if it has a planar, monocyclic system of conjugated $4n + 2$ π electrons where $n = 0$, 1, 2, 3, …. Thus, molecules with 2, 6, 10, 14 π … electrons can be aromatic.

For example, in Benzene, C_6H_6



Benzene

No. of π electrons = $6e^-$ (3π bonds × $2e^-$ = $6e^-$)

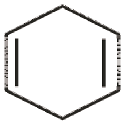
Using formula,

$4n + 2$ = No. of π electrons

$4n + 2 = 6$ gives $n = 1$

Hence, benzene is aromatic.

Let us take another example, i.e. 1,4-hexadiene



Hex-1,4-diene

For this compound, No. of π electron = $4e^-$ (2π bond × $2e^-$)

Using formula,

$4n + 2$ = No. of π electrons

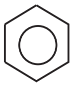
$$4n + 2 = 4$$

$$n = \frac{\cancel{2}}{\cancel{4}} = 0.5$$

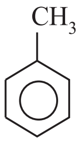
Hence, the value of n is 0.5. So, it does not obey Huckel rule and is non aromatic.

24.4.3 Physical Properties of Aromatic Hydrocarbons

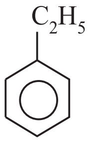
1. Benzene and its homologues are colourless liquids having a characteristic odour.
2. They are immiscible in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc. They dissolve fats and many other organic substances.
3. Most of the aromatic hydrocarbons are lighter than water.
4. Their boiling points show a gradual increase with increasing molecular mass e.g. benzene (b.p. 353 K), toluene (b.p. 383 K) and ethylbenzene (b.p. 409 K) and so on.



Benzene
(b.p. 353 K)



Toluene
(b.p. 383 K)

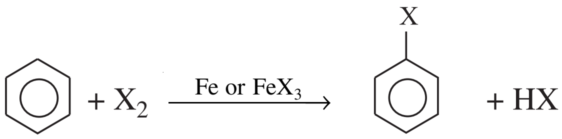


Ethylbenzane
(b.p. 409 K)

24.4.4 Chemical Properties of Aromatic Hydrocarbons

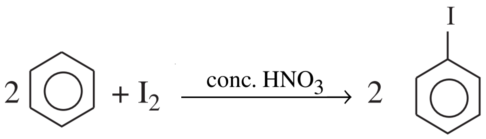
Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(i) Halogenation : The reaction in which a hydrogen atom of benzene is replaced by a halogen atom is called halogenation of benzene. Halogenation takes place in the presence of iron, or ferric halides (FeX_3, where X = Cl or Br).



Halobenzene

In case of iodination the HI formed can reduce iodobenzene back to be benzene which is prevented by carrying out this reaction in the presence of HNO_3 or HIO_3. These acids react with HI as soon as it is formed.



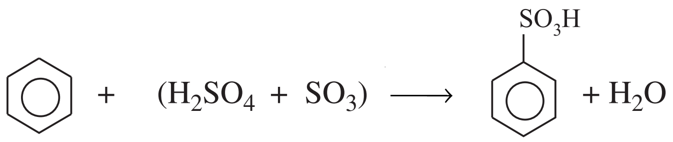
Iodobenzene

(ii) **Nitration :** The chemical reaction in which a hydrogen atom of benzene ring is replaced by $-NO_2$ group, is called nitration. It is carried out in the presence of nitrating mixture, i.e. a mixture of conc. HNO_3 and conc. H_2SO_4. Nitronium ion (NO_2^+) so formed acts as an electrophile.

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^- + NO_2^+ + H_3O^+$$

Nitrobenzene

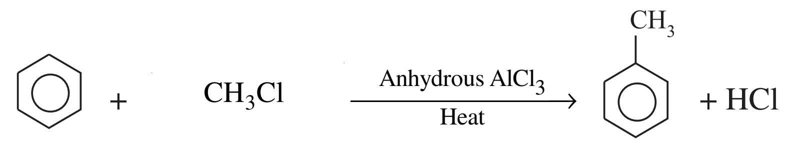
(iii) **Sulphonation :** The chemical reaction in which the hydrogen atom of benzene is replaced by $-SO_3H$ group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.



Fuming sulphuric acid **Benzenesulphonic acid**

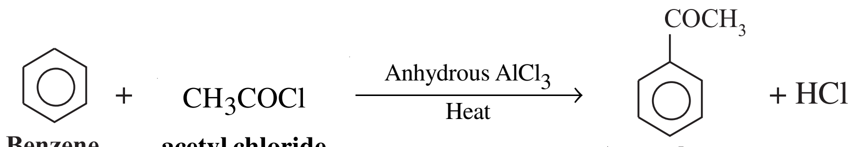
(iv) **Friedel–Craft's Reactions :** In Friedel-Craft's reaction, benzene is heated either with alkyl halide **(alkylation)** or acyl halide **(acylation)** in the presence of a catalyst (anhydrous $AlCl_3$). The products formed are alkyl or acyl derivatives of benzene.

Alkylation



Benzene **Chloromethane** **Toluene**

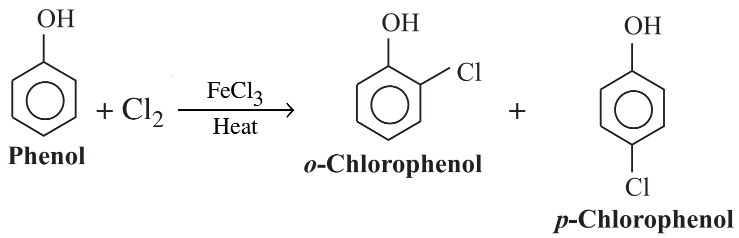
Acylation



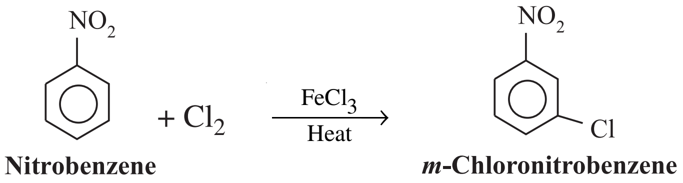
Benzene **acetyl chloride** **Acetophenone**

24.4.5 Directive Influence of Functional Groups

In case of substituted aromatic compounds, the functional group(s) already present directs the next incoming group to a particular position in the aromatic ring.. It is called directive influence of the group already attached to the benzene ring. For example, phenol on chlorination gives a mixture of *ortho* – chlorophenol and *para*– chlorophenol as – OH groups is an *ortho* and *para* directing group.



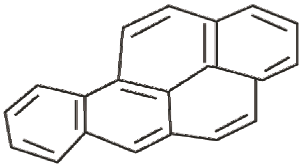
In case of nitrobenzene, we find that $-NO_2$ group is a *meta* directing group and hence, the product obtained on chlorination is *meta*-chloronitrobenzene.



24.4.6 Carcinogenicity & Toxicity

There exist several aromatic compounds-many of them being very important for the life while there are some others which are harmful. A large number of them are toxic in nature. For example benzene is carcinogenic in nature.

Another such hydrocarbon, is benzo[α] pyrene which has been found in cigarette smoke and in the exhaust from automobiles. This compound is also carcinogenic and can cause skin cancer in mice.



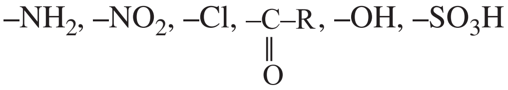
Benzo [a] pyrene

24.4.7 Uses of Aromatic Hydrocarbons

Benzene is used as a solvent for several organic compounds and thus, acts as a medium for carrying out synthetic reactions. It is the basic aromatic hydrocarbon and can be converted to other organic compounds by carrying out substitution in the benzene ring. **Toluene,** a higher homologue of the benzene, finds its uses for dry-cleaning, as a solvent, and as a starting material for the manufacture of dyes, drugs, explosive (trinitrotoluene, T.N.T.), benzaldehyde, benzoic acid etc.

INTEXT QUESTIONS 24.4

1. What is the value of resonance energy of benzene?
2. Name the product formed when :
   (i) benzene reacts with chlorine in the presence of light.
   (ii) phenol reacts with chlorine in the presence of $FeCl_3$.
   (iii) nitrobenzene reacts with chlorine in the presence of $FeCl_3$.
3. Classify the following into *o*-and *p*- or *m*-directing groups :



$-NH_2, -NO_2, -Cl, -\underset{\underset{O}{\|}}{C}-R, -OH, -SO_3H$

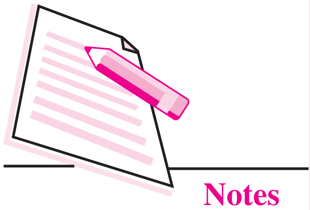
WHAT YOU HAVE LEARNT

- Alkanes can be prepared by (i) the reduction of haloalkanes, (ii) action of water or alcohol on Grignard's reagent, (iii) Wurtz reaction and (iv) hydrogenation of unsaturated hydrocarbons.
- Physical properties of hydrocarbons depend on the intermolecular forces of attraction. which in turn depend upon the shapes of molecules and their surface area.
- The melting points of hydrocarbons depends upon the symmetry of the molecules i.e. hydrocarbons with even number of carbon atoms are more symmetrical and have higher melting points.
- Rotation about carbon-carbon single bond leads to various conformations of a molecule. Ethane has many conformations out of which the staggered conformation is the most stable one and the eclipsed conformation is the least stable one.
- Alkenes can be prepared by dehydrohalogenation of alkyl halides and by dehydration of alcohols.
- Alkenes and alkynes undergo addition reactions e.g. addition of hydrogen, halogens, halogen acids, water, sulphuric acid etc. due to the presence of carbon-carbon double or triple bonds.
- Addition of halogen acids and other unsymmetrical reagents to unsymmetrical alkenes and alkynes takes place according to the Markownikoff's rule.
- Alkenes undergo polymerization on heating under pressure.

- All hydrocarbons (saturated as well as unsaturated) form CO_2 and H_2O on combustion and liberate energy.
- An alkaline solution of $KMnO_4$ can oxidize alkenes and alkynes forming different products such as carboxylic acids, aldehydes and/or ketones and carbon dioxide.
- Ozone can oxidize unsaturated hydrocarbons (alkenes and alkynes) forming ozonides which when further reacted with water in the presence of zinc dust either form aldehydes or ketones or both.
- Reaction of ozone with alkenes can be used to determine the position of double bond.
- Ethyne can be prepared by the action of water on calcium carbide and by dehydrogenation of dihaloalkanes.
- Alkynes are acidic in nature due to *sp*-hybridization of carbon atoms. Because *sp* hybridized carbon atoms are more electronegative than sp^2 and sp^3, and the bond between C—H is weakened. Hence, hydrogen atoms in alkynes can be replaced by certain metal atoms.
- Alkanes, alkenes and alkynes can be distinguished by using:
  - a) Br_2 dissolved in carbon tetrachloride.
  - b) Ammoniacal solution of $AgNO_3$
  - c) Ammoniacal solution of Cu_2Cl_2
  - d) Alkaline solution of $KMnO_4$
- Benzene is obtained by destructive distillation of coal.
- A ring structure of benzene was suggested by Kekule. Actual structure of benzene is the resonance hybrid of the canonical structures.
- Aromatic hydrocarbons undergo substitution reactions i.e. the reactions in which hydrogen atom of hydrocarbons is replaced by another atom or group of atoms. Halogenation, sulphonation, nitration and Friedel Craft's reaction are substitution reactions of benzene.
- The position of second substituent on a benzene ring depends upon the nature of the group already present.

TERMINAL EXERCISE

1. What happens when : (Write chemical equations)
   - (i) Iodoethane is heated with HI in the presence of red phosphorus.
   - (ii) 2-Chlorobutane reacts with sodium metal.



(iii) Ethyl magnesium bromide is reacted with methyl alcohol (methanol).

(iv) 2-Chloropropane reacts with alcoholic solution of KOH.

(v) 1,1-Dichloroethane reacts with alcoholic solution of KOH.

2. Give reasons for the following :

   (i) The boiling point of neopentane is less than that of n-pentane.

   (ii) Stability of benzene ring

   (iii) Boiling points of hydrocarbons decrease with the increase in branching.

3. How will you prepare the following?

   (i) Ethane from ethene

   (ii) Ethene from ethanol

   (iii) Cyclohexane from benzene

   (iv) Methane from sodium acetate

   (v) Butane from bromoethane

4. What happens when (write balanced chemical equations):

   (i) Hydrochloric acid is added to ethene.

   (ii) Hydrobromic acid (HBr) is added to propene in the presence of benzoyl peroxide.

   (iii) Benzene reacts with chloromethane in the presence of anhydrous $AlCl_3$.

   (iv) Br_2 is added to ethyne.

   (v) Methane is oxidized with oxygen in the presence of copper at 475K and a high pressure of 120 atm.

5. How are the following conversions carried out?

   (i) Ethyne to ethane

   (ii) Benzene to nitrobenzene

   (iii) Ethyl alcohol (ethanol) to ethene

   (iv) Ethyne to ethanedioic acid

   (v) Benzene to *o*-nitrochlorobenzene.

6. You are provided with three gas jars containing ethane, ethene and ethyne. Give the suitable chemical tests to identify the three hydrocarbons.

7. What is ozonolysis? How is it used to determine the position of a double bond?

8. Give reasons for the following :

   (i) Alkanes do not undergo addition reactions like alkenes and alkynes.

   (ii) Ethyne is more acidic than ethane.

(iii) Ethene undergoes polymerization but not ethane.

(iv) Benzene undergoes electrophilic substitution reactions.

ANSWERS TO INTEXT QUESTIONS

24.1

1. They are used as fuels and to prepare detergents, dyes, drugs, explosives etc. Hydrocarbons are used to prepare some important organic compounds like alcohols, aldehydes, carboxylic acids etc.
2. The alkyl magnesium halides (R-MgX) are called Grignard's reagent.
3. Easily replaceable hydrogen present in a molecule is called active hydrogen.
4. The physical properties of hydrocarbons differ from one another due to difference in molecular mass, surface area, intermolecular force of attraction.
5. Methane and ethane are gases, pentane and hexane are liquids.
6. Three isomers of pentane are : *n*-pentane, isopentane and neopentane.
7. *n*-pentane has higher boiling point than n-butane.
8. $C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$

24.2

1. *Trans*-2-butene has higher boiling point than *cis*-isomer.
2. Ethane-1, 2-diol
3. Hydrogen in presence of catalist Ni, Pt or Pd
4. Epoxyethane is produced.

24.3

1. Calcium carbide is reacted with water to prepare ethyne.

   $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

2. Reaction with sodium metal confirms the acidic nature of ethyne.

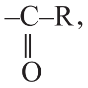
   $$\underset{\textbf{Ethyne}}{H-C\equiv C-H} + 2\ Na \longrightarrow \underset{\textbf{Disodium acetylide}}{Na-C\equiv C-Na} + H_2$$

3. The *s*-character in : Ethane = 25%,
   Ethene = 33%,
   Ethyne = 50%

24.4

1. The resonance energy of benzene is 150.3 KJ mol^{-1}.
2. (i) Benzene hexachloride (BHC).

   (ii) *o*-Chlorophenol and *p*-chlorophenol.

   (iii) *m*-Chloronitrobenzene.
3. *o* – and *p* – directing groups : $-NH_2$, $-Cl$, $-OH$
   m-directing groups : NO_2,  $-\underset{\underset{O}{\|}}{C}-R$, $-SO_3H$

25

COMPOUNDS OF CARBON CONTAINING HALOGENS (HALOALKANES AND HALOARENES)

You have studied about the hydrocarbons in the previous lesson.When a hydrogen attached to a carbon atom in the hydrocarbons is replaced by a halogen atom (i.e. F,C1,Br or I), the compounds formed are called **haloalkanes or haloarenes.**The halogen derivatives do not occur in nature and they are synthesized in the laboratory. These compounds have wide applications in industry and domestic uses. They are used as industrial solvents, in the manufacture of pharmaceuticals, as dry cleaning agents, as pesticides, as anesthetics in medicine, as refrigerants, as fire extinguishers and as antiseptics. In this lesson, you will study the nomenclature, methods of preparation and properties of this important class of carbon compounds.

OBJECTIVES

After reading this lesson, you will be able to :

- define haloalkanes and haloarenes;
- name haloalkanes and haloarenes according to IUPAC rules;
- explain methods of preparation, physical properties, chemical properties and uses of haloalkanes and haloarenes;
- distinguish between haloalkanes and haloarenes, and
- explain the preparation, properties and uses of some important polyhalogen compounds.

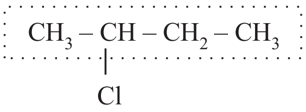
25.1 NOMENCLATURE OF HALOALKANES AND HALOARENES

You have learnt the nomenclature of hydrocarbons in lesson 25. In this section, you will learn the nomenclature of halogen derivatives of both aliphatic and aromatic hydrocarbons i.e. haloalkanes and haloarenes.

Nomenclature of Haloalkanes

The following rules are used for naming haloalkanes according to the IUPAC system.

1. The longest chain of the carbon atoms bearing the halogen atom is selected.

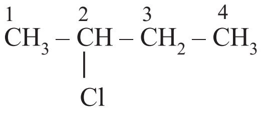


$$\boxed{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3}$$

The longest chain of carbon atoms in the above example is shown in the box.

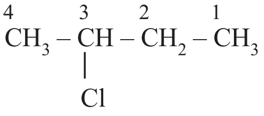
2. Numbering of the carbon atoms in the chain is done in such a way that the carbon atom bearing the halogen atom gets the lowest number.

For example.



$$\overset{1}{C}H_3-\underset{\underset{Cl}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

(Correct) I



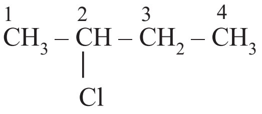
$$\overset{4}{C}H_3-\underset{\underset{Cl}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

(Incorrect) II

In the above example, numbering shown in (I) is correct while in (II), it is incorrect since the carbon atom bearing halogen atom gets lower number in I than in II.

3. The word chloro, is prefixed to the parent hydrocarbon name.

So, the correct name for the above halocompound is

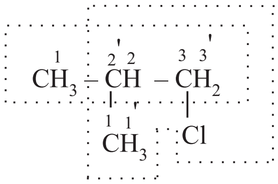


$$\overset{1}{C}H_3-\underset{\underset{Cl}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

2-Chlorobutane

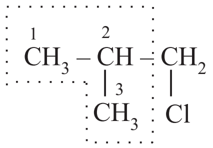
4. In case of alkyl substituted haloalkanes, the longest chain containing halogen atom is selected for numbering.

For example :



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

I

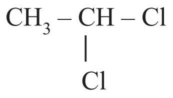


$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

II

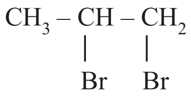
In structure I, the selection of chain is shown by two different ways. Both the ways of selection are correct since they include chloro group. In structure II numbering shown is not correct since it does not include chloro group.

5. When two or more halogen atoms are present in a compound, the longest chain selected must contain the maximum number of halogen atoms. The multiplicative prefixes (*di, tri, tetra,* etc.) are added before the name of halogen atom to indicate the number of halogen atoms. The following examples illustrate this rule.



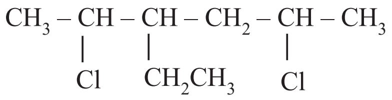
$CH_3-\underset{\underset{Cl}{|}}{CH}-Cl$

1, 1 - Dichloroethane



$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$

1, 2 - Dibromopropane

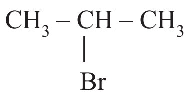
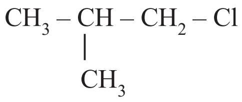


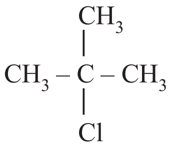
$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

2,5 - Dichloro - 3 - etylhexane

Some more examples are given in Table 25.1 to illustrate the above rules.

Table 25.1: Names of Some Haloalkanes

Compound	IUPAC name	Common name
CH_3CH_2Br	Bromoethane	Ethyl bromide
$CH_3CH_2CH_2Br$	1-Bromopropane	*n*-Propyl bromide
 $CH_3-\underset{\underset{Br}{\vert}}{CH}-CH_3$	2-Bromopropane	*iso*-Propyl bromide
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-Cl$	1-Chloro-2-methylpropane	*iso*-Butyl chloride
 $CH_3-\underset{\underset{Cl}{\vert}}{CH}-CH_2-CH_3$	2-Chlorobutane	*sec*- Butyl chloride



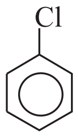
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large Cl}{|}}{C}}-CH_3$$

2-Chloro-2-methylpropane *tert*-Butyl chloride

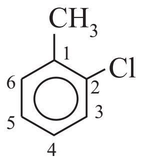
* All compounds essentially do not have common names.

Nomenclature of Haloarenes

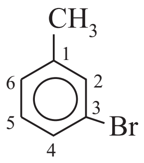
Haloarenes are those aromatic halogen compounds in which the halogen atom is directly linked to an aromatic ring. Their general formula is Ar-X where Ar- represents an aromatic ring and X denotes the halogen. In naming a haloarene, the prefix *chloro, bromo-or iodo-* etc. is are added to name of arene according to halogen(s) present. The relative positions of halogen atoms are indicated by appropriate numbers. The prefixes *ortho (o-), meta(m-) and para (p-)* are also commonly used respectively to indicate the relative positions i.e. 1,2- ;1,3 – and 1,4- of substituents in a benzene ring. Following examples illustrate the nomenclature of some haloarenes.



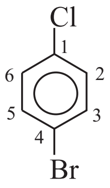
Chlorobenzene



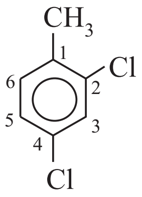
2-Chlorotoluene
(*o*-Chlorotoluene)



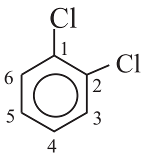
3-Bromotoluene
(*m*-Bromotoluene)



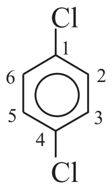
4-Bromochlorobenzene
(*p*-bromochlorobenzene)



2, 4-Dichlorotoluene



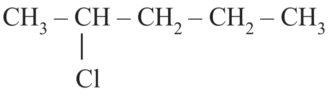
1, 2-Dichlorbenzene
(*o*-Dichlorobenzene)



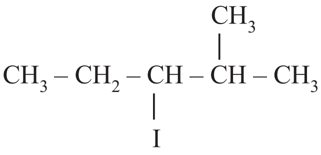
1, 4-Dichlorobenzene
(*p*-Dichlorobenzene)

INTEXT QUESTIONS 25.1

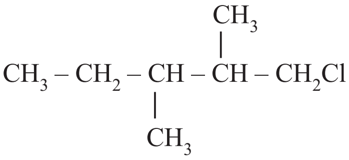
1. Write the IUPAC names of each of the following compounds :

(i) 

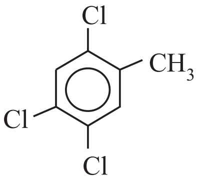
$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-CH_3$

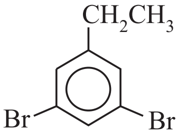
(ii) 

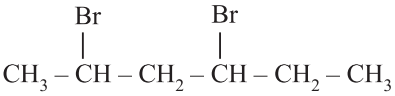
$CH_3-CH_2-\underset{\underset{I}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(iii) 

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl$

(iv) 

(v) 

(vi) 

$CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3$

2. Draw structural formulae of the following compounds:

(i) 2-Bromo-3-methylbutane

(ii) 3-Chloro-4-methylhexane

(iii) 3-Bromochlorobenzene

(iv) 2,4-Dibromotoluene

25.2 PREPARATION OF HALOALKANES AND HALOARENES

25.2.1 Preparation of Haloalkanes

(i) **From Hydrocarbons :** Direct halogenation of hydrocarbons takes place in the presence of sunlight or at high temperature in dark. For example, chloroethane is prepared by monochlorination of ethane.

$$\underset{\textbf{Ethane}}{CH_3-CH_3}+Cl_2\xrightarrow{\text{Sunlight}}\underset{\textbf{Chloroethane}}{CH_3-CH_2Cl}+HCl$$

This reaction follows a free radical mechanism. You have already learnt the mechanism of chlorination of methane in lesson 26.

Bromo derivatives of alkanes are also prepared by direct bromination.

$$\underset{\textbf{Ethane}}{CH_3-CH_3}+Br_2\xrightarrow{\text{Sunlight}}\underset{\textbf{Bromoethane}}{CH_3-CH_2-Br}+HBr$$

Direct iodination is not possible with iodine as the reaction is reversible. Direct fluorination is also not possible because due to the high reactivity of the fluorine, the reaction cannot be controlled.

(ii) **From Alcohols :** Alcohols are converted into haloalkanes by treating with (a) hydrogen halides (b) phosphorus halides or (c) thionyl chloride.

(a) **Reaction with Hydrogen Halides :** Hydrogen halides react with an alcohol in presence of a dehydrating agent such as anhydrous zinc chloride to produce a haloalkane.

Chloroethane is conveniently prepared by the reaction of ethanol with concentrated hydrochloric acid in presence of anhydrous zinc chloride.

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH}+HCl\xrightarrow{\text{anhy.}ZnCl_2}\underset{\textbf{Chloroethane}}{CH_3-CH_2Cl}+H_2O$$

Zinc chloride absorbs water from the reaction mixture and thus prevents the reverse reaction.

Bromoethane is obtained by refluxing ethanol with HBr in presence of little concentrated H_2SO_4 as the catalyst.

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH}+HBr\xrightarrow[\Delta]{\text{conc. }H_2SO_4}\underset{\textbf{Bromoethane}}{CH_3CH_2Br}+H_2O$$

(b) Reaction with Phosphorus Halides : Haloalkanes are conveniently prepared by the reaction of an alcohol with a phosphorus halide $(PCl_3, PCl_5 \text{ or } PBr_3)$ according to the following equations.

$$3\ C_2H_5OH + PCl_3 \longrightarrow 3\ C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3\ C_2H_5OH + PBr_3 \longrightarrow 3\ C_2H_5Br + H_3PO_3$$

(c) Reaction with Thionyl Cholride : Thionyl chloride ($SOCl_2$) is another reagent which reacts with an alcohol to yield a chloroalkane.

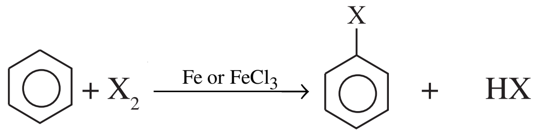
$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2\uparrow + HCl\uparrow$$

Ethanol **Chloroethane**

As both the byproducts, SO_2 and HC1 are gases, the purification of final product is not required.

25.2.2 Preparation of Haloarenes

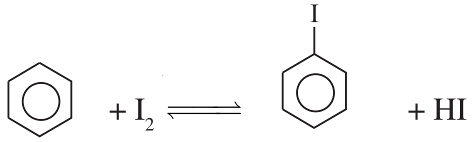
(i) From Aromatic Hydrocarbons : Haloarenes are obtained by direct halogenation of aromatic hydrocarbons in the presence of a catalyst. Usually iron filings or iron (III) halide is used as the catalyst.



Benzene **Halobenzene (Haloarene)**

where X = Cl or Br

The direct iodination of aromatic hydrocarbons is not a useful reaction since the HI produced reduces the aryl iodide back to the aromatic hydrocarbon.



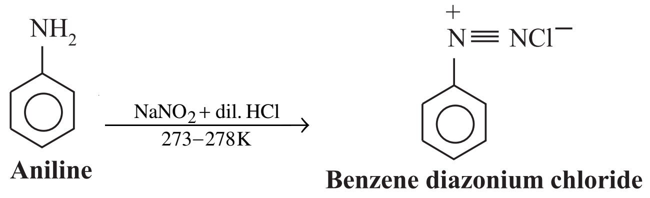
Benzene **Iodobenzene**

However, in the presence of an oxidizing agent such as nitric acid, iodic acid (HIO_3), mercury oxide, the HI produced is either oxidized to iodine or is eliminated as mercuric iodide and, thus, iodobenzene is obtained.

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3H_2O$$

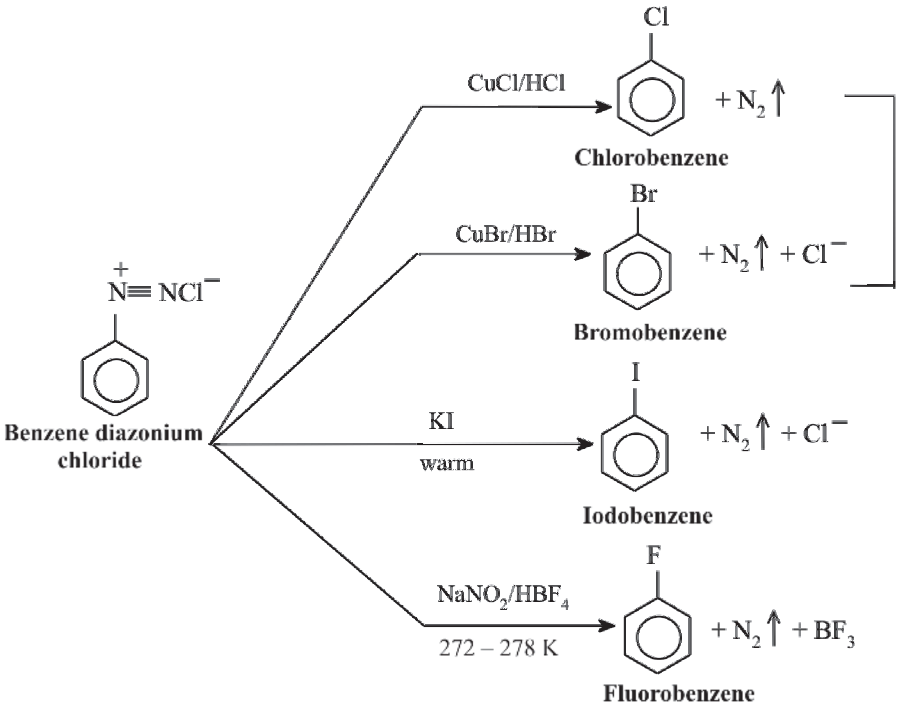
Fluorobenzene cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be controlled.

(ii) From Diazonium Salts : Benzene diazonium salt is formed by treating an aromatic primary amine with $NaNO_2$ and dil. HCl at low temperature. The process is known as **diazotisation**.

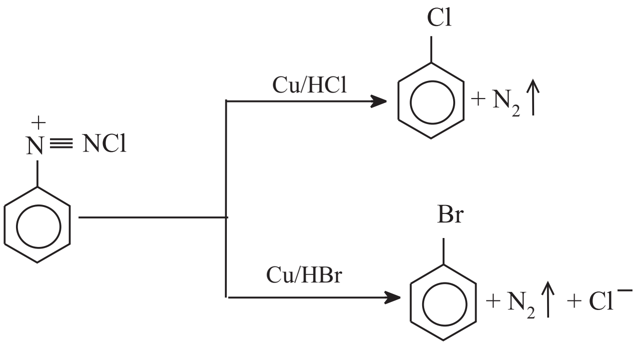


Diazonium salts are highly reactive compounds. They are used in the preparation of a large number of arene derivatives. When a diazonium salt is treated with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2), the corresponding haloarene is formed.

This reaction is known as **Sandmeyer reaction**. It is used for introducing a chloro or bromo group in the benzene ring.

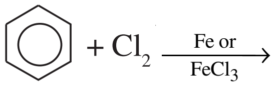


Haloarenes can also be prepared by reacting benzene diazonium chloride with copper powder in presence of corresponding halogen acid. This reaction is called **Gattermann reaction** and is shown below :



INTEXT QUESTIONS 25.2

1. Write the structure of the main product obtained by treating 1-propanol with excess of hydrogen chloride in the presence of anhydrous zinc chloride.
2. What will be the product obtained on treatment of 1-propanol with thionyl chloride?
3. Give one example of preparation of chlorbenzene using Sandmeyer reaction?
4. Complete the following reaction :

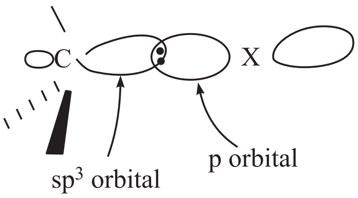


25.3 PROPERTIES OF HALOALKANES AND HALOARENES

Before we discuss the important physical and chemical properties of alkylhalides and aryl halides, let us consider the nature of C—X bond.

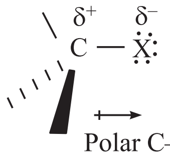
25.3.1 The Nature of C–X Bond

In alkyl halides, the carbon – halogen bond is formed by the overlap of the sp^3 hybrid orbital of carbon atom with the *p*-orbital of the halogen atom.



As one moves from fluorine to iodine, the size of the halogen atom increases and hence the overlap decreases. Hence, the C–X bond becomes longer and weaker on going from alkyl fluorides to alkyl iodides.

Also, the halogens are more electronegative than carbon. Thus, the electron density along the C–X bond is displaced in the direction of the halogen. Thus, *the C–X bond in polar in nature*. The carbon atom bears a partial positive charge (δ^+) and the halogen atoms bears a partial negative charge (δ^-).



Polar C–X bond

You will now study that this bond polarity has important impact on the physical and chemical properties of alkyl halides.

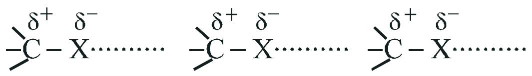
The partially positively charged carbon in haloalkanes can be easily attached by anions and electron rich species which are called *nucleophiles*. On the other hand, the partially negatively charged halogen atom can be attacked by the cations and electron deficient species.

25.3.2 Physical Properties

1. The lower alkyl halides (CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl) are gases at room temperature. The other alkyl halides containing upto C_{18} are liquids having high boiling points.

2. Haloalkanes and haloarenes are moderately polar molecules ($\overset{\delta+}{>C}-\overset{\delta-}{X}$). Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.

3. The melting and boiling points of haloalkanes and haloarenes are higher than those of their parent hydrocarbons (Table 25.2) This is due to (i) the greater molecular mass and hence greater magnitude of van der Waals forces of attraction in halocompounds than in the parent hydrocarbons and (ii) the existence of intermolecular dipole-dipole interaction, as shown below:

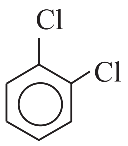


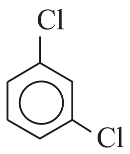
For a given alkyl or aryl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 25.2 to show this variation.

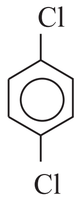
Table 25.2 : Boiling Points of Haloalkanes and Haloarenes

Compound	Boiling Point (K)				
	X=H	X=F	X=Cl	X=Br	X=I
CH_3-X	111.5	194.6	248.8	276.6	315.4
C_2H_5-X	184.3	241	285	311.4	345
C_6H_5-X	351	358	405	429	461

4. All monohalobenzenes are liquids at room temperature. Among dihalobenzenes, the *para* isomers have the highest melting points. It is due to the greater symmetry that causes a better packing of molecule in the *para* isomer.

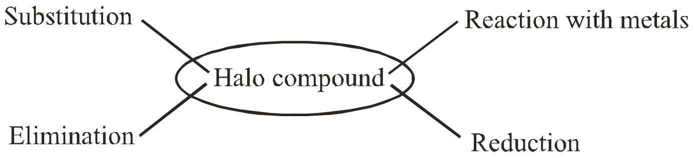

256 K


249 K


325 K

25.3.4 Chemical Properties

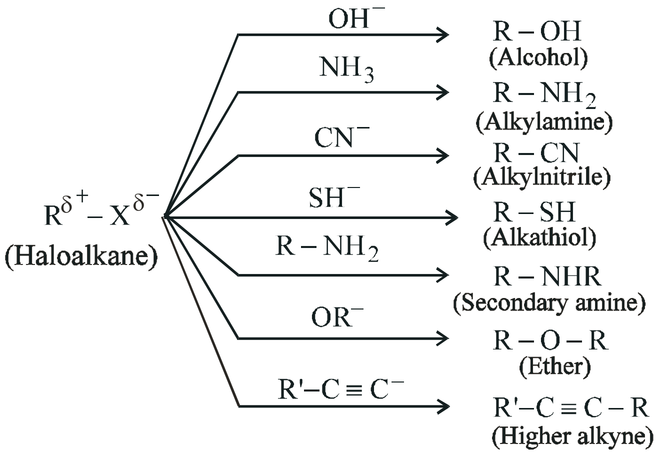
Halo compounds can undergo the following types of reactions :



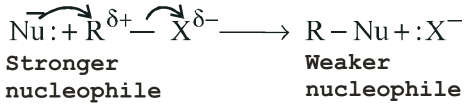
1. Substitution : Substitution reactions are those in which an atom or a group of atoms from the reactant molecule is displaced by another atom or a group of atoms. For example, on treating chloroethane with sodium hydroxide, the chlorine atom of chloroethane is substituted by the hydroxyl group and ethanol is formed as the reaction product.

$$C_2H_5-Cl+OH^- \longrightarrow C_2H_5OH+Cl^-$$

In this reaction, it is to be noted that the hydroxide ion (nucleophile) displaces the chlorine atom from C_2H_5Cl as chloride ion (another nucleophile). Such reactions which are initiated by the attack of a nucleophile are known as **nucleophilic reactions**. In haloalkanes, the carbon atom carrying the halogen atom is electron deficient due to – I effect of halogen atom. This electron deficient carbon atom is susceptible to attack by a nucleophile. Thus, you may conclude that haloalkanes undergo **nucleophillic substitution reactions**. Following are a few examples of nucleophilic substitution reactions of haloalkanes.



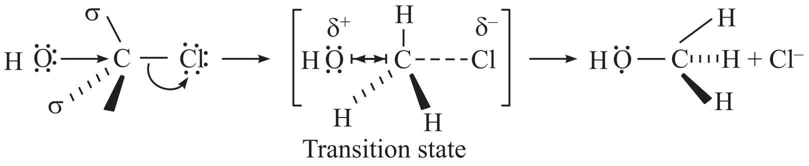
In all the above reactions, the stronger nucleophile $\left(HO^-, C_2H_5O^-, CN^- \text{ or } NH_3 \text{ etc.}\right)$ displaces a weaker nucleophile X^- as



25.3.3 Mechanism of Nucleophilic Substitution Reactions

The nucleophilic substitution reactions could be either S_N1 or S_N2 type.

When the nucleophilic attacks the haloalkane, and simultaneously the leaving groups leaves then, the reaction is called **nucleophilic substitution bimolecular** i.e. S_N2.

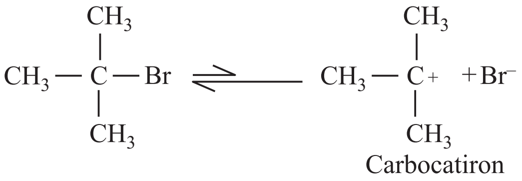


Also, note that it is a one step process and the transition state involves *two* species. The formation of this transition state is the rate determining step in this mechanism.

Here, the bond making and the bond breaking takes place simultaneously. The nucleophilie (^-OH) attacks from one side of the carbon atom whereas the leaving group (Cl^-) leaves from the opposite direction. Hence, there is an *inversion* of configuration at the carbon atom.

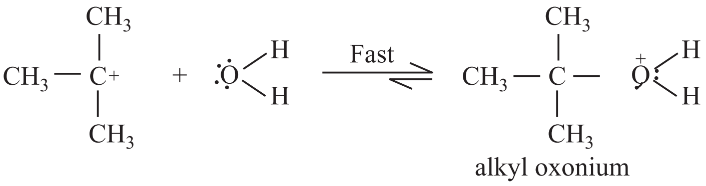
Primary alkyl halides undergo substitution by S_N2 mechanism.

However, in case of tertiary alkyl halides, the substitution takes place by an alternative mechanism, i.e. *substitution nucleophilic*, unimolecular or SN^1 mechanism. For example, in the hydrolysis of 2-bromo-2-methylpropane, any one molecule participates in the rate determining step which is the dissociation of the alkyl halide to alkyl cation and bromide ion.

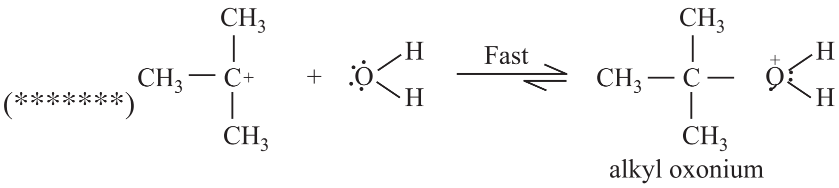


This alkyl cation is a carbocation and its formation is a slow and rate determining step.

After this, as soon as this carbocation is formed, the nucleophile, which is water (solvent) molecule, attacks on it which is a fast step.



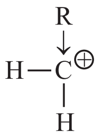
Finally, the alkyl oxonium ion loses a proton to give the alcohol as the product.



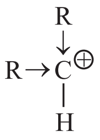
Since, the S_N1 reactions proceed via the formation of carbocations, the stability of the carbocation formed is an important factor in the S_N1 reactions.

Stability of Carbocations

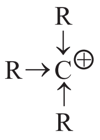
Let us consider the following carbocations.



I
A primary carbocation



II
A secondary carbocation



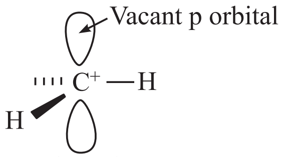
III
A tertiary carbocation

A carbocation is classified as *primary, secondary* or *tertiary* depending upon whether the positively charged carbon atom is linked to *one, two or three* carbon atoms, respectively.

Here, as the *number of alkyl groups* attached to the positively charged carbon atoms increases, the stability of the carbocation *also increases*. This is because alkyl groups are electron releasing in nature and help in the stabilization of the positive charge on the carbon atom of the carbonation.

Thus, a tertiary carbocation is more stable than a secondary carbocation which, in turn, is more stable than a primary carbonation.

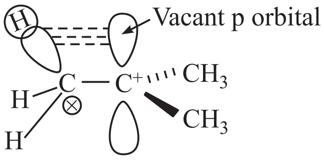
The above order of stability of carbocations is also explained on the basis of ***hyperconjugation***. Hyperconjugation results from the overlap of a *p* orbital with a neighbouring bonding molecular orbital. In a carbocation, the *p* orbital on the carbon carrying positive charge is vacant.



Carbocation

This vacant *p* orbital can overlap with the neighboring orbital of C–H bond and stabilize the charge. The more the number of such neighboring orbitals, the move will be the stabilization.

If we see the extent of hyper conjugation possible in primary, secondary and tertiory carbocation we can observe that in a primary carbocation cation 3 C–H bonds are available for hyperconjugation and in secondary carbocation 6 C–H bonds are available for hyperconjugation. Similarly, in a tertiary carbocation, 9 C–H bonds are available for hyperconjugation.

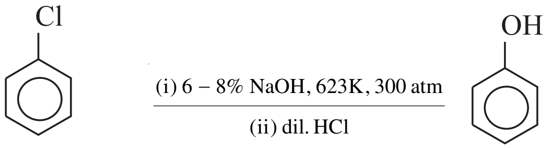


Hyper conjugation

Hence, a tertiary carbocation is more stable than a secondary carbocation which is, in turn, more stable than a primary carbocation.

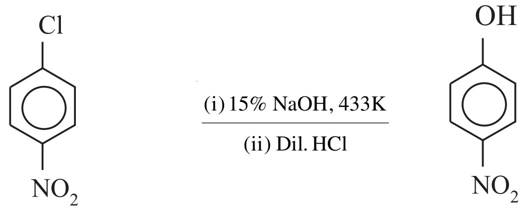
Thus, this also explains why tertiary halides undergo nucleophilic substitution reactions by S_N1 mechanism.

Haloarenes are almost unreactive to reagents such as NaOH, C_2H_5ONa, NaCN and NH_3 under ordinary laboratory conditions but can show nucleophillic substitution reactions under drastic conditions.



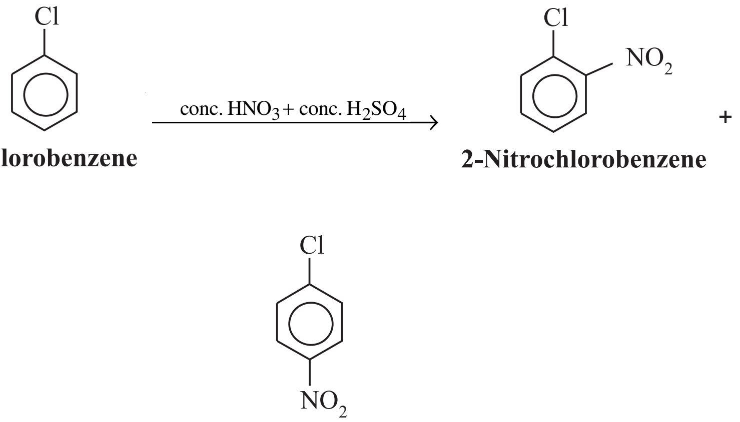
Chlorobenzene **Phenol**

It is also observed that the presence of electron withdrawing groups such as $-NO_2$ groups at *o*- and *p*-position (but not a *m*-position) with respect to halogen activates the halogens towards nucleophillic displacement.For example:



4-Nitrochlorobenzene **4-Nitrophenol**

Haloarenes can also readily undergo substitution reactions in benzene ring. The benzene ring is an electron rich species. Therefore, it is attacked by an electron deficient species such as NO_2^+. As *ortho* and *para* positions in haloarenes are electron rich due to resonance (Fig. 25.1), the electrophilic substitution takes place mainly at these positions. For example, the nitration of chlorobenzene, with a mixture of concentrated HNO_3 and H_2SO_4, gives a mixture of 2-nitrochlorobenzene and 4-nitrochlorobenzene.



Chlorobenzene **2-Nitrochlorobenzene**

4-Nitrochlorobenzene

Haloalkanes are highly reactive compounds due to the presence of a polar carbon-halogen bond in their molecules. The bond energy values of C–X bonds in haloalkanes and haloarenes are given in Table 25.3.

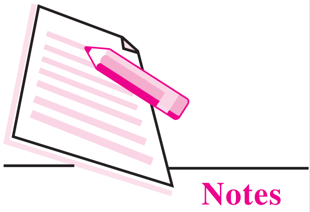


Table 25.3 : C–X bond energy Values

Bond	Bond Energy/kJ mol^{-1}
C–F	485
C–C1	339
C–Br	284
C–I	213

These bond energy values show that C-I bond is the weakest bond and C-F bond is the strongest bond. Therefore, the order of reactivity of haloalkanes is iodoalkane >bromoalkane > chloroalkane> fluoroalkane.

Comparing the haloalkanes and haloarenes, haloalkanes are found to more reactive than haloarenes in reactions involving the breaking of C–X bond (X = F,C1,Br, or I). It is due to the existernce of the phenomenon of resonance which cause carbon–halogen bond to acquire double bond character in haloarenes. The resonating structures of chlorobenzene are shown below :

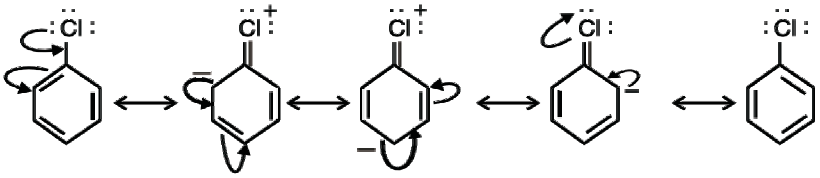


Fig. 25.1 : *Resonance Structures of Chlorobenzene*

2. Elimination reactions : When haloalkanes are heated with aqueous solution of potassium or sodium hydroxide, the major product formed is the alcohol, produced by nucleophilic displacement of the halogen atom by HO^{-}.

$$C_2H_5Cl \xrightarrow{\text{aq. KOH}} C_2H_5OH + Cl^{-}$$

Chloroethane **Ethanol**

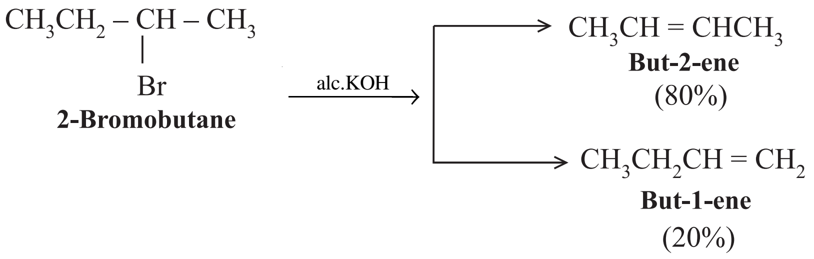
If a haloalkane is heated with concentrated alcoholic potassium hydroxide, the major product formed is an alkene due to the elimination of hydrogen halide. This is called β-elimination or dehydrohalogenation.

$$C_2H_5Cl \xrightarrow{\text{alc.KOH}} CH_2 = CH_2$$

Chloroethane **Ethene**

In this reaction, the OH^{-} ion acts and a base removes a proton from the molecule.

If the structure of alkyl halide is such that it can undergo elimination in two different ways, then the more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of elimination. This is known as **Saytzeff's rule**. For example, elimination reaction of 2-bromobutane gives 2-butene as major product according to the Saytzeff's rule, (refer lesson 26).



3. Reactions with metals : Haloalkanes and haloarenes react with a variety of metals (zinc, magnesium and lithium). The compounds so obtained have a metal atom directly bonded to a carbon atom. Such compounds in which the metal atom is directly bonded to a carbon atom are known as **organometallic compounds**. The organometallic compounds of magnesium with alkyl and aryl halides are known as **Grignard reagents.**

$$C_2H_5-Cl+Mg \xrightarrow{\text{dry ether}} C_2H_5-Mg-Cl$$

Chloroethane **Ethyl magnesium chloride**

These are named after the French chemist Victor Grignard.

Alkyl halides react with metallic sodium in presence of dry ether to form symmetrical higher alkanes. This reaction is called **Wurtz reaction.**

French Chemist

Victor Grignard was awarded Nobel Prize in 1912. He introduced **organomagnesium halide as a** common synthetic reagent.

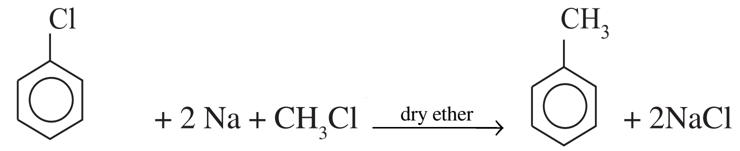
$$2\,R-X+2\,Na \xrightarrow{\text{dry ether}} R-R+2\,Na^+X^-$$

Ethyl bromide can react with lead in presence of dry ether to form tetraethyl lead (TEL) which is used as antiknocking agent in gasoline used for running automobiles.

$$4\,CH_3CH_2Br+4\,Pb \xrightarrow{\text{dry ether}} (CH_3CH_2)_4\,Pb$$

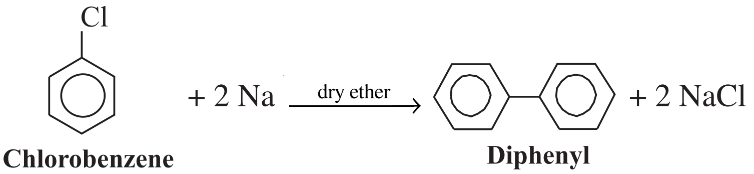
Bromethane **Tetraethyl lead**

When haloarenes react with alkyl halides in presence of sodium and dry ether, the alkyl derivatives of benzene are formed. This reaction is called **Wurtz-Fittig reaction.**



Chlorobenzene **Toluene**

When haloarenes are treated with sodium, diaryls are produced. This reaction is called **Fittig reaction.**



4. Reduction : Haloalkanes can be reduced to the corresponding alkanes. For example, bromoethane can be reduced to ethane by using metal catalyst such as nickel or palladium or platinum or by using hydroiodic acid (HI) in presence of red phosphorus.

$$\underset{\textbf{Bromethane}}{CH_3CH_2Br} + H_2 \xrightarrow[\text{or Pd}]{\text{Ni or Pt}} \underset{\textbf{Ethane}}{CH_3-CH_3} + HBr$$

$$\underset{\textbf{Iodoethane}}{CH_3CH_2I + HI} \xrightarrow{\text{red P}} \underset{\textbf{Ethane}}{CH_3-CH_3} + I_2$$

Distinction between haloalkanes and haloarene

Haloalkane and haloarenes can be distinguished by silver nitrate ($AgNO_3$). Haloalkanes react with $AgNO_3$ to give white precipitate of AgCl while haloarenes do not react.

$$RCl + NaOH \longrightarrow NaCl + ROH$$

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow NaNO_3$$

INTEXT QUESTIONS 25.3

1. Although haloalkanes are polar in nature, they are immiscible in water. Explain.
2. Which one of the following isomers has the higher boiling point and why?
   (i) *o*-dichlorobenzene (ii) *p*-dichlorobenzene
3. What will be the products of nitration of chlorobenzene?
4. What products will obtained when ethylbromide reacts with
   (i) aq. KOH and (ii) alc. KOH
5. What is the major product of elimination reactions of 2- bromobutane?

25.4 SOME USEFUL POLY HALOGEN COMPOUNDS

A large number of polyhalogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform ($CHCl_3$), iodoform (CHI_3), carbon tetrachloride (CCl_4), benzene hexachloride (BHC), DDT, etc.

Let us now study some of these compounds.

25.4.1 Chloroform

Chlorofom is a derivative of the simplest hydrocarbon, methane. Its IUPAC name is trichloromethane.

1. From Ethanol

Chlorofom is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali :

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\textbf{Ethanal}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\substack{\textbf{Trichloroethanal}\\\textbf{(Chloral)}}}{Cl_3CCHO}$$

$$Ca(OH)_2 + 2Cl_3C-CHO \longrightarrow \underset{\substack{\textbf{Calcium}\\\textbf{formate}}}{(HCOO)_2\,Ca} + \underset{\textbf{chloroform}}{2\,CHCl_3}$$

$$\underset{\textbf{Propanone}}{CH_3COCH_3} \xrightarrow[-3HCl]{3Cl_2} Cl_3C-CO-CH_3$$

$$Ca(OH)_2 + 2\,CCl_3CO-CH_3 \longrightarrow \underset{\substack{\textbf{Calcium}\\\textbf{acetate}}}{(CH_3COO)_2\,Ca} + \underset{\textbf{chloroform}}{2\,CHCl_3}$$

Chlorofom is a colourless sweet smelling liquid (b.p. 334K). It is slowly oxidized by air in the presence of light to a poisonous gas, phosgene. Chemically phosgene is carbonyl chloride, ($COCl_2$). Therefore, chloroform is stored in dark coloured bottles to protect it from light. The bottle are completely filled so that the air is kept out. A small amount of ethanol is added to chloroform to convert toxic phosgene, if formed, into a nontoxic compound, ethyl carbonate.

$$CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\textbf{Phosgene}}{COCl_2} + 2\,HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\textbf{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCl$$

Chloroform is used in isocyanide test for the detection of primary amines. In this test, a mixture of amine and chloroform is heated with alcoholic NaOH. A foul smelling isocyanide is obtained. This test is also known as **carbylamine test.** It can be used to test aliphatic and aromatic primary amines.

$$\underset{\textbf{Ethylamine}}{C_2H_5NH_2} + CHCl_3 + 3\,NaOH \longrightarrow \underset{\textbf{Ethyl isocynanide}}{C_2H_5NC} + 3\,NaCl + 3\,H_2O$$

25.4.2 Iodoform

Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

Preparation

Iodoform is prepared by heating ethanol or acetone with iodine in the presence of alkali.

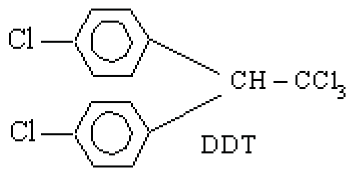
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3CONa + 3NaI + 3H_2O$$

Yellow crystals of iodoform can easily be recognized by the characteristic smell. Formation of iodoform is used to test compounds containing $CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\substack{|\\ OH}}{CH}-$ group. This test is known as **iodoform test**. Iodoform is used as an antiseptic.

25.4.3 Dichlorodiphenyltrichloroethane (DDT)

It is available in several different forms : powder, aerosols, granules, etc.



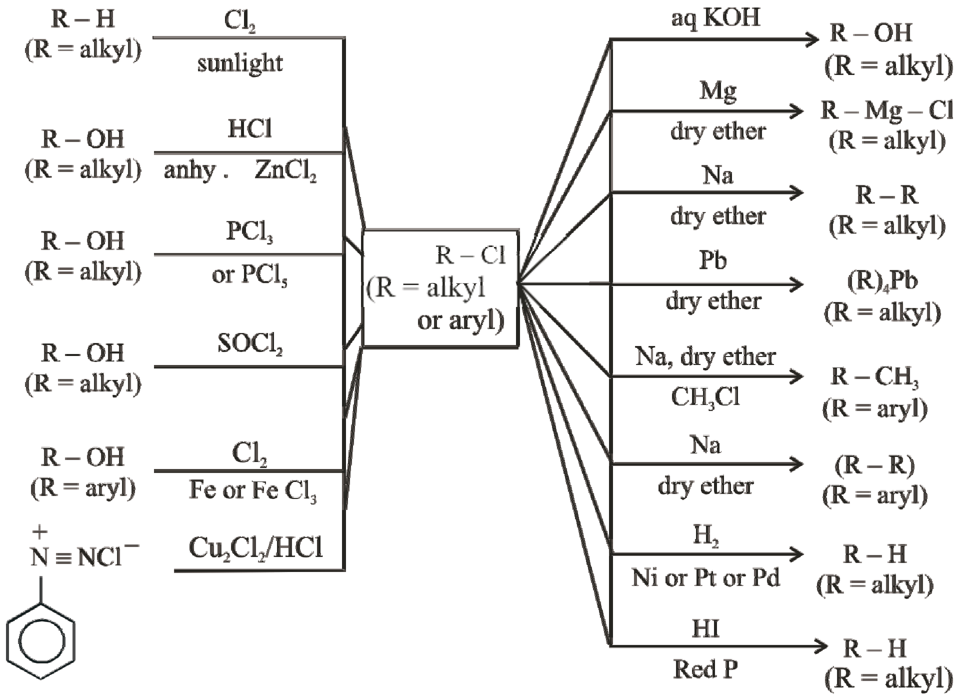
Uses : It is used mainly to control mosquito-borne malaria. It is also used as an agricultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

INTEXT QUESTIONS 25.4

1. Write IUPAC names of chloroform and iodoform.
2. Why is chloroform stored in dark coloured bottles?
3. What type of of compounds will give a positive iodoform test?
4. Name two commonly used polyhalogen compounds.

WHAT YOU HAVE LEARNT

- Haloalkanes and haloarenes are important organic compounds having wide industrial and household applications.
- Various rules for IUPAC naming of haloalkanes and haloarenes.
- Methods of preparation and chemical properties of haloalkanes and haloarenes which are summarized below :

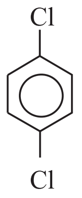


- Due to the polar nature, halo compounds have higher melting and boiling points than the corresponding hydrocarbons.
- Chemically, fluoro compounds are comparatively least reactive and iodo compounds are the most reactive. Also, haloalkanes are more reactive than haloarenes in reactions involving cleavage of C–X bond.

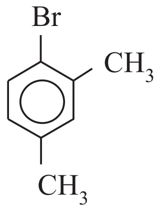
- Haloalkanes undergo nucleophilic substitution reactions. But in haloarenes, the substitution in the benzene ring is an electrophilic substitution reaction.
- Grignard reagents are produced by the reaction of a haloarene or haloalkane with magnesium metal.
- Chloroform and idoform are useful trihalo derivatives of methane. Chloroform is prepared in the laboratory from ethanol or propanone by reacting with chlorine in presence of alkali.
- Iodoform test is given by compounds containing either $CH_3-\overset{|}{C}O = O$ or $CH_3-\overset{|}{C}H-OH$ group.

TERMINAL EXERCISE

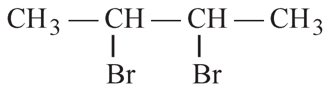
1. Give IUPAC names of the following compounds:
   (i) *sec*-butyl chloride
   (ii) *iso*- propyl bromide
   (iii)



   (iv)



   (v)



$$CH_3-\underset{Br}{CH}-\underset{Br}{CH}-CH_3$$

2. Name the product obtained by treating 2-propanol with hydrogen chloride in presence of anhydrous zinc chloride. Also write reaction involved.
3. Alkyl halides are more reactive towards nucleophilic reagents than aryl halides. Discuss briefly.
4. Write chemical equations for the reactionss of :
   (i) *n*-propanol with PCl_5.
   (ii) chlorine gas with benzene in presence of $FeCl_3$ as catalyst.

(iii) bromoethane with aqueous KOH solution.

(iv) nitrous acid with aniline at 278 K.

(v) chlorobenzene with magnesium.

(vi) chlorobenzene with a mixture of conc. HNO_3 and H_2SO_4 .

5. Give reason for the following :
   (i) Haloalkanes undergo nucleophilic substitution reactions.
   (ii) Haloarenes undergo electrophilic substitution reactions.

6. What is a Grignard reagent ? How is it prepared?

7. Disucss briefly the following :
   (i) Iodoform test
   (ii) Carbylamine test
   (iii) Diazotization
   (iv) Releative reactivities of chloroethane and bromoethane

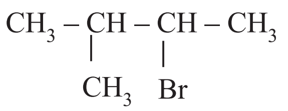
8. How is chloroform prepared in the laboratory? Write the reaction for its prepartion from ethanal.

ANSWERS TO INTEXT QUESTIONS

25.1

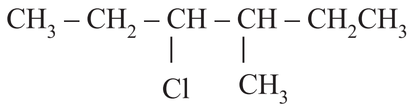
1. (i) 2-Chloropentane
   (ii) 3-Iodo-2-methylpentane
   (iii) l-Chloro-2,3-dimethylpentane
   (iv) 1,3,4-Trichloro-6-methylbenzene or 2,4,5 - Trichlorotoluene
   (v) 1,3-Dibromo-5-ethylbenzene
   (vi) 2,4-Dibromohexane

2. (i)



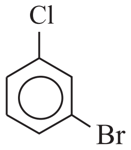
$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-\underset{\substack{|\\ Br}}{CH}-CH_3$$

(ii)

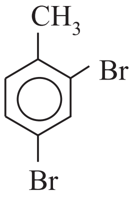


$$CH_3-CH_2-\underset{\substack{|\\ Cl}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH_2CH_3$$

(iii)

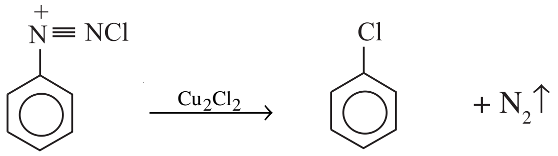


(iv)



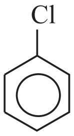
25.2

1. $CH_3CH_2CH_2Cl$
2. 1-chloropropane
3. The Diazonium salt on treatment with copper (I) chloride Cu_2Cl_2 gives chlorobenzene.



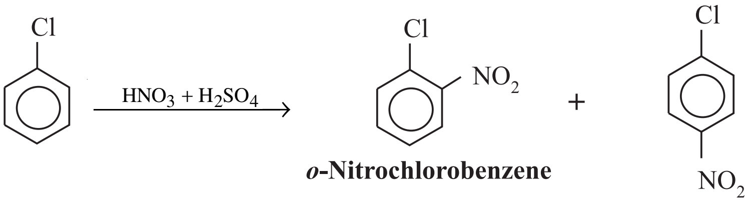
Chlorobenzene

4.



25.3

1. Due to their inability to form hydrogen bonds.
2. *Para* dichlorobenzene; due to greater symmetry and hence a better packing.
3.



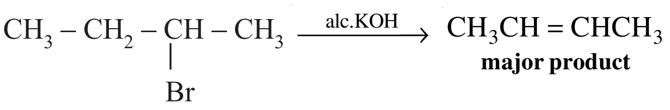
***o*-Nitrochlorobenzene**

***p*-Nitrochlorobenzene**

4. (i) $C_2H_5Cl \xrightarrow{\text{aq.KOH}} C_2H_5OH$

   (ii) $C_2H_5Cl \xrightarrow{\text{alc.KOH}} CH_2 = CH_2$

5.



$$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{alc.KOH}} \underset{\textbf{major product}}{CH_3CH = CHCH_3}$$

25.4

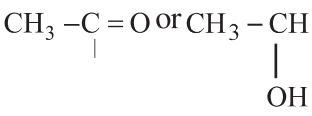
1. (i) Trichloromethane

   (ii) Triiodomethane

2. Chloroform oxidises to phosgene in the presence of air and sunlight. Dark coloured bottles reduce formation of poisionous phosgene

$$CHCl_3 + O_2 \xrightarrow{\text{sunlight}} COCl_2 + HCl$$

3. Compounds having $CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\substack{|\\ OH}}{CH}-$ units in their structure.



$CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\substack{|\\ OH}}{CH}-$

   Dark coloured bottles reduce formation of poisonous phosgene.

4. DDT, BHC, $CHCl_3$ and CHI_3.

26

ALCOHOLS, PHENOLS AND ETHERS

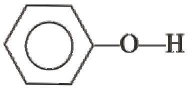
So far you have learnt the chemistry of hydrocarbons which serve as basic skeleton for the attachment of various functional groups to give a large number of their derivatives. In the last lesson, we discussed one such class of compounds *viz halogen derivatives of hydrocarbons*. Another very useful and important catagory of hydrocarbon derivatives is that of compounds containing functional groups in which the carbon atom is linked to an oxygen atom.

We have devoted two lessons for the study of these compounds. In this lesson, you will study about compounds containing carbon-oxygen single bond (–C–O) whereas the next lesson deals with compounds containing carbon-oxygen double-bond ($>C=O$).

Among the compounds with carbon-oxygen single bond are the classes of *alcohols, phenols* and *ethers* having the following general structures.

$R-O-H$

Alcohol



Phenol

$R-O-R'$

Ether

R/R′ can also be aromatic

These are very important categories of compounds both in the industry and in the synthesis of other organic compounds. You will study each of these classes of compounds in this Lesson.

OBJECTIVES

After reading this lesson, you should be able to

- classify alcohols as primary, secondary or tertiary;
- name simple alcohols according to IUPAC system of nomenclature;
- list general methods of preparation of alcohols;
- discuss the properties of alcohols in the light of their structure;
- explain various reactions exhibited by alcohols to give other categories of organic compounds;
- describe important uses of alcohols;
- give the names of common phenolic compounds;
- describe the laboratory and industrial methods of preparation of phenols;
- explain the greater acidity of phenols as compared to alcohols;
- discuss the reactions of phenols;
- name ethers according to the IUPAC system of nomenclature;
- describe the general methods of preparation of ethers and
- explain the important reactions of ethers.

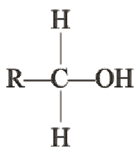
26.1 ALCOHOLS

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded to the *carbon atoms in aliphatic compounds*. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methanol and ethanol are two industrially important alcohols.

$CH_3–OH$	$CH_3CH_2–OH$
Methanol	**Ethanol**
(Methyl alcohol)	**(Ethyl alcohol)**

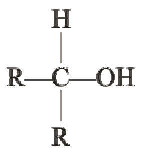
26.1.1 Classification and Nomenclature of Alcohols

Alcohols are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon whether the number of alkyl groups bonded to the carbon atom bearing the hydroxy group is one, two or three, respectively.



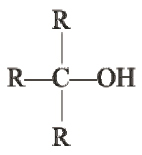
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

primary alcohol
1°



$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OH$$

secondary alcohol
2°



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-OH$$

tertiary alcohol
3°

According to the IUPAC system of nomenclature, alcohols are called **alkanols**. They are named as the derivatives of the corresponding alkane in which the -*e* of the alkane is replaced by *-ol* .

The procedure for nomenclature involves the following steps:

Step 1: Select the longest carbon chain which contains the carbon atom bearing the –OH group. Count the number of carbon atoms and identify the corresponding alkane. From the name of this alkane, drop the final *e* and suffix *-ol* in its place. This gives the root name or the parent name.

Step 2: Number the carbon chain starting from the end nearest to the hydroxy group. The number of the carbon atom bearing the hydroxy group is indicated before *-ol* in the name.

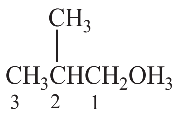
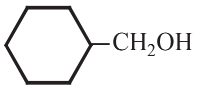
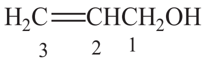
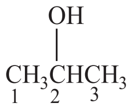
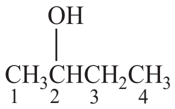
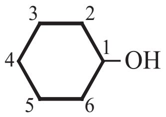
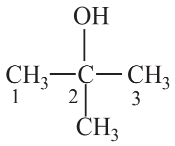
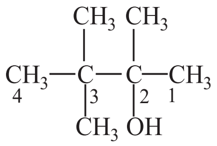
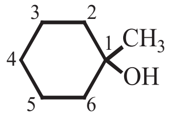
Step 3: Number the other substituents according to their position on the chain.

Step 4: Write the name of the alcohol by listing the substituents in the alphabetical order alongwith their position.

You may remember from Lesson 25 that the hydroxyl group takes precedence over double and triple bonds.

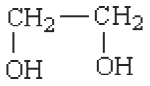
Table 26.1 illustrates some common alcohols and their IUPAC and common names. Go through them in light of the steps given above for nomenclature.

Table 26.1 : Some common Alcohols and their Names

Primary Alcohol	 $\underset{3}{CH_3}\underset{2}{\overset{\overset{CH_3}{\vert}}{CH}}\underset{1}{CH_2OH_3}$ **2-Methyl propan-l-ol** **(Isobutyl alcohol)$^+$**	 **Pheaylmethanol** **(Benzyl alcohol)**	 $\underset{3}{CH_3}\underset{2}{CH}\underset{1}{CH_2OH}$ **1-Propanol** **(n-Propyl alcohol)**  $\underset{3}{H_2C}{=}\underset{2}{CH}\underset{1}{CH_2OH}$ **Prop-2-en-1-ol**
Secondary Alcohol	 $\underset{1}{CH_3}\underset{2}{\overset{\overset{OH}{\vert}}{CH}}\underset{3}{CH_3}$ **Propan-2-ol** **(Isobutyl alcohol)$^+$**	 $\underset{1}{CH_3}\underset{2}{\overset{\overset{OH}{\vert}}{CH}}\underset{3}{CH_2}\underset{4}{CH_3}$ **Butan-2-ol** **(*sec* Benzyl alcohol)**	 **Cyclohexanol** **(Cyclohexyl alcohol)**
Tertiary Alcohol	 **2-Methyl propan-2-ol** **(*tert*-Benzyl alcohol)**	 **2,3,3-Trimethylbutan-2-ol**	 **1-Methyloyclohex-1-ol**

* The names given in the brackets are common names.

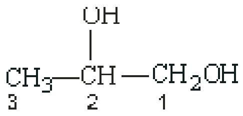
In the above examples, only one -OH group is present in the molecule. These alcohols are called **monohydric** alcohols. Alcohols having **two hydroxyl** groups in a molecule are known as **dihydric alcohols** or **diols** or **glycols**. Examples of some diols are shown below :



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

Ethane-1,2-diol

(Ethylene glycol)



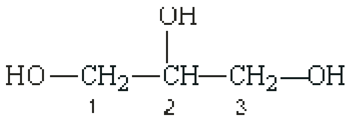
$$\underset{3}{CH_3}-\underset{2}{\overset{OH}{CH}}-\underset{1}{CH_2OH}$$

Propane-1,2-diol

(Propylene glycol)

Note that the term *glycol* generally means 1,2-diol or a **vicinal** diol. In these diols, the two hydroxyl groups are present on the adjacent carbon atoms.

Similarly, alcohols having *three* hydroxyl groups are called *trihydric* alcohols. 1,2,3-propanetriol which is commanly known as *glycerol*, is a trihydric alcohol.



$$HO-\underset{1}{CH_2}-\underset{2}{\overset{OH}{CH}}-\underset{3}{CH_2}-OH$$

1,2,3-Propanetriol

(Glycerol)

26.1.2 General Methods of Preparation

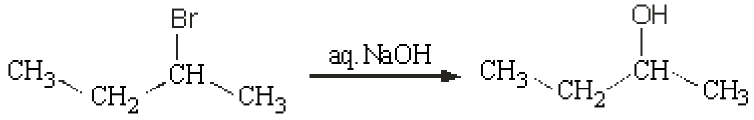
Alcohols are synthesized by the following general methods. You might have come across some of these methods in previous lessons. Let us now study these methods.

1. Hydrolysis of Haloalkanes

Haloalkanes can be converted to corresponding alcohols using aqueous sodium or potassium hydroxide or water as nucleophiles.

$$CH_3CH_2Cl + NaOH(aq.) \longrightarrow CH_3CH_2OH + NaCl$$

Chloroethane **Ethanol**



2-Bromobutane

Butan-2-ol
(90%)

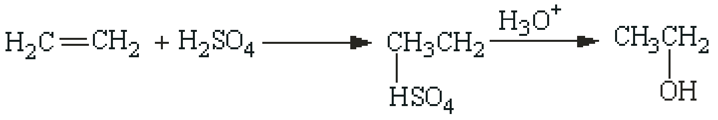
2. From hydration of Alkenes

Hydration means addition of water molecule. In case of alkenes, hydration is the addition of H^+ and OH^- across the double bond to give alcohols.

Alkenes can be hydrated by the following methods:

(i) Acid-catalysed Hydration

Alkenes can be hydrated to yield alcohols in the presence of acid catalysts.

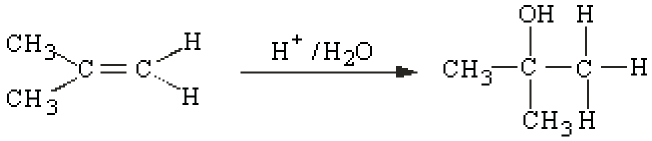


$$H_2C{=}CH_2 + H_2SO_4 \longrightarrow \underset{\displaystyle HSO_4}{CH_3CH_2} \xrightarrow{H_3O^+} \underset{\displaystyle OH}{CH_3CH_2}$$

Ethene **Ethyl hydrogen sulphate** **Ethanol**

The reaction proceeds via alkyl hydrogen sulphate and this method is used for the industrial preparation of ethanol.

In case of unsymmetric alkenes, the addition follows Markovniokov's rule.



$$(CH_3)_2C{=}CH_2 \xrightarrow{H^+/H_2O} CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

2-Methylpropene **2-Methyl-2-propanol**

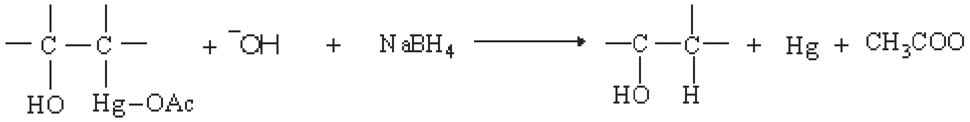
(ii) Oxymercuration-demercuration

Alkenes react with mercury (II) acetate, i.e. mercuric acetate [$Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2$ also represented as $Hg(OAc)_2$] in aqueous tetrahydrofuran (THF) solvent to give hydroxyalkyl mercury compounds which are reduced to alcohols by sodium borohydride.

Step 1: Oxymercuration

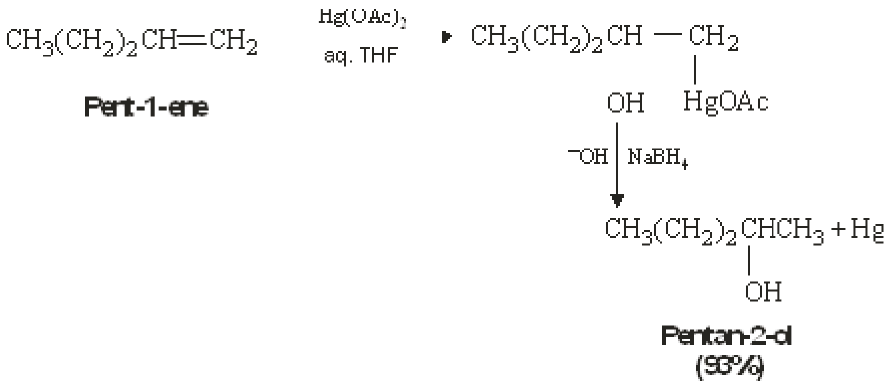
$$>C{=}C< + H_2O + Hg(OAc)_2 \xrightarrow{THF} -\underset{\displaystyle HO}{C}-\underset{\displaystyle Hg-OAc}{\overset{|}{C}}- \quad + \quad CH_3COOH$$

Step 2: Demercuration



$$-\underset{\displaystyle HO}{\overset{|}{C}}-\underset{\displaystyle Hg-OAc}{\overset{|}{C}}- \quad + \ {}^-OH \quad + \quad NaBH_4 \longrightarrow -\underset{\displaystyle HO}{C}-\underset{\displaystyle H}{\overset{|}{C}}- \ + \ Hg \ + \ CH_3COO$$

This method gives very good yield of alcohols and here also, the addition takes place in Markovnikov's fashion.

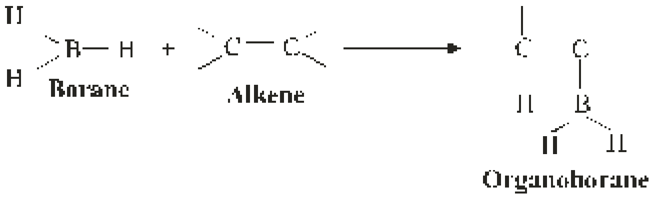


Pent-1-ene

Pentan-2-ol (93%)

(iii) Hydroboration - Oxidation

When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained.

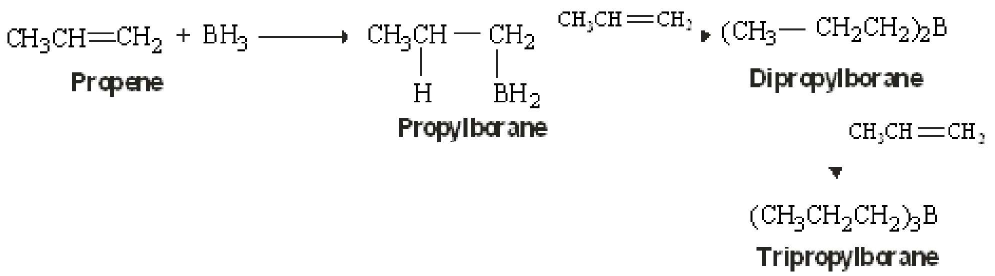


Borane

Alkene

Organoborane

Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane (R_3B). This is shown below for propene.



Propene

Propylborane

Dipropylborane

Tripropylborane

The trialkylborane so obtained is oxidised using alkaline hydrogen peroxide solution to give three molecules of alcohols and boric acid.

$$(CH_3CH_2CH_2)_3\ B \xrightarrow{H_2O_2/^-OH} 3CH_3CH_2CH_2OH + B(OH)_3$$

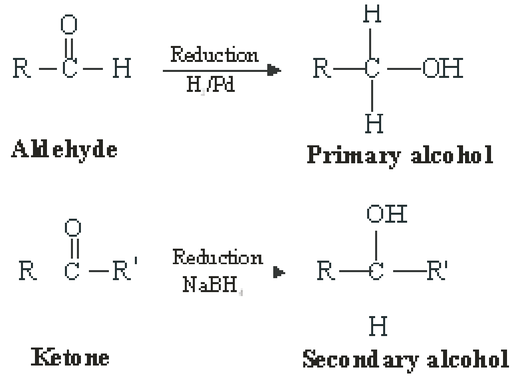
Tripropylborane **Propanol** **Boric acid**

Note that hydroboration-oxidation yields the anti-Markovnikov addition of water although the reaction proceeds according to Markonikov's rule.

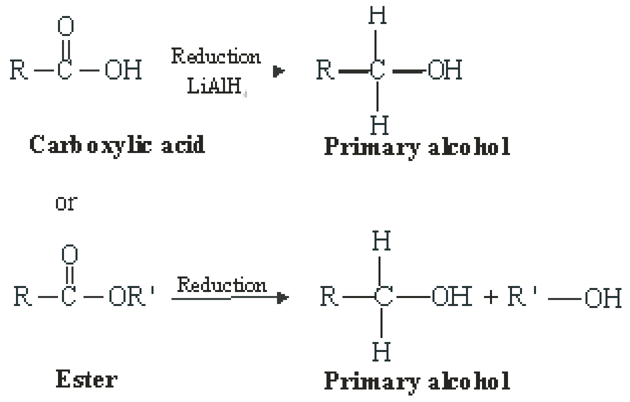
3. Reduction of Carbonyl Compounds

Carbonyl compounds (which contain $-\overset{O}{\overset{\|}{C}}-$ group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols.

Aldehydes give primary alcohols while ketones yield secondary alcohols on reduction.

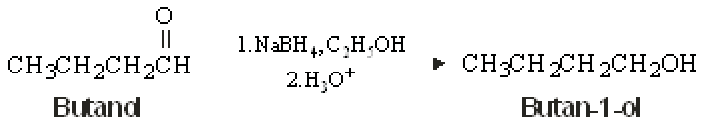


Carboxylic acids and esters also give primary alcohols on reduction.



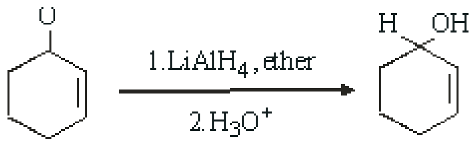
The reduction is carried out using hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). $LiAlH_4$ is stronger and reacts explosively with water while $NaBH_4$ is convenient to handle and reacts slowly.

Lithium aluminium hydride reduces all of the above classes of compounds while sodium borohydride reduces only aldehydes and ketones and does not reduce carboxylic acids and esters. Hence, it can be used to selectively reduce aldehydic/ketonic carbonyl group in presence of carboxylic acid/ester function. Some examples below illustrate the use of these reagents.



$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[2.H_3O^+]{1.NaBH_4, C_2H_5OH} CH_3CH_2CH_2CH_2OH$$

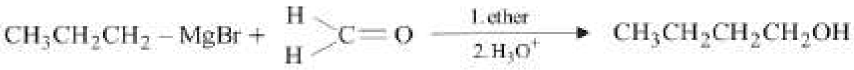
Butanal Butan-1-ol



Cyclohexex-2-enone Cyclohex-2-enol

4. From Aldehydes and Ketones using Grignard Regents

Grignard reagents react with methanal (or formaldehyde) to give a *primary alcohol*.



$$CH_3CH_2CH_2-MgBr + \begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow[2.H_3O^+]{1.ether} CH_3CH_2CH_2CH_2OH$$

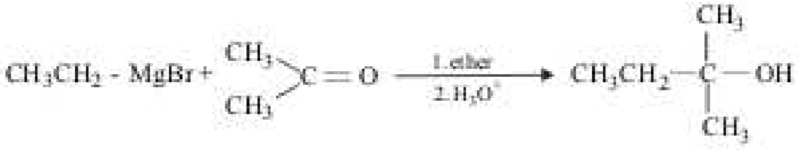
Propyl magnesium bromide **Methanal** **Butan-1-ol (Primary alcohol)**

All other aldehydes yield *secondary alcohols* on reaction with Grignard reagents.

$$CH_3CH_2-MgBr + \begin{matrix}CH_3\\H\end{matrix}\!\!>C=O \xrightarrow[2.H_3O^+]{1.ether} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Ethyl magnesium bromide **Ethanal (Acetaldehyde)** **Butan-2-ol (Secondary alcohol)**

With ketones, Grignard reagents give *tertiary alcohols*.



$$CH_3CH_2-MgBr + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[2.H_3O^+]{1.ether} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

Ethyl magnesium bromide **Propanone** **2-Methylbutan-2-ol**

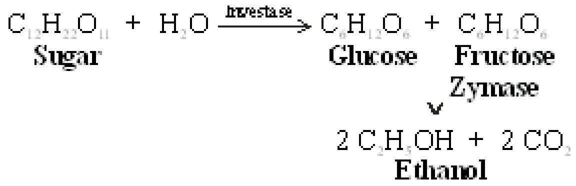
5. Diazotization of Primary Aliphatic Amines

This reaction also yields alchols and will be discussed in Lesson 30.

6. Fermentation

Ethanol is prepared on a large scale using fermentation. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes.

The fermentation of sugar is shown below :



$$\underset{\textbf{Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\textbf{Glucose}}{C_6H_{12}O_6} + \underset{\textbf{Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\textbf{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2$$

26.1.3 Structure and Physical Properties

The structure of alcohols is similar to that of water. The structures of water and methanol molecules are shown in Fig. 26.1.

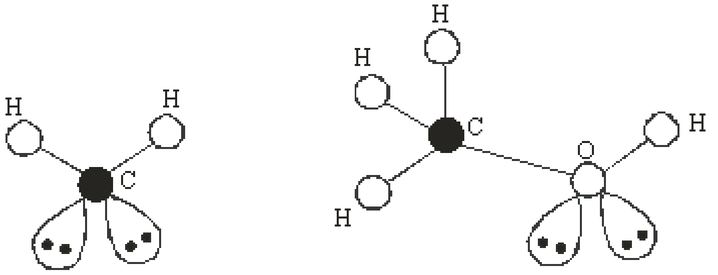


Fig. 26.1: *Water and Methanol molecule*

You know that the electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the O–H bond is polar in nature. In other words, oxygen has a slight negative charge on it whereas hydrogen has a slight positive charge. This bond polarity alone cannot explain the higher boiling points of alcohols as compared to hydrocarbons or similar haloalkanes, as listed in Table 26.2.

Normally, hydrogen bonding is responsible for higher boiling points of alcohols. Hydrogen bonding amongst alcohol molecules is depicted in Fig. 26.2.

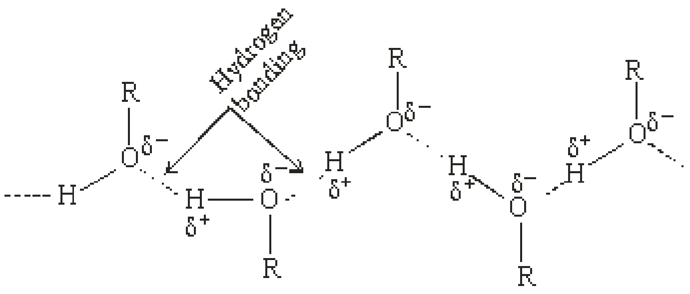
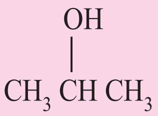
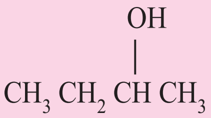


Fig. 26.2: *Hydrogen bonding in alcohol molecules*

You can see that the negatively polarised oxygen atom of one alcohol molecule attracts the positively polarised hydrogen atom of the other molecule. Thus, alcohol molecules are associated or are held together. This force of attraction is to be overcome before a molecule is set free from the liquid state and vaporises. Thus, more heat energy is required to break the hydrogen bonds and hence, the boiling points of alcohols are higher than alkanes and haloalkanes of comparable molecular mass.

Table 26.2: Physical Properties of some Alcohols, Hydrocarbons and related Haloalkanes

Compound	IUPAC Name	Melting Point (K)	Boiling Point (K)	Solubility g/100 mL of water
CH_3OH	Methanol	175.2	322.8	∞
CH_4	Methane	90.5	181.13	–
CH_3Cl	Chloromethane	175.3	248.8	–
CH_3CH_2OH	Ethanol	158.3	351.5	∞
CH_3CH_3	Ethane	189.7	184.4	–
CH_3CH_2Cl	Chloroethane	136.6	285.3	–
$CH_3CH_2CH_2OH$	Propan-1-ol		378.04	∞
$CH_3CH_2CH_3$	Propane	85.3	230.9	–
 $CH_3\overset{\overset{OH}{\vert}}{C}HCH_3$	Propan-2-ol	184	355	∞
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	183	391	8.3
 $CH_3CH_2\overset{\overset{OH}{\vert}}{C}HCH_3$	Butan-2-ol	159	373	10.0

From the last column of Table 26.2, you must have noticed that alcohols have high solubilities in water. The lower alcohols are completely miscible and their solubilities decrease as the hydrocarbon portion of the molecule becomes larger. The higher solubility of alcohols can be again attributed to the hydrogen bonding. In this case, hydrogen bonding takes place between the alcohol and water molecules as is shown below in Fig. 26.3.

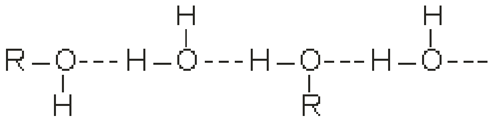


Fig. 26.3: *Hydrogen bonding in a solution of methanol and water*

26.1.5 Reactions of Alcohols

Alcohols exhibit the following reactions:

1. Acidic and Basic behaviour

Alcohol behave both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H^-) in sodium hydride (NaH), can remove the proton from the alcohol molecule and an alkoxide ion results.

$$R-\ddot{\underset{\cdot\cdot}{O}}-H + B\!:^- \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}\!:^- + B-H$$

Alcohol **Base** **Alkoxide ion** **Protonated base**

$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + B\!:^- \rightleftharpoons CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}\!:^- + BH$$

Ethanol **Base** **Ethoxide ion** **Protonated base**

When water is used as a base, the *acid dissociation constant* (K_a) and pK_a can be written as follows:

$$R-O-H + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} R-O^- + H_3O^+$$

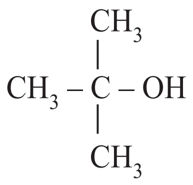
$$K_a = \frac{[H_3O^+][RO^-]}{[ROH]}$$

$$pK_a = -\log K_a$$

Some pK_a values are listed in Table 26.3.

Table 26.3: pK_a **values of some compounds**

Compound	pK_a
CH_3OH	15.5
H_2O	15.74
CH_3CH_2OH	15.9
$CH_3\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_3$	16.5



$$CH_3-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-OH$$

18.0

Remember that the lower the pK_a *value, higher is the acidity of the compound.*

Alcohols can behave as weak bases also. They have lone pair of electrons on oxygen atom and hence they can be protonated by strong acids to give oxonium ions as shown below:

$$R-\ddot{\underset{..}{O}}-H + H-X \rightleftharpoons R-\overset{\overset{H}{|}}{\underset{..}{O^+}}-H + X^-$$

Alcohol **Acid** **Oxonium ion**

2. Formation of Alkoxides

Alcohols react with sodium or potassium metals to give the respective alkoxides.

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

Ethanol	Sodium metal	Sodium ethoxide

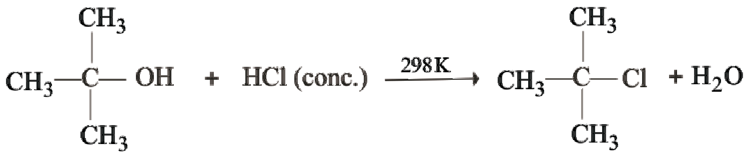
$$(CH_3)_3C-OH + K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

tert-Butyl alcohol	Potassium metal	Potassium *tert*-butoxide

Alkoxides are used in the synthesis of organic compounds.

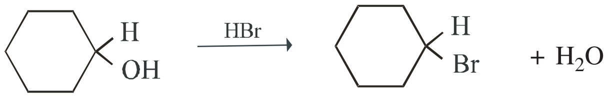
3. Conversion to Alkyl Halides

You have already studied in Lesson 27 that alcohols react with a variety of reagents to form alkyl halides. These are hydrogen halides (such as HCl, HBr or HI), phosphorus tribromide (PBr_3) and thionyl chloride ($SOCl_2$). The reaction involves the breaking of $R-OH$ bond of alcohol molecule.

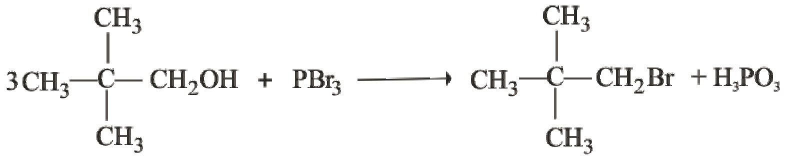


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + HCl\,(conc.) \xrightarrow{298K} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl + H_2O$$

2-Methyl propan-2-ol **2-chloro-2-methyl propane**



Cyclohexanol **Bromocyclohexane**



$$3\,CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH + PBr_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br + H_3PO_3$$

2, 2-Dimethylpropan-1-ol **1-Bromo-2, 2-Dimethylpropane**

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2(g) + HCl(g)$$

Propan-1-ol **1-Chloropropane**

Tertiary alcohols are readily converted to alkyl halides by HCl or HBr while the best method with primary and secondary alcohols is by using PBr_3 or $SOCl_2$ as the reagents. Another advantage of using $SOCl_2$ is that both the by-products in this reaction, i.e. SO_2 and HCl are gases and hence can be easily eliminated to yield pure alkyl halide.

Lucas Test

The formation of alkyl halides from alcohols is the basis of this test. In involves the reaction of the alcohol with Lucas reagent (i.e. anhyd. $ZnCl_2$ + conc. HCl). Since the reactivity of alcohols is in the following order :

primary alcohols < secondary alcohols < tertiary alcohols

With primary alcohols turbidity does not appear. In case of secondary alcohols, turbidity appears within 5 mintues whereas it appears immediately with tertiary alcohols. The turbidity is due to the formation of alkyl chlorides from the corresponding alcohols.

4. Formation of Alkenes

Alcohols can be dehydrated to alkenes. This reaction requires an acidic catalyst and is favoured at higher tempratures. Usually sulphuric and phosphoric acid are used as acidic catalysts. You have come across this reaction in Lesson 26 also. The ease of dehydration follows the following order amongst alcohols.

tertiary alcohols > secondary alcohols > primary alcohols

26.1.4 Mechanism of Dehydrations of Alcohols

The dehydration of alcohols to give alkenes follows an E1 mechanism. The reaction is acid catalysed. Here, E stands for dimination and 1 denotes that it is unimolecular in nature which means only one molecule is involved in the rate determining step.

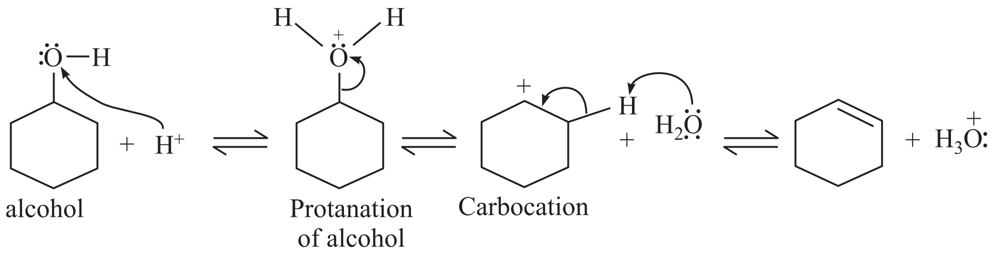
The reaction occurs in three steps :

(i) Protonation of the oxygen of OH group

(ii) Loss of water to give a carbocation

(iii) Loss of a proton from a neighboring carbon atom which produces an alkene

This is shown below:



5. Dehydration to form Ethers

Intermolecular dehydration of alcohols yields ethers. This reaction takes place at a lower temperature than that for dehydration to give alkenes.

$$\begin{tikzcd} & CH_2=CH_2 \\ CH_3CH_2OH \arrow[ur, "H_2SO_4", "435\ K"'] \arrow[dr, "H_2SO_4", "413\ K"'] & \\ & CH_3CH_2OCH_2CH_3 \end{tikzcd}$$

Ethanol **Ethene (Alkene)** **Ether**

The formation of ethers by dehydration is a substitution type of reaction and gives only symmetrical ethers. You will study a better method of synthesis of ethers later under the section of ethers in this lesson.

6. Oxidation

Alcohols can be oxidised to carbonyl compounds. Primary alcohols give aldehydes or carboxylic acids on oxidation while secondary alcohols yield ketones. The tertiary alcohols do not usually undergo oxidation. Normally $KMnO_4$, CrO_3 and $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ are used as oxidising agents.

$$CH_3CH_2CH_2OH \xrightarrow[H_2O]{K_2Cr_2O_7, H_2SO_4} CH_3CH_2CHO$$

Propan-1-ol **Propanal**

$$\xrightarrow{\text{Further oxidation}} CH_3CH_2COOH$$

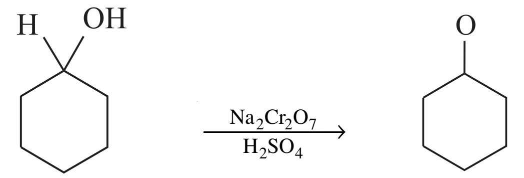
Propanoic acid

The aldehydes obtained by oxidation of the primary alcohols get further oxidised to carboxylic acids as shown above. You will study more about these classes of compounds in the next lesson.

The oxidation can be controlled and aldehydes are obtained as the products by using pyridium chlorochromate (PCC) which is a mild reagent.

$$\underset{\textbf{Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{PCC} \underset{\textbf{Decanal}}{CH_3(CH_2)_8CHO}$$

Secondary alcohols can be oxidised to ketones as shown below :



Cyclohexanol **Cyclohexanone**

7. Formation of Esters

Alcohols react with carboxylic acids to form esters. This reaction is discussed in the next lesson.

$$\underset{\textbf{Ethanoic acid}}{CH_3COOH} + \underset{\textbf{Ethanol}}{CH_3CH_2OH} \xrightleftharpoons{H+} \underset{\textbf{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + \underset{\textbf{Water}}{H_2O}$$

This reaction is called **esterification reaction** and is reversible in nature.

Uses

Alcohols find a large variety of uses as follows :

1. As solvents
2. As laboratory reagents
3. In medicines
4. As thinners in paints, varnishes, etc.

Uses of Methanol and Ethanol

Methanol is toxic to humans and even its small quantities can cause blindness. In larger quantities, its consumptions can cause death. However, it is useful industrially both as a solvent and in the production of formaldehyde and acetic acid, as a starting material. It is also used in the synthesis of which is used as an to gosoline MTBE

$$CH_3OC(CH_3)_3$$

Methyl tert-butyl ether
(MTBE)

Ethanol, obtained by the fermentation of sugars is present in all alcoholic beverages.

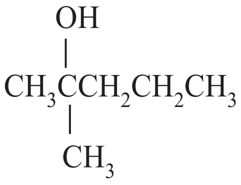
It is also an important industrial chemical. Thus, ethanol used for scientific and industrial purposes is made purposely toxic to prohibit people from consuming it.

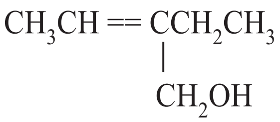
Ethanol can be used as a fuel and as a fuel additive. It is also used as a solvent in the manufacture of varnishes and perfumes.

It is also used in hand sanitizers as an antiseptic.

INTEXT QUESTIONS 26.1

1. Give the IUPAC names of the following alcohols :

(i) 
$CH_3\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$

(ii) 
$CH_3CH{=}{=}\underset{\underset{CH_2OH}{|}}{C}CH_2CH_3$

(iii) 
$CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2OH$

2. How will you prepare propan-1-ol from propanal?
3. Give the synthesis of 2-methylpropan-2-ol using Grignard reagent.
4. Give the product of the following reactions:

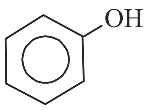
(i) Hexan-1-ol $\xrightarrow[H_2O,\,H^+]{CrO_3}$

(ii) Hexan-1-ol $\xrightarrow[\text{Chlorochromate}]{\text{Pyridium}}$

5. What is MTBE? GIve its use.
6. What is the product obtained when alcohols are dehydrated?

26.2 PHENOLS

The name phenol is specifically used for the following compound (hydroxybenzene) in which one hydroxyl group is attached to the benzene ring.

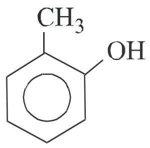


Phenol

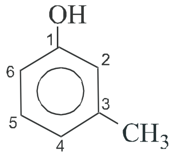
It is also used as a general name for the class of compounds derived from the above compound. Phenol is a disinfactant. Phenols are widely distributed in nature. They are also important in the synthesis of organic compounds such as aspirin and in the preparation of dyes. Phenol is also used in the manufacture of bakelite which is a very useful polymer.

26.2.1 Nomenclature of Phenols

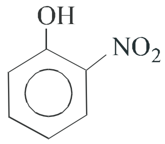
Some representative examples of phenolic compounds are given below:



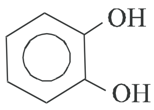
2-Methylphenol
(*o*-Cresol)



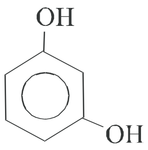
3-Methylphenol
(*m*-Cresol)



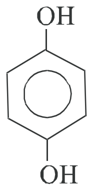
2-Nitrophenol
(*o*-Nitrophenol)



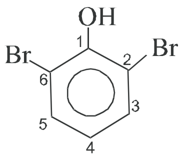
1,2-Benzenediol
(Catechol)



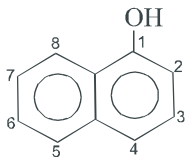
1,3-Benzenediol
(Resorcinol)



1,4-Benzenediol
(Hydroquinone)



2,6-Dibromophenol



1-Naphthol
(α – Naphthol)

Note that the term *phenol* is used as a parent name and the other substituents present in the compound are given a specific number according to their position on the aromatic ring. As done before the common names of the above compounds are given in the brackets below their IUPAC names.

26.2.2 General Methods of Preparation

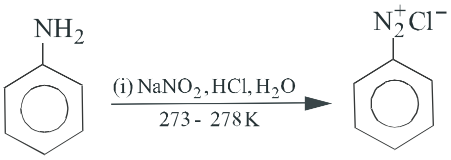
We can categorise the methods of preparation as methods of *laboratory synthesis* and *industrial synthesis* of phenols.

A. Laboratory Synthesis of Phenols

1. From Arenediazonium Salts

It is the most general method of preparation of phenols and requires mild conditions.

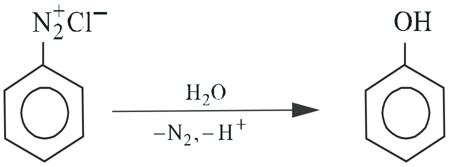
Arenediazonium salts or aromatic diazonium salts are obtained by the *diazotization* of primary aromatic amines as given below :



Benzenamine **(Aniline)** **(an aromatic amine)**

Benzenediazonium chloride

The arenediazonium salt on hydrolysis yields phenol.



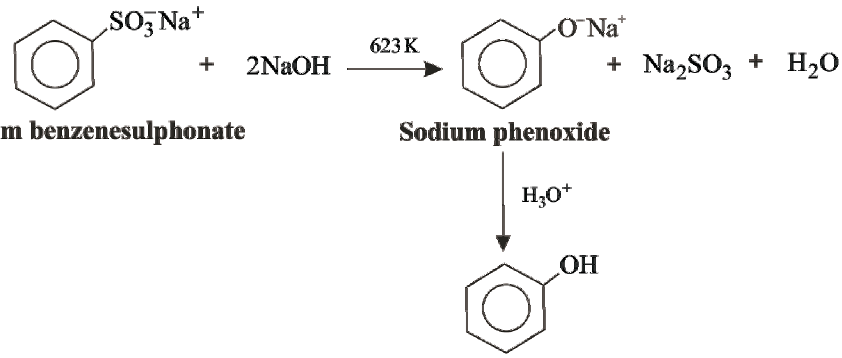
Benzenediazonium chloride

Phenol

2. Alkali Fusion of Sodium Benzenesulphonate

This was the first commercial synthesis of phenol developed in Germany in 1890. It can also be used as a laboratory method for synthesis of phenol.

Sodium benzenesulphonate is fused with sodium hydroxide to give sodium phenoxide which on acidification yields phenol.



Sodium benzenesulphonate

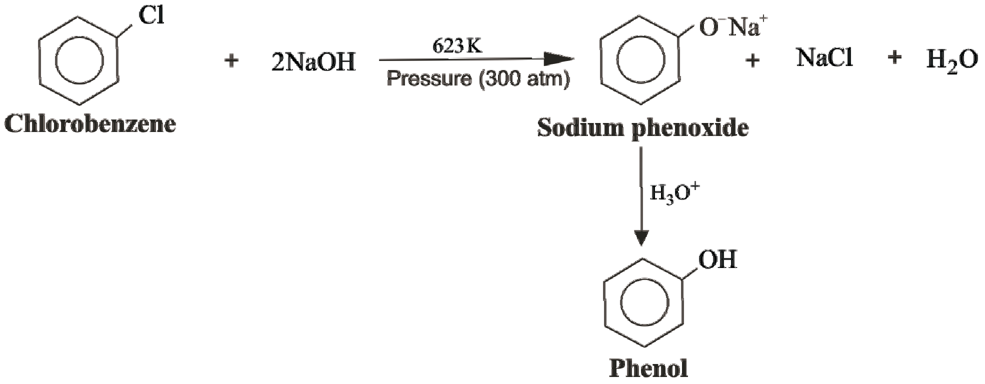
Sodium phenoxide

Phenol

B. Industrial Synthesis of Phenols

1. Dow Process

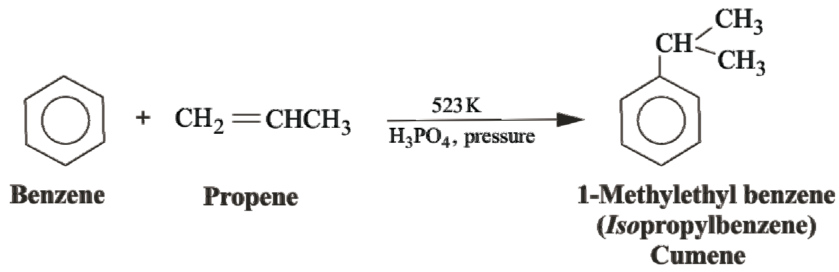
In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.



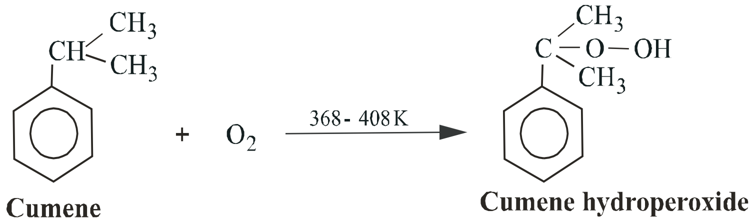
This method was in use for many years but now phenol is synthesised via cumene hydroperoxide which is discussed below.

2. From Cumene Hydroperoxide

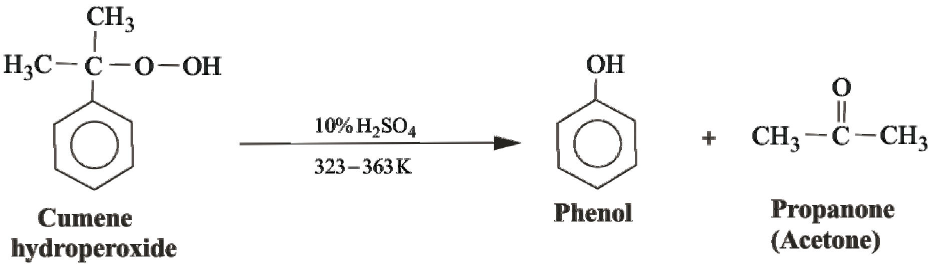
The reaction between benzene and propene in presence of phosphoric acid yields cumene.



Cumene is then oxidised to cumene hydroperoxide by air.



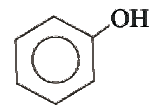
In the final step, cumene hydroperoxide is treated with 10% sulphuric acid to give phenol and acetone on hydrolytic rearrangement.



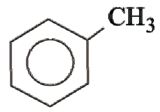
Note that propanone is obtained as a valuable byproduct in this reaction.

26.2.3 Physical Properties

Similar to alcohols, phenols also have hydrogen atom linked to the electronegative oxygen atom. Thus, phenols also exhibit hydrogen bonding and hence have higher boiling points as compared to the hydrocarbons of similar molecular weight.



b.p. = 454.7 K
Phenol



b.p. = 383.6 K
Methylbenzene (Toluene)

Due to their ability to form hydrogen bonds, phenols show some water solubility. For example, the solubility of phenol is 9.3 g per 100 mL of water.

26.2.4 Reactions of Phenols

Let us now study the reactions exhibited by phenols.

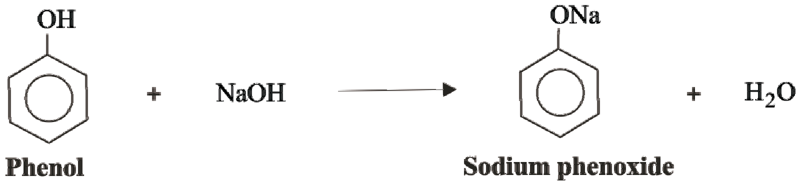
1. Acidic and Basic Nature

Phenols are much more acidic than alcohols. pK_a values of some phenols are listed in Table 26.4.

Table 26.4: pK_a values of phenols

Name	pK_a
Phenol	9.89
2- Methylphenol	10.20
2-Chlorophenopl	8.11
3-Chlorophenol	8.80
2-Nitrophenol	7.17
3-Nitrophenol	8.28
4-Nitrophenol	7.15
2,4,6-Trinitrophenol (Picric acid)	0.38

Since phenols are acidic in nature, they are soluble in dilute sodium hydroxide.



The greater acidity of phenols can be attributed to the resonance stablisation of the phenoxide ion. The resonance structures of pheoxide ion are shown in Fig. 26.4.

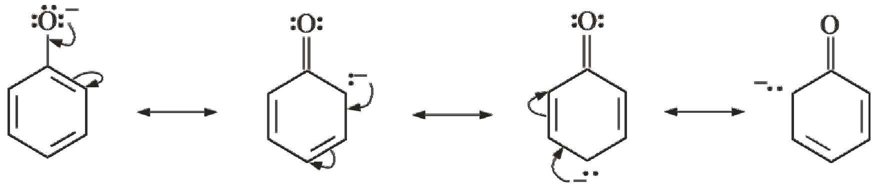


Fig. 26.4: *Resonance structures of phenoxide ion*

The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions.

Similar resonance is also shown in phenol itself, see Fig 26.5. But the resonance structures of phenol are less stable as compared to those of phenoxide ion as they involve the separation of charge.

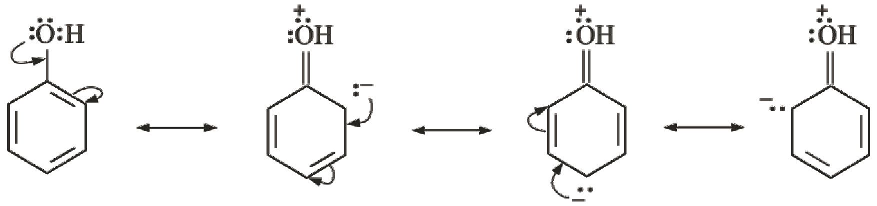
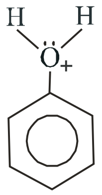


Fig. 26.5: *Resonance structures of phenol*

If you carefully go through the pK_a values given in Table 26.4, you would see that the electron donating substituents such as methyl group decrease the acidity of phenol and hence alkylphenols have greater pK_a values as compared to phenol itself. On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents (–Cl, $-NO_2$, etc.) have lower pK_a values than phenol. In fact, 2,4,6-trinitrophenol is more acidic than many carboxylic acids.

Phenols behave as weak bases also. Similar to alcohols, they can also be protonated to give phenyloxonium ion.

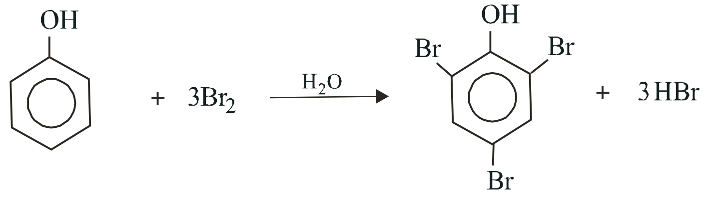


Phenyloxonium ion

2. Electrophilic Substitution Reactions

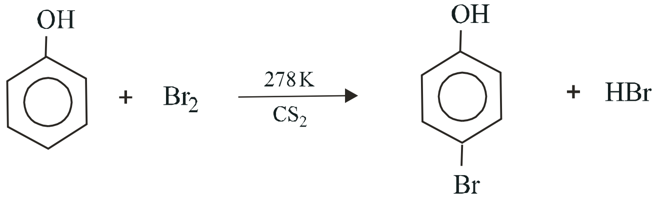
The hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. In this reaction, an **electrophile** (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are electron rich, the substitution takes place at these positions. Two such reactions are **halogenation** and **nitration** reactions. Let us now study them in details.

(i) Halogenation: Phenol reacts with bromine in aqueous solution to give 2,4,6-tribromophenol in about 100% yield.



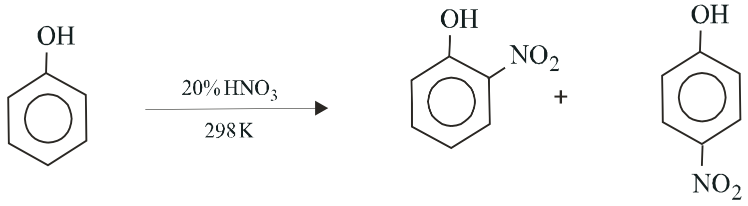
Phenol **2,4,6-Tribromophenol**

Bromination can be limited to monobromination to give mainly 4-bromophenol using low temprature and less polar solvent such as carbon disulphide. The other product formed in minor quantity is 2-bromophenol.



Phenol **4-Bromophenol**

(ii) Nitration: Phenol gives a mixture of 2-nitro and 4-nitrophenols on nitration with dilute nitric acid.

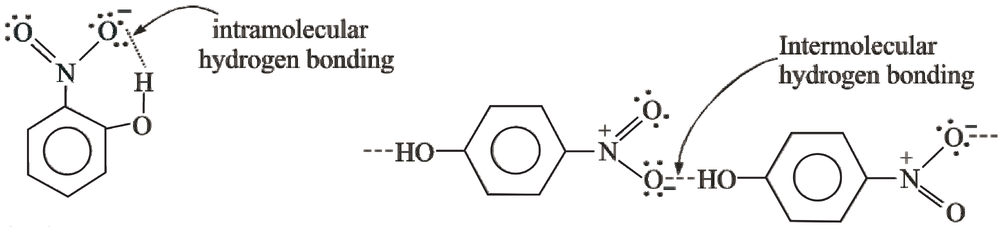


Phenol

2-Nitrophenol
(*o*-Nitrophenol)
(30-40%)

4-Nitrophenol
(*p*-Nitrophenol)
(15%)

The mixture of nitrophenols so obtained is separated using steam distillation. Both these products show hydrogen bonding. In case of 2-nitrophenol, the hydrogen bonding is **intramolecular** (in the same molecule) whereas in case of 4-nitrophenol, it is **intermolecular** (between different molecules). These are depicted in Fig. 26.5.



2-Nitrophenol **4-Nitrophenol**

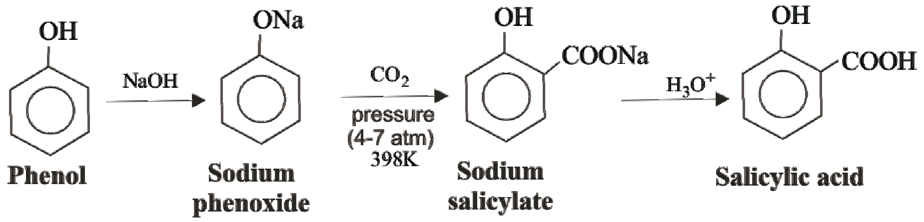
Fig. 26.5 : *Intramolecular and intermolecular hydrogen bonding in nitrophenols*

2-Nitrophenol is steam volatile and distills out on passing steam whereas 4-nitrophenol is less volatile due to intermolecular hydrogen bonding.

Treatment of phenol with a mixture of conc. nitric acid and conc. sulphuric acid at 323K yields 2,4,6-trinitrophenol also known as picric acid.

3. Kolbe Reaction

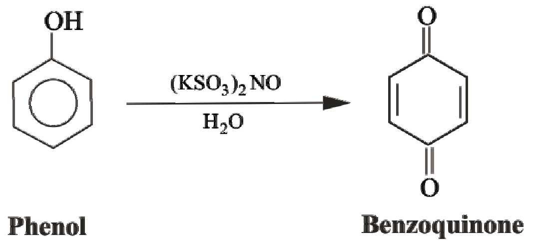
It involves sodium phenoxide which is allowed to absorb carbon dioxide and then heated under a pressure of CO_2 to 398 K. Sodium salicylate so obtained on acidification yields salicylic acid.



By reaction with acetic anhydride, salicylic acid yields *aspirin*, which is the common pain reliever.

4. Oxidation

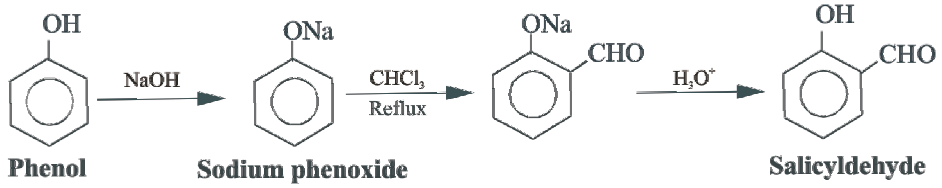
Phenols undergo oxidation reactions to give products which are diffrent from those obtained by alcohols. They can be oxidised using a variety of oxidising agents such as sodium dichromate or silver oxide to give quinones. These days Fremy's salt $[(KSO_3)_2NO]$ is preferred for oxidation.



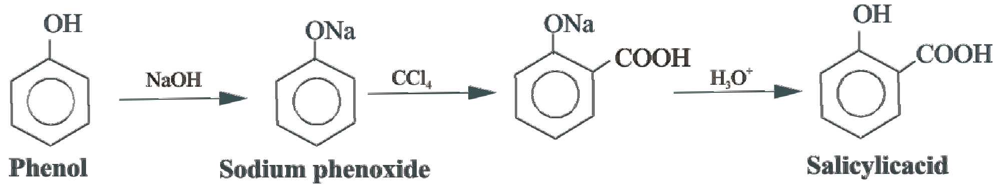
Notes

5. Reimer Tiemann Reaction

Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.

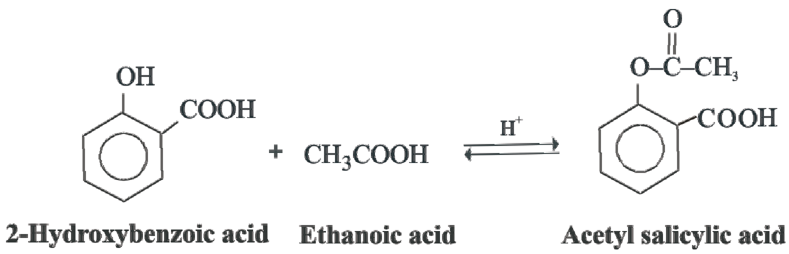


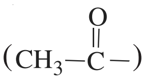
Use of carbon tetrachloride in place of chloroform gives salicylic acid.



6. Esterification

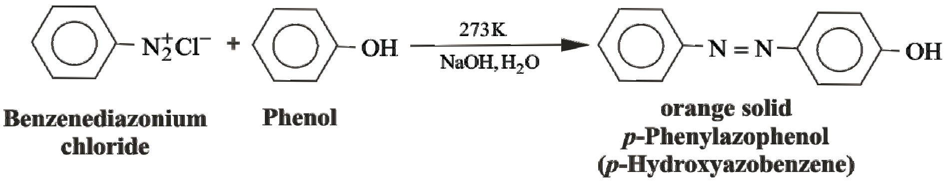
Similar to alcohols, phenols react with carboxylic acids to give esters.



This reaction is an acetylation reaction as the H of –OH the phenol is replaced by the acetyl  $(CH_3-\overset{O}{\overset{\|}{C}}-)$ group.

7. Coupling Reaction

Phenols react with aromatic diazonium salts in slightly alkaline conditions to give *azo* compounds. These *azo* compounds are brightly coloured and are used as *azo dyes*.



Uses

1. Phenol is used as a disinfectant.
2. It is also used in the synthesis of polymers.
3. Phenols are used in the synthesis of many organic compounds.
4. Substituted phenols are used in dyeing and tanning industries.

INTEXT QUESTIONS 26.2

1. How will you convert aniline to phenol?
2. What is the starting material in Dow's process?
3. Arrange the following in the increasing order of their acidity:
   Phenol, 2-Methylphenol, 2-Chlorophenol
4. How will you prepare salicylic acid from phenol?
5. What is an azo dye?

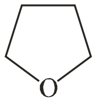
26.3 ETHERS

Ethers are organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups. Thus, ethers can be represented as $R-O-R'$ where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R') are identical, then the ether is called a **symmetrical ether,** otherwise if these two groups are different, then the ether is known as an **unsymmetrical ether.**

$CH_3CH_2 - O - CH_2CH_3$ $\quad$ $CH_3 - O - CH_2CH_3$

A symmetricalether $\quad$ **An unsymmetrical ether**

The oxygen atom of the ether can also be part of a ring, in which case the ether is known as a **cyclic ether**. Tetrahydrofuran is one such cyclic ether which is used as a solvent.



Tetrahydrofuran (THF)

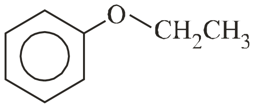
Ethers are commonly used as solvents for organic reactions. The symmetrical ether shown above is diethyl ether and is commonly also referred to simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years.

26.3.1 Nomenclature of Ethers

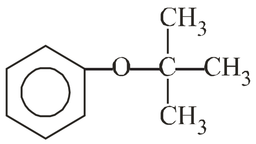
Common names of ethers are arrived by alphabetically naming the two groups attached to the oxygen followed by the word ether. The common names for some ethers are given below :

$CH_3OCH_2CH_3$
Ethyl methyl ether

$CH_3CH_2OCH_2CH_3$
Diethyl ether



Ethyl phenyl ether



***tert*-Butyl phenyl ether**

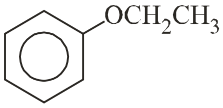
$Cl-CH_2-O-CH_3$
Chloromethyl methyl ether

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane* and the smaller alkyl group is treated as an *alkoxy* substituent on this alkane. For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

$CH_3OCH_2CH_3$
Ethyl methyl ether

The remaining portion , *i.e.*, $-OCH_3$ part in this case, is called the methoxy substituent. Hence, the above ether is called **methoxyethane.** Some more examples of IUPAC names of ethers are given below :

$CH_3CH_2OCH_2CH_3$
Ethoxy ethane



Ethoxybenzene

$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2OCH_3$
1,2-Dimethoxyethane

26.3.2 General Methods of Preparation

You have already studied under the reactions of alcohols that ethers can be obtained by the dehydration of alcohols. Ethers can also be prepared by Williamson synthesis which is explained below :

Williamson Synthesis : It involves the reaction of a metal alkoxide with a primary alkyl halide. The metal alkoxide is prepared by adding sodium or potassium metal or sodium hydride (NaH) to the alcohol.

$$< ROH + Na \longrightarrow \underset{\textbf{Metal alkoxide}}{RO^-Na^+} + \frac{1}{2}H_2 >$$

$$< ROH + NaH \longrightarrow RO^{-}Na^{+} + H_2 >$$

Metal alkoxide

$$< RO^{-}Na^{+} + R'-X \longrightarrow R-O-R' + NaX >$$

Metal alkoxide **Alkyl halide** **Ether**

$$CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2ONa \xrightarrow{CH_3CH_2I}$$

propan-1-ol **Sodium propoxide**

$$CH_3CH_2CH_2OCH_2CH_3 + NaI$$

1-Ethoxypropane
(Ethyl propyl ether)

Williamson synthesis involves the displacement of the halide ion by the alkoxide ion.

26.3.3 Sturcture and Properties of Ethers

Ethers have geometry similar to water and alcohols. The oxygen atom is sp^3 hybridised. There are two lone pairs of electrons present on the oxygen atom as is shown in Fig. 26.6.

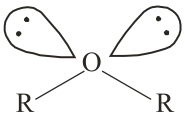


Fig. 26.6 : *Geometry of an ether molecule*

Note that the ether molecule has a bent structure. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar is nature (Fig. 26.7). Ethers, thus, act as polar solvents.

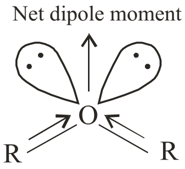
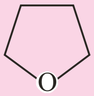
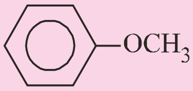


Fig. 26.7 : *Polar ether molecule*

Since ethers do not have a hydrogen atom linked to the oxygen atom, they cannot form hydrogen bonds amongst their own molecules. Due to the absence of hydrogen bonding, they have lower boiling points as compared to alcohols having similar molecular masses. The boiling boints of some ethers are listed in Table 26.5.

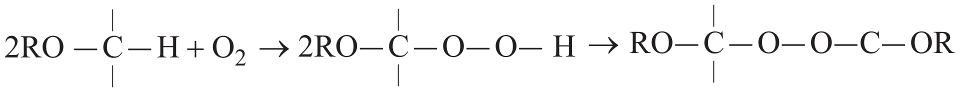
Table 26.5 : Boiling points of some common ethers

Ether	Boiling point (K)
CH_3OCH_3	248.1
$CH_3OCH_2CH_3$	283.8
$CH_3CH_2OCH_2CH_3$	307.6
$CH_3OCH_2CH_2OCH_3$	356
	338.4
	431.3

26.3.4 Reactions of Ethers

Ethers are normally unreactive in nature. Their unreactivity makes them good solvents. However, they show some reactions which are discussed below :

1. Reaction with Oxygen : Ethers slowly react with oxygen to form hydroperoxides and peroxides.



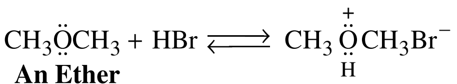
$$2RO-\overset{|}{\underset{|}{C}}-H + O_2 \rightarrow 2RO-\overset{|}{\underset{|}{C}}-O-O-H \rightarrow RO-\overset{|}{\underset{|}{C}}-O-O-C-OR$$

Ether **Ahydroperoxideofether** **Aperoxide of ether**

Peroxides have a tendency to explode. Therefore, one should be very careful in handling ethers which may have been stored for sometime because they may contain some peroxide.

2. Reaction wtih Acids

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature.



$$CH_3\ddot{\underset{..}{O}}CH_3 + HBr \rightleftharpoons CH_3\overset{+}{\underset{H}{\ddot{O}}}CH_3Br^-$$

An Ether **Anoxoniumsalt**

3. Acidic Cleavage

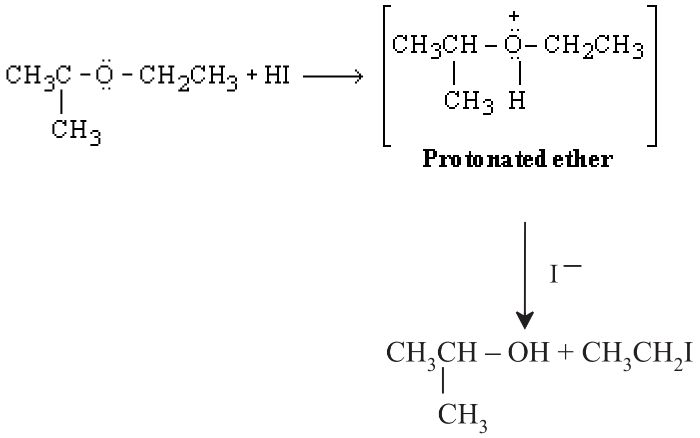
Heating dialkyl ethers with strong acids such as HI, HBr or H_2SO_4 leads to their cleavage.

$$\underset{\textbf{Ethoxyethane}}{CH_3CH_2OCH_2CH_3} + HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3CH_2Br} + \underset{\textbf{Ethanol}}{CH_3CH_2OH}$$

The alcohol formed further reacts with additional HBr to give bromoethane. Hence,

$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

In case of ethers having primary or secondary alkyl groups, the nucleophile (Br^- or I^-) attacks the less hindered alkyl group. Thus, in case of the following unsymmetrical ether, the products contain alkyl halide formed by the attack of the halide ion on the less hindered primary alkyl group, *i.e.*, ethyl group.



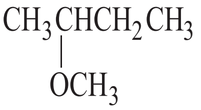
$$\underset{\substack{|\\CH_3}}{CH_3C}-\ddot{\underset{..}{O}}-CH_2CH_3 + HI \longrightarrow \left[\underset{\substack{|\\CH_3}}{CH_3CH}-\overset{+}{\underset{\substack{..\\|\\H}}{\ddot{O}}}-CH_2CH_3\right]$$

Protonated ether

$$\xrightarrow{I^-} \underset{\substack{|\\CH_3}}{CH_3CH}-OH + CH_3CH_2I$$

INTEXT QUESTIONS 26.3

1. What are the IUPAC names of the following ethers ?

   (i) 
   $\underset{\substack{|\\OCH_3}}{CH_3CH}CH_2CH_3$

   (ii) $CH_3–O–CH_3$

2. (i) How will you prepare methyl propyl ether using Williamson synthesis?

   (ii) What is the IUPAC name of methyl propyl ether ?

3. Why should you be careful in using old stock of ethers.

4. Why are ethers good solvents ?

5. What is tetrahydrofuran ? Give its structure and use.

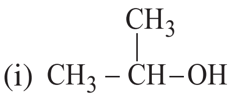
WHAT YOU HAVE LEARNT?

In this lesson, you have learnt that

- Alcohols can be classified as primary, secondary or tertiary.
- Alcohols can be monohydric, dihydric or polyhydric.
- Alcohols can be prepared by the following general methods :
  - – Hydrolysis of haloalkanes
  - – Hydration of alkenes
  - – Reduction of carbonyl compounds
  - – From aldehydes and ketones using Grignard reagents
- Alcohols behave both as weak acids and weak bases.
- Alcohols can be converted to alkyl halides, alkenes, ethers, aldehydes, ketones, carboxylic acids and esters.
- In the laboratory, phenols can be prepared from arenediazonium salts and sodium benzene sulphonate. Their industrial preparation is done by Dow's process and from cumene hydroperoxide.
- Similar to alcohols, phenols can also behave both as acids and bases.
- Typical reactions of phenols being electrophilic substitution reactions such as halogenation, sulphonation, nitration, etc.
- Phenols undergo oxidation and also exhibit Reimer Tiemann reaction. They react with aromatic diazonium salts to give azo dyes.
- Ethers can be symmetrical or unsymmetrical.
- Ethers can be prepared by Williamson synthesis.
- Dialkyl ethers are cleaved on heating with strong acids .

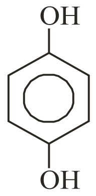
TERMINAL EXERCISE

1. Give the IUPAC names of the following compounds :



(i) $CH_3-\underset{}{\overset{\overset{CH_3}{|}}{CH}}-OH$

(ii) $C_6H_5OCH_2CH_3$

(iii) 

2. Compare the boiling points of ethyl alcohol and dimethyl ether. Which one has higher boiling point and why ?
3. Which ester would give ethanol and methanol on reduction?
4. Complete the following reactions :

   (i) $CH_3CH_2CH_2Cl \quad + \quad NaOH\ (aq.) \longrightarrow$ ....

   (ii) $CH_3CHO \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ ether}$ ....

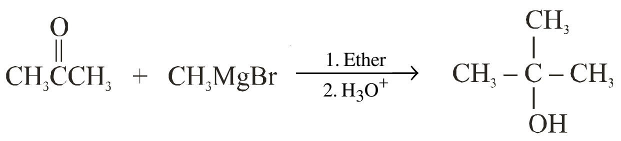
   (iii) $CH_3OH + Na \longrightarrow$ ....
5. How is ethanol prepared using fermentation?
6. What is Lucas test? What is its use?
7. Which reagent is used for oxidising primary alcohols to aldehydes?
8. Why are phenols more acidic than alcohols? Explain.
9. Why are ethers polar in nature?

ANSWERS TO INTEXT QUESTIONS

26.1

1. (i) 2-Methylpentan-2-ol

   (ii) 2-Ethylbut-2-en-1-ol

   (iii) 1, 4-Pentanediol
2. By reduction with $NaBH_4$ or $LiAlH_4$
3. 

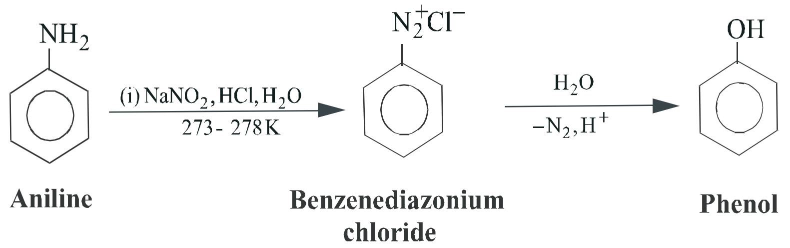
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ Ether} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$
4. (i) Hexanoic Acid

   (ii) Hexanal

5. MTBE is methyl tert-butyl ether. It is used as an additive to gasoline.
6. Alkenes.

26.2

1.



2. Chlorobenzene
3. 2-Methylphenol < Phenol < 2-Chlorophenol
4. By Kolbe reaction
5. Azo dyes are azo compounds formed by the reaction of phenols with aromatic diazonium salts. They are brightly coloured.

26.3

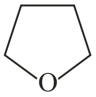
1. (i) 2-Methoxybutane

   (ii) Methoxymethane

2. (i) $CH_3CH_2CH_2O^- + CH_3Br \longrightarrow CH_3CH_2 - O - CH_3 + Br^-$

   (ii) Methoxypropane

3. They may explode due to the presence of peroxides.
4. Because they are unreactive in nature.
5. It is a cyclic ether.



It is used as a solvent.

28

COMPOUNDS OF CARBON CONTAINING NITROGEN

In the previous lesson, you have studied the chemistry of organic compounds containing oxygen atom as a part of the functional group. Now, you will learn about organic compounds containing nitrogen atom as a part of the functional group. An historical importance can be associated with these compounds as the first ever organic compound synthesised in the laboratory was urea which contains nitrogen. Nitrogen containing compounds have wide applications in our daily life. They form a part of dyes, drugs, fertilizers, alkaloids, proteins, etc. Only two classes of nitrogen containing compounds, *viz*. amines and nitro compounds are discussed in this lesson. First, the IUPAC nomenclature of amines has been explained followed by their preparation and chemical properties. The difference in the basicities of aliphatic and aromatic amines has also been described. Finally, the chemistry of nitro compounds is briefly discussed.

OBJECTIVES

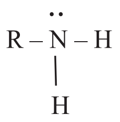
After reading this lesson, you will be able to:

- classify amines as primary, secondary, or tertiary amines;
- write the IUPAC names of amines and nitro compounds;
- describe the general methods of preparation, properties and uses of primary amines;
- explain the relative basicities of primary, secondary and tertiary aliphatic amines and compare them with the basicities of ammonia and aromatic amines;
- differentiate primary, secondary and tetracy amines;
- discuss the important reactions of diazonium salts and explain their utility in synthesis of organic compounds;
- describe the methods of preparation of nitro compounds;

- discuss important reactions of nitro compounds, and
- list important uses of nitro compounds;

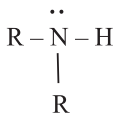
28.1 AMINES

Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified into three different types as primary (1°), secondary (2°) and tertiary (3°) depending on the number of hydrogen atoms replaced by alkyl or aryl groups. In primary amines, only one alkyl or aryl group is attached to the nitrogen atom. In secondary amines, two alkyl or aryl groups are attached to the nitrogen while tertiary amines contain three alkyl or aryl groups attached to the nitrogen atom.
This is illustrated below.



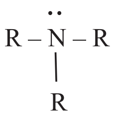
$$\begin{array}{c} R-\ddot{N}-H \\ | \\ H \end{array}$$

A primary amine



$$\begin{array}{c} R-\ddot{N}-H \\ | \\ R \end{array}$$

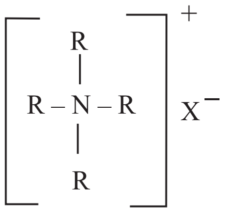
A secondary amine



$$\begin{array}{c} R-\ddot{N}-R \\ | \\ R \end{array}$$

A tertiary amine

If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.

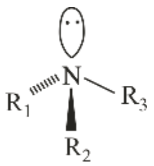


$$\left[\begin{array}{c} R \\ | \\ R-N-R \\ | \\ R \end{array}\right]^{+} X^{-}$$

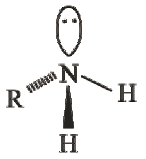
A quaternary ammonium salt

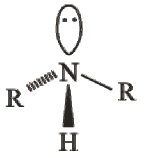
Structure of Amines

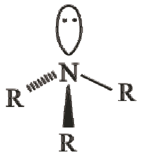
The nitrogen atom of amines is approximately sp^3 hybridised. The three alkyl groups or hydrogen atoms occupy the three corners of the tetrahedron while the unshared pair of electrons is directed towards the other corner of the tetrahedron.



If we consider the three groups attached to the nitrogen as R_1, R_2 and R_3 then the shape of the molecule can be described as *trigonal pyramidal*. These three groups could be either alkyl groups or hydrogen atoms. Accordingly, the amine is called primary, secondary or tertiary,

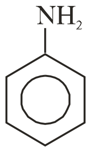

Primary amine


Secondary amine


Tertiary amine

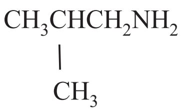
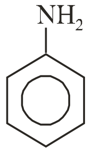
However, if we consider lone pair of electrons also as a group attached to the nitrogen, then the geometry of the molecule is called *tetrahedral.* The bond angles R –N–R are close to the tetrahedral angle of 109.5°.

The amino group in aromatic amines is directly bonded to the benzene ring. Aromatic amines are aryl derivatives of ammonia. The parent aromatic amine is known as aniline.

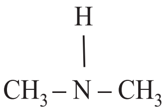
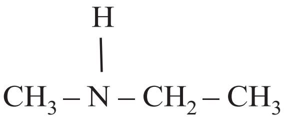
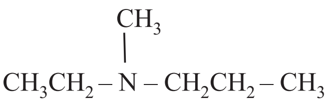

Aniline

28.2.1 IUPAC Nomenclature of Amines

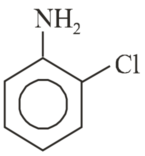
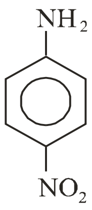
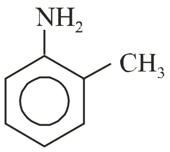
Similar to other classes of compounds which you have studied, amines can also be named according to the IUPAC system. In case of primary aliphatic amines, the longest continuous chain of carbon atoms determines the root name of the compound. The ending –*e* in the name of the corresponding alkane is changed to-*amine*. The other substituents along the carbon chain are given numbers. This is illustrated by the following examples.

Compounds	***IUPAC name***	***Common name***
CH_3NH_2	Methanamine	Methyl amine
$CH_3CH_2NH_2$	Ethanamine	Ethyl amine
$CH_3CH_2CH_2NH_2$	Propan-1-amine	Propyl amine
 $CH_3\underset{\substack{\vert \\ CH_3}}{C}HCH_2NH_2$	2-Methyl propan-l-amine	—
	Benzenamine	Aniline

Secondary and tertiary amines are named by using the prefix *N* for each substituent on the nitrogen atom.

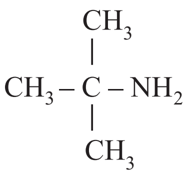
Compound	***IUPAC name***	***Common name***
 $CH_3-\overset{H}{\overset{\vert}{N}}-CH_3$	*N*-Methylmethanamine	Dimethylamine
 $CH_3-\overset{H}{\overset{\vert}{N}}-CH_2-CH_3$	*N*-Methylethanamine	Ethylmethylamine
 $CH_3CH_2-\overset{CH_3}{\overset{\vert}{N}}-CH_2CH_2-CH_3$	*N*-Ethyl-*N*-methylpropan-1-amine	—

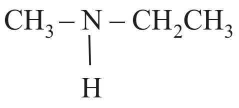
The IUPAC names of other aromatic amines are given as derivatives of aniline shown below :

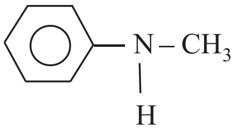
Compound	***IUPAC name***	***Common name***
	2-Chloroaniline	*o*-Chloroaniline
	4-Nitroaniline	*p*-Nitroaniline
	2-Methylaniline	*o*-Toluidine

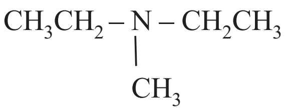
INTEXT QUESTIONS 28.1

1. Classify the following as primary, secondary, tertiary amines and quaternary ammonium salts :

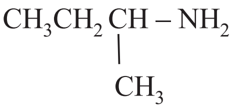
(i)  $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-NH_2$

(ii)  $CH_3-\underset{H}{\underset{\vert}{N}}-CH_2CH_3$

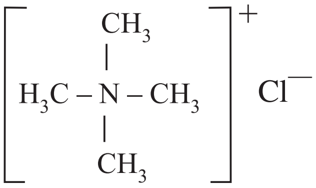
(iii) 

(iv) 

$$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2CH_3$$

(v) 

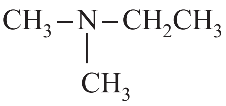
$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$$

(vi) 

$$\left[H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N}}}}-CH_3\right]^+ Cl^-$$

2. Write IUPAC names for the following amines :

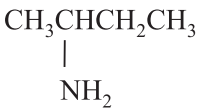
(i) $CH_3CH_2CH_2CH_2NH_2$

(ii) 

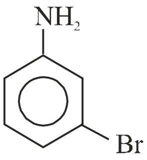
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2CH_3$$

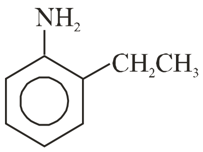
(iii) 

$$CH_3-\underset{\displaystyle H}{\underset{|}{N}}-CH_2CH_2CH_2CH_3$$

(iv) 

$$CH_3\underset{\displaystyle NH_2}{\underset{|}{CH}}CH_2CH_3$$

(v) 

(vi) 

28.2.2 Preparation of Amines

Several methods are available for the preparation of primary aliphatic and aromatic amines. In this section, you will learn some of the methods which are generally used for their perparation.

(i) ***From alkyl halides***

Alkyl halides react with ammonia to form primary amines.

$$R-X+2\,NH_3 \longrightarrow R\,NH_2+NH_4X$$

The primary amine so formed may further react to give a secondary amine, tertiary amine or a quaternary ammonium salt. So in order to get good yield of the primary amine, the reaction is carried out using excess of ammonia. For example, bromoethane on reaction with excess of ammonia gives ethanamine.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br}+2\,NH_3 \longrightarrow \underset{\textbf{Ethanamine}}{C_2H_5NH_2}+NH_4Br$$

(ii) ***By reduction of nitriles (cyanides), amides and nitro compounds***

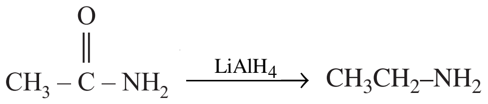
Compounds containing cyano, amido or nitro groups can be reduced into the corresponding primary amines.

Nitriles can be reduced by hydrogen in the presence of platinum catalyst or by sodium in presence of ethanol to corresponding primary amines. For example, propanenitrile (cyano ethane) on reduction gives propan-l-amine.

$$CH_3CH_2C{\equiv}N \xrightarrow[\text{or } Na/C_2H_5OH]{H_2/Pt} CH_3CH_2CH_2{-}NH_2$$

Propanenitrile **Propan-l-amine**

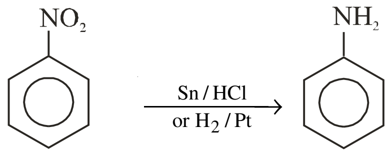
Similarly, amides are reduced by $LiAlH_4$ to primary amines having same number of carbon atoms as in the starting amide. For example, ethanamide gives ethanamine on reduction.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2{-}NH_2$$

Ethanamide **Ethanamine**

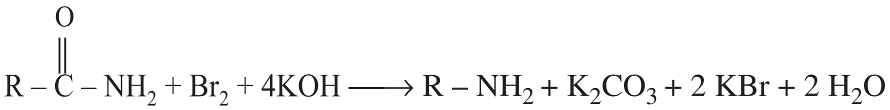
Reduction of nitro compounds can be carried out by using hydrochloric acid and a metal such as Sn or Fe. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. Such a reduction of nitrobenzene by any of these methods provides aniline.



Nitrobenzene **Aniline**

(iii) ***By Hofmann bromamide reaction***

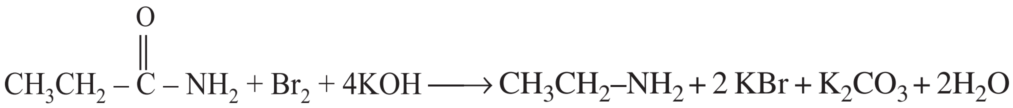
Aliphatic amides on treatment with bromine and a strong base like potassium hydroxide are converted into primary amines having one carbon less than those present in the starting amide.



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

Amide **Amine**

Thus, ethanamine is obtained by treating propanamide with bromine and KOH.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3CH_2{-}NH_2 + 2\,KBr + K_2CO_3 + 2H_2O$$

Propanamide **Ethanamine**

28.2.4 Physical Properties of Amines

Aliphatic amines containing up to three carbon atoms are gases whereas higher amines are liquids. Some higher aromatic amines are even solids. Methyl and ethyl amines have smell like ammonia. Amines have higher boiling points than the corresponding hydrocarbons because they form hydrogen bonds amongst themselves. Lower amines are soluble in water and the solubility decreases with the increase in size of the alkyl group. This solubility is because of the presence of hydrogen bonding between the amino group and water molecules. All amines are soluble in organic solvents like benzene, alcohol, ether etc.

28.2.5 Chemical Properties of Amines

(i) ***Basic Character***

Amines are basic in nature due to the presence of a lone pair of electrons on nitrogen. You know that the strength of a base depends upon the availability of electrons. Basicities of amines can be compared with respect to ammonia, by comparing the availability of pair of electrons on nitrogen. Ammonia and amines, both when dissolved in water, attract a proton from water to form an ammonium or alkylammonium ion, respectively, and a hydroxide ion.

$$\ddot{\mathrm{N}}\mathrm{H}_3 + \mathrm{H-O-H} \longrightarrow \underset{\textbf{Ammonium ion}}{\mathrm{NH}_4^+} + \mathrm{OH}^-$$

$$\mathrm{R-\ddot{N}H_2 + H-O-H} \longrightarrow \underset{\textbf{Alkylammonium ion}}{\mathrm{R-NH}_3^+} + \mathrm{OH}^-$$

You know that aliphatic amines contain one or more alkyl groups in place of hydrogen atoms of ammonia. Since alkyl groups are electron releasing groups, they increase the electron density on nitrogen. This makes the lone pair of electrons on nitrogen atom to be easily available for sharing and hence, this increases the basicity of the amine. So, we expect that the basicities of the amines would increase as we move from primary to secondary to tertiary amines.

But the order of the basicities has been found to be

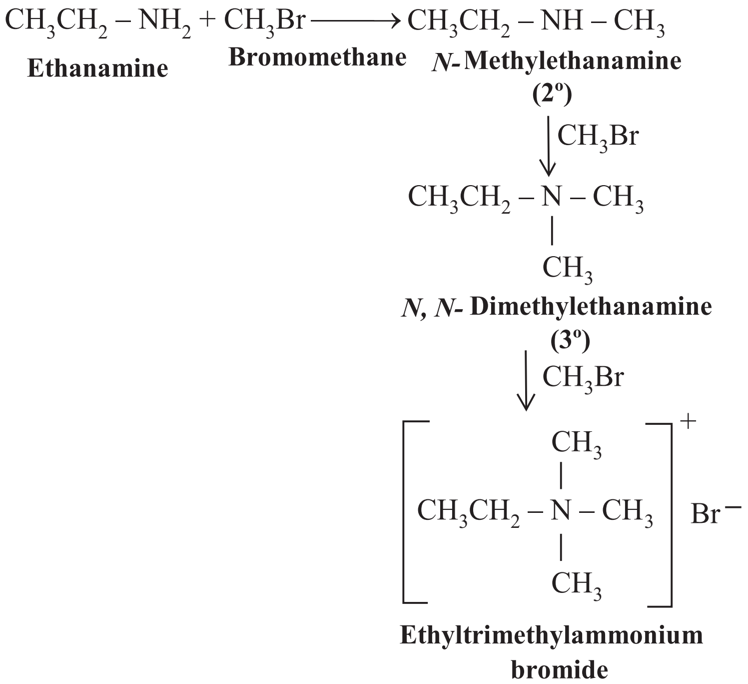
$$\underset{\textbf{Primary }(1^0)}{\mathrm{R-NH_2}} < \underset{\textbf{Secondary }(2^0)}{\mathrm{R_2\,NH}} > \underset{\textbf{Tertiary }(3^0)}{\mathrm{R_3N}}$$

The tertiary amines are less basic than secondary amines. The reason is that a tertiary amine, though has three alkyl groups which can donate electrons to the nitrogen atom but they also cause crowding (also called *steric hinderance*) around nitrogen. This hinders the protonation at nitrogen atom and hence, reduces the basicity.

The aromatic amines are weaker bases than ammonia because the aromatic ring is electron withdrawing. It reduces the electron density at nitrogen and makes the aromatic amines less basic. So we can express the basic character of aliphatic and aromatic amines as shown below.

Aromatic amines < Ammonia < Aliphatic amines

(ii) ***Alkylation :*** Primary amines react with alkyl halides to give secondary amines. The reaction may continue further to form a tertiary amine and a quaternary ammonium salt. For example, the reaction of ethanamine with bromomethane proceeds as shown below.



$$CH_3CH_2-NH_2 + CH_3Br \longrightarrow CH_3CH_2-NH-CH_3$$

Ethanamine **Bromomethane** ***N*-Methylethanamine (2°)**

$$\downarrow CH_3Br$$

$$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$$

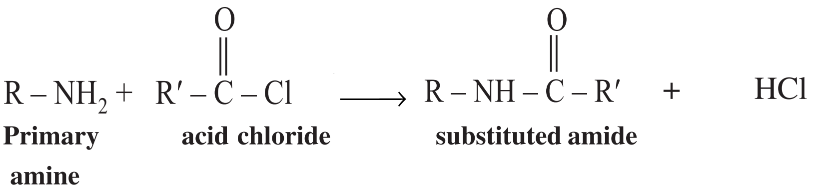
***N, N*- Dimethylethanamine (3°)**

$$\downarrow CH_3Br$$

$$\left[CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N}}}}-CH_3\right]^+ Br^-$$

Ethyltrimethylammonium bromide

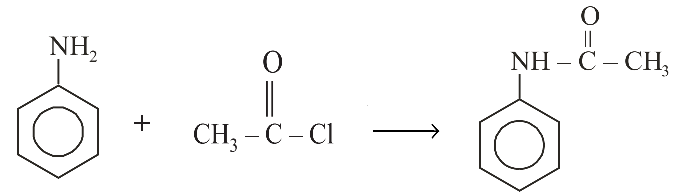
(iii) ***Acylation :*** Primary amines on reaction with acid chlorides or acid anhydrides give *N*-substituted amides.



$$R-NH_2 + R'-\overset{\displaystyle O}{\overset{\|}{C}}-Cl \longrightarrow R-NH-\overset{\displaystyle O}{\overset{\|}{C}}-R' + HCl$$

Primary amine **acid chloride** **substituted amide**

For example, aniline on reaction with ethanoyl chloride (acetyl chloride) gives acetanilide.



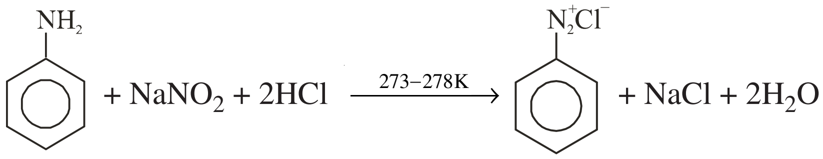
Aniline **Ethanoyl chloride** **Acetanilide**

(iv) ***Carbylamine reaction :*** When a primary amine is heated with chloroform in the presence of alcoholic potassium hydroxide, then the corresponding isocyanide is formed. Isocyanides are also known as **carbylamines**, hence this reaction is called as **carbylamine reaction**. For example, aminoethane on undergoing this reaction, gives ethyl carbylamine.

$$\underset{\textbf{Ethylamine}}{CH_3CH_2{-}NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\textbf{Ethyl carbylamine}}{CH_3CH_2\,N \equiv C} + 3KCl + 3H_2O$$

Isocyanides give a very offensive odour, so this reaction is also used as a test for primary amines.

(v) ***Reaction with nitrous acid :*** Primary aromatic amines react with nitrous acid to give diazonium salts and this reaction is known as **diazotisation**. Nitrous acid is an unstable compound and can not be stored, so it is prepared during the reaction by mixing sodium nitrite and hydrochloric acid. The reaction is specifically carried out at low temperature between 273 – 278 K. For example, aniline reacts with nitrous acid to give benzene diazonium chloride.



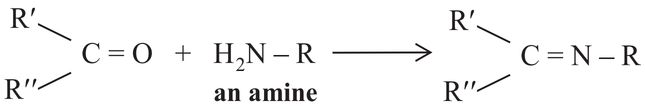
Aniline **Benzene diazonium chloride (a diazonium salt)**

Primary aliphatic amines also react in a similar way but the diazonium salts formed are unstable and decompose to give alcohols and nitrogen gas. Thus, ethanamine gives ethanol when subjected to this reaction.

$$\underset{\textbf{Ethanamine}}{CH_3CH_2{-}NH_2} \xrightarrow{NaNO_2/HCl} \underset{\substack{\textbf{Ethyldiazonium chloride}\\ \textbf{Unstable diazonium salt}}}{[CH_3CH_2\,N_2^+\,Cl^-]} \xrightarrow{H_2O}$$

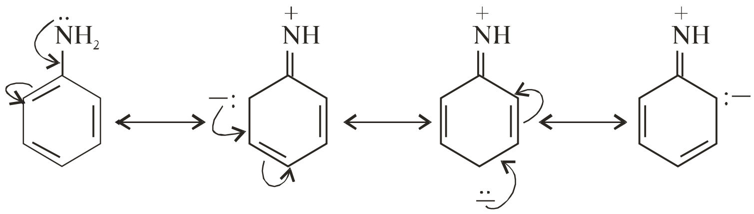
$$\underset{\textbf{Ethanol}}{CH_3CH_2{-}OH} + N_2\uparrow + HC$$

(vi) Primary amines undergo condesnsation with aldehydes or ketones to form **imines**. These products are also called **Schiff's bases**. The reaction can be shown as follows :



an amine **a Schiff's base**

(vii) ***Ring substitution in aromatic amines :*** You know that – NH_2 group is a strong activating and *ortho*-, *para*- directing group for electrophilic aromatic substitution reactions. This directive influence can be explained by the following resonating structures of aniline.

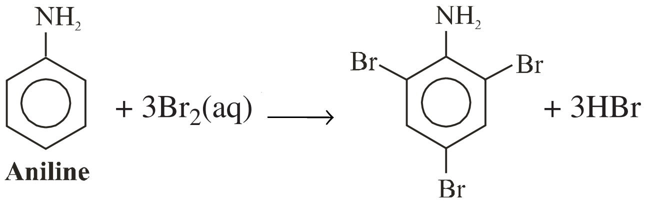


Resonance structures of aniline

As a result of this resonance, the electron density is more at *ortho*- and *para*-positions; hence, the electrophilic substitution occurs at these positions.

Some important ring substitution reactions of aromatic amines are halogenation, nitration and sulphonation.

(a) ***Halogenation :*** Aniline on treatment with an aqueous solution of bromine gives 2,4,6 - tribromoaniline.



2,4,6-Tribromoaniline

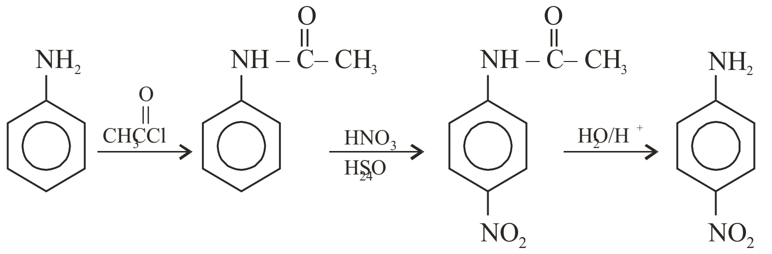
Aniline is very reactive and all the three hydrogen atoms at *ortho*- and *para*-positions are substituded with bromine atoms.

(b) ***Nitration :*** Nitration of aniline is carried out on the acetylated amine (acetanilide) rather than on the free amine itself. There are two reasons for this.

(i) The free amine is very susceptible to oxidation and thus much of it is lost in the form of a black-sticky material which is fomed as result of its oxidation.

(ii) The free amine is very reactive but acetyl the group protects it and reduces its reactivity.

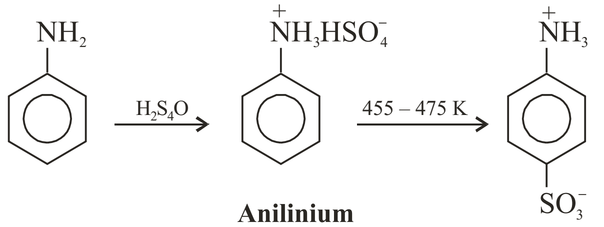
The nitration of aniline with the protection of the amino group is shown below:



Aniline **Acetanilide** ***p*-Nitroacetanilide** ***p*-Nitroaniline**

The first step consists of acetylation of the amino group in aniline. The conversion of $-NH_2$ to $-NH-\overset{\overset{O}{||}}{C}-CH_3$, lowers the activity of $-NH_2$ group because of electron withdrawal by $-\overset{\overset{O}{||}}{C}-CH_3$. This step is followed by nitration (conc. HNO_3 / H_2SO_4) which gives mainly the *p*-nitroacetanilide. This, 'on acid hydrolysis' yields the desired product *p*-nitroaniline.

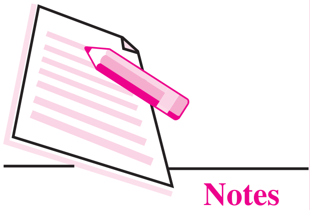
(c) ***Sulphonation :*** Sulphonation is carried out in the presence of sulphuric acid. The amino group in aniline is a basic group. Therefore, an acid-base reaction takes place to form anilinium hydrogensulphate salt. This salt undergoes rearrangement at a high temperature to give sulphanilic acid.



Aniline **Anilinium hydrogensulphate** **Sulphanilic acid**

28.2.6 Uses of Amines

Amines are very useful compounds. They are used for a variety of purposes in the laboratory as well as in the industry. Some aliphatic amines are used as solvents and intermediates in drug synthesis. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents. Aromatic amines e.g. aniline and its derivatives, are used for the production of dyes, drugs and photographic developers. 1,4-Diaminobenzene is the main ingredient of all hair dyes. Many dithiocarbamates which are the compounds derived from primary amines, are used as herbicides. Diazonium salts obtained from primary aromatic amines form the basis of synthesis of many other organic compounds.

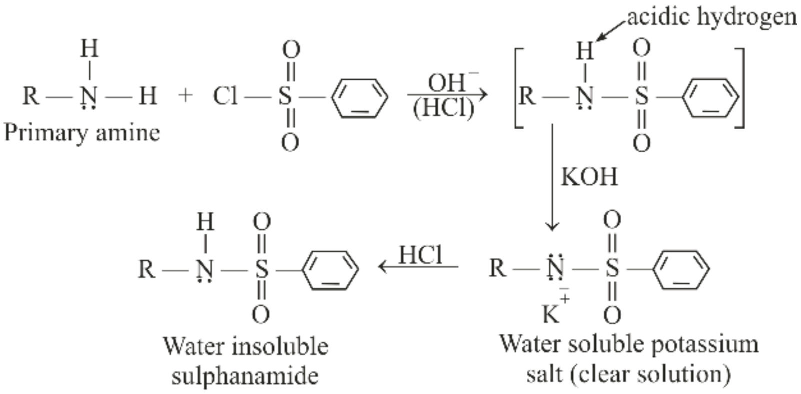


28.2.7 Identification of Primary, Secondary and Tertiary amines

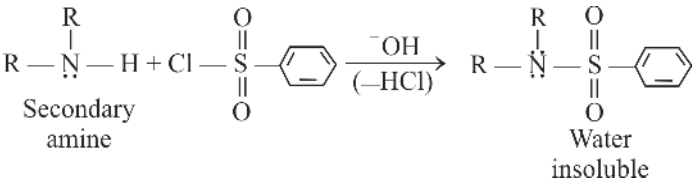
Primary, secondary and tertiary amines can be distinguished from each other using **Hinsberg test**. In this test, a small amount of the amine and benzene sulphonyl chloride is shaken with excess of potassium hydroxide. After allowing the reaction to take place, the mixture is acidified. The following is observed for different types of amines.

The **primary amines** react with benzene sulphonyl chloride to form *N*-substituted benzene sulphonamide which in turn, forms, water soluble potassium salt, with excess of potassium hydroxide.

This clear solution on acidification gives water-insoluble *N*-substituted sulphonamide which precipitates out.



The **secondary amines** react with benzene sulphonyl chloride in aqueous potassium hydroxide to give insoluble *N*, *N*-disubstituted sulphonamides which form a precipitate. These sulphonamides are not soluble in aq. KOH because they do not have an acidic hydrogen. Hence, on further acidification also, there is no change in the reaction mixture.

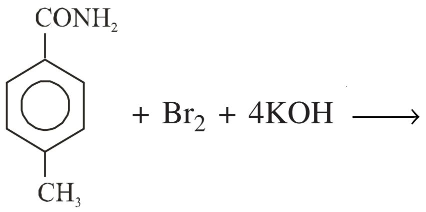


In case of tertiary amines, if the amine is water insoluble then no change will take place on addition of benzene sulphonyl chloride and aq. KOH as no reaction will take place. However, when we acidify this mixture, the tertiary amine will dissolve as a water soluble salt will form.

INTEXT QUESTIONS 28.2

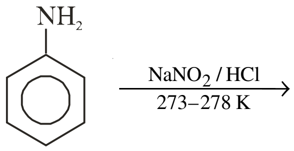
1. Predict the major product of the following reactions :

(a)

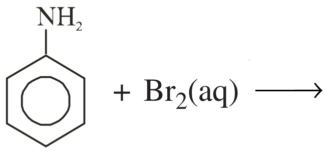


(b) $CH_3CH_2NH_2 \xrightarrow{NaNO_2/HCl}$

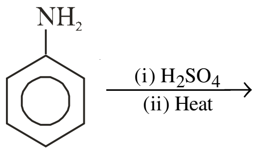
(c)



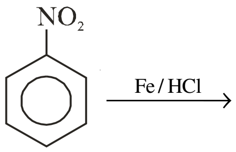
(d)



(e)



(f)



2. Why is aniline very reactive towards bromination?

3. Name the test which uses potassium hydroxide and chloroform for identifying a primary amine.

4. Can aniline be nitrated directly?

5. How will you obtain sulphanilic acid from benzene?

28.3 DIAZONIMUM SALTS: REACTIONS AND IMPORTANCE IN SYNTHETIC CHEMISTRY

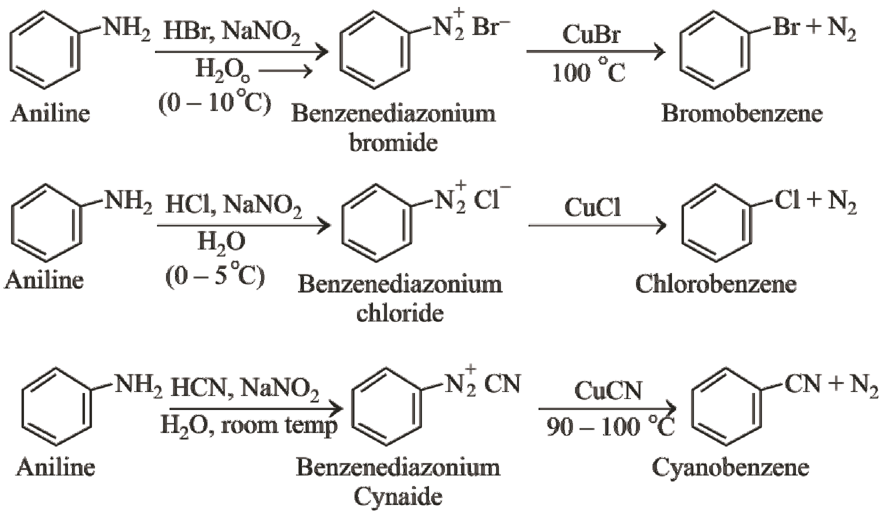
Most of the arenediazonium salts (formed from aromatic amines) are unstable at temperatures above 5–10°C. These salts explode when dry.

Therefore, many of their further reactions are carried out without isolating them.

The reactions of diazonium salts are very important synthetically because the diazonium group can be replaced by a variety of other groups such as –F, –Cl, –Br, –I, –CN, –OH and –H. These reactions are given below.

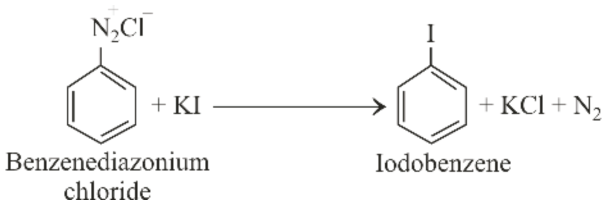
(i) The Sandmeyer reaction

In this reaction, the arene diazonium salts are reacted with cuprous bromide, cuprous chloride and cuprous cyanide in the presence of HBr, HCl and HCN, respectively. Some of the examples of **Sandmeyer reaction** are given below: You can see in these reactions that the diazonium group is replaced by –Br, –Cl and –CN group.



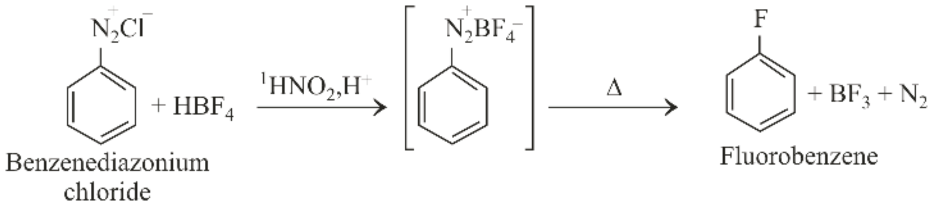
(ii) Replacement of diazonium group by –I group

In this reaction, the dizonium salt is treated with potassium iodide to give the product in which diazonium group has been replaced by –I group.



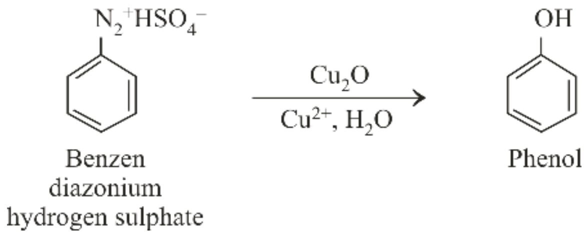
(iii) Replacement of diazonium group by –F group

Here, the diazonium salt is first treated with fluoroboric acid (HBF_4) and the diazonium fluoroborate precipitated is isolated and dried. It is then heated until it starts decomposing to give the aryl fluoride product.



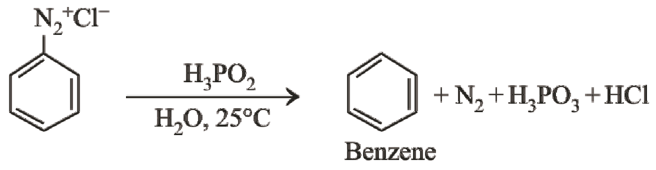
(iv) Replacement of dizonium group by –OH group

If cuprous oxide is added to a dilute solution of the diazonium salt containing a large excess of cupric nitrate, then the diazonium group is replaced by a hydroxyl group.



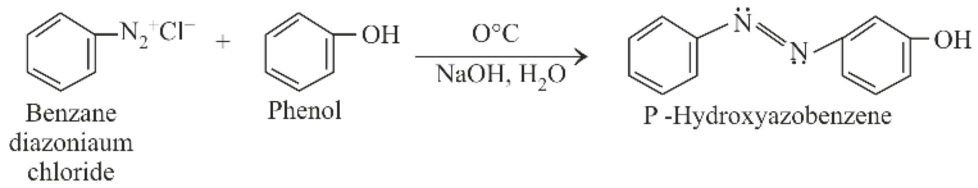
(v) Replacement of diazonium group by a hydrogen atom

The reaction of diazonium salts with hypophosphorous acid (H_3PO_2) replaces the diazonium group by a hydrogen atom.



(vi) Coupling Reactions of Arenediazonium Salts

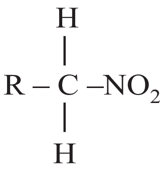
Arenediazonium salts react with phenols and tertiary aryl amines to give azo compounds which are known *azo dyes*. This reaction is called *diazo coupling reaction*.



Hence, by using the above reactions, we can synthesize a variety of compounds.

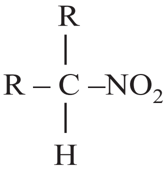
28.4 NITRO COMPOUNDS

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom is replaced by a nitro ($-NO_2$) group. They may be aliphatic or aromatic. Nitroalkanes are divided into primary (1°), secondary (2°) or tertiary (3°) nitro alkanes depending upon the attachment of nitro group to primary, secondary or tertiary carbon atom, respectively.



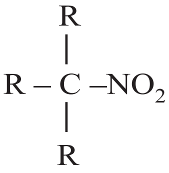
$$\begin{array}{c} H \\ | \\ R-C-NO_2 \\ | \\ H \end{array}$$

***p*-nitroalkane**



$$\begin{array}{c} R \\ | \\ R-C-NO_2 \\ | \\ H \end{array}$$

sec-nitroalkane

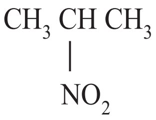
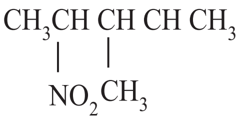
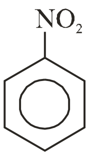
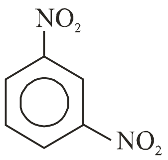


$$\begin{array}{c} R \\ | \\ R-C-NO_2 \\ | \\ R \end{array}$$

tert-nitroalkane

28.4.1 IUPAC Nomenclature of Nitro Compounds

According to IUPAC system, nitro compounds are named by prefixing the word nitro before the name of the parent hydrocarbon. The number of nitro groups and their positions are suitably indicated as shown in some examples given below.

Compound	**IUPAC Name**
CH_3-NO_2	Nitromethane
$CH_3CH_2-NO_2$	Nitroethane
 $\begin{array}{l} CH_3\,CH\,CH_3 \\ \quad\;\, | \\ \quad\; NO_2 \end{array}$	2-Nitropropane
 $\begin{array}{l} CH_3CH\,CH\,CH\,CH_3 \\ \quad\;\;\; | \quad\; | \\ \quad\; NO_2\,CH_3 \end{array}$	2-Nitro - 3- methylbutane
	Nitrobenzene
	1, 3 - Dinitrobenzene (*m* - Dinitrobenzene)

28.4.2 Preparation of Nitro Compounds

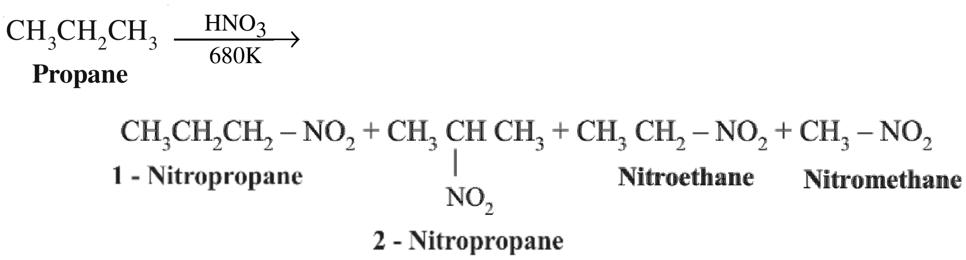
(i) ***From alkyl halides :*** Nitroalkanes are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite. In this reaction, a small amount of isomeric alkyl nitrites (R–O–N = O) is also obtained.

$$R - X + AgNO_2 \longrightarrow R - NO_2 \ + \ AgX$$

For example. bromoethane on reaction with silver nitrite gives nitroethane.

$$\underset{\textbf{Bromoethane}}{CH_3CH_2Br} + AgNO_2 \longrightarrow \underset{\textbf{Nitroethane}}{CH_3CH_2NO_2} + AgBr$$

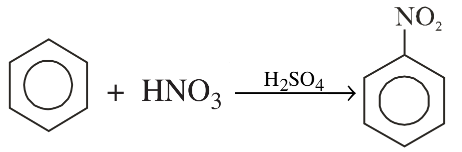
(ii) ***By nitration of alkanes :*** Nitroalkanes can also be prepared by the nitration of alkanes in vapour phase. For this reaction, a mixture of the alkane and nitric acid is passed through a metal tube at about 680 K. This reaction always yields a mixture of compounds due to the cleavage of the starting alkane. For example, propane on nitration gives a mixture of following compounds.



$$\underset{\textbf{Propane}}{CH_3CH_2CH_3} \xrightarrow[680K]{HNO_3}$$

$$\underset{\textbf{1 - Nitropropane}}{CH_3CH_2CH_2 - NO_2} + \underset{\textbf{2 - Nitropropane}}{CH_3\underset{\substack{| \\ NO_2}}{CH}CH_3} + \underset{\textbf{Nitroethane}}{CH_3CH_2 - NO_2} + \underset{\textbf{Nitromethane}}{CH_3 - NO_2}$$

(iii) ***By nitration of aromatic compounds :*** Aromatic nitro compounds are almost always prepared by direct nitration. For example, nitration of benzene gives nitrobenzene. The reaction is generally carried out with a mixture of concentrated nitric acid and concentrated sulphuric acid.



Benzene **Nitrobenzene**

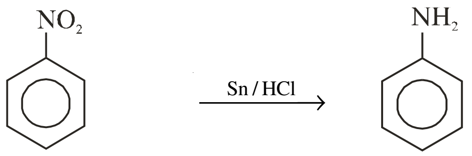
28.4.3 Physical Properties of Nitro Compounds

Nitroalkanes are colourless oily liquids in the pure state. They have pleasant smell. They possess higher boiling points than the corresponding alkanes because of their polar nature. Amongst the aromatic nitro compounds, nitrobenzene is a yellow liquid with the smell of bitter almonds. Most other aromatic nitro compounds are yellow crystalline solids. All the nitro compounds are heavier than water and insoluble in it. They are, however, soluble in organic solvents like alcohol, ether, benzene, chloroform etc.

28.4.4 Chemical Properties of Nitro Compounds

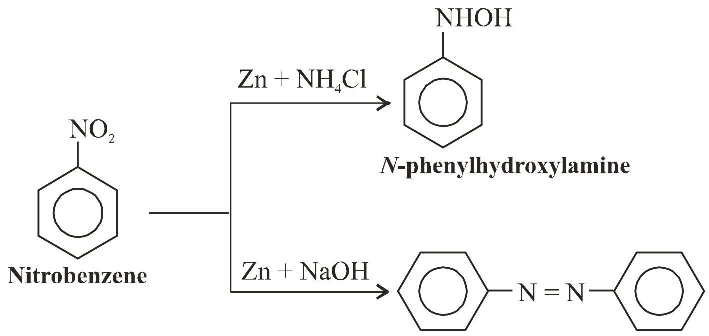
(i) ***Reduction :*** One of the important reactions of nitro compounds is reduction. Nitro compounds can be readily reduced to primary amines by a variety of reducing agents. For example, (a) hydrogen in presence of catalyst like nickel or platinum (b) a metal like tin or iron in presence of hydrochloric acid and (c) lithium aluminium hydride. Reduction of nitroethane and nitrobenzene provides ethanamine and aniline, respectively.

$$\underset{\textbf{Nitroethane}}{CH_3CH_2-NO_2} + 3H_2 \xrightarrow{Ni} \underset{\textbf{Ethanamine}}{CH_3CH_2-NH_2} + 2H_2O$$



Nitrobenzene **Aniline**

Nitrobenzene on reduction in neutral medium, using zinc dust and ammonium chloride yields *N*-phenylhydroxylamine whereas its reduction in alkaline medium using zinc and sodium hydroxide yields azobenzene.



***N*-phenylhydroxylamine**

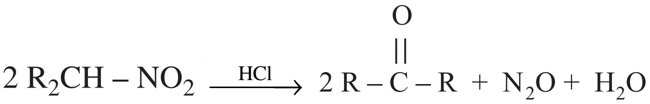
Nitrobenzene

Azobenzene

(ii) ***Hydrolysis :*** Primary nitroalkanes on reaction with dilute hydrochloric acid or sulphuric acid undergo hydrolysis to produce carboxylic acids and hydroxylamine.

$$RCH_2-NO_2 + H_2O \xrightarrow{HCl} \underset{\textbf{A carboxylic acid}}{R-COOH} + \underset{\textbf{Hydroxylamine}}{NH_2OH}$$

Secondary nitroalkanes on hydrolysis form ketones.

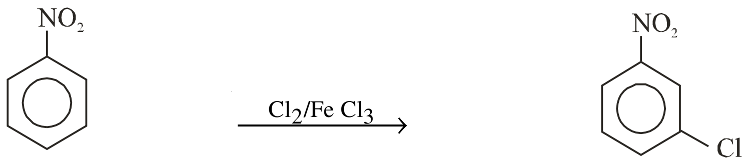


$$2\,R_2CH-NO_2 \xrightarrow{HCl} 2\,\underset{\textbf{ketone}}{R-\overset{\overset{\displaystyle O}{||}}{C}-R}} + N_2O + H_2O$$

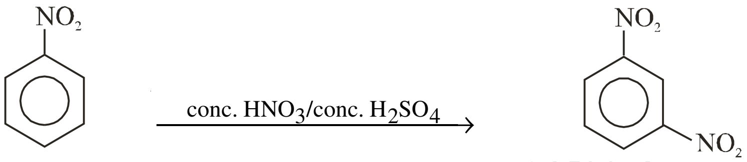
(iii) ***Thermal decomposition :*** Nitroalkanes decompose with explosion on heating. Advantage is taken of this reaction in the commercial use of nitroalkanes as explosives. It is due to the formation of large volume of gaseous products on heating which produce high pressure.

$$2\,CH_3NO_2 \xrightarrow{\Delta} N_2 + 2\,CO_2 + 3\,H_2$$

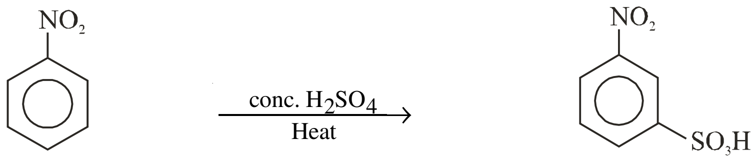
(iv) ***Ring substitution in aromatic nitro compounds*** : You know that $-NO_2$ group is a deactivating and *meta* - directing group for electrophilic substitution reactions. It is due to the electron withdrawing tendency of $-NO_2$ group. Thus, nitrobenzene on halogenation, nitration or sulphonation gives the *meta*-substituted products as shown below.



Nitrobenzene **3-Chloronitrobenzene**



Nitrobenzene **1, 3-Dinitrobenzene**



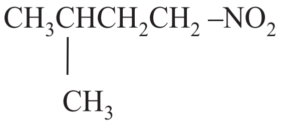
Nitrobenzene **3-Nitrobenzenesulphonic acid**

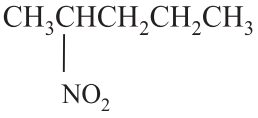
28.4.5 Uses of Nitro Compounds

1. Nitroalkanes are used as solvents for rubber, cellulose acetate etc.
2. They are used as intermediates in the industrial production of explosives, detergents, medicines, amines etc.
3. Nitro compounds are also used as fuel in small engines and rockets.

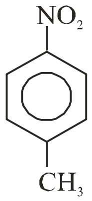
INTEXT QUESTIONS 28.4

1. Write IUPAC names of the following :

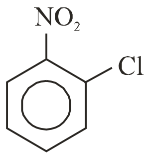
(a) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2-NO_2$

(b) 
$CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_2CH_2CH_3$

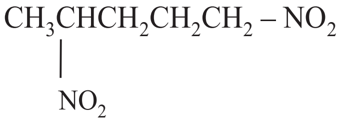
(c)



(d)



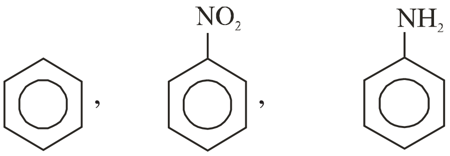
(e)



$CH_3\underset{\substack{| \\ NO_2}}{CH}CH_2CH_2CH_2-NO_2$

2. Write the product formed when 1,3 - dinitrobenzene is treated with tin and hydrochloric acid.

3. Arrange the following compounds in increasing order of their reactivity towards halogenation.



4. Which reaction of nitroalkanes makes them suitable to be used as rocket fuel?

WHAT YOU HAVE LEARNT

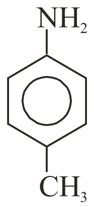
- Amines are considered as derivatives of ammonia. They are classified as primary, secondary or tertiary based on how many alkyl groups have replaced the hydrogen atoms of ammonia.
- Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines alongwith quaternary ammonium salts.
- Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms.
- In Hofmann bromamide reaction, the amine formed has one carbon less than the starting amide.
- Both aliphatic and aromatic amines are basic in nature. But aromatic amines are less basic and aliphatic amines are more basic than ammonia. An aliphatic secondary amine is more basic than primary and tertiary amines.
- Primary amines can be differentiated from secondary and tertiary amines by carbylamine reaction.
- Aliphatic primary amines undergo diazotisation to form alcohols whereas aromatic primary amines form diazonium salts.

- The amino group (–NH_2) is an activating and *ortho-, para*-directing group towards the electrophilic aromatic substitution reactions.
- Nitroalkanes are obtained by the reaction of alkyl halides with alcoholic silver nitrite.
- Nitrobenzene is obtained by the direct nitration of benzene with conc. HNO_3 in the presence of conc. H_2SO_4.
- Primary nitroalkanes are hydrolysed in acidic medium to give carboxylic acids whereas secondary nitroalkanes give ketones.
- All nitro compounds are reduced into amino compounds by (i) hydrogen in presence of catalyst or (ii) tin or iron in presence of hydrochloric acid.
- Nitro group is deactivating and *meta*-directing group towards electrophilic aromatic substitution reactions.

TERMINAL EXERCISE

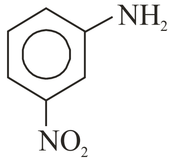
1. Write the structural formula of the following compounds :
   (i) 2-Methylpropan - 2-amine
   (ii) Butan - 2-amine
   (iii) *N* - Ethyl - *N* - methylbutan - 1- amine
   (iv) 2 - Methyl - 2-nitropropane
   (v) 4 - Nitrotoluene
2. What do you understand by diazotisation? Write the product of following reactions.

(i)



$\xrightarrow[273-278\ K]{NaNO_2\,/\,HCl}$

(ii)

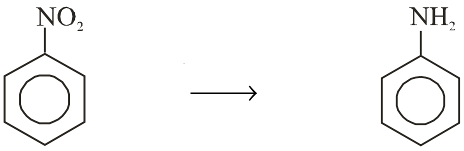


$\xrightarrow[273-278\ K]{NaNO_2\,/\,HCl}$

(iii) $CH_3–CH_2–CH_2–NH_2 \xrightarrow[273-278\ K]{NaNO_2\,/\,HCl}$

3. How will you prepare butan-1-amine starting from a suitable amide? Name the reaction involved.

4. What different reagents can be used for the following conversion?



5. Arrange the following amines in increasing order of their basicities :

Ethanamine, *N*-Methylethanamine, Aniline

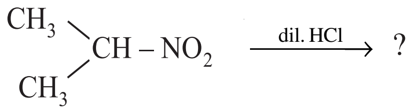
6. How will you prepare sulphanilic acid from nitrobenzene?

7. What happens when ethanamine is treated with excess of chloroethane?

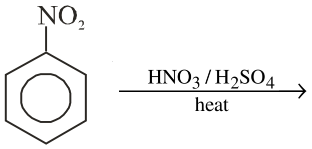
8. Write the reaction sequence to convert nitromethane into ethanamine.

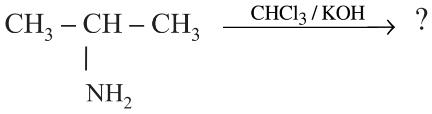
9. How will you prepare *para*-bromoaniline from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.

10. Complete the following reactions :

(i) 

(ii) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2 / KOH} ? \xrightarrow[273-278\ K]{NaNO_2 / HCl} ?$

(iii) 

(iv) 

$$\underset{\displaystyle NH_2}{\underset{|}{CH_3 - CH - CH_3}} \xrightarrow{CHCl_3 / KOH} ?$$

(v) $CH_3CH_2CH_2– Br + AgNO_2 \xrightarrow{alcohol} ?$

ANSWERS TO INTEXT QUESTIONS

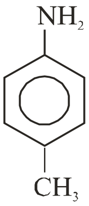
28.1

1. (i) Primary amine (ii) Secondary amine
(iii) Secondary amine (iv) Tertiary amine
(v) Primary amine (vi) Quaternary ammonium salt

2. (i) Butan-1-amine
   (ii) *N*, *N*-Dimethylethanamine
   (iii) *N*-Methylbutan-1- amine
   (iv) Butan-2-amine
   (v) 3-Bromoaniline
   (vi) 2-Ethylaniline

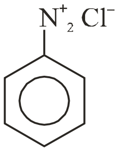
28.2

1. (i)

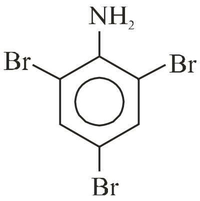


(ii) CH_3CH_2OH

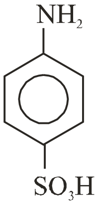
(iii)



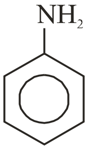
(iv)



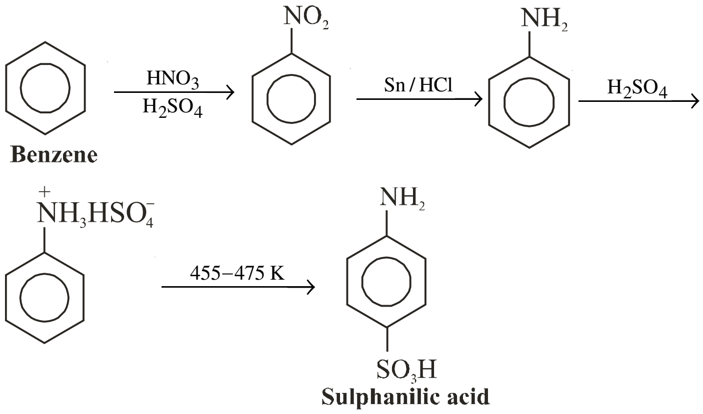
(v)



(vi)

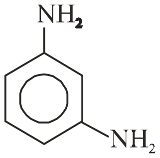


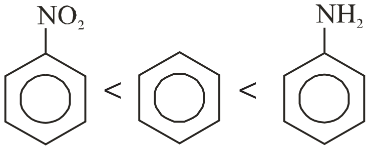
2. Aniline is very reactive towards bromination because the $–NH_2$ group is a highly activating group.
3. Carbylamine test.
4. No
5.



28.3

1. (i) 3-Methyl-1-nitrobutane
   (ii) 2-Nitropentane
   (iii) 4- Nitrotoluene
   (iv) 2-Chloronitrobenzene
   (v) 1,4 –Dinitropentane

2. 

3. 

4. Nitroalkanes decompose on heating and produce large volume of gases. The formation of gaseous products at high pressure produces the thrust which is necessary for the movement of rocket.

29

BIOMOLECULES

You are aware that our body, plants and other animals are made up of many chemical substances. There are certain complex organic molecules which form the basis of life. These build up living organisms and are also required for their growth and maintenance. Such molecules are called **biomolecules.** The main classes of biomolecules are carbohydrates, proteins, lipids, nucleic acids, enzymes, hormones etc. In this lesson, you will study about the structures and functions of some important biomolecules.

OBJECTIVES

After reading this lesson you will be able to :

- discuss different types of biomolecules;
- describe the important structural features of biomolecules;
- classify carbohydrates, proteins and lipids on the basis of their structure and functions;
- give the composition of proteins and nucleic acids;
- explain the difference between DNA and RNA;
- differentiate between oils and fats;
- explain the action of enzymes and their characteristic features and
- discuss important hormones and their importance
- name some important vitamins and give their deficiency symptoms.
- list the functions of biomolecules in biological systems.

29.1 CARBOHYDRATES

Carbohydrates form a very large group of naturally occurring organic compounds which play a vital role in daily life. They are produced in plants by the process of

photosynthesis. The most common carbohydrates are glucose, fructose, sucrose, starch, cellulose etc. Chemically, the carbohydrates may be defined as **polyhydroxy aldehydes** or **ketones** or **substances which give such molecules on hydrolysis**. Many carbohydrates are sweet in taste and all sweet carbohydrates are called as **sugars**. The chemical name of the most commonly used sugar in our homes is sucrose.

29.1.1 Classification of Carbohydrates

Carbohydrates are classified into three groups depending upon their behaviour on hydrolysis.

(i) **Monosaccharides**: A polyhydroxy aldehyde or ketone which cannot be hydrolysed further to a smaller molecule containing these functional groups, is known as a *monosaccharide*. About 20 monosaccharides occur in nature and glucose is the most common amongst them.

Monosaccharides are further classified on the basis of the number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an **aldose** and if it contains a keto group, it is known as a **ketose**. The number of carbon atoms present is also included while classfying the compound as is evident from the examples given in Table 29.1. Name of some naturally occuring monosaccharides are given in brackets.

Table 29.1 Classification of monosaccharides

No. of carbon atoms	Type of monosaccharide	
present	Aldose	Ketose
3	Aldotriose (Glyceraldehyde	Ketotriose
4	Aldopentose ((Xylose)	Ketopentose
5	Aldotetrose (Erythrose)	Ketotetrose
6	Aldohexose (Glucose)	Ketohexose
7	Aldoheptose	Ketoheptose

(ii) **Disacccharides:** Carbohydrates which give two monosaccharide molecules on hydrolysis are called disaccharides e.g. sucrose, maltose, lactose etc.

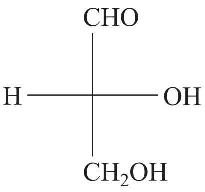
(iii) **Oligosacharides:** Carbohydrates that yield 2–10 molecules of monosascharides are called **oligosaccharides.**

(iv) **Polysaccharides:** Carbohydrates which yield a large number of monosaccharide units on hydrolysis e.g. starch, glycogen, cellulose etc.

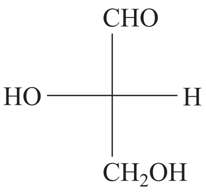
29.1.2 Structure of Monosaccharides

Although a large number of monosaccharides are found in nature.

D-or L-before the name of monosaccharides indicates the configuration of particular stereoisomer. Various stereoisomers are assigned relative configurations as D– or L –. This system of assigning the relative configuration refers to their relation with the glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and hence exists in two enantiomeric forms as shown below.

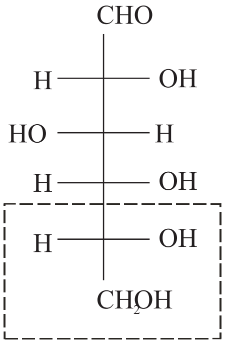


D-(+) –glyceraldehyde

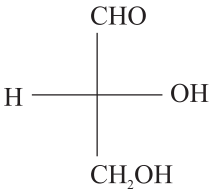


L-(–) –glyceraldehyde

All those compounds which can be correlated to (+) -glyceraldehyde are said to have D-configuration and those can be correlated to (–) -glyceraldehyde are said to have L–configuration. In monosaccharides, it is the lowest asymmetric carbon atom (shown in the box) by which the correlation is made. As in (+) glucose, the lowest asymmetric carbon atom has –OH group on the right side which matches with (+) glyceraldehyde; hence, it is assigned D-configuration.



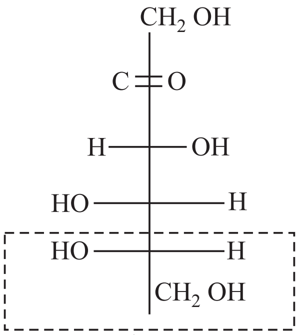
(+) – glucose or D-glucose



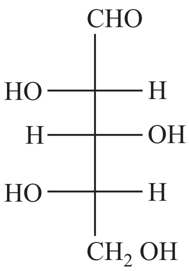
(+) – glyceraldehyde or D-glyceraldehyde

L-Configuration Examples

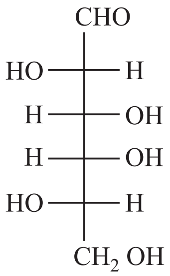
Some example of molecules having L-configuration are shown below:



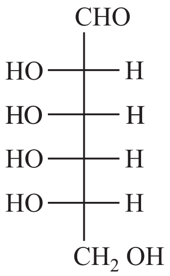
L - fructose



L - Xylose



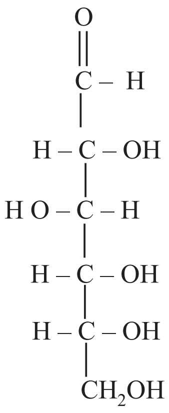
L - Galactose



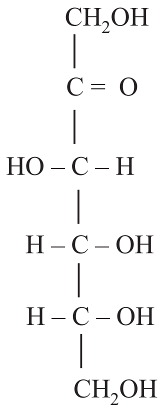
L - Allose

We will confine our discussion here to four of them only viz. D-glucose, D-fructose,D-ribose and 2-deoxy-D-ribose.

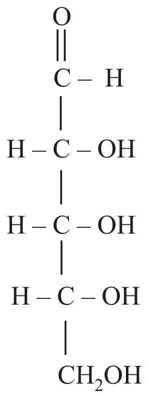
D-Glucose (an aldohexose) is the monomer for many other carbohydrates. Alone or in combination, glucose is probably the most abundant organic compound on the earth. D-Fructose (a ketohexose) is a sugar that is found with glucose in honey and fruit juices. D-Ribose (an aldopentose) is found in ribonucleic acids (RNA) while. 2-Deoxy-D-ribose is an important constituent of the deoxyribonucleic acids(DNA). Here, the prefix 2-Deoxy indicates that it lacks oxygen at carbon no. 2.



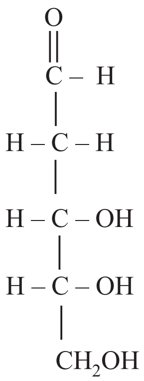
D-Glucose



D-Fructose



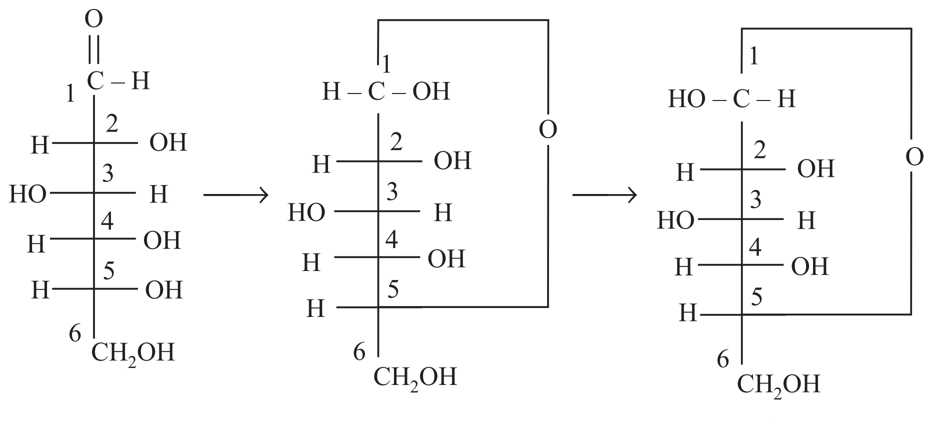
D-Ribose



2-Deoxy-D-ribose

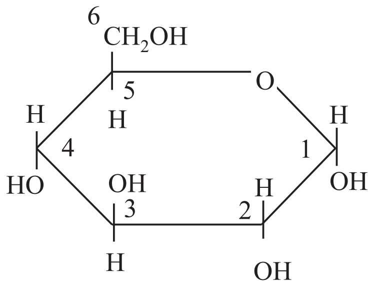
These monosaccharides generally exist as cyclic compounds in nature. A ring is formed by a reaction between the carbonyl group and one of the hydroxyl groups present in the molecule. Glucose preferentially forms the six membered ring which can be in two different isomeric forms called α- and β-forms (shown below as I and II). The two forms differ only in the arrangement of the hydroxyl group at carbon No.1. Such isomers are called **anomers**.

Formation of these cyclic structures (I and II) from the open chain structure can be shown as follows.

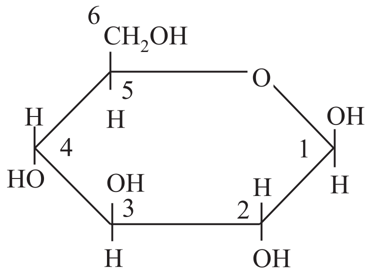


(I) α – D – glucose (II) β – D –glucose

The cyclic structures I and II are more appropriately represented as Ia and IIa.

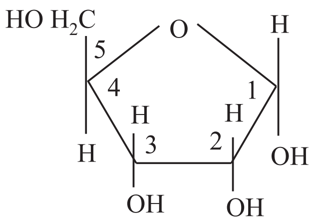


(Ia)

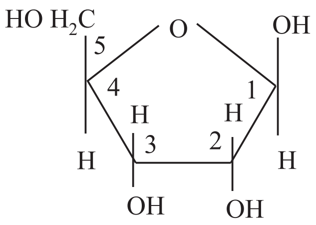


(IIa)

The α- and β-forms of other sugars also exist in the cyclic form. D-Ribose forms a five membered ring structure as shown below :



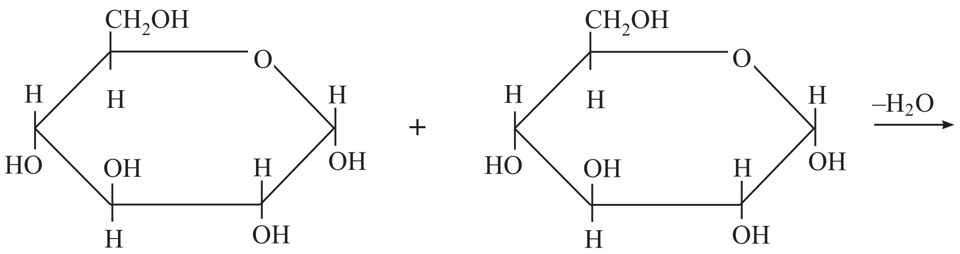
α – D – ribose



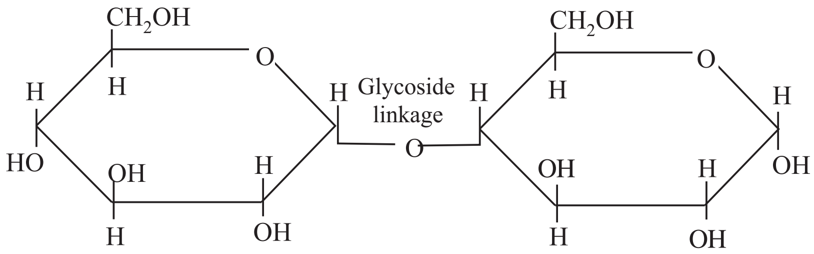
β – D – ribose

29.1.3 Structure of Di-Saccharides, Oligo Saccharides and Polysaccharides

Disaccharides are formed by the condensation of two monosaccharide molecules. These monosaccharides join together by the loss of a water molecule between one hydroxyl group on each monosaccharide. Such a linkage, which joins the monosaccharide units together is called **glycoside linkage**. If two α-glucose molecules are joined together, the disaccharide maltose is formed.

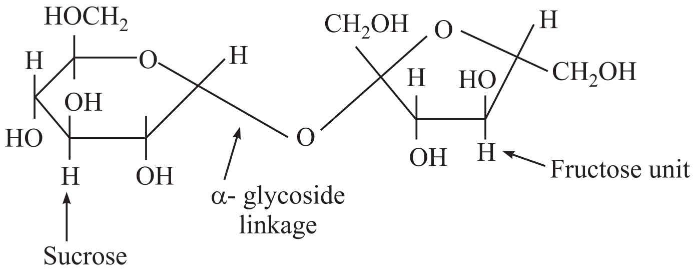


2 molecules of α – glucose

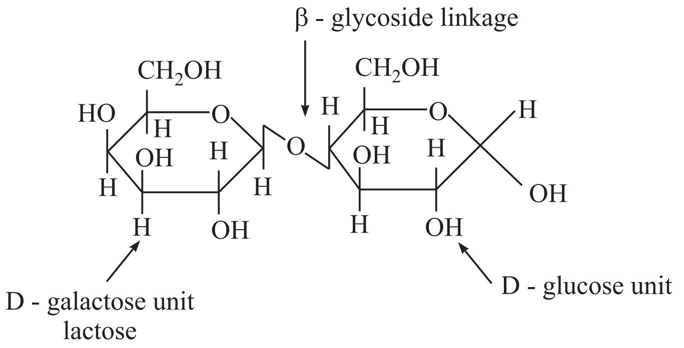


Maltose

Similarly, sucrose (the common sugar) consists of one molecule of glucose and one molecule of fructose joined together.



Lactose(or milk sugar) is found in milk and is formed by joining of one molecule of glucose and one molecule of galactose.



If a large number of monosaccharide units are joined together, we get polysaccharides. These are the most common carbohydrates found in nature. They have mainly one of the following two functions- either as food materials or as structural materials. Starch is the main food storage polysaccharide of plants. It is a polymer of α-glucose and consists of two types of chains- known as **amylose** and **amylopectin**.

Amylose is a water soluble fraction of starch and is a linear polymer of α-D-glucose. On the other hand, amylopectin is a water insoluble fraction and consists of branched chain of α-D-glucose.

Cellulose is another natural polysaccharide which is the main component of wood and other plant materials. It consists of long chain of β-D-glucose molecules.

Glycogen

The carbohydrates are stored in animal body as glycogen and its structure is similar to amylopectin.

It is a polysaccharide containing the α-D-glucose monosaccharide and does the same energy storage function in animals which the starch does in plants. The carbohydrates which are not needed immediately by the body are converted by the body to glycogen for long term storage. Glycogen molecules are larger than those of amylopectin and are having more branched structure.

29.1.4 Biological Importance of Carbohydrates

(i) Carbohydrates act as storage molecules. For example they are stored as starch in plants and as glycogen in animals.

(ii) D-Ribose and 2-deoxy-D-ribose are the constituents of RNA and DNA, respectively.

(iii) Cell walls of bacteria and plants are made up of cellulose. It may be of interest to note that human digestive system does not have the enzymes required for the digestion of cellulose but some animals do have such enzymes.

(iv) Some carbohydrates are also linked to many proteins and lipids. These molecules are known as glycoproteins and glycolipids, respectively. These molecules perform very specific functions in organisms.

INTEXT QUESTIONS 29.1

1. Name three constituents of your diet which provide carbohydrates.
2. How are carbohydrates produced in nature?

3. What are the hydrolysis products of starch and sucrose?
4. Write the linear and ring forms of D-glucose.

29.2 PROTEINS

Proteins are the most abundant macromolecules in living cells. The name protein is derived from the Greek word **'proteios'** meaning 'of prime importance'. These are high molecular mass complex amino acids. You will study about amino acids in the next section. Proteins are most essential class of biomolecules because they play the most important role in all biological processes. A living system contains thousands of different proteins for its various functions. In our every day food pulses, eggs, meat and milk are rich sources of proteins and are must for a balanced diet.

29.2.1 Classification of Proteins

Proteins are classified on the basis of their chemical composition, shape and solubility into two major categories as discussed below.

(i) **Simple proteins:** Simple proteins are those which, on hydrolysis, give only amino acids. According to their solubility, the simple proteins are further divided into two major groups **fibrous** and **globular proteins**.

(a) **Fibrous Proteins:** These are water insoluble animal proteins eg. collagen (major protein of connective tissues), elastins (protein of arteries and elastic tissues), keratins (proteins of hair, wool, and nails) are good examples of fibrous proteins. Molecules of fibrous proteins are generally long and thread like.

(b) **Globular Proteins:** These proteins are generally soluble in water, acids, bases or alcohol. Some examples of globular proteins are albumin of eggs, globulin (present in serum), and haemoglobin. Molecules of globular proteins are folded into compact units which are spherical in shape.

(ii) **Conjugated proteins:** Conjugated proteins are complex proteins which on hydrolysis yield not only amino acids but also other organic or inorganic components. The non-amino acid portion of a conjugated protein is called **prosthetic group**.

Unlike simple proteins, conjugated proteins are classified on the basis of the chemical nature of their prosthetic groups. These are

a. Nucleoproteins (protein + nucleic acid)

b. Mucoproteins and glycoproteins (protein+ carbohydrates)

c. Chromoproteins (proteins + a coloured pigment)

d. Lipoproteins (proteins + lipid)

e. Metalloproteins (metal binding proteins combined with iron, copper or zinc)

f. Phosphoproteins (proteins attached with a phosphoric acid group).

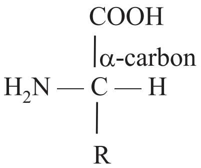
Proteins can also be classified on the basis of functions they perform, as summarized in table 29.2.

Table 29.2 : Classification of proteins according to their biological functions

Class	Functions	Examples
1. Transport Proteins	Transport of oxygen, glucose and other nutrients	Haemoglobin Lipoproteins
2. Nutrient and storage Proteins	Store proteins required for the growth of embryo	Gliadin(wheat) Ovalbumin(egg) Casein (milk)
3. Structural Protiens	Give biological structures, strength or protection	Keratin(Hair, nails,etc.) collagen(cartilage)
4. Defence Proteins	Defend organisms against invasion by other species	Antibodies Snake venoms
5. Enzymes	Act as catalysts in biochemical reactions	Trypsin,Pepsin
6. Regulatory Proteins	Regulate cellular or physiological activity	Insulin

29.2.2 Structure of Proteins

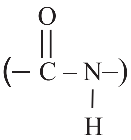
Protein molecules are polymers of different sizes and shapes with different physical and chemical properties. The monomer units for proteins are amino acids. All the amino acids that are found in proteins have an amino group(-NH_2) on the carbon atom adjacent to carbonyl group, hence are called α-amino acids. The general formula of α-amino acids is shown below.

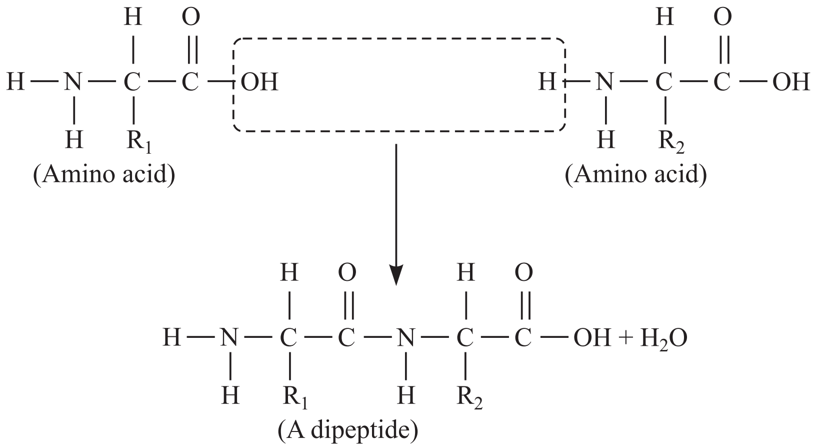


$$H_2N-\overset{\overset{\displaystyle COOH}{|\ \alpha\text{-carbon}}}{\underset{\underset{\displaystyle R}{|}}{C}}-H$$

All proteins found in nature are the polymers of about twenty (20) different α-amino acids and all of these have L-configuration. Out of these ten (10) amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called **essential amino acids**.

All proteins have one common structural feature that their amino acids are connected to one another by *peptide linkages*. By a peptide linkage we mean an

amide  $(-\overset{\overset{\displaystyle O}{||}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-)$ bond formed when the carboxyl group of one amino acid molecule reacts with the α-amino group of another. In the process, a molecule of water is given off. The product of the reaction is called a *peptide* or more precisely a dipeptide because it is made by combining two amino acids, as shown below:



If a third amino acid is joined to a **dipeptide** in the same manner, the product is a **tripeptide**. Thus, a tripeptide contains three amino acids linked by two peptide linkages. Similar combinations of four, five, six amino acids give a **tetrapeptide**, a **pentapeptide**, a **hexapeptide**, respectively. Peptides formed by the combination of more than ten amino acid units are called **polypeptides**. **Proteins are polypeptides** formed by the combination of **large number of amino acid units**. There is no clear line of demarcation between polypeptides and proteins. For example insulin, although it contains only 51 amino acids, is generally considered a small protein.

The amino acid unit with the free amino group is known as the ***N***-terminal residue and the one with the free carboxyl group is called the ***C***-terminal residue. By convention, the structure of peptide or proteins written with the ***N***-terminal residue on the left and the ***C***-terminal on the right.

The actual structure of a protein can be discussed at four different levels.

(i) **Primary structure**: Information regarding the sequence of amino acids in a protein chain is called its primary structure. The primary structure of a protein determines its functions and is critical to its biological activity.

(ii) **Secondary structure**: The secondary structure arises due to the regular folding of the polypeptide chain due to hydrogen bonding between $-\underset{\underset{\text{O}}{\|}}{\text{C}}-$ and >N – H group. Two types of secondary structures have been reported. These are – α helix (Fig. 29.1) when the chain coils up and β-pleated sheet (Fig. 29.2) when hydrogen bonds are formed between the chains.

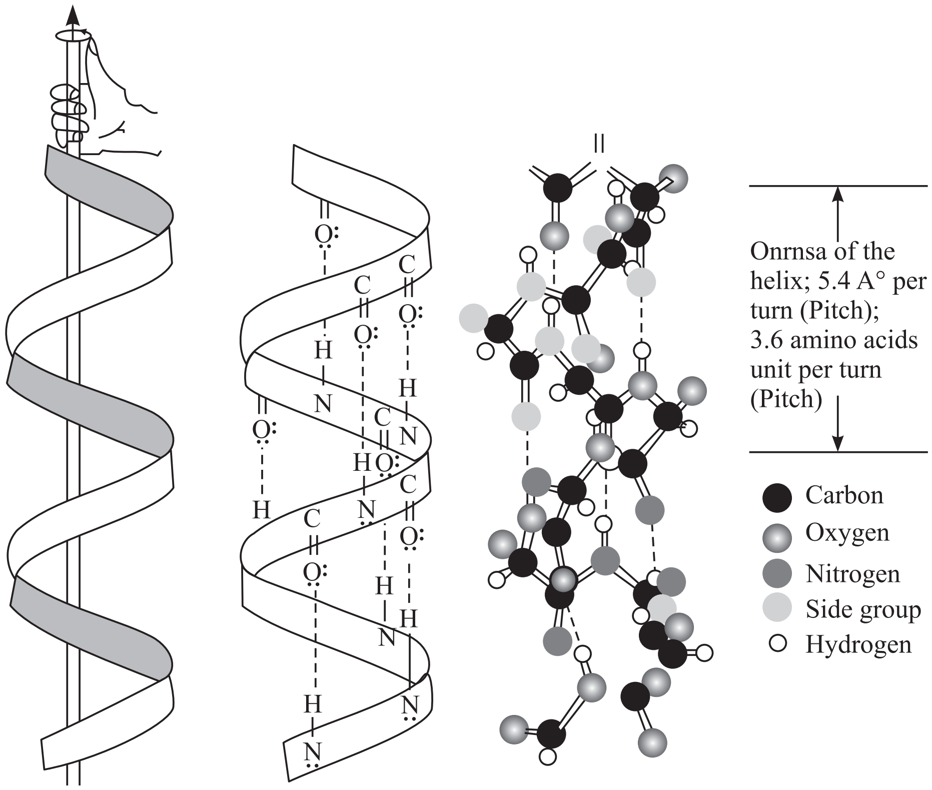
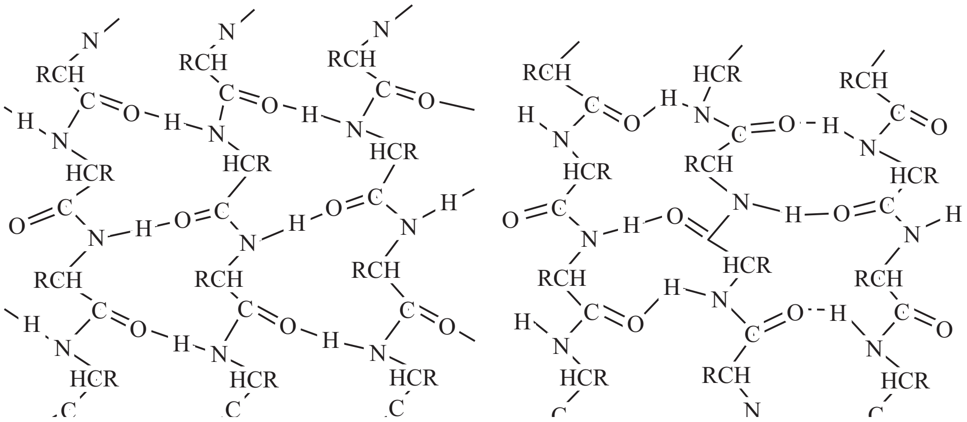


Fig. 29.1 : *The a-helix structure of protein*



Parallel β-Conformation **Antiparallel β-Conformation**

Fig. 29.2 : *The β-pleated-sheet structure of protein*

(iii) Tertiary structure: It is the three-dimensional structure of proteins. It arises due to folding and superimposition of various a-helical chains or b-plated sheets. For example Fig. 29.3 represents the tertiary structure for the protein myoglobin.

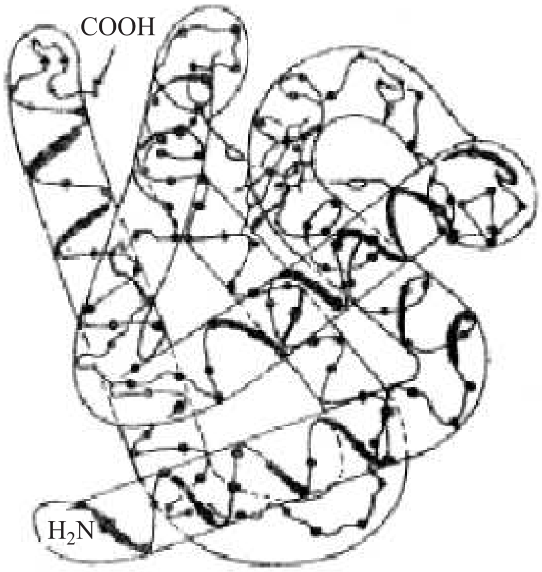


Fig. 29.3 : *Structure of myoglobin*

(iv) **Quaternary structure:** The quaternary structure refers to the way in which simple protein chains associate with each other resulting in the formation of a complex protein.

By different modes of bonding in secondary and tertiary structural levels a protein molecule appears to have a unique three-dimensional structure.

29.2.3 Denaturation

One of the great difficulties in the study of the structure of proteins is that if the normal environment of a living protein molecule is changed even slightly, such as by a change in pH or in temperature, the hydrogen bonds are disturbed and broken. When attractions between and within protein molecules are destroyed, the chains separate from each other, globules unfold and helices uncoil. We say that the protein has been denatured.

Denaturation is seen in our daily life in many forms. The curdling of milk is caused by bacteria in the milk which produce lactic acid. The change in *p*H caused by the lactic acid causes denaturation, coagulation and precipitation of the milk proteins. Similarly, the boiling of an egg causes precipitation of the albumin proteins in the egg white. Some proteins (such as those in skin, fingernails, and the stomach lining) are extremely resistant to denaturation.

29.2.4 Biological Importance of Proteins

(i) Proteins are structural components of cells.

(ii) The biochemical catalysts known as enzymes are proteins.

(iii) The proteins known as immunoglobins serve in defence against infections.

(iv) Many hormones, such as insulin and glucagon are proteins.

(v) Proteins participate in growth and repair mechanism of body tissues.

(vi) A protein called fibrinogen helps to stop bleeding.

(vii) Oxygen is transported to different tissues from blood by haemoglobin which is a protein attached to haeme part.

INTEXT QUESTIONS 29.2

1. What do you understand by primary structure of protein ?
2. What do you mean by a peptide bond?
3. Write the general structural formula of an a-amino acid?
4. What are conjugated proteins ?

29.3 LIPIDS

The lipids include a large number of biomolecules of different types. The term lipid originated from a Greek word '*Lipos*' meaning fat. In general, those constituents of the cell which are insoluble in water and soluble in organic solvents of low polarity (such as chloroform, ether, benzene etc.) are termed as *lipids*. Lipids perform a variety of biological functions.

29.3.1 Classification of Lipids

Lipids are classified into three broad categories on the basis of their molecular structure and the hydrolysis products.

(i) Simple Lipids: Those lipids which are esters and yield fatty acids and alcohols upon hydrolysis are called simple lipids. They include oils, fats and waxes.

(ii) Compound Lipids: Compound lipids are esters of fatty acids and alcohol with additional compounds like phosphoric acid, sugars, proteins etc.

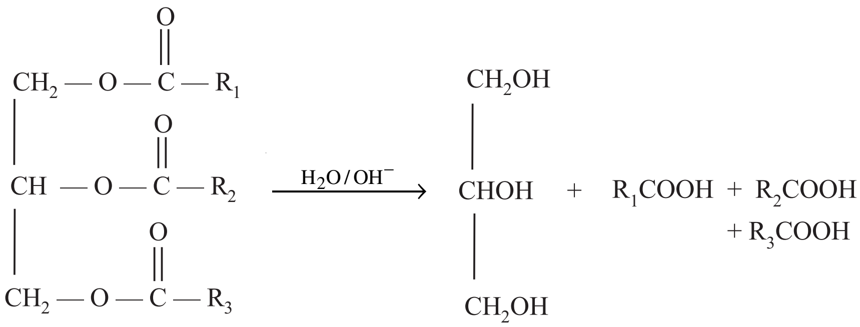
(iii) Derived Lipids: Compounds which are formed from oils, fats etc. during metabolism. They include steroids and some fat soluble vitamins.

29.3.2 Structure of lipids

The structure of all three types of lipids are breifly discussed below.

(i) Simple Lipids

The simple lipids are esters. They are subdivided into two groups, depending on the nature of the alcohol component. Fats and oils are triglycerides, i.e. they are the esters of glycerol with three molecules of long chain fatty acids. Variations in the properties of fats and oils is due to the presence of different acids. These long chain acids may vary in the number of carbon atoms (between C_{12} to C_{26}) and may or may not contain double bonds. On hydrolysis of a triglyceride molecule, one molecule of glycerol and three molecules of higher fatty acids are obtained as shown below:

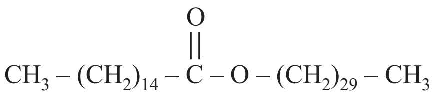


(Oil or fat) **Glycerol** **(Fatty acids)**

By definition, a fat is that triglyceride which is solid or semisolid at room temperature and an oil is the one that is liquid at room temperature. Saturated fatty acids form higher melting triglycerides than unsaturated fatty acids. The saturated triglycerides tend to be solid fats, while the unsaturated triglycerides tend to be oils. The double bonds in an unsaturated triglyceride are easily hydrogenated to give a saturated product, and in this way an oil may be converted into a fat. Hydrogenation is used in the manufacture of *vanaspati ghee* from oils.

Fats and oils are found in both plants and animals. Our body can produce fats from carbohydrates. This is one method that the body has for storing the energy from unused carbohydrates. The vegetable oils are found primarily in the seeds of plants.

The second type of simple lipids are waxes. They are the esters of fatty acids with long chain monohydroxy alcohols 26 to 34 carbons atoms. Waxes are widespread in nature and occur usually as mixtures. They form a protective coating on the surfaces of animals and plants. Some insects also secrete waxes. The main constitutent of bees wax obtained from the honey comb of bees is myricyl palmitate:



$$CH_3-(CH_2)_{14}-\overset{\overset{\displaystyle O}{||}}{C}-O-(CH_2)_{29}-CH_3$$

myricyl palmitate

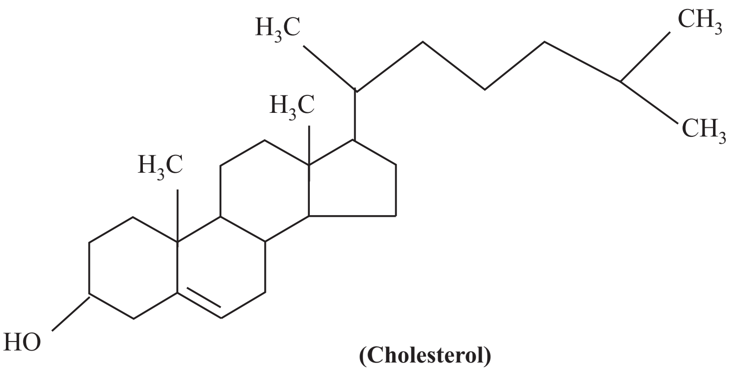
The waxes discussed above should not be confused with household paraffin wax which is a mixture of straight chain hydrocarbons.

(ii) Compound Lipids

Compound lipids on hydrolysis yield some other substances in addition to an alcohol and fatty acids. The first type of such lipids are called phospholipids, because they are the triglycerides in which two molecules of fatty acids and one molecule of phosphoric acid are present. Glycolipids contain a sugar molecule in addition to fatty acid attached to an alcohol.

(iii) Derived Lipids

Steroids are another class of lipids which are formed in our body during metabolism. These are the compounds with a distinctive ring system that provides the structural backbone for many of our hormones. Steroids do not contain ester groups and hence cannot be hydrolysed. Cholesterol is one of the most widely distributed steroids in animal and human tissues.



(Cholesterol)

Another important group of derived lipids is that of fat-soluble vitamins. This includes vitamins A, D, E and K, whose deficiency causes different diseases.

29.3.3 Biological Importance of Lipids

(i) Fats are main food storage compounds and serve as reservoir of energy.

(ii) Presence of oils or fats is essential for the efficient absorption of fat soluble vitamins A, D, E and K.

(iii) Subcutaneous fats serve as biological insulator against excessive heat loss.

(iv) Phospholipids are the essential component of cell membrane.

(v) Steroids control many biological activities in living organisms.

(vi) Some enzymes require lipid molecules for maximum action.

INTEXT QUESTIONS 29.3

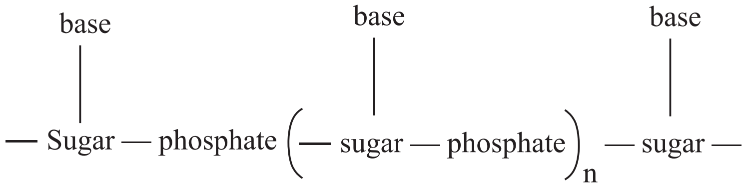
1. What are lipids?
2. What are the products of hydrolysis of an oil?
3. Name two important types of compound lipids.
4. What is the basic difference between fats and oils?

29.4 NUCLEIC ACIDS

Why is a dog a dog and not a cat? Why do some people have blue or brown eyes and not black? From a chemical standpoint, how does the body know what particular type of protein is to be synthesized? How is this information transmitted from one generation to the next? The study of the chemistry of heredity is one of the most fascinating fields of research today. It was recognized in the 19th century that the nucleus of a living cell contains particles responsible for heredity, which were called chromosomes. In more recent years, it has been discovered that chromosomes are composed of nucleic acids. These are named so because they come from the nucleus of the cell and are acidic in nature. Two types of nucleic acids exist which are called DNA (deoxyribonucleic acid) and RNA(ribonucleic acid).They differ in their chemical composition as well as in functions.

29.4.1 Structure of Nucleic Acids

Like all natural molecules, nucleic acids are linear polymeric molecules. They are chain like polymers of thousands of nucleotide units, hence they are also called polynucleotides. A nucleotide consists of three subunits: a nitrogen containing heterocyclic aromatic compound (called base), a pentose sugar and a molecule of phosphoric acid. So a nucleic acid chain is represented as shown below.



$$-\overset{\text{base}}{\overset{|}{\text{Sugar}}}-\text{phosphate}\left(-\overset{\text{base}}{\overset{|}{\text{sugar}}}-\text{phosphate}\right)_n-\overset{\text{base}}{\overset{|}{\text{sugar}}}-$$

In DNA molecules, the sugar moity is 2-deoxyribose, whereas in RNA molecules it is ribose. In DNA, four bases have been found. They are adenine (A), guanine (G), cytosine (C) and thymine (T). The first three of these bases are found in RNA also but the fourth is uracil (U).

The sequence of different nucleotides in DNA is termed as its primary structure. Like proteins, they also have secondary structure. DNA is a double stranded helix. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The hydrogen bonds are specific between pairs of bases that is guanine and cytosine form hydrogen bonds with each other, whereas adenine forms hydrogen bonds with thymine. The two stands are complementary to each other. The overall secondary structure resembles a flexible ladder (Fig. 29.4). This structure for DNA was proposed by James Watson and Francis Crick in 1953. They were honoured with a Nobel Prize in 1962 for this work.

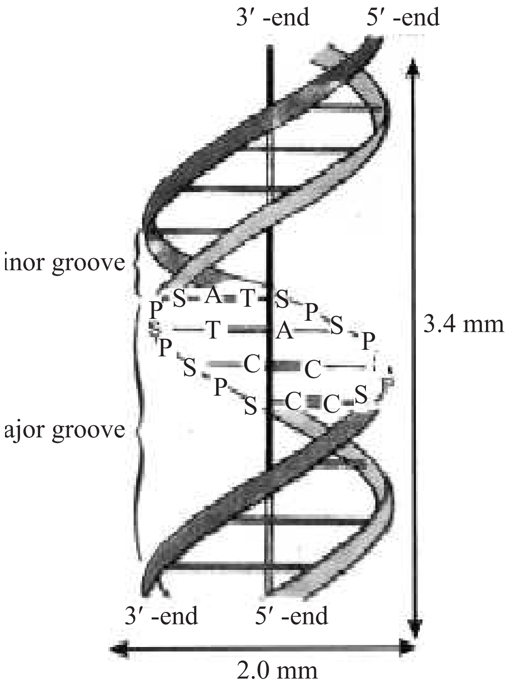


Fig. 31.4 : *Watson and Crick's double helix structure of DNA*

Unlike DNA, RNA is a single stranded molecule, which may fold back on itself to form double helix structure by base pairing in a region where base sequences are complimentary. There are three types of RNA molecules which perform different functions. These are named as messenger RNA(*m*-RNA), ribosomal-RNA(*r*-RNA) and transfer RNA (*t*-RNA)

29.4.2 Biological Functions of Nucleic Acids

A DNA molecule is capable of self duplication during cell divisions. The process starts with the unwinding of the two chains in the parent DNA. As the two strands separate, each can serve as a master copy for the construction of a new partner. This is done by bringing the appropriate nucleotides in place and linking them together. Because the bases must be paired in a specific manner (adenine to thymine and guanine to cytosine), each newly built strand is not identical but complimentary to the old one. Thus when replication is completed, we have two DNA molecules, each identical to the original. Each of the new molecule is a double helix that has one old strand and one new strand to be transmitted to daughter cells (Fig. 3.15).

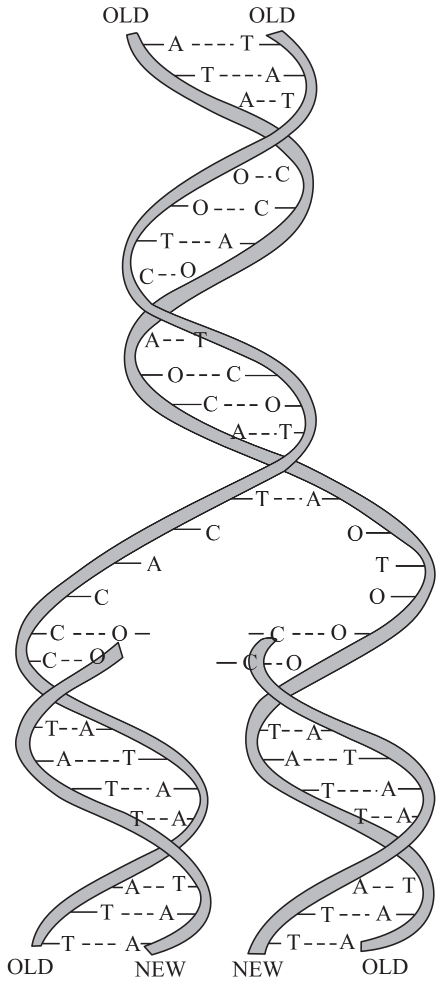


Fig. 29.5 : *Replication of DNA*

Another important function of nucleic acids is the protein synthesis. The specific sequence of bases in DNA represents coded information for the manufacture of specific proteins. In the process, the information from DNA is transmitted to another nucleic acid called messenger RNA, which leaves the nucleus and goes to the cytoplasm of the cell. Messenger RNA acts as template for the incorporation of amino acids in the proper sequence in protein. The amino acids are brought to the messenger RNA in the cell, by transfer RNA. Where they form peptide bonds. In short it can be said that DNA contains the coded message for protein synthesis whereas RNA actually carries out the synthesis of protein.

INTEXT QUESTIONS 29.4

1. What is a nucleotide?
2. Why structure DNA is called a “doublehelix”?
3. Write two main structural differences between DNA and RNA.

29.5 ENZYMES

In a living system, many complex reactions occur at the temperature of about 310K. An example of this is the digestion of food, during which stepwise oxidation to CO_2 and water and energy production. These reactions are carried out under such mild conditions due to presence of certain chemicals which are called enzymes. They act as catalysts for biochemical reactions in living cells. Almost all the enzymes are globular proteins.

Enzymes are very selective and specific for a particular reaction. They are named after the compound or class of compounds upon which they work or after the reaction that they catalyze. The ending of an enzyme name is- **ase**. For example, maltase is an enzyme that specifically catalyzes the hydrolysis of maltose into glucose. Similarly, an esterase is an enzyme which induces hydrolysis of ester linkage.

29.5.1 Mechanism of Enzyme Action

Just like chemical catalysts, enzymes are needed only in small quantities. Similar to the action of chemical catalysts, enzymes lower the energy barrier that reactants must pass over to form the products. For example, hydrolysis of the ester that needs boiling with aqueous NaOH in the laboratory, whereas it occurs at nearly neutral pH and at moderate temperature when catalyzed by an enzyme.

There is a particular enzyme for each substrate and they are said to have lock and key arrangement. It is said that first the substrate molecule binds to the active site of the enzyme which results in the formation of an enzyme-substrate complex. In this complex, the substrate is placed in the right orientation to facilitate a given reaction (Fig.29.6). This complex then breaks to give the molecule of the product and regenerates the enzyme for the next molecule of the substrate.

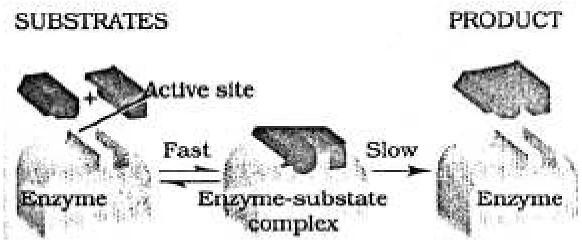


Fig. 29.6 : *Lock and Key arrangement of enzyme action*

29.5.2 Characteristics of Enzymes

(i) Enzymes speed up biochemical reactions up to ten million times compared to the uncatalysed reaction.

(ii) Enzyme catalysed reactions rapidly attain equilibrium.

(iii) Enzymes function in dilute aqueous solutions, at moderate temperatures and at a specific *p*H.

(iv) They are very specific and selective in their action on substrates.

(v) Enzymes are highly efficient and are needed in small amounts only.

(vi) In addition to the protein structure, most active enzymes are associated with some non-protein component required for their activity, called *coenzymes*. For example nicotinamide adenine dinucleotide (NAD) is a coenzyme which is associated with a number of dehydrogenation enzymes.

29.6 HORMONES

Hormones are chemical messengers which are secreted by endocrine glands. They are carried through the blood stream to the target tissues.

Majority of the hormones in humans are steroids. The two important classes of steroid hormones are **sex hormones** and **adrenocortical hormones**. The sex hormones control maturation, tissue growth and reproduction whereas the adreno-cortical hormones regulate various metabolic processes. Two most important male sex hormones or **androgens are testosterone** and **androterone**. They are responsible for the development of male secondary sex characteristics during puberty and for promoting tissue and muscle growth.

The female sex hormones or **estrogens** include **estrogen** and **estradiol** as examples. These hormones are responsible for the development of female secondary sex characteristics and for regular of menstrual cycle.

Another important female hormone is **progesterone** which prepares the lining of the uterus for the implantation of the fertilized ovum. The continued secretion of progerterone is important for the completion of the pregnancy.

Synthetic estrogens have been developed and they are used in combination with synthetic pregnancy hormones as oral contraceptines.

The adrenocritical hormones are secreted by adrenal glands which are small organs located near the upper end of each kidney. The **aldosterone** controls the tissue swelling by regulating cellular salt balance between Na^+ and K^+. Another hormone called **hydrocortisone** is involved in the regulation of glucose metabolism and in the control of inflammation.

Two important hormones which are polypeptides in nature are **vasopressin** and **oxytocin**. Oxytocin occurs in females only and stimulates uterine contraction during child birth. Vasopression occurs both in males and females and causes contraction of peripheral blood vessels and an increase in blood pressure.

Insulin, another important polypeptide hormone, is secreted from pancreases. It regulates the metabolism of glucose in the body. The deficiency of insulin in human causes diabetes mellitus.

INTEXT QUESTIONS 29.5

1. Name two important classes of steroid hormones.
2. What is oxytocin? Give its role.

29.7 VITAMINS : CLASSIFICATION AND THEIR FUNCTIONS

A variety of organic molecules act as coenzymes. Many of them are vitamins. Vitamins are small organic molecules which are taken in diet and there are required in trace amounts for proper growth.

Vitamins can be fat soluble or water soluble. A list of important vitamins and their deficiency symptoms is given below.

	Vitamin	**Deficiency Symptom**
A. Water Soluble		
(i)	Ascorbic Acid (Vitamin C)	Bleeding gums, Bruising
(ii)	Thiamin (Vitamin B_1)	Fatigue, Depression
(iii)	Riboflavin (Vitamin B_2)	Cracked lips, Scaly skin
(iv)	Pyridoxine (Vitamin B_6)	Anemia, Irritability
(v)	Niacin	Dermatitis, Dementis
(vi)	Folic acid (Vitamin M)	Megalobastic Anemia
(vii)	Vitamin B_{12}	Megalobastic Anemia, Neuro degeneration
(viii)	Pantothenic acid	Weight loss, Irreitability
(ix)	Biotin (Vitamin H)	Dermatitis, anorexia, depression
B. Fat Soluble		
(x)	Vitamin A	Night blindness, dry skin
(xi)	Vitamin D	Rickets, osteomalacia
(xii)	Vitamin E	Hemolysis of RBCs
(xiii)	Vitamin K	Hemorrahage, delayed blood clotting

INTEXT QUESTIONS 29.6

1. Match the following vitamins mix their deficiency symptoms:

   (i) Vitamin C
   (ii) Vitamin B_2
   (iii) Vitamin B_6

   (a) Anemia
   (b) Bleeding guns
   (c) Scaly skin

2. What is night blindness? Why is it caused?
3. How do enzymes increase the rate of a reaction?
4. What do you understand by lock and key arrangement?

WHAT YOU HAVE LEARNT

- Carbohydrates are polyhydroxy aldehydes or ketones or substances which provide such molecules on hydrolysis.
- They are classified as mono-, di-and polysaccharides.
- Proteins are the polymers of α-amino acids which are linked by peptide bonds.
- All proteins are the polymers of twenty different α-amino acids. Out of these 10 amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called essential amino acids.
- Proteins are very important to us and perform many functions in a cell that are absolutely necessary for our survival.
- Chief sources of proteins are pulses, milk, meat, eggs, etc.
- Biomolecules which are insoluble in water and soluble in organic solvents are called lipids. They are classified as simple, compound and derived lipids.
- Nucleic acids are the compound which are responsible for the transfer of characters from parents to offsprings.
- There are two types of nucleic acids- DNA and RNA. They are polymers composed of repeating units called nucleotides.
- DNA contains a five carbon sugar molecule called 2-deoxyribose whereas RNA contains ribose.
- The four bases present in DNA are adenine, cytosine, guanine and thymine whereas RNA contains uracil in place of thymine.

- DNA is a double strand molecule whereas RNA is a single strand molecule.
- DNA is present in the nucleus and have the coded message for proteins to be synthesized in the cell.
- Proteins are actually synthesized by RNA which are of three types – messenger-RNA (*m*-RNA), ribosomal-RNA (*r*-RNA) and transfer- RNA (*t*-RNA).
- Enzymes are biocatalysts which speed up the reactions in biosystems.
- Chemically all enzymes are proteins. They are very specific and selective in their action on substrates.

TERMINAL EXERCISE

1. How is excess glucose stored in our body?
2. What is a disaccharide? Give an example.
3. What are the products formed by the hydrolysis of lactose?
4. What are essential amino acids?
5. Differentiate between globular and fibrous proteins with suitable examples.
6. What are triglycerides? Mention one of its important uses.
7. What is a nucleotide?
8. Differentiate between the nucleotides of RNA and DNA.
9. What are different types of RNA found in the cell? Mention their functions.
10. What are enzymes?
11. What is insulin? Why is it important for us?
12. List the deficiency symptoms caused by deficiency of vitamin B12 and vitamin D.

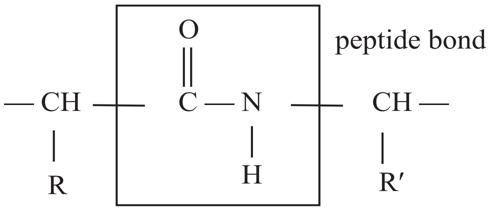
ANSWERS TO INTEXT QUESTIONS

29.1

1. Cereals, fruits and sugar.
2. Plants produce carbohydrates during photosynthesis.
3. Starch on hydrolysis gives glucose whereas sucrose on hydrolysis gives glucose and fructose.
4. Refer to section 29.1.2.

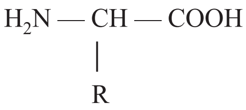
29.2

1. Information regarding the sequence of amino acids in a protein chain is called its primary structure.
2. Proteins are made up of many α-amino acids which join together by the formation of an amide bond between $-NH_2$ group of one amino acid and $-COOH$ group of another. When two amino acids combine in this way, the resulting product is called a dipeptide and the amide bond between them is called a peptide bond.



$$-\underset{\displaystyle R}{\underset{|}{CH}}-\boxed{\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{\underset{|}{N}}}-\underset{\displaystyle R'}{\underset{|}{CH}}- \quad \text{peptide bond}$$

3. An α-amino acid may be represented as



$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$$

4. Refer to section 29.2.1.

29.3

1. Biomolecules which are insoluble in water and soluble in organic solvents like benzene, ether or chloroform are called lipids.
2. Oils on hydrolysis give glycerol and long chain fatty acids.
3. Two types of compound lipids are phospholipids and glycolipids.
4. A triglyceride which is solid at room temperature is called a fat and if it is liquid then it is called an oil.

29.4

1. A nucleotide consists of three subunits which are (i) a nitrogen containing heterocyclic aromatic compound, also called a base; (ii) a pentose sugar (ribose or 2-deoxy ribose) and (iii) a molecule of phosphoric acid.
2. In DNA, two chains are wound around each other in the form of helix, hence the structure is called a double helix.
3. Two main structural differences between DNA and RNA are :
   (i) DNA molecules are double stranded whereas RNA are single strand molecules.

Notes

(ii) In DNA molecules, the sugar moity is 2-deoxyribose whereas in RNA molecules, it is ribose.

29.5

1. Refer to section 29.5.1
2. Refer to section 29.5.1

29.6

1. Six hormones and adrenocortical hormones.
2. Oxytocin is a female hormone. It stmulates uterine contraction during child birth.
3. (i) – (b)

   (ii) – (c)

   (iii) – (a)
4. Night blindness is a deficiency sympton. It is caused by the deficiency of vitamin A.

MODULE - VIII

CHEMISTRY IN EVERYDAY LIFE

30. Drugs and Medicines
31. Soaps, Detergents and Polymers
32. Environmental chemistry

30

DRUGS AND MEDICINES

The association of mankind with pain and disease is probably as old as man himself. Humans have always been looking for remedies to overcome their pain and suffering. The earliest attempts at this, involved use of various plants. The knowledge was based on experience and was handed on from generation to generation. It is being used even today.

In an attempt to conquer pain and disease, a large number of synthetic chemicals have been discovered. The chemicals used as medicines are known as pharmaceuticals. Today pharmaceutical industry has grown to be one of the biggest industries in the world.

In this lesson we will try to introduce you to the area of drugs and medicines. In the process we would attempt to differentiate between drugs and medicines (though commonly used interchangeably). You will also learn about classification of medicines and other important aspects of drugs and medicines.

OBJECTIVES

After reading this lesson you will be able to :

- define drugs and medicines;
- differentiate between drugs and medicines;
- classify medicines on the basis of their action (use);
- cite examples and effects of analgesics, antipyretic, antiseptics, disinfectants, antacids, antimalarials, anaesthetics, antimicrobials (sulpha drugs and antibiotics), anti-fertility drugs, etc.;
- differentiate between analgesics and antipyretics;
- differentiate between antiseptics and disinfectants;

- explain habit forming and non-habit forming drugs;
- differentiate between broad spectrum and narrow spectrum antibiotic;
- differentiate between local and general anaesthetics;
- describe self-medication and
- alternate systems of medicine.

30.1 WHAT ARE DRUGS AND MEDICINES?

When we fall ill we take some tablets, pills, injections or apply some ointments to get well. All these are collectively known as medicines. Some time we may use some parts of plants or some preparations made from herbs, minerals, animals, etc. All these substances used for the treatment or prevention of diseases, can also be called medicines. Medicines contain a single chemical or a number of chemicals in different amounts to have the desired effect.

The mode of action of the chemicals of a medicine is quite varied and complicated. In many a cases mode of action may not be fully known to us, but we continue to use them as they are useful to us.

Early man used several plants or parts of plants to cure diseases, without knowing of the chemical components, responsible for it. For example bark of willow tree was used for relieving pain (as analgesic). Later, it was found that its bark contained 2-hydroxy benzoic acid, which is closely related to acetyl salicylic acid (also known as aspirin). Parts of a plant *Rauwolfia serpentina* (Hindi name, sarpagandha) have been used in Ayurvedic drugs for the treatment of hypertension (high blood pressure). Later on it was discovered that a compound called reserpine was responsible for reducing blood pressure. Thus reserpine became the first modern medicine to control blood pressure.

In most of the cases nature led to the discovery of modern medicine. Thousands of chemists all over the world are constantly searching for better, efficient, cheaper and safer medicines.

As mentioned earlier the term drugs and medicines are used interchangeably, but there is a difference between the two. Let us try to understand the difference between drugs and medicines. The term drug is often used for preparations or formulation whose chemical components and their quantities are not known fully. These may be extracts of certain plants, herbs, animal parts or may be minerals.

The term medicine is used when the chemical composition and the quantities of various chemical components are known. Further, the effects of the chemical compounds present in a medicine and their side effects have been properly and extensively studied. The medicines are approved by the relevant governmental authorities like Drug Controller of India.

The term drug is also used for substances, which are habit forming and are often abused, for example, narcotics like cocaine, morphine, heroine, marijuana, etc.

As you read in newspapers terms like illegal drug trade, drug trafficking, drug mafia, drug peddler are used to refer to illegal dealing with habit forming substances, referred to as drugs.

However the difference between drug and medicine is far from clear.

INTEXT QUESTIONS 30.1

1. Write a definition of medicines.
2. Most of the chemicals used in medicines are poisonous. Is this statement true or false?
3. What are pharmaceuticals?
4. Name the compound which is present in the plant sarpagandha and is responsible for reducing blood pressure.

30.2 CLASSIFICATION OF MEDICINES

You may be familiar with some of the common medicines used for relieving pain, reducing fever or for treating common cold, etc. The number of medicines is very large therefore medicines are classified according to their action or use. Table 30.1 provides a list of some important classes of medicines. The terms like analgesics, antibiotics, antiseptics, etc. are common household words. Let us try to understand the meaning of this classification in a little more detail.

Table 30.1 : Some Important Classes of Medicines and their Action

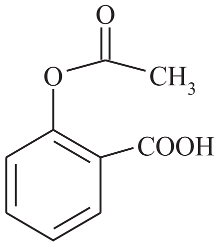
S.No.	Class	Action or Usage
1.	Antipyretics	Reduce body temperature
2.	Anti histamines	Reduce allergy
3.	Analgesics	Reduce pain
4.	Antimalarials	Used for treatment of malaria
5.	Germicides	Kill germs
6.	Antiseptics	Kill germs (can be safely used on living tissue)
7.	Disinfectant	Kill germs (cannot be used on living tissue)
8.	Antacids	Reduce acidity in stomach
9.	Anaesthetics	Loss of sensation
10.	Antimicrobials, Sulpha drugs and Antibiotics	Kill microorganisms
11.	Tranquilizers and hypnotics	Reduce anxiety and bring calmness
12.	Birth Control Medicines (Contraceptives)	Birth control

1. Antipyretics

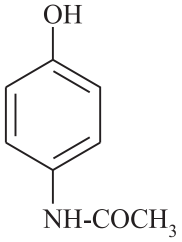
Antipyretics are the substances which are used to reduce body temperature or to control fever.

The word antipyretic is derived from pyro which means fire (means hot) anti means against. Thus antipyretic means it counteracts heat (high body temperature).

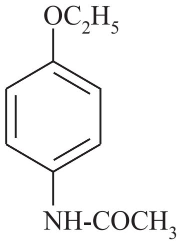
Aspirin, paracetamol and phenacetin are commonly used antipyretics. You get them in the market with different trade names like crocin, anacin, disprin, etc.



Aspirin



Paracetamol



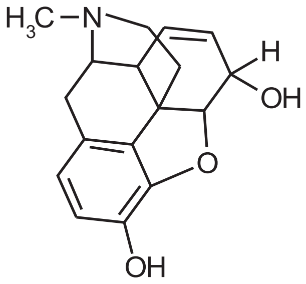
Phenacetin

Aspirin is the most popular antipyretic in use. It gets hydrolyzed in stomach and salicylic acid is released. Overdose and using it over a long time may cause side effects. It may cause bleeding in the stomach wall and even ulcers. Therefore, overdose and prolonged use should be avoided. However, calcium and sodium salts of aspirin are more soluble in water and are less harmful than aspirin.

2. Analgesics

Analgesics are the substances, that reduce pain which may be due to swelling of tissues, injury, inflammation or some other disorders. Analgesics are of two types, namely narcotic & non-narcotic.

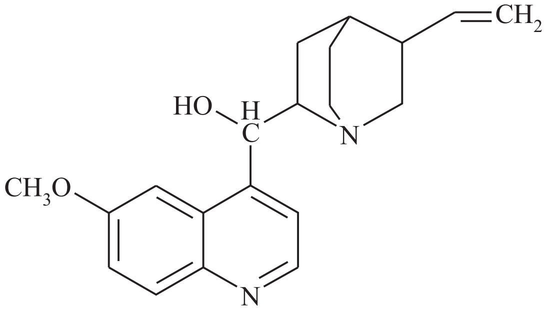
Narcotic analgesics are the ones which induce sleep and thus help to reduce the feeling of pain alkaloids present in opium, viz. morphine, codeine, etc. are common examples of narcotics. In higher doses these may cause unconsciousness. These are habit-forming and cause addiction. Due to addiction a person wants to have it regularly and in larger amounts. Such a person feels upset and uncomfortable if he doesnot get it. Narcotic analygesies do not induce sleep and are not habit forming. A common example of this type of narcotics is morphine.



Morphine

3. Antimalarials

Antimalarial medicines are used to treat malaria. Quinine and chloroquine are widely used antimalarials. Quinine is one of the earliest drugs, which was first obtained from the bark of a plant (cinchona) and later on synthesized in laboratories.



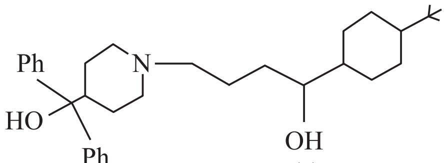
Quinine

4. Antihistamines

Some persons are hypersensitive towards some medicines like penicillin, sulpha drugs and may be sensitive to food and environment due to different sensitizing substances (antigens) derived from them. The hypersensitivity is called allergy. It is due to release of a chemical substance called histamine in the body.

"Anthistamine are the chemical substances (drugs) which control or abolish the effect of histamines released in the body." These drugs are also called anti-allergic drugs.

Histamine is also responsible for the nasal congestion (discharge), mild asthama associated with common cold, cough, allergic response to pollengrains etc. Histamine contract the smooth muscles in bronchi and gut, relaxes other muscles present in the walls of fine blood versels. Antihistamine are widely used for treatment of hay-fever, itching of eyes, nose and throat, conjuctivities. Some antihistamine drugs are diphenhydramine (Benadryl) pheniramine maleate (Avil) chlorspheniramine maleate (zect), citrazine and terfenadine (seldane)



Seldane

5. Germicides, Disinfectant and Antiseptic

Germicides are the chemicals, which prevent growth of germs (microorganisms). Germicides are classified as antiseptic and disinfectant. Both kill microorganisms but the difference lies in the way we use them.

Antiseptics kill microorganisms and are safe to be used on living beings (tissues). Antiseptics are used on wounds, cuts or skin abrasions. These are used to dress wounds, etc. For example, iodoform (CHI_3), tincture of iodine, ethyl alcohol, a 0.2 percent aqueous solution of phenol and boric acid (H_3BO_3) are common antiseptics.

Some dyes have the ability to kill microorganisms. These dyes were the earliest compounds to be used as antiseptics. Examples are acriflavine (a yellow coloured dye), mercurochrome (a red coloured dye), methylene blue (a blue coloured dye). These dyes are still in use as antiseptics.

Iodine is a powerful antiseptic. It is used as tincture of iodine. Tincture of iodine is 2 to 3 percent solution of iodine dissolved in ethyl alcohol. Iodoform is a yellow coloured solid, which is used as an antiseptic.

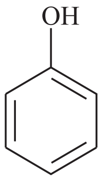
Disinfectants kill germs (microorganisms) but are used on non-living substances like surgical instruments, floors, bathrooms, lavatories, etc. Disinfectants are harsh and are not safe to be used on living beings as disinfectants can damage living tissues.

Chlorine is a powerful oxidizing agent. It is used for disinfecting water. A concentration of 0.2 to 0.4 ppm (parts per million) is enough to kill microorganisms present in water.

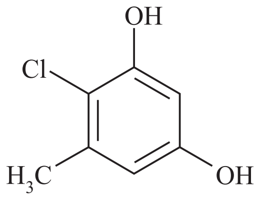
Low concentration of sulphur dioxide is used to kill microorganisms in jams, jellies and squashes. Thus it acts as a food preservative. Sulphur dioxide is used for fumigation in rooms, operation theaters, etc. to sterilize them. Bleaching powder ($CaOCl_2$), chlorine (Cl_2), mercuric chloride ($HgCl_2$), sodium hypochlorite (NaClO), sulphur dioxide (SO_2) etc. are other examples of disinfectants.

Is Phenol Antiseptic or Disinfectant?

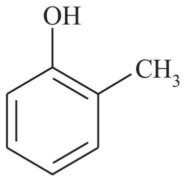
It is interesting to note that 0.2 percent aqueous solution of phenol is used as antiseptic by making. It is safe to be used on living tissues in low concentrations (less than 0.2 percent). If concentration of phenol is high then it can damage tissues. Therefore, at higher concentration (1 percent or more) phenol is used as disinfectant.



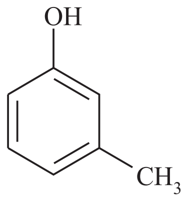
Phenol



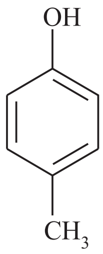
Chloro-xylenol



***o*-Cresol**



***m*-Cresol**



***p*-Cresol**

Most antiseptics and disinfectaints are powerful poisons (Table 30.2). They are able to kill microorganisms as they interfere with their metabolism. While some others are able to kill microorganisms because of their powerful oxidizing or reducing nature (Table 30.2).

Table 30.2 : Nature of Some Important Antiseptics and Disinfectants

Poisons	Oxidising agents	Reducing agents
Dyes		
Acriflavine (a yellow dye)	Bleaching powder	Sulphur dioxide
Gentian violet	Chlorine	
Mercurochrome	Hydrogen peroxide	
Methylene blue	Iodine	
	Tincture of iodine	
Phenols	Iodoform	
	Potassium permanganate	
Phenol	Sodium hypochlorite	
Cresols		
Resorcinol		
Chloroxylenol		
Others		
Formaldehyde		
Boric acid		
Mercuric chloride		
Silver nitrate		

Notes

6. Antacids

Antacids are the medicines which neutralize the excess acid present in the stomach.

Stomach juice contains hydrochloric acid (HCl). This acid helps the process of digestion of food. Due to illness or anxiety or some other reasons more acid is produced in the stomach. The stomach juice becomes more acidic than necessary. This causes problems in digestion, bleeding in the lining of stomach or even ulcers. Some medicines are used to neutrialise the excess acid and correct the pH of the stomach fluid.

For example, sodium bicarbonate ($NaHCO_3$) or a suspension of magnesium hydroxide is used to neutralize excess of acid present in the stomach. Milk of magnesia contains magnesium hydroxide, 'ENO fruit salt' contains sodium bicarbonate which helps to neutralise excess acidity in the stomach juice. Medicine like digene, gelusil, used as an antacid contain magnesium hydroxide.

7. Antimicrobials

Many diseases are caused due to infection in the body by certain microorganisms (bacteria, fungus or viruses). Some examples of diseases caused by microbes are dysentry, pneumonia, typhoid, urinary tract infection, etc.

Antimicrobials are the chemicals, which are used to kill microorganisms (which has infected the body) without causing much damage to the body of the patient.

Thus an antimicrobial is a chemical, which is capable of curing diseases caused by various microbes.

An ideal antimicrobial should kill disease-causing microbe and should not have any harmful effect on the patient. In fact there may not be any such antimicrobial which is totally safe and without any side effect.

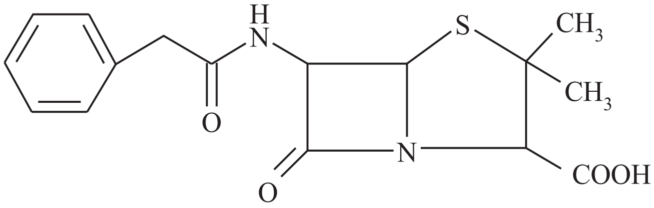
The most common antimicrobials available are the sulhpa drugs and antibiotics.

8. Antibiotics

Antibiotics are the metabolic products produced by some microorganisms (mould or fungi). They inhibit growth and even kill disease causing microorganisms (like bacteria, fungi, etc) by inhibiting their life processes. Therefore they are referred to as antibiotics (anti means against and biotic means life).

Penicillin was the first antibiotic to be discovered. Alexander Fleming isolated penicillin in 1929 from a mould *Pencillium notatum*. Penicillin has been used for the treating diseases caused by several bacteria. It has been effectively used for treatment of pneumonia, bronchitis, sore throat, abscesses, etc.

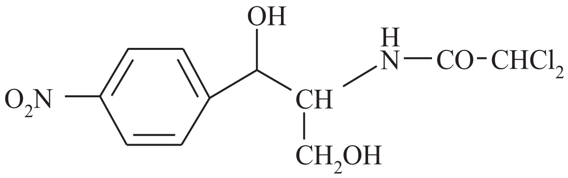
Later on attempts have been made to improve the quality of penicillin. It has led to the discovery of different varieties of penicillin. For example, Penicillin G (also known as benzyl penicillin), penicillin F, penicillin K are the more common varieties of penicillin.



Penicillin G (benzyl peniclin)

Ampicillin and amoxicillin are the semi-synthetic modifications of penicillin. In this case the metabolic product of mould is obtained and then some reactions are carried out to bring the desired changes in the antibiotic molecule to get ampicillin or amoxicillin.

Attempts are being made to discover better and better antibiotics. This search for finding better antibiotics is a never-ending process. Now a large number of antibiotics are available. Some examples are streptomycin and chloromycetin (chloroamphenicol) and tetracycline.



Chloroamphenicol

Streptomycin is used for the treatment of tuberculosis (TB). Chloromycetin is used for the treatment of typhoid. Tetracycline is used for the treatment of several diseases.

Broad-spectrum antibiotics are those antibiotics, which kill a wide range of disease-causing microorganisms.

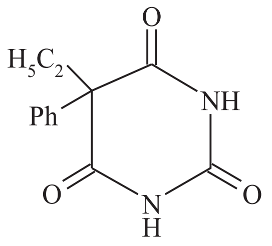
Broad-spectrum antibiotics can be used for the treatment of several diseases. For example, streptomycin, tetracycline and chloroamphenicol are broad-spectrum antibiotics. Narrow spectrum antibiotics are effective in the treatment of a few diseases.

9. Allergic Reactions of Antibiotics

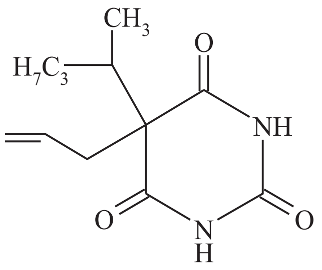
Some people may show allergic reactions to some antibiotics. These reactions may be mild like rashes appearing on the skin or may be very serious and can even be fatal. You might have observed that a doctor gives a small dose of antibiotic by injection and then waits for some time to watch if there is any unwanted reaction. If there is no adverse (bad) reaction, then only the doctor gives the full dose of the antibiotic.

10. Tranquilizers and Hypnotics

Tranquilizers and hypnotics are used to reduce anxiety, and they also make a person calm. Sleeping pills are made up of these compounds. Most of them are habit-forming. Their indiscriminate and over use should be avoided. Otherwise it may lead to addiction and many other complications,

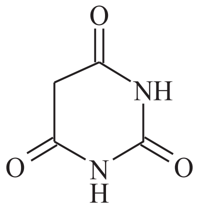


Luminal

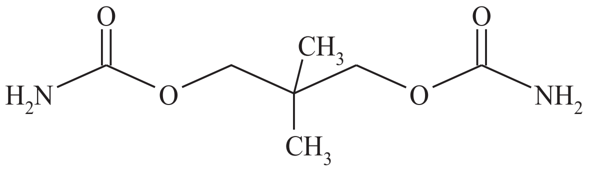


Seconal

Luminal, seconal and equanil are the most commonly used tranquilizers. Barbituric acid and some other compounds related to barbituric acid are used in making sleeping pills.



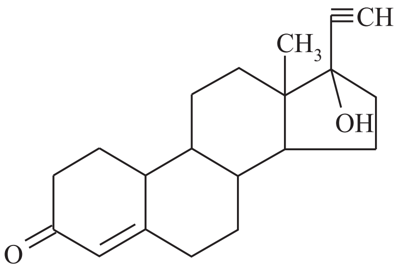
Barbituric acid



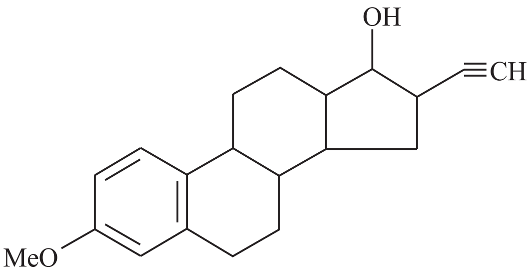
Equanil

11. Fertility Control Medicines

It is a concern of everyone to control human population. Medicines are available which help prevent pregnancy. The medicines, which help prevent pregnancy, are known as contraceptives. These are generally available in the form of tablets and are to be taken regularly by females. Chemicals like norethindrone and mestranol are used as contraceptives (birth control pills). Chemically these are similar to female sex hormones.



Norethindrone



Mestranol

The birth control pills may have some side effects in some cases. Therefore, the birth control pills should be used under the guidance of some expert.

30.3 HAZARDS OF SELF MEDICATION

When medicines are taken by a patient without the advice of a qualified doctor, it is called self-mediation.

Self-medication is very harmful and a dangerous practice. One should never try self-medication. Some of the harmful effects are:

1. A medicine, which has worked well for some one, may not be good for you and can even cause some serious harm.
2. You may take a medicine in quantity more than necessary. It may be harmful for you.
3. You may take quantity less than necessary. The disease-causing microorganisms may gain resistance to the medicine and the medicine may become ineffective.

You should avoid self-medication. Without advice of a doctor avoid use of common medicines over prolong periods. Improper use of even most common medicines, which are readily available without a prescription of a doctor, can have harmful effect.

The medicines, which you can buy without a prescription of a doctor, are called over-the-counter medicines. For example cough syrups, crocin, aspirin, etc are over the counter medicines.

The medicines, which you can buy after showing a prescription of a qualified doctor, are known as scheduled drugs. Improper use of scheduled drugs is likely to cause more serious problems. Therefore, their sale is controlled and regulated by the government.

Most of good chemists do not sell scheduled medicines without a proper prescription. Some irresponsible chemists may sell such medicines without a prescription. It is not a good practice you should not encourage it.

INTEXT QUESTIONS 30.2

1. Give two examples of antipyretics.
2. Give one example of a narcotic type analgesic.
3. What is the difference between an antiseptic and disinfectant?
4. What are antacids? Name two chemicals commonly used as antacids.
5. What is the difference between local anaesthetic and general anaesthetic.
6. Define antibiotics. Give one example of an antibiotic.
7. Which type of medicines are usd in hey-fever, itching of eyes; nose and throuts.
8. What is the use of tranquilizers and hypnotics?
9. Give one example of a tranquilizer.
10. What are contraceptives?
11. What are over the counter medicines?

30.3.1 Chemicals in foods – Preservatives and artificial sweetening agents

Food Preservatives: "Chemical substances which are used to protect food materials against microorganisms (bacteria yeasts and moulds) are called preservatives."

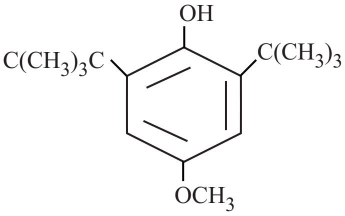
Some commonly used preservatives are

1. **Common Salt, Sugar and oils:** The sufficient amount of salt resist the activity of microorganisms in food it is called salting. It is used to preserve raw mango, bean, fish and meat, etc. Sugar syrup used for preserving like apple, mango, amla and carrot etc. Sugar, oil, vinegar & citric acid are used to preserve pickles, ketchups and jams, etc.
2. **Sodium benzoate (C_6H_5COONa):** It is used for preserving of food material like fruit juices, soft drinks, squashes and jams. It is soluble in water. It is metabolized as hippuric and which is excreted in urine.
3. **Sodium meta bisulphite ($Na_2S_2O_5$):** Its preservative action is due to SO_2 which from sulphurous acid when dissolved in water. It also inhibits the growth of yeasts, moulds and bacteria. It is used to preserve fruitams, juices, squashes, pickles, apples, etc.
4. Sodium and Potassium Salts of propionic acid, sorbic acid are also used as preservatives.

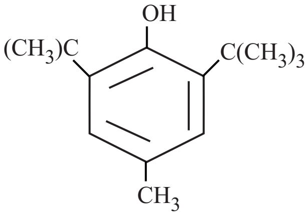
30.3.2 Antioxidants

The unsaturated fat and oils are readily oxidized on storage, the taste and smell are changed and become rancid. To prevent this oxidation, rancidity and spoilage, certain chemical substances are added, are called antioxidant (food additives).

When these are added to food items containing fats and oils retard the oxidation because they are more reactive towards oxidation than fats and oils. So the oxidation of food is prevented. Antioxidants react with free radicals and stop the oxidation of food. The most familiar antioxidants are butylated hydroxyl toluene (BHT) and butylated hydroxyl anisole (BHA)



(BHA)



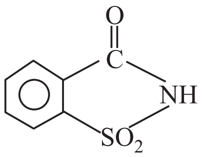
(BHT)

These are added to butter, meats, cereals chewing gum, snack gum, baked food and beer etc. It increases the life of food from months to years. It shows more active synergetic effect when added with Vitamin C (ascorbic acid) and citric acid.

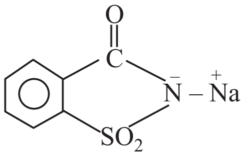
30.2.3 Artificial Sweetening Agents

“The chemical compounds which give sweetening effect to the food are called sweeting agent.” Sucrose and Glucose are widely used as natural sweetening agent. The excess intake of natural sugar cause to obesity diabetics and tooth decay. Natural sugar is a good source of energy. While the artificial sweetening agents does not provide energy. It is excreted from the body in urine unchanged. Some commonly used artificial sweetening agents are saccharin, aspartame, alitame, sucrolose, etc.

1. Saccharin (O-Sulpho benzimide) Saccharin is insoluble in water but sodium salt is highly soluble in water. It is 550 times sweeter than sugar. It is not metabolized by our body. So it does not provide energy and has no calorific values.

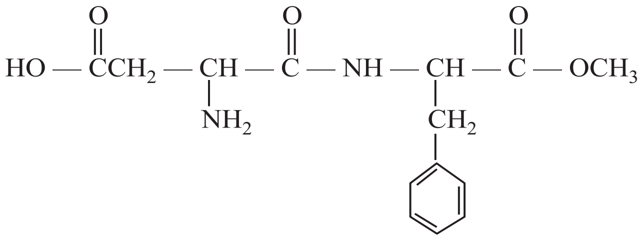


Saccharine
(Insoluble inwater)



Sodium salt of
Saccharine
(Solube in water)

2. **Aspartame –** It is methyl ester of dipetide derivative derived from aspartic acid and phenylalanine. It is 100 times as sweet as sugar. It is unstable at cooking temperatures. It is used in cold drinks and soft drinks. It is an exception because the body breakes it down in to amino acid and menthol.



(Aspartame)

3. **Alitame:** It is very high potency sweetener, It is about 2000 times sweeter than sugar. It is more stable at cooking temperatures. It is very difficult to control the sweetness of food.
4. **Sucrolose:** It is trichloro derivative of sucrose. It's taste is like sugar. It is also stable at cooking temperatures. It is about 600 times sweeter than sugar.

Sucrolose is expected to become a great commercial artificial sweeting agent.

INTEXT QUESTIONS 30.3

1. What type of change take place on storage the fat & oil?
2. Write the name of preservative used with soft drinks.
3. What change will take inner body on taking exercise sugar (N).

WHAT YOU HAVE LEARNT

- Medicines are the chemicals or mixture of chemicals used for the prevention, cure, treatment, management of diseases and disorders or recovery of patients
- Medicines are obtained from plants or parts of plants or synthesized in laboratories.
- Medicines may contain only one chemical compound or it may be a mixture of several compounds.
- Drugs may be the crude mixtures and the identity of all the chemical components and their amount present in them may not be accurately known.
- Antipyretics are used to reduce body temperature for example aspirin and paracetamol.

- Analgesics reduce body pain for example aspirin and morphine.
- Antiseptics kill microorganisms and are safe to be used on a living tissue while disinfectants are used on inanimate objects.
- Aqueous solution (less than 0.2 percent) of phenol is used as an antiseptic. In higher concentrations phenol is used as a disinfectant.
- Antibiotics are the metabolic products produced by certain microorganisms which can kill some microorganisms. For example penicillin, streptomycin, tetracycline, etc.
- Broad spectrum antibiotics can kill several different microorganisms, therefore, can cure several diseases.
- On storage the taste and smell are changed and become rancid.
- Certain chemical substances are added to control oxidation spoilage and rancidity.
- Butylated hydroxyl toluene (BHT) and Butylated hydroxyl anisole (BHA).
- Common Salt, sugar and oils are natural food preservatives.
- Sodium benzrate is familiar food predervative.
- Aspartame is unstable at cooking temp. so used in cold drinks and soft drinks.
- Alitame is more stable at cooking temp.
- Suerolose is mare stable at cooling tamp and easy to control the sweetness of food.

TERMINAL EXERCISE

1. How are medicines classified?
2. Who isolated the first antibiotic?
3. Name a medicine, which is used as analgesic as well as antipyretic.
4. What is a non-narcotic analgesic?
5. Why is 2.0 percent aqueous solution of phenol used as a disinfectant?
6. What do you understand by allergic reactions of antibiotics?
7. What are scheduled drugs?
8. Which medicines can you purchase without the prescription from a doctor?
9. What is self-medication? Describe some of its ill effects.
10. Write the two names of chemicals which increases the life of food from months to years.
11. Which artificial sweatening agents is more suitable at cooking temperatures.
12. Which is responsible for perservation action of sodium meta bisulphite?

ANSWERS TO INTEXT QUESTIONS

30.1

1. Medicines are all those substances or formulations which are used for cure, treatment, prevention of diseases or disorders and recovery of a patient.
2. True
3. Pharmaceuticals are the chemicals which are used as medicines.
4. Reserpine

30.2

1. Aspirin and Paracetamol.
2. Morphine.
3. Disinfectants kill germs but can damage living tissues Anticeptics are safe for living tissues and yet kill germs.
4. Medicines used to neutralise excess acid in the stomach. Magnesium hydroxides and sodium carbonate.
5. Local anesthetics cause loss of sensation of pain over a small area while general anesthetics cause loss of concsiousness.
6. Metabolic products of certain microorganisms and can kill some other microorganisms. Penicilin is an example of antibiotic.
7. Anti histomines are used.
8. Tranquilizers and hypnotics are used to reduce anxiety and these also make a person calm.
9. luminal
10. Contraceptives are the medicines used for prevention of pregnancy.
11. Over-the-counter medicines are those which can be purchased without a prescription from a doctor.

30.3

1. On storage of fat and oil get oxidised, the taste and smell are changed and become rancid.
2. Sodium benzoate (C_6H_5COONa) is used as perservative with soft drinks.
3. The excess intake of natural sugar cause to obesity and tooth decay.

Notes

31

SOAP, DETERGENTS AND POLYMERS

In the previous lesson module VII you have studied about the chemistry of organic compounds. In this module you would learn about the meaning of soaps, detergents and polymers. The synthetic detergents are better than soaps but due to non biodegradibility causes water pollution and soil pollution. You would also learn about type of soaps and detergents. Today polymers have influenced our life style to the extent that it would not be wrong to say that we are in polymer age. Now-a-days polymers find wide range of uses starting from common household utensils, automobiles, clothes, furniture, etc., to space-aircraft and biomedical and surgical components.

Polymeric materials are light weight but can possess excellent mechanical properties and can be easily processed by different methods. In this lesson you would learn more about polymers, their types and some important-synthetic and natural polymers.

OBJECTIVES

After reading this lesson, you will be able to :

- distinguish between soaps and detergents;
- explain types of detergents;
- list advantages and disadvantages of detergents over soaps;
- explain cleansing action of soaps and detergents;
- define the terms like monomers, polymer, homopolymer, copolymer and polymerization;
- classify polymers on the basis of their source, molecular forces and method of preparation;

Notes

- list the monomers of the polymers like natural and synthetic rubber;
- list the monomer of the polymer like polythene, polystyrene, Buna- S, PMMA, PVC, teflon, polyester, Nylon 66 and Nylon 6;
- define biodegradable polymers; and
- cite examples of some biopolymers.

31.1 CLEANSING AGENTS (SOAPS AND DETERGENTS)

Soaps and detergents are widely used as cleaning agents. Chemically soaps and detergents are quite different from each other. The common feature of soaps and detergents is that when dissolved in water the molecules of soap and detergent tend to concentrate at the surface of the solution or at interface. Therefore, the surface tension of the solution is reduced, it causes foaming of the solution.

Soaps and detergents lower the surface tension of the solution. Such substances are called surface-active agents or surfactants.

To sum up, soaps and detergents:

1. are used as cleansing agents
2. cause foaming of the solution
3. lower surface tension
4. molecules tend to concentrate near the surface of the solution
5. are the surface active agents
6. are the surfactants
7. can emulsify grease
8. can remove dirt, etc.

Hydrophilic and Lipophilic Parts

Both soap and detergent molecules have two parts. One part of the molecule is polar (ionic) in nature. Polar nature is due to the presence of groups like carboxylate ($-COO^-$) or sulphonate ($-SO_3^-$). The polar group is a hydrophilic group. The hydrophilic group makes soaps and detergents soluble in water. The other part of the soap or detergent molecule is non polar (nonionic) that is lipophilic. The lipophilic part (a long chain alkyl or a long chain substituted aryl group) makes the molecule oil soluble.

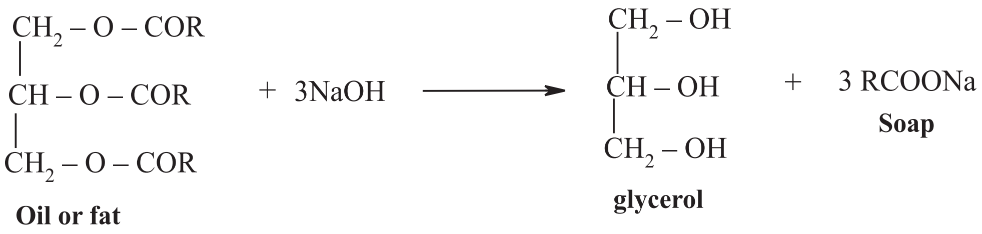
Depending on the nature of the hydrophilic (polar) part in the soap or detergent molecule these are classified as anionic, cationic or non-ionic type. For example, soap has a carboxylate anion therefore soap is anionic type (table 8.5.1). Synthetic detergents have sulphonate anion thus they are also classified as anionic type. Anionic types are the most common. However, cationic and non-ionic detergents are also known.

Soaps

Soaps are the sodium or potassium salts of long chain fatty acids. These fatty acids are present in oils and fats in the form of glycerides. The glycerides present in oils and fats are the esters of glycerol and long chain carboxylic acids for example palmitic acid and stearic acid.

Saponification

Saponification is the process of making soap. Saponification is done by hydrolysis of oils or fats (of vegetable or animal origin) with the help of alkali like sodium hydroxide (NaOH) or potassium hydroxide (KOH)

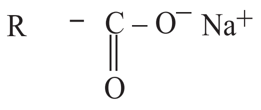


$$\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-COR \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3\ RCOONa$$

(where R= long chain alkyl group containing 11 to 17 carbon atoms)

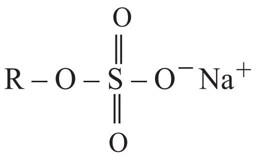
Synthetic Detergents

Synthetic detergents are used as cleaning agents much like soaps. Chemically, detergents are sodium salts of long-chain alkyl hydrogen sulphate or sodium salts of long-chain alkyl benzene sulphonic acids. (Remember that soap is a sodium or potassium salt of long-chain fatty acid.)



$$R-\underset{\underset{O}{\|}}{C}-O^-\ Na^+$$

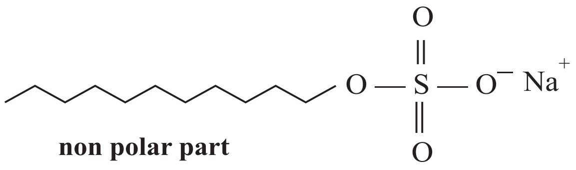
(Soap)

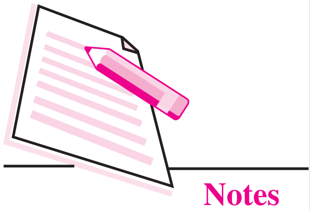


$$R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-\ Na^+$$

(Detergent)

Detergent molecules are similar to that of soap molecules, that is they have an oil-soluble (lipophilic) long chain of carbon atoms and a polar (hydrophilic) water-soluble part. For example, sodium lauryl sulphate ($C_{12}H_{25}$–O – SO_3Na) has a 12 carbon atom hydrocarbon like alkyl chain. The long carbon chain is oil-soluble (lipohilic) part and the sulphate is polar (hydrophilic) part that makes the molecule water-soluble. The water-soluble part is referred to as water-soluble head and the long chain of carbon atoms is referred to as oil-soluble tail.





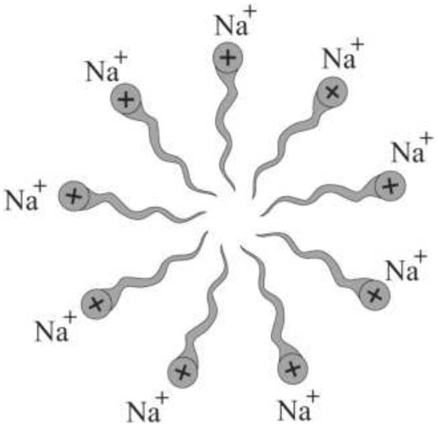
Notes

31.1.1 Cleansing action of soap and detergents

The molecules of soaps and detergents are smaller than the colloidal particles. These molecules associate and get the colloidal particle size range. This associate form is known as micelles. Soap and detergents dissociate in ions when dissolve in water being electrolyte in nature.

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} \longrightarrow C_{17}H35COO^{-} + Na^{+}$$

The long chain of hydrocarbon, which is hydrophobic is nature (insoluble in water) directed towards the centre while the head (hydrophylic water soluble part) is on the surface in control of water.



The initial concentration at which micellization begins is called critical micellization concentration (CMC). The formation of micelles starts above a definite temp, that is called kraft temperature (TK).

The cleansing action of soap is due to micelles. The micelles are absorbed by grease/dirt in cloth. Because both are non polar. The polar head is directed towards water the rubbing by hands or mechanical stirring break the grease particles in to smaller droplets and form emulsion with water. As a result, the cloth gets free from dirt and grease. The droplets and washed away with water.

31.1.2 Advantages and Disadvantages of Synthetic Detergents

The synthetic detergents are better than soaps in certain respects. Synthetic detergents can be used for washing of clothes even if the water is hard. Calcium and magnesium ions present in hard water make corresponding salts with detergent molecules. The calcium and magnesium salts of detergent molecules are soluble in water (unlike that formed by soap molecules).

However, detergent containing branched alkyl benzene sulphonate is not completely biodegradable (Table 32.2). Soap is completely biodegradable. Therefore, excessive use of synthetic detergents is a cause of worry. The problem has been partly solved by using linear alkyl benzene sulphonate, which has better bio-degradability then the branched alkyl benzene sulphonate (Table 31.1)

Table 31.1 : Bio-degradability and class of soaps and some synthetic detergents

Detergent	Class	Polar Group	Bio-degradable
Soaps	anionic	Carboxylate	100%
Branched alkyl benzene sulphonate	anionic	Sulphonate	50-60%
Linear alkyl benzene sulphonate	anionic	sulphonate	90%
Lauryl alcohol	anionic	Sulphate	100%

INTEXT QUESTIONS 31.1

1. What is the active component in soaps ?
2. What are the raw materials used for the manufacture of soaps ?
3. What is the polar part in a soap molecule ?
4. What is the polar part (hydrophilic) in a synthetic detergent molecule ?
5. What is the oil-soluble (lipophilic) part in the soap molecule ?
6. Branched alkyl benzene sulphonate is more bio-degradable than linear alkyl benzene sulphonate. Is it true or false ?

31.2 WHAT ARE POLYMERS

A Polymer is a giant molecule formed by inter molecular linkage between same or different types of smaller molecules called **monomers**. If a large number of monomers (A) are linked together then the polymer is represented as $(-A_n-) - (-A-A-A-A-A)_{\overline{n}}$ is a polymer of the monomer of (A). For example, polyethene $-\!(\!-CH_2-CH_2)_{\overline{n}}$ is a polymer of the monomer ethylene ($CH_2 = CH_2$).

Polymer is a high molecular mass molecule formed by linking up of two or more small molecules called monomers.

Monomers are the small molecule which are capable of linking amongst themselves to form big molecules called polymers.

In some polymers more than one type of monomers combine with each other to give the polymer. For example, a polymer may be obtained from two monomers (A) and (B) viz,

$$-A-B-A-B- \quad \text{or} \quad -\!(\!-A-B-\!)\!-_n$$

31.2.1 Types of Polymers

Depending upon the nature of the repeating structural units (monomers), polymers are divided into two broad categories viz., homopolymers and copolymers

(a) **Homopolymer**

A polymer formed from only one kind of monomers is called homopolymer. Polyethene $-\!\left(CH_2-CH_2\right)\!-_n$ is an example of homopolymer.

(b) **Copolymer**

A polymer formed from more than one kind of monomer units is called **copolymer or mixed polymer**. For example, Buna-S rubber which is formed from 1, 3-butadiene ($CH_2=CH-CH=CH_2$) and styrene ($C_6H_5CH=CH_2$) is an example of copolymer.

31.3 POLYMERIZATION

The process by which the monomers get linked up is called **polymerization**.

Polymerization is represented as :

$$M+M \longrightarrow \underset{\text{Dimer}}{M-M} \xrightarrow{+M} \underset{\text{Trimer}}{M-M-M} \xrightarrow{+M^*} \underset{\text{Polymer}}{M-(M)_n-M}$$

where M stands for the monomer

31.3.1 Types of Polymerization

Depending upon the mode of reaction, polymerisation is classified as :

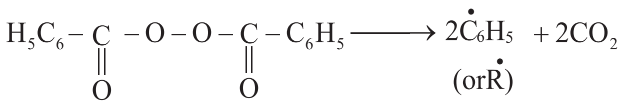
(a) addition polymerization and

(b) condensation polymerization.

(a) Addition Polymerization : This process involves the addition of monomer units to themselves to form a growing chain by a chain reaction mechanism. It is for this reason that the process is also known as **chain growth polymerization**.

Addition polymerization is achieved by adding a catalyst (known as initiator), which provides some reactive species like free radicals.

For example benzoyl peroxide provides free radical 'benzyl' to initiate the chain polymerization reaction.



$$H_5C_6-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \longrightarrow \underset{(\text{or}\,\dot{R})}{2\dot{C}_6H_5} + 2CO_2$$

Initiation $\dot{R} + \underset{\text{(Monomer)}}{CH_2 = CH_2} \longrightarrow R - CH_2 - \dot{C}H_2$

These free radicals (R) then attack the unsaturated monomer and form a new free radical which goes on successively adding monomers and thus grows the chain, this is called **Chain propagation** :

$$R - CH_2 - \dot{C}H_2 + CH_2 = CH_2 \longrightarrow R - CH_2 - CH_2 - CH_2 - \dot{C}H_2$$

or $M - MMMMMMMMM^{\bullet}$

The final **termination** of the two growing chains leads to a polymer. This is called **chain termination** :

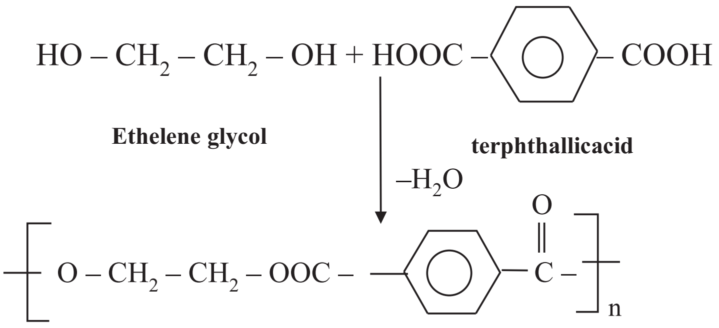
$$\begin{array}{c} MMMMMMMMM^{\bullet} + {}^{\bullet}MMMMMMMMM \\ \downarrow \\ M\ MMMMMMMMMMMMMMMMMM \end{array}$$

Polymer

Condensation Polymerization : In this, the monomers combine with the elimination of a small molecule like H_2O, ROH or NH_3, etc. The reaction is called (step growth) condensation polymerization and the product formed is called condensation polymer.

The process involves the elimination of by product molecules, therefore, the molecular mass of the polymer is not the integral multiple of the monomer units.

For example polyester or Terylene is a condensation polymer of ethylene glycol and terphthallic acid.



Poly (ethylene terphthalate) or (Terylene)

These two processes of making polymers have several characteristics which distinguish them from each other. These are shown in (Table 31.2).

Table 31.2 : Some differences between addition polymerization and condensation polymerization

Addition Polymerization	Condensation polymerization (Polycondensation)
1. Involves unsaturated monomer like ethylene, vinyl chloride, styrene etc.	1. Involves substances with at least 2 functional groups like ethylene glycol (2-OH groups), adipic acid (2-COOH groups).
2. Fast addition of monomers	2. Step-wise slow addition
3. At any instant, only monomer and polymers are present.	3. No monomer. Mixtures of dimers, trimers and tetramers etc. are present
4. Initiator is necessary to catalyse the polymerization.	4. Catalyst is not necessary.
5. No small molecules are eliminated.	5. Small molecules like H_2O, HCl, CO_2, CH_3OH are often eliminated.
6. Polymers are made for example, polyethene, polypropylene, polybutadiene, polyvinylchloride.	6. Polymer are made for example, terylene, nylon, Formaldehyde-resins, silicones.

INTEXT QUESTIONS 31.2

1. Define the terms :

   (i) Polymer (ii) Monomer

2. Write one example of each of :

   (i) Addition polymerization (ii) Condensation polymerization.

3. Differentiate between homopolymers and copolymers.

4. Write monomers of Terylene and Nylon-66.

31.4 CLASSIFICATION OF POLYMERS

The polymers can be classified in a number of ways. Some of these are discussed below for a systematic investigation of their properties and uses.

(a) Classification of Polymers on the Basis of Origin.

On the basis of origin, polymers are classified as :

1. Natural polymers
2. Synthetic polymers

1. **Natural Polymers :** The polymers obtained from nature (plants and animals) are called natural polymers. Starch, cellulose, natural rubber, proteins, etc. are some examples.

2. **Synthetic Polymers :** The polymers which are prepared in the laboratories are called **synthetic polymers.** These are also called **man-made polymers.** Polyethene, PVC, nylon, feflon, bakelite, terylene, synthetic rubber, etc. are common examples.

(b) Classification of Polymers on the Basis of structure

On the basis of structure of polymers, these can be classified as :

1. Linear polymers
2. Branched chain polymers
3. Cross-linked polymers.

1. **Linear polymers :** These are polymers in which **monomeric units** are linked together to form linear chains. These linear polymers are well packed (Fig. 31.1) and therefore, have high densities, high tensile (pulling) strength and high melting points. For example, polyethelene, nylons and polyesters are examples of linear polymers.

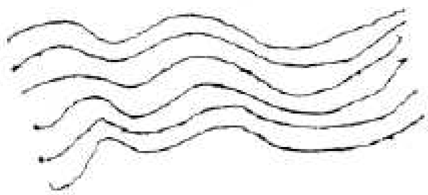


Fig. 31.1 : *Linear Polymers*

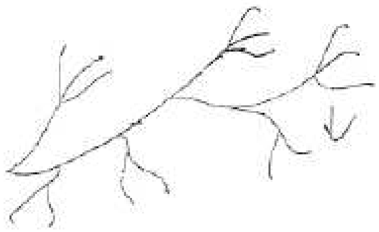


Fig. 31.2 : *Branched chain polymers*

2. **Branched chain polymers :** These are polymers in which the monomers are joined to form long chain with side chains or branches of different lengths (Fig. 31.2). These branched chains polymers are irregularly packed and therefore, they have lower tensile strength and melting points than linear polymers. For example, low density polyethene, glycogen, starch, etc.

3. **Cross-linked polymers :** These are polymers in which long polymer chains are cross-linked together to from a three dimensional network. These polymers are hard, rigid and brittle because of the network structure. (Fig. 31.3 bakelite, melamine and formaldehyde resin are some examples of this type.

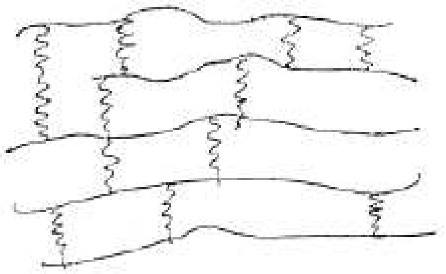


Fig. 31.3 : *Cross linked polymers*

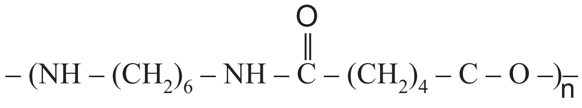
(c) Classification of Polymers on the Basis of Method of Polymerisation

On the basis of method of polymerisation the polymers are classified as :

1. **Addition polymer :** A polymer formed by direct addition of repeated monomers without the elimination of any small molecule is called **addition polymer.** In this type, the monomers are unsaturated compounds and are generally derivatives of ethene. The addition polymers have the same empirical formula as their monomers. Examples are polyethene, polypropylene and polyvinyl chloride, etc.

2. **Condensation polymer :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc. is called **condensation polymer.** In this type, each monomer generally contains two functional groups. For example, nylon – 66 is obtained by the condensation of two monomers; hexa methylenediamine and adipic acid with the loss of water molecules.

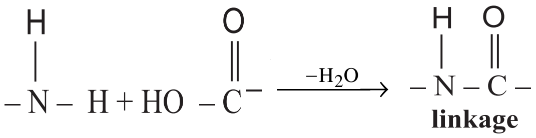
$$n\,H_2N-(CH_2)_6-NH_2+nHOOC-(CH_2)_4-COOH-\xrightarrow{-n\,H_2O}$$



$$-(NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-C-O-)_{\overline{n}}$$

nylon - 66

In this polymerization reaction – NH_2 group of hexamethylenediamine reacts with – COOH group of adipic acid forming – NH –CO – linkage with the elimination of H_2O.



$$-\overset{\overset{\displaystyle H}{|}}{N}-\;H+HO\;-\overset{\overset{\displaystyle O}{\|}}{C}-\xrightarrow{-H_2O}\underset{\textbf{linkage}}{-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-}$$

Examples of condensation polymers are Nylon 66, terylene, bakelite, alkylresins, etc.

(d) Classification of Polymers on the Basis of Molecular Forces

Depending upon the intermolecular forces between monomer molecules, the polymers have been classified into four types.

Notes

1. Elastomers
2. Fibers
3. Thermoplastics
4. Thermosetting

1. **Elastomers :** In case of elastomers the polymer chains are held together by weak **van der waals forces.** Due to weak forces, the polymers can be easily stretched on applying small stress and they regain their original shape when the stress is removed. This is due to the presence of few- ‘cross links’ between the chains, which help the polymer to retract to its original position after the force is removed, as in vulcanized rubber.

   The most important example of elastomer is **natural rubber.**

2. **Fibres :** These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of the strong forces, the chains are closely packed, giving them high tensile strength and less elasticity. These polymers can be drawn into long, thin and thread like fibres and therefore can be woven into fabrics. The common examples are nylon-66, dacron, silk, etc.

3. **Thermoplastics :** These are linear polymers with very few cross linkages or no cross linkages at all. The polymeric chains are held by weak VANDER WAAL forces and slide over one another. Due to lack of cross linkages these polymers soften on heating and harden or become rigid on cooling. Thus they can be moulded to any shape. Polythene, PVC, polystyrene are addition type thermoplastics and Terylene, nylon are condensation type thermoplastics.

   Plasticizers : Certain plastics do not soften much on heating. These can be easily softened by the addition of some organic compounds which are called **plasticizers.** For example, polyvinyl chloride (PVC) is very stiff and hard but is made soft by adding di-n-butylphthalate (a plasticizer). Some other common plasticizers are dialkyl phthalates and cresyl phthalate.

4. **Thermosetting polymers :** Usually thermosetting polymer can be heated only once when it permanently sets into a solid which can not be remelted and remoulded. Thermosetting polymers are produced from relatively low molecular mass semi fluid polymers (called polymers) which on heating develop extensive cross-linkage by themselves or by adding some cross-linking agents and become infusible and insoluble hard mass. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked and is permanently rigid. The common example are bakelite, melamine, formaldehyde resin, etc.

   Some important differences in the properties of thermosetting and thermoplastic polymers are summerized in Table 31.3.

Table 31.3 : Distinction between Thermoplastic and Thermosetting polymers

Themoplastic	Thermosetting polymers
1. Linear Polymers.	1. Cross-linked polymers.
2. Weak van der Waals intermolecular forces and thus soften/melt on heating.	2. Chemical cross-linking make them infusible materials. Do not melt on heating.
3. Molten polymer can be moulded in desired shape. It can be remoulded by heating again.	3. Cross-linking is usually developed at the time of moulding where they harden irreversibly.
4. Examples are polystyrene, PVC, SBR, Teflon, PMMA terylene.	4. Examples are Glyptals, epoxy polymers, formaldehyde resins.

INTEXT QUESTIONS 31.3

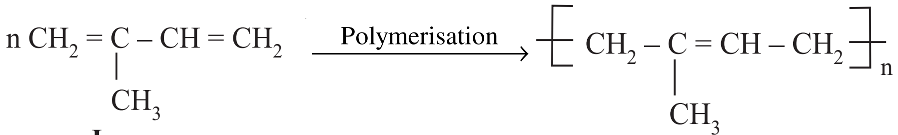
1. Define natural and synthetic polymers with examples?
2. What are cross linked polymers? Give one example of this type.
3. How do thermoplastic differ from thermosetting polymers?
4. Arrange the following polymers in the increasing order of their intermolecular forces. Also classify them as addition and condensation polymers.
   Nylon – 66, Buna-S, Polyethene.

31.5 SOME COMMERCIALLY IMPORTANT POLYMERS

31.5.1 Polydiens

These polymers are obtained when an unsaturated hydrocarbon with two double bonds or when a diene (2 double bond compound) is polymerized with a substituted alkene. The polymers belonging to this class are rubbers or elastomer. They can be natural or artificial. Consequently we have natural rubber and synthetic rubber.

(1) Natural Rubber : It is a polymer of unsaturated hydocarbon, 2-methyl-1, 3-butadiene also called isoprene. It is obtained from the latex of rubber trees found in tropical and semi-tropical countries such as India (southern part), Indonesia, Malayasia, Ceylon, South America, etc. The latex contains about 25-40% of rubber hydrocarbons dispersed in water alongwith stabilizer proteins and some fattyacids. It is a natural polymer and possess remarkable elasticity.



$$n\,CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2 \right]_n$$

Isoprene
2-methyl–1, 3–butadiene

Polyisoprene
(natural rubber)

In natural rubber 10,000 to 20,000 isoprene units are linked together.

Drawbacks of raw rubber

Raw natural rubber has a number of drawbacks. For example :

1. Rubber is brittle at low temperature and becomes very soft at high temperatures. Thus it can be used only in the limited temperature range of 10-60°C
2. It is too soft to be used for heavy duty operation.
3. On stretching, it undergoes permanent deformation.
4. Not resistant to mineral oils, organic solvents and even action of water. It has large water absorption capacity.

Vulcanization of Rubber

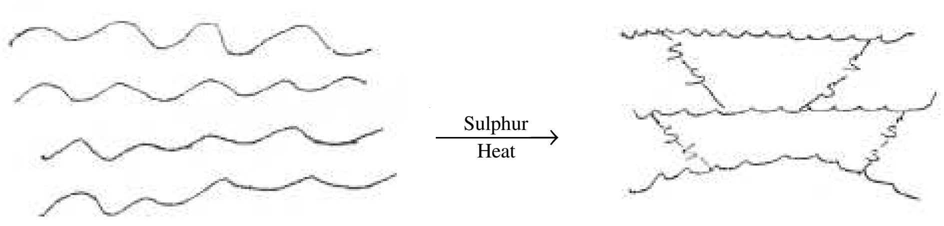
The wide applications of rubber are due to its property called elasticity and that is why rubber is said to be an **elastoplastic** or **elastomer.** Accidentally, in 1893, Charles Goodyears discovered that addition of sulphur to hot rubber cause changes that improve its physical properties in a spectacular manner. This process is called **vulcanization.** It is carried out by heating crude rubber in presence of sulphur or dipping it in a solution of S_2Cl_2 in CS_2. **Vulcanisation depends upon :**

(i) The amount of sulphur used : by increasing the amount of sulphur rubber can be hardened

(ii) Temperature

(iii) Duration of heating.

Crude rubber is intimately mixed with about 3% ground sulphur, an accelerator and activator and then heated to about 150^0C (for tyres it is 153^0C). Vulcanisation is a progressive reaction and is allowed to a definite stage. The detailed mode of vulcanization process may be difficult to visualize, but probable structure of vulcanized rubber is depicted below (Fig. 33.4).



Natural rubber *Vulcanized rubber*

Fig. 31.4 : *Process of vulcanization of rubber*

Table 31.4 Comparison of some properties of natural rubber and vulcanized rubber :

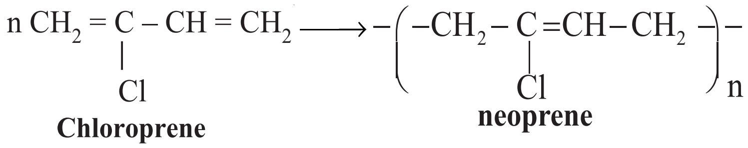
Natural Rubber	Vulcanised rubber
1. Natural rubber is soft and sticky.	1. Vulcanized rubber is hard and non-sticky.
2. It has low tensile strength.	2. It has high tensile strength.
3. It has low elasticity.	3. It has high elasticity.
4. It can be used over a narrow range of temperature (from 10^0 to 60^0C).	4. It can be used over a wide range of temperature (- 40^0 to 100^0C).
5. It has low wear and tear resistance.	5. It has high wear and tear resistance.
6. It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	6. It is insoluble in most of the common solvents.

(2) Synthetic Rubbers

Synthetic high polymers possessing similar physical properties as that of natural rubber are called **synthetic rubber.** Usually synthetic rubber is an improvement over natural rubber, specially with respect to its resistance to oils, gas, solvents.

Some synthetic rubbers are made by polymerization of only one monomer, for example Neoprene is made by polymerization of chloroprene, while synthetic rubbers like Buna-S, Buna N and Butyl rubber etc. are copolymers as these have more then one monomer.

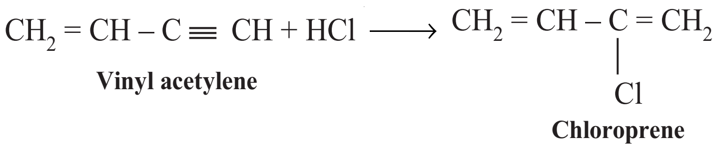
Neoprene : This synthetic rubber resembles natural rubber in its properties. It is obtained by polymerization of chloroprene.



$$n\,CH_2=\underset{\substack{|\\ Cl}}{C}-CH=CH_2 \longrightarrow -\left(-CH_2-\underset{\substack{|\\ Cl}}{C}=CH-CH_2-\right)_n-$$

Chloroprene **neoprene**

Chloroprene is obtained by the reaction of HCl with vinylacetylene



$$CH_2=CH-C\equiv CH+HCl \longrightarrow CH_2=CH-\underset{\substack{|\\ Cl}}{C}=CH_2$$

Vinyl acetylene **Chloroprene**

Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to oils, gasoline and other solvents

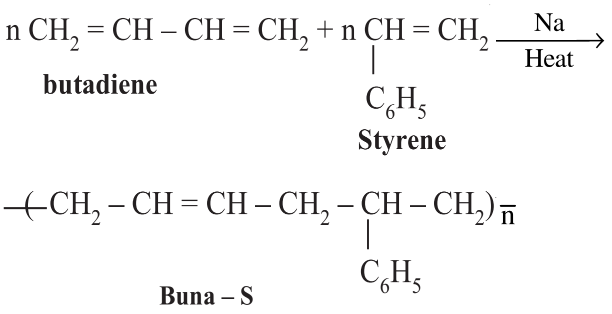
Neoprene is used for

(i) making belts, hoses, shoe heals, stoppers, etc. and

(ii) manufacture of containers for storing petrol, oil and other solvents.

Buna – S:

It is obtained by polymerization of butadiene and styrene in presence of sodium metal.



$$n\,CH_2=CH-CH=CH_2 + n\,\underset{\underset{C_6H_5}{|}}{CH}=CH_2 \xrightarrow[\text{Heat}]{Na}$$

butadiene **Styrene**

$$-\!\!\left(CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2\right)_{\overline{n}}$$

Buna – S

In Buna – S, Bu stands for butadiene, Na for sodium and S stands for styrene. It is also called S.B.R. (Styrene Butadiene Rubber). It has slightly less tensile strength than natural rubber.

Buna-S is used for

(i) making automobile tyres.

(ii) rubber soles, belts and hoses etc.

Buna – N : It is obtained by copolymerization of two parts of butadiene and one part of acrylonitrile in presence of sodium metal.

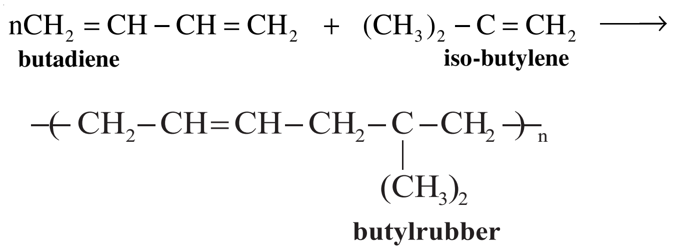
Buna – N is hard and extremely resistant to the swelling action by oils (petrol), solvents and is resistant to heat, etc.

Uses :

(i) It is used for the manufacture of storage tanks for solvents and

(ii) For making oil seals.

Butyl Rubber : This is obtained as a result of co-polymerization of butadiene and isobutylene. It is generally carried out in the presence of small quantity of isoprene. The function of isoprene is not exactly known.



$$nCH_2=CH-CH=CH_2 + (CH_3)_2-C=CH_2 \longrightarrow$$

butadiene **iso-butylene**

$$-\!\!\left(CH_2-CH=CH-CH_2-\underset{\underset{(CH_3)_2}{|}}{C}-CH_2\right)_n$$

butylrubber

Butyl rubbers are inert towards acids and alkalies, but have poor resistance towards petroleum products.

Uses :

(i) It is used for making inner tubes of tyres and

(ii) For making conveyor belts, tank linings and insulation of high voltage wires and cables etc.

INTEXT QUESTION 31.4

1. Write the IUPAC names and structures of monomers of the following polymers:

   (i) Natural rubber (ii) Neoprene

2. What is the function of sulphur in the vulcanization of rubber?

3. What is Buna – S? How is it synthesized?

4. Compare the properties (at least three) of natural rubber and vulcanized rubber?

After the detailed discussion of rubbers, we shall now discuss some other commercially important polymers.

31.5.2 Polyolefins

Polyolefins is a major class of synthetic polymers made by the polymerization of an olefin (alkene) or its suitable derivative. Most of these are obtained from petro chemical industry. Polyethylene, polypropylene, PVC, Teflon, etc. belong to the class of polyolefins. Some important members of this class are discussed here with.

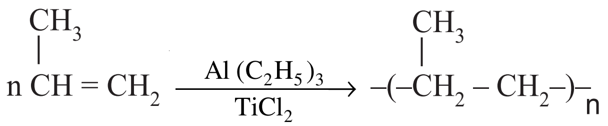
(1) Polyethylene or polyethene is formed by polymerization of ethylene ($CH_2 = CH_2$). It is manufactured in large quantities and is the most common polymer which you find almost every where.

Polyethene is of two types Low Density Polyethene (LDPE) and High Density Polyethene (HDPE) depending upon the nature of has branching in polymer chain and is not compact in polymer molecules. Low density polyethene has branching in polymer chains and is not compact in packing. While high density polyethere has linear chain of molecules which are packed in a more compact fashion (Fig. 33.1 and Fig. 33.2).

$$\underset{\textbf{ethylene}}{n\,CH_2 = CH_2} \longrightarrow \underset{\textbf{Polyethylene}}{-(CH_2 - CH_2)_{\overline{n}}}$$

Polyethylene is used for making pipes, insulators, packing films, carry-bags, etc.

(2) Polypropylene : The monomer units are propylene molecules. It is generally manufactured by passing propylene through n-hexane (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethyl aluminium and titanium chloride)



$$n\,\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{CH}} = CH_2 \xrightarrow[TiCl_2]{Al(C_2H_5)_3} -\!\!\left(\!-CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH_2}-\!\right)\!\!-_n$$

Propylene **Polypropylene**

Polypropylene is harder, stronger and lighter than polyethene Polypropylene is used for packing of textile material and food, lining of bags, gramophone records, ropes, carpet fibres, etc.

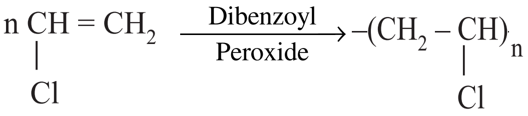
(3) Teflon or Polytetrafluoro ethylene (PTFE) : The monomer unit is terafluoroethylene molecule. Teflon is prepared by heating tetra fluoroethylene under pressure in the presence of ammonium peroxosulphate. $[(NH_4)_2S_2O_8]$.

$$n\,CF_2 = CF_2 \xrightarrow[\text{Heat, pressure}]{(NH_4)_2S_2O_8} -\!\!\left(CF_2 - CF_2\right)\!\!-_n$$

Tetrafluoroethylene **Teflon**

Teflon is a very tough material and is resistant towards heat, action of acids or bases. It is bad conductor of electricity. Teflon is used for coating utensils to make them non-sticking, making seals and gaskets which can with stand high pressures, insulation for high frequency electrical installations.

(4) Polyvinylchloride (PVC) : The monomer units are vinyl chloride molecules. PVC is prepared by heating vinyl chloride in an inert solvent in the presence of dibenzoyl peroxide.

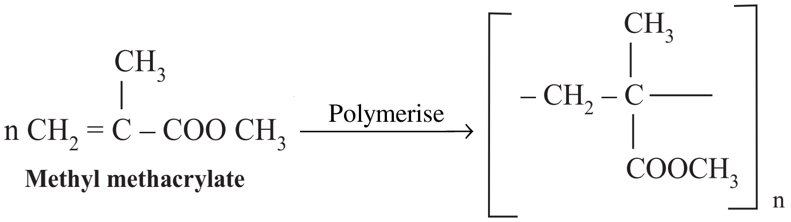


$$n\,\underset{\underset{\displaystyle Cl}{|}}{CH} = CH_2 \xrightarrow[\text{Peroxide}]{\text{Dibenzoyl}} -\!\left(CH_2 - \underset{\underset{\displaystyle Cl}{|}}{CH}\right)_n$$

Vinyl chloride PVC

PVC is a hard horny material. However, it can be made to acquire any degree of pliability by the addition of a plasticizer. It is resistant to chemicals as well as heat. It is used for making rain coats, hand bags, toys, hosepipes, gramophone records, electrical insulation and floor covering.

(5) Polymethyl Methacrylate (PMMA) : Its monomer unit is methyl methacrylate.



$$n\,CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - COO\,CH_3 \xrightarrow{\text{Polymerise}} \left[- CH_2 - \underset{\underset{\displaystyle COOCH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - \right]_n$$

Methyl methacrylate

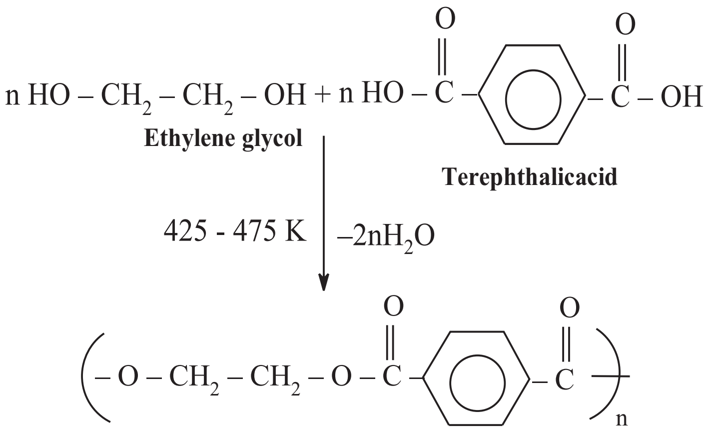
Polymethyl metha acrylate
(PMMA)

PMMA is a hard and transparent polymer and quite resistant to the effect of heat, light and ageing. It has high optical clarity. It is used in the manufacture of lenses, transparent domes and skylights, dentures, aircraft windows and protective coatings. Its commercial names are Lucite, Plexiglass, Acrylite and Perspex.

31.5.3 Polyester

Some synthetic polymers have ester group $(-\underset{\underset{\textstyle O}{\|}}{C}-O-)$ in them. These are condensation polymers. The important members of this class are polyester and glyptal resins.

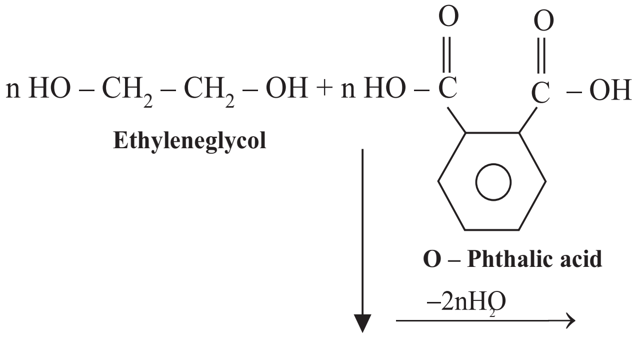
Terelene : It is a polymer obtained by the condensation reaction between ethylene glycol and terephthalic acid.

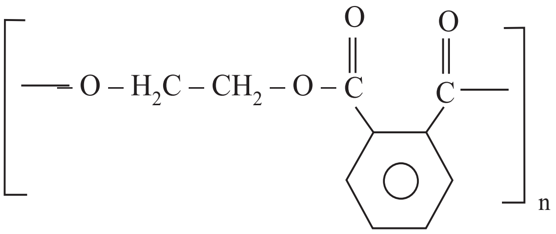


Polyester or terelene

Terelene is resistant to the action of most of the common chemicals and biological substances and also to abrasion. It has a low moisture absorbing power. As such it is widely used in making wash and wear fabrics. The polyester textile fibres made from the polymer are marketed under the trade name terelene or dacron. It is also blended with cotton and wool in clothing.

Glyptal or Alkyl resin : Glyptal is a general name of all polymers obtained by condensation of di-basic acids, and polyhydroxy alcohols. The simplest glyptal is (poly ethelene glycol phthalate) which is obtained by a condensation reaction between ethylene glycol and ortho-phthalic acid.



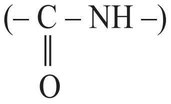


(Poly ethylene glycol
phthalate)

Glyptal resins are three dimensional cross-linked polymers. Poly (ethylene glycol phthalate) dissolves in suitable solvents and the solution on evaporation leaves a tough and non-flexible film. Thus, it is used in adherent paints and lacquers.

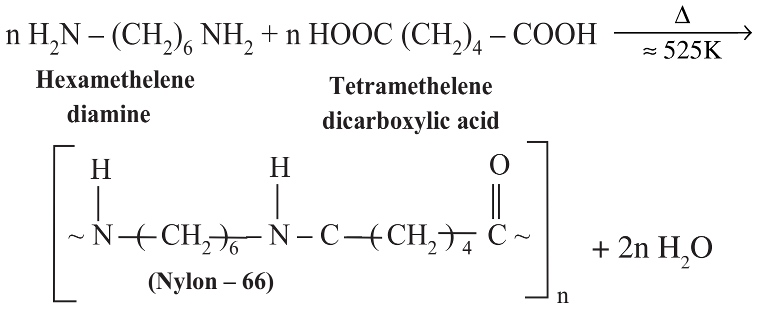
31.5.4 Polyamide

Polyamides are the polymers having amide group $(-\underset{\underset{O}{\|}}{C}-NH-)$ in them. The important polyamide is Nylon-66 which is a synthetic polymer. In nature also the polymer have amide linkages in their molecules.



$(-\underset{\underset{O}{\|}}{C}-NH-)$

Nylon – 66 : It is a polymer of adipic acid (tetra methelene dicarboxylic acid) and hexamethelene diamine



$$n\,H_2N-(CH_2)_6\,NH_2 + n\,HOOC\,(CH_2)_4-COOH \xrightarrow[\approx 525K]{\Delta} \left[\sim \overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - C - (CH_2)_4 - \overset{\overset{O}{\|}}{C} \sim \right]_n + 2n\,H_2O$$

Hexamethelene diamine

Tetramethelene dicarboxylic acid

(Nylon – 66)

Nylon – 66 (read as nylon – six-six) can be cast into a sheet or fibres by spinning devices. Nylon fibres have high tensile strength. They are tough and resistant to abrasion. They are also somewhat elastic in nature.

Nylon finds use in making bristles and brushes, carpets and fabrics in textile industry, elastic hosiery in the form of crinkled nylon.

INTEXT QUESTIONS 31.5

1. What does PMMA represent?
2. Write the names of monomers of terylene?

3. How is nylon - 66 synthesised?
4. Write equations for the synthesis of the following polymers :
   (i) glyptal (ii) Teflon

In this section we shall discuss about Biopolymers. (Natural Polymers)

31.5.5 Biopolymers

Many polymers which are present in plants and animals such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are called **biopolymers.**

(i) **Starch :** It is polymer of glucose. It is a chief food reserve of plants.

(ii) **Cellulose :** It is also a polymer of glucose. It is a chief structural material of the plants. Both starch and cellulose are made by plants from glucose produced during photosynthesis.

(iii) **Proteins :** These are polymers of **amino acids.** They have generally 20 to 1000 amino acids joined together in a highly organized arrangement. These are building blocks of animals and constitute an essential part of our food.

(iv) **Nucleic acids :** These are polymers of various nucleotides. For example, RNA and DNA are common nucleotides. These biopolymers are very essential for our life.

31.6 ENVIRONMENTAL PROBLEMS AND BIODEGRADABLE POLYMERS

In this section we shall discuss those polymers which will not cause any environmental pollution.

With the increasing use of polymers, the problem of disposal of waste of these products is posing alarming curse. Since most of the synthetic polymers are in the form of plastics, it is frequently used in abundance in the form of packing material and throw away bags. Since ordinary polymers do not degrade naturally by light, oxygen, water or micro-organisms, there is a serious problem of their disposal. The environmental problems caused by careless use of non-biodegradable polymers can be reduced by proper disposal of these materials and reusing them and remoulding them for other uses. Another way is to collect them and depolymerise them back to monomers. Though it has a limited application.

Another option is to produce biodegradable polymers which can be broken into small segments by enzyme-catalysed reactions. The required enzymes are produced by micro-organisms. It is a known fact that the carbon-carbon bonds of chain growth polymers are inert to enzyme catalysed reactions, and hence they are non-biodegradable. To make such polymers biodegradable we have to insert certain bonds in the chains so that these can be easily broken by the enzymes. When such polymers are buried as waste, micro organisms present in the soil can degrade the polymer, so that they do not cause any serious affects on the environment.

One of the best method of making a polymer biodegradable is by inserting hydrolysable ester group into the polymer.

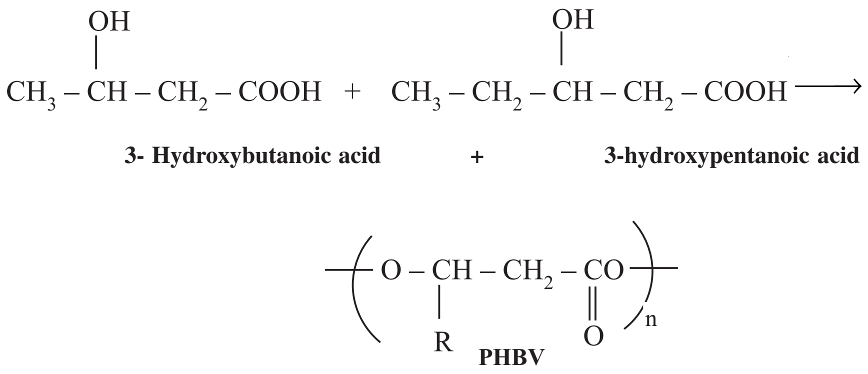
31.6.1 Some Biodegradable Polymers

A large number of bio degradable polymers are now available and more are being added to the list. However, these are expensive, therefore, these find use in special situations where cost factor can be ignored. In future, as their cost reduces these will find greater use in daily life and will replace non-bio-degradable polymers.

Some important biodegradable polymers are PHBV, PGA, PLA and PCL.

(PHBV) Poly-Hydroxybutyrate – co – β - Hydroxyvalerte

PHBV is a copolymer of 3 – hydroxy butanoic acid, and (3 – hydroxypentanoic acid), in which, the monomer units are connected by ester linkages.



$$\underset{\text{3- Hydroxybutanoic acid}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-COOH} + \underset{\text{3-hydroxypentanoic acid}}{CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_2-COOH} \longrightarrow$$

$$\underset{\text{PHBV}}{\left(O-\underset{\underset{R}{|}}{C}H-CH_2-\underset{\underset{O}{\|}}{C}O \right)_n}$$

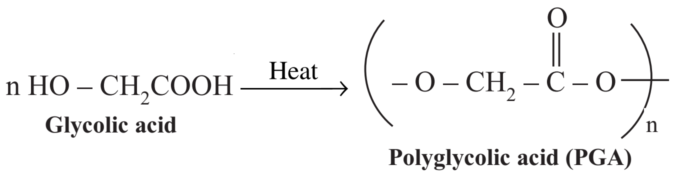
$R = -CH_3$ or $-CH_2-CH_3$

The properties of PHBV vary according to the ratio of both the acids. 3 – Hydroxybutanoic acid provides stiffness and 3 – hydroxypentanoic acid imparts flexibility to the copolymer.

(i) PHBV is used in orthopaedic devices and

(ii) In controlled drug release. The drug put in PHBV capsule is released after this polymer is degraded by enzymatic action. It can also be degraded by bacterial action.

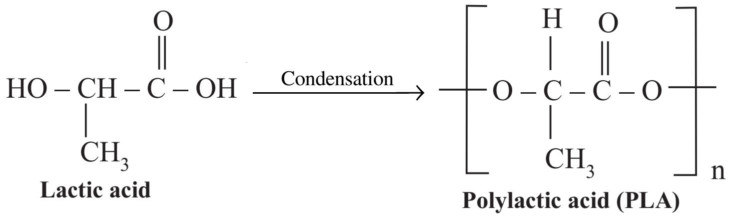
PGA Polyglycolic acid is obtained by the chain polymerization of dimer of glycolic acid, HO – CH_2COOH.



$$n\,HO-CH_2COOH \xrightarrow{Heat} \left(-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)_n$$

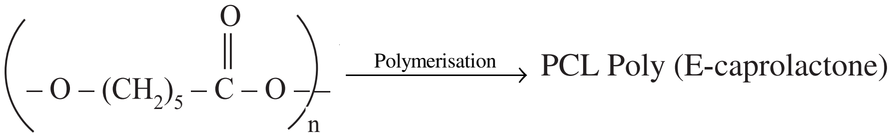
Glycolic acid **Polyglycolic acid (PGA)**

PLA Polyactic acid is obtained by polymerization of the dimer of lactic acid ($HO–CH(CH_3)\ COOH$) or by micro biological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.



Lactic acid **Polylactic acid (PLA)**

PCL Poly (E–caprolactone) is obtained by chain polymerization of the lactone of 6 – hydroxy hexanoic acid.



$$\left(-O-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)_n \xrightarrow{Polymerisation} \text{PCL Poly (E-caprolactone)}$$

Most of the biodegradable polymers find use in stiching wounds and cuts.

1. In medical goods such as surgical sutures.
2. In agriculture materials such as films, seed coatings.
3. In food wrappers, personal hygiene products, etc.

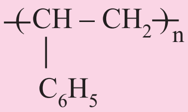
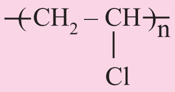
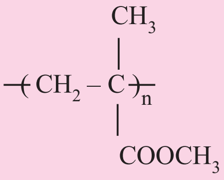
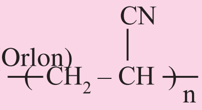
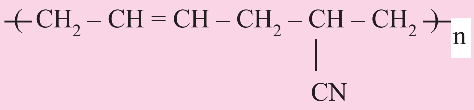
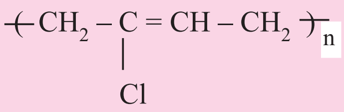
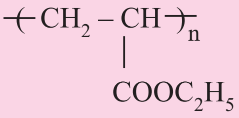
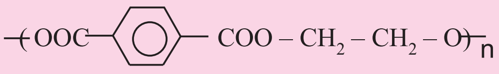
INTEXT QUESTIONS 31.6

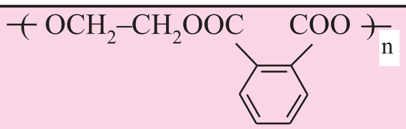
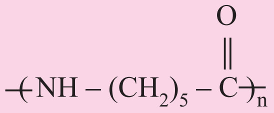
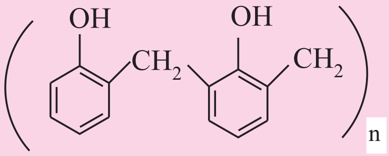
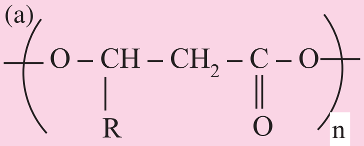
1. What is PHBV?
2. Give two examples of biopolymers?
3. Define biodegradable polymers? Give three examples?
4. Which polymer is used for post-operative stitches?

In the following Table 33.4 we shall now give a brief account of the various commercially important polymers alongwith their structures and uses.

Notes

Table 31.5

S. No.	Name of Polymer	Structure	Uses
1.	Polythene	$-\!\left(CH_2-CH_2\right)_n\!-$	As Insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	 $\left(\underset{\underset{C_6H_5}{\mid}}{CH}-CH_2\right)_n$	As Insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	 $\left(CH_2-\underset{\underset{Cl}{\mid}}{CH}\right)_n$	In manufacture or raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$-\!\left(CF_2-CF_2\right)_n\!-$	As lubricant, insulator and making cooking wares.
5.	Polymethyl metha acrylate (PMMA) or Flexi glass	 $\left(CH_2-\overset{\overset{CH_3}{\mid}}{\underset{\underset{COOCH_3}{\mid}}{C}}\right)_n$	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)	 $\left(CH_2-\overset{\overset{CN}{\mid}}{CH}\right)_n$	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or BuNa-S)	 $\left(CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{\mid}}{CH}-CH_2\right)_n$	In making automobile tyres and footwear.
8.	Nitrile rubber (Buna-N)	 $\left(CH_2-CH=CH-CH_2-\underset{\underset{CN}{\mid}}{CH}-CH_2\right)_n$	In making oil seals manufacture of hoses and tank linings.
9.	Neoprene	 $\left(CH_2-\underset{\underset{Cl}{\mid}}{C}=CH-CH_2\right)_n$	As insulator, making conveyor belts and printing rollers.
10.	Poly ethyl acrylate	 $\left(CH_2-\underset{\underset{COOC_2H_5}{\mid}}{CH}\right)_n$	In making films, hose pipes and furnishing fabrics.
11.	Terylene (Dacron)		For making fibres, safety belts, tyre cords, tents, etc.

12.	Glyptal		As binding material in preparation of mixed plastics and paints.
13.	Nylon 6	 $-\!\!\left(NH-(CH_2)_5-\overset{\overset{O}{\parallel}}{C}\right)\!\!_n$	In making fibres, plastics, tyre cords and ropes.
14.	Nylon 66	$-\!\!\left(NH-(CH_2)_6-NHCO\,(CH_2)_4\,CO\right)\!\!-_n$	In making brushes synthetic fibres, parachutes, ropes and carpets.
15.	Bakelite		For making gears, protective coating and electrical fittings.
16.	Urea formaldehyde resin	$-\!\!\left(NH-CO-NH-CH_2\right)\!\!-_n$	For making unbreakable cups and laminated sheets.
17.	Melamine formaldehyde resin		Formaking plastic crockery, un breakable cups and plates.
18.	Poly-β-hydroxy butyrate-co-βhydroxy valerate (PHBV)	(a)  $-\!\!\left(O-\underset{\underset{R}{\vert}}{CH}-CH_2-\overset{}{\underset{\underset{O}{\parallel}}{C}}-O\right)\!\!-_n$ $R = CH_3, -C_2H_5$	As packging, orthopaedle devices and in controlled drug release.

WHAT YOU HAVE LEARNT

- Difference between soaps and detergents
- Lipophilic and hydrophilic parts of soap and detergent molecules
- Advantages and disadvantages of detergents over soaps
- Cleansing action of soaps and detergents
- Soap does not make leather with hardwater due to formation of salt with calcium and magnesium.

- Linear Alkyl benzene sulphonate is better biodegrable than branched alkyl benzene sulphonates detergents.
- Polymers, the high molecular mass macrosized molecules consisting of repeating units of monomers of synthetic or natural origin.
- Synthetic polymers are classified with respect to their composition, mode of poly merization and nature of molecular forces.
- Polymerization is classified into two categories (i) addition polymerization (ii) condensation polymerization.
- Addition polymers are formed by addition of large number of monomers without the elimination of any smaller molecules.
- Condensation polymers are formed by elimination of smaller molecules such as H_2O, NH_3 etc.
- Natural rubber is a linear polymer of isoprene, and is vulcanized by heating with sulphur, which forms cross link between different chains.
- Vulcanized rubber has much improved physical properties.
- Synthetic rubbers are usually obtained by copolymerization of an alkene and 1,3-butadiene derivatives.
- Synthetic polymers due to their inertness to degradation have created environmental problems.
- Since biopolymers degrade enzymatically, synthetic biodegradable polymers having functional groups such as ester, amide etc. have potential use as sutures, implants, drug release materials, are developed as alternatives. For example, PHBV, PLA, etc. constitute such materials.

TERMINAL EXERCISE

1. What is the difference in between soaps and detergents?
2. Write the cleansing action of soap sand detergents.
3. Write the names of two anti oxidants.
4. Which type of soap and detergents are biodegradable?
5. What is spanification?
6. Explain the difference between chain growth and step growth polymerization.
7. Define the terms thermosetting and thermo-plastics. Give one example of each.
8. What is a copolymer. Give one example.

9. Differentiate between addition polymer and condensation polymer with the help of one example each.
10. What are elastomers? Give the chemical equation for the preparation of Buna-S.
11. Write the information asked for the following polymers :
    (i) Neoprene : Materials required for preparation.
    (ii) PVC : monomer unit.
    (iii) Synthetic rubber : monomer units
12. What is vulcanization of rubber? What are the advantages of vulcanized rubber?
13. Give examples of two plasticizers.
14. How are polymers classified into different categories on the basis of intemolecular forces? Give one example of a polymer of each of these categories.
15. What are biodegradable polymers? Give three examples.
16. Write the names and structures of monomers of the following polymers :
    (a) Polystyrene
    (b) Teflon
    (c) PMMA
    (d) PVC
    (e) PHBV
    (f) Polypropylene.
17. How will you prepare the following? Give chemical reaction only :
    (a) PVC
    (b) Nylon-66
    (c) PMMA

ANSWERS TO INTEXT QUESTIONS

31.1

1. Sodium or potassium salt of higher fatty acid.
2. Sodium or potassium hydroxide and oils and fats.
3. Carboxylate anion
4. Sulphonate anion.
5. Long normal alkyl chain.
6. False

31.2

1. (i) Polymer is a giant chain like molecule obtained by inter-molecular combinations of similar or different types of smaller molecules.

   (ii) Monomers are the low molecular mass simple molecules capable of forming inter-molecular linkage to give gaint molecules called polymers.

2. (i) Polyethene (ii) Terelene

3. (i) Hompolymers are polymers made of single monomer units, for example, polythene, polystyrene, or polybuta diene.

   (ii) A copolymer is one which is formed by the co–polymerisation of two monomers. For example, Buna (or SBR, styrene - butadiene rubber)

4. (i) Ethelene glycol and terephthallic acid

   (ii) Hexamethelene diamine and adipic acid.

31.3

1. (i) Natural polymers are found in nature, (in animals and plants) e.g. proteins and nucleic acids.

   (ii) Synthetic polymers are man-made. e.g. Nylon, polyesters and rubbers.

2. The polymers in which the linear polymer chains are cross linked to form a three-dimensional network structure are called cross-linked polymers. The common example of this type of polymer is bakelite.

3. Thermoplastics differ from thermosetting plastics in terms of mode of linkage and intermolecular forces. Thermoplastic polymer can be moulded in desired shape but thermosetting polymers set to shape on heating and can not be moulded.

4. Polyethene < Buna-S< Nylon-66

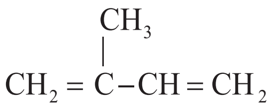
   Nylon 66 : Condensation polymer

   Buna-S : Addition polymer

   Polyethene : Addition polymer

31.4

1. (i) Monomer of natural rubber is

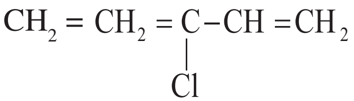


$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$

Isoprene

2-methyl buta-1,3-diene

   (ii) Monomer of Neoprene is



$$CH_2=CH_2=\underset{\underset{\displaystyle Cl}{|}}{C}-CH=CH_2$$

Chloroprene

2-Chlorobuta – 1,3-diene

2. Sulphur makes the rubber more elastic, more ductile, less plastic and non-sticky.
3. Buna-S is obtained by co-polymerization of butadiene and styrene in presence of sodium metal. Bu stands for butadiene, na for sodium and S stands for styrene, It is also called S.B.R.
4. 1. Natural rubber is soft and sticky, but vulcanised rubber is hard and non-sticky.
    2. Natural rubber has less tensile strength while vulcanised rubber has high tensile strength.
    3. Natural rubber is soluble in solvents like ether, carbon tebrachloride, petrol etc. whereas vulcanised rubber is insoluble in all common solvents.

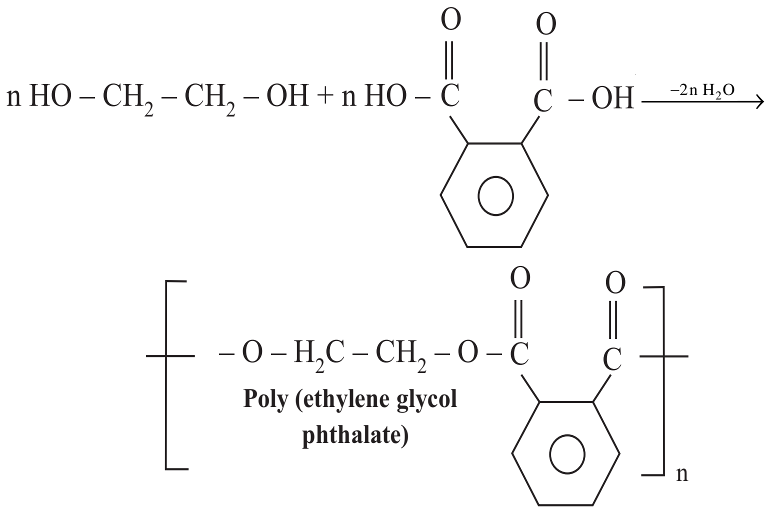
31.5

1. Polymethyl methacrylate (PMMA)
2. Ethelene glycol and terphthalic acid.
3. Nylon – 6, 6 is synthesised by the polymerisation of two monomer units adipic acid and hexamethelene diamine.

$$n\,H_2N\left(CH_2\right)_6 NH_2 + n\,HOOC\left(CH_2\right)_4 COOH \xrightarrow[525K]{\Delta}$$

$$\underbrace{\left[-N\left(CH_2\right)_6 NH-CO\left(CH_2\right)_4 CO-\right]_n}_{\textbf{Nylon – 66}} + 2n\,H_2O$$

4. (i) Glyptal



(ii) Teflon $n\,CF_2 = CF_2 \xrightarrow[\Delta,\ \text{pressure}]{(NH_4)_2S_2O_8} \left(-CF_2-CF_2-\right)_n$

31.6

1. PHBV is a copolymer of 3 – Hydroxy butanoic acid and 3-hydroxypentanoic acid. It is used in making capsules. It is biodegradable in nature.
2. Nucleic Acids, proteins.
3. Polymers, which are degraded by microorganisions are called biodegradable polymers. For examples, PHBV, Polyglycolic acid, Polylactic acid, etc.
4. Polyglycolic acid (PGA) and poly Lactic Acid (PLA).

32

ENVIRONMENTAL CHEMISTRY

The earth has just the right kind of conditions of temperature range, air, water, soil for supporting life and is protected from harmful rays from the outer space by the ozone layer. With progressive increase in human population and human activities, the quality of air, water, soil and other natural sources get degraded and become unfit for use by organisms. Increasing population, urbanisation and industrialisation has led to the decreased availability of water. The quality of water used is also being deteriorated as it is getting more and more polluted. You may be aware of at least some health hazards and harmful effects of water pollution. The main components of soil are 90–95%. Inorganic matter and 5–10% organic matter besides soil contains water and air, the composition of the soil varies considerably place to place.

Soil has become dumping ground of most of the waste products There will be a great loss of earth crust. The dumping of nuclear waste is a world side problem, cause of soil pollution. In this lesson a detailed account of various types, sources and effects of water pollutants is given. Some methods of water pollution control and legislatures involved have also been discussed.

It causes unwanted effects. In this lesson you shall learn about the sources of pollutants and their effects on environment. Thus the pollution in many ways threaten the existence of many organisms including human being on the earth. Therefore, any threat of degradation or damage to the environment should be a matter of concern the green chemistry is environment friendly living on design of chemical products with their impacts on human health and on environment. it reduces the use of hazardous substances.

OBJECTIVES

After reading this lesson you will be able to :

- define environment and biosphere;

- differentiate the varions environmental segments;
- explain nature of threats to environment;
- define pollutants and its types;
- list sources of pollutants and
- explain the effects of pollutants on environment, organisms and humans in particular.
- list earth's water resources;
- define water pollution and its different parameters;
- list the major types of water pollutants, their sources and effects;
- distinguish between natural and man -made pollutants;
- use the concept of biological oxygen demand (BOD) and account for the changes in a water body;
- state methods for the prevention of water pollution;
- compare primary, secondary and tertiary treatment of sewage;
- identify the sources of soil pollution;
- how to control of soil pollution,
- explain the principles of green chemistry;
- the achievements of green chemistry; and
- explain strategies to control environmental pollution.

32.1 COMPONENTS OF ENVIRONMENT

Different organisms live in different types of surroundings such as air, water and soil. Different kinds of living organisms share these surroundings. The surroundings are the "environment" of an organism.

Environment has two components

(i) physical or abiotic (non-living) components and

(ii) living or biotic components.

Abiotic components of environment are air, water, soil, energy radiation, etc. **Biotic components** of environment are microbes (such as bacteria, algae and fungi), plants, animals, etc.

Environment is the sum total of living and non living components surrounding an organism.

Environment consists of four segments such as

(i) Biosphere (ii) Atmosphere (iii) Hydrosphere, and (iv) Lithosphere

Biosphere : All the parts of the earth are not suitable for survival of organisms. Some parts are too hot or very cold to support life.

The part of earth on which organisms can survive and reproduce is called biosphere.

Survival of organisms depend upon a delicate balance between themselves and with the various components of the environment. Any disturbance, damage or adverse change in the quality of environment poses a threat to the survival and well being of organisms. Therefore, any threat of degradation or damage to environment should be a cause of concern to all of us.

Atmosphere : Atmosphere is the only place where free oxygen and water vapour exist.

Atmosphere is a thin layer of air (mixture of gases) around the earth which is a great source to all living organisms.

Hydrosphere : Water plays an important role in the biosphere, without it life is impossible.

Hydrosphere is the part of earth on which all types of water resources exists, viz., oceans, seas, rivers, lakes, glaciers, ice caps, ground water, etc.

Lithosphere : Soil is a part of lithosphere which supports life.

Lithosphere is the part of the earth where all types of minerals, metals, organic matters, rocks, soils, etc. exist

Global Environmental Damages

Some example of global damages are discuss below.

(i) Chloroflouro carbons (CFCs), used as refrigerants, and various kinds of sprays or sols (eg. perfumes, air freshner, etc.). CFCs cause ozone holes in the ozone layer. Ozone hole refer to depletion of ozone molecules in the ozone layer due to the reacton of CFCs.The holes in the ozone layer appear elsewhere and not where these chemicals are used.

(ii) More ultraviolet radiations reach the earth through the ozone holes and the reflected radiations from the earth are absorbed by CO_2 water vapour, etc. The traped radiations release more and more heat resulting in the phenomenon of **Global Warming.** This effect is also known as **Green House Effect.**

Global environment damage affects quality of environment over a much larger area and is not localised to the area where the damage is initiated. Global warming will cause ill effects and are not confined to the area causing the damage. It causes wide range of effects like melting of glaciers, polar caps, rise in water level of sea and flooding of costal plains, etc.

INTEXT QUESTIONS 32.1

1. Define environment.
2. What are the two components of environment?
3. List three biotic components?
4. How do CFCs affect the ozone layer?
5. What are the different segments of environment?

32.2 POLLUTION

In ancient times human settlements began and flourished along river banks as rivers provided them basic facilities. Growth of population forced people to move to other places. They started utilising natural resources such as trees and soil (mud) to build shelters. More waste material started collecting at places they inhabited. Humans themselves created conditions for disposal of waste (sanitation). Humans then started industries to manufacture goods for their own comforts. Pesticides and chemical fertilisers were manufactured to grow more food for the growing demand by population. Industries also generated wastes, which ultimately finds its way to water sources. Pesticides and chemicals were washed into natural water bodies such as sea, river, lakes and ponds and affected the aquatic organisms. Supply of potable (safe for drinking) water diminished. All this badly affects life of organism including humans. All such waste generated through human activities and spoiling the natural environment is termed as **pollutants**. Damaging the natural environment by pollutants is termed as **pollution.**

Pollution refers to deterioration or unclean objectionable conditions in the quality of natural resources such as air, water and soil because of the action or presence of unwanted substances beyond a certain limit.

32.3 POLLUTANTS

Pollutants are the substances or effect introduced into the environment in significant amounts in solid, semi solid, liquid gas or sub molecular particle form which has a detrimental (bad) effect on the environment.

The pollutants may be classified in the following ways (Fig.32.1).

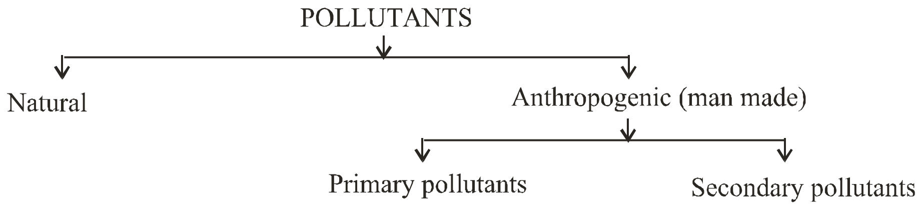


Fig. 32.1 : *Classification of pollutants*

32.3.1 Natural Pollutants

There can be several natural sources which are the cause of pollution. Some of them are listed below :

(i) Fires in forests may be caused when lightening strikes the trees. Burning of tree produces a lot of CO_2 which is released to the atmosphere.

(ii) Soil erosion increases suspended particulate matter and dust in air. These may even enter water bodies as they are washed down by rain or natural water falls.

(iii) Volcanic eruptions also add pollutants like SO_2 and solid particles to the environment.

(iv) Volatile organic compounds from leaves, trees and dead animals naturally enter the atmosphere.

(v) Natural radioactivity and the other natural pollutants have been entering the environment since ages. (But the low level of pollution has rarely endangered lives of organisms).

32.3.2 Anthropogenic Pollutants

Increased human activities releases a large amount of pollutants to the environment and poses a threat to the human life. Pollutants added to the environment through human activities are termed *anthropogenic pollutants*. These are of two kinds**.**

(i) **Primary pollutants:** Primary pollutants are added directly in a harmful form to the atmosphere. eg CO_2 and CO from burning of fossil fuel; SO_2 and oxides of nitrogen from vehicular combustion, thermal power stations, etc.

(ii) **Secondary Pollutants:** Secondary pollutants are the products of reaction between the primary pollutants and normal environmental constituents.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

Thus, SO_2 a primary pollutant which reacts with oxygen of air to give SO_3. Further, SO_3 reacts with water vapour present in the atmosphere and forms H_2SO_4. Thus SO_3 and H_2SO_4 are secondary pollutants.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$2NO + O_2 \longrightarrow 2NO_2$$

Nitric oxide (NO), a primary pollutant reacts with oxygen to give NO_2 which is a secondary pollutant.

Depending on the sources. anthropogenic pollutants may be classified further into

(i) Industrial Pollutants

(ii) Domestic Pollutants

(i) Industrial Pollutants: Paper, textile industries, tanneries and distilleries dispose various effluents like oil, grease, plastic and metallic wastes into the environment.

(ii) Domestic Pollutants: Detergents, fluoride toothpastes, edible colours, food flavouring agents, polythene bags and wrappers find their way into the environment as pollutants. Methane is produced in cattle stomach and in stagnant paddy fields is also a domestic pollutant.

INTEXT QUESTIONS 32.2

1. Define a pollutant.
2. Name two sources of natural pollution.
3. Define a secondary pollutant.
4. What do you mean by environmental pollution?

32.4 SOURCES OF POLLUTANTS

Many of the pollutants in our environment have natural as well as human related origins. For example, the natural origin of pollutants includes the release of sulphur dioxide (SO_2) from volcanic eruptions, erosion of soil by wind and water, dissolved minerals carried on to rivers and ocean by surface run off, etc.

The sources of pollutants are also classified :

(i) Stationary and

(ii) Mobile sources

Stationary Sources : The pollutants relased from a fixed location or a well defined area is known as stationary source. e.g. smokestacks of power plants, smelters, surface mines, etc.

Mobile Sources : The pollutants released from diffused sources or the sources that move from place to place is termed as a mobile source. e.g. automobiles, buses, aircrafts, ships, trains, etc.

The various pollutants of water, their sources and effects are given in Table 32.1

Table No. 32.1 : Major Air Pollutants their Sources and Effects

Major Pollutants of Air	Some of the Sources	Some of the Effects
SO_2	Vehicular combustion, fossil fuel burning	Irritation to the eyes, acid rain premature falling of leaves
CO and CO_2	Vehicular combustion and burning of fuels and hydrocarbons	Global warming, green house effect CO has great affinity for haemoglobin and forms the carboxy haemoglobin
Smoke, fly ash and soot	Thermal power stations	Respiratory diseases.
Lead and mercury	Auto exhaust from gasoline, paints, storage batteries. fossil fuel burning	Affects the nervous system and circulatory system causing nerve and brain damage.
CFCs	Refrigerants and aerosol	Kidney damage and ozone depletion.

The various pollutants of water, their sources and effects are summerised in Table No. 32.2

Table 32.2 : Major Water Pollutants their Sources and Effects

Major Pollutants of Water	Some of the Sources	Some of the Effect
Pesticides and insecticides like DDT, BHC	Improper use in agriculture, mosquitos repellants	Toxic to fishes, predatory birds and mammals.
Plastics	Homes and industries	Kills fishes and animals like cows.
Chlorine compounds	Water disinfection with chlorine, paper and bleaching powder	Fatal for plankton (organisms floating on the surface of industries water) foul taste and odour, can cause cancer in humans.
Lead	Leaded gasoline, paints, etc.	Toxic to organisms
Mercury	Natural evaporation and dissolved industrial wastes, fungicides	Highly toxic to humans
Acids	Mine drainage, industrial wastes	Kills organisms
Sediments	Natural errosion, run off from fertilizer and other factories, mining and construction activities.	Reduces ability of water to assimilate oxygen.

The general effects of pollutants are produced due to interactions of pollutants among themselves.

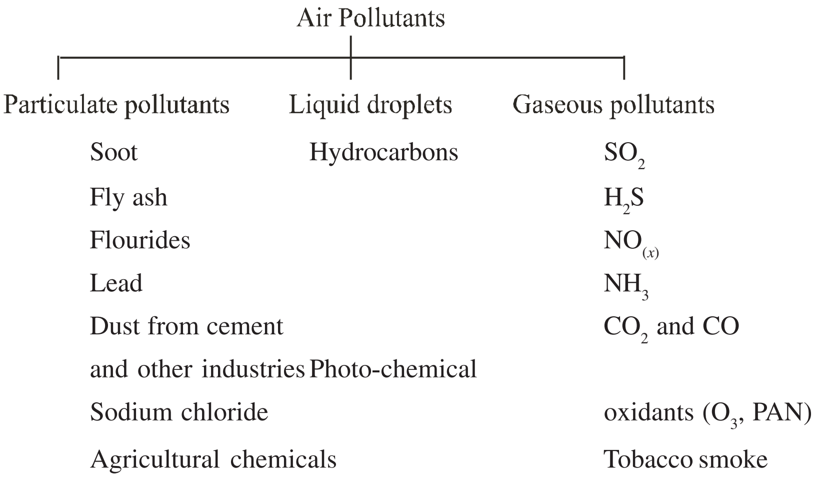
Contamination

Contaminations refer to the mere presence of undesirable materials to a medium like air, water, soil, etc. making it unfit for a particular use. For example, contamination of air by hazardous exhaust from automobiles. It becomes a pollutant if its concentration exceeds the level which can cause harmful effect.

32.5 AIR POLLUTION

You have just learnt how nature has its own means of using up and getting back its components such as CO_2, O_2 and N_2. If the balance of CO_2, O_2 or N_2 is disturbed by human activity then it will have adverse affect on life on the earth. Now you know why environmentalists are deeply concerned about environmental pollution, tree plantations and afforestation.

Undesirable changes have occurred in the physical and chemical constituents of air due to human activities. Undesirable change in the atmosphere is air pollution. Pollutant gases such as SO_2 oxides of nitrogen, CO and excessive amount of CO_2 have been added to the atmosphere. Air pollutant may be classified as particulate matter, liquid droplets and gaseous pollutants (Fig 32.2) :



Air Pollutants

Particulate pollutants	Liquid droplets	Gaseous pollutants
Soot	Hydrocarbons	SO_2
Fly ash		H_2S
Flourides		$NO_{(x)}$
Lead		NH_3
Dust from cement		CO_2 and CO
and other industries	Photo-chemical	
Sodium chloride		oxidants (O_3, PAN)
Agricultural chemicals		Tobacco smoke

Fig. 32.2 : *Classification and Example of Air pollutants*

32.5.1 Particulate Pollutants

Particulate pollutants such as soot and fly ash are released by various industries as by products of industrial processes. They are blown away by wind when they come out of the chimneys and other outlets of industries and mix with air.

Suspended particulate matter is also emitted by exhaust of polluting diesel vehicles and ill managed coal fired power plants. In nature, forest fires, wind erosion and volcanic eruptions add suspended particulate matter into air. Examples of particulate pollutants are soot, flyash from thermal power plants, cement dust, petrocoke from petroleum refineries. Some of the particulate pollutants are discussed in detail below:

Fluoride: Aluminium, steel and electrochemical plants, blast furnaces, brick kilns, coal combustion, tile and glass etching factories add fluoride particles which settle on vegetation. They burn tips of leaves and when cattle eat the vegetation they suffer from fluorosis resulting in loss of teeth, weight and lameness. Humans also suffer from fluorosis. Volcanoes also release fluorides which form gaseous as well as particulate pollutant.

Lead: Lead particles come into air from automobile exhausts. Lead is used as an antiknock agent in automobile gasoline which contains tetraethyl lead. Paint, ceramic and pesticide industries also add lead particles to the atmosphere. Manufacture of lead storage battries and recycling of discarded battries add to lead pollution. Lead interferes with development of red blood corpuscles and causes anaemia (lack of haemoglobin - the oxygen carrying pigment of blood). Lead is a cumulative poison and prolonged exposure even in low concentration may damage kidneys and liver.

Dust: Particulate matter less than 10 microns in size is dust. It reaches lungs, deposits along the respiratory tract and causes asthma or even lung cancer. Dust from stone crushers is another example of particular pollutant.

Sodium chloride: Sodium chloride is used to remove snow in winter and remains in the enviromnent. Some sodium chloride is also added to the environment when waves of the sea spray it. Excess sodium chloride has been found to cause defoliation (leaf falling), suppression of flowering and breaking of terminal shoots of apple.

Agricultural chemicals: Chemical insecticides, herbicides and other pesticides are known to have damaging effects on plants. They are toxic to animals and humans also. Residues of pesticides get suspended as particulate matter in air.

32.5.2 Hydrocarbons

Hydrocarbons which may be in the form of liquid droplets or gas pollute air. As liquid droplets they spill or are added through seepage of oil fields and natural gas leakage. Methane is emitted in the swamps and paddy fields by methanogenic bacteria. Methane (CH_4) is also generated in stomachs of ruminant animals. Incomplete combustion of fuels release 3, 4 benzopyrene which causes lung cancer. Pesticides, paints and solvents also release hydrocarbons. Hydrocarbons are a source of photochemical smog.

32.5.3 Gaseous Pollutants

SO_2, CO_2, nitrogen oxides are commonly added to the air by human activities. Excess of these have very serious damaging effects on the physical environment as well as on humans.

SO_2 and H_2S : These are released into atmosphere through smelting of ores containing sulphur, manufacture of H_2SO_4 petroleum refining, combustion of fossil fuels, paper making, burning of sulphur containing refuse and in nature through volcanic eruptions. Plants exposed to SO_2 and H_2S show defoliation (leaves falling off) and reduced growth.

In humans, SO_2 pollution causes headache, vomiting, irritation of eye and respiratory passages. SO_2 reacts with water to form H_2SO_4 which is washed down as acid rain about which you shall study later in the chapter.

Nitrogen Oxides: Anaerobic breakdown of nitrogenous compounds by bacteria is the natural source of nitrogen oxides. Burning fossil fuel also releases them. Power generators, automobile exhausts, explosives and nitrogenous fertilizer industries and the other anthropogenic sources produce nitrogen oxides.

NO_2: causes early dropping off of leaves and fruits in plants. Nitrogen oxides are one source of photochemical smog, acid deposition and greenhouse effect. .

CO_2 and CO : Combustion of oil, gas, coal and wood releases CO_2 in the atmosphere. CO is released chiefly from gasoline engines and burning of coal in defective furnaces. Motor vehicles with internal combustion engines emit high levels of CO and hydrocarbons. Excess of CO_2 can cause global warming, CO causes photochemical smog and has a fatal effect when inhaled by humans.

CO poisoning: CO has a high affinity for haemoglobin. It combines with the blood pigment haemoglobin to form carboxyhaemoglobin. The normal function of haemoglobin is to carry O_2. But CO combines with haemoglobin about two hundred times faster than O_2. Tissues do not get oxygen and die due to lack of oxygen. Carboxy haemoglobin is dark red in colour, the victims of CO poisoning have dark red lips. Mild CO poisoning causes lung disorders like bronchitis and emphysema. CO from cigarette smoke makes haemoglobin non functional in smokers.

Photochemical oxidants: Primary pollutants such as nitrogen oxides and hydrocarbons mix in the atmoshpere and form secondary pollutants like peroxyacetyl nitrate (PAN) and ozone, under the influence of UV radiation from the sun. Both PAN and O_3 form photochemical smog. PAN and O_3 are toxic to plants. In humans they cause irritation of eyes coughing, headache, dry throat, respiratory problems and haemorrhage.

Tobacco smoke: Smoke from burning cigarettes or bidis contains nicotine, aromatic hydrocarbons and tar. These cause problems of blood pressure and heart, windpipe and lungs in the smoker as well as those around the smoker. Cigarette smoke is also carcinogenic. The various human and natural activities which introduce air pollutants into the atmosphere are summarised in Table 32.2

Table 32.3 : Common air pollutants, their sources and contribution of Natural and Anthropogenic pollution

Air Pollutants	Some Sources	Emission (% of total) Natural	Anthropogenic
Sulphur oxide (SO_x)	Fossil fuel burning, industry biomass biomass burning, volcanoes, oceans.	50	50
Carbon monoxide (CO)	Incomplete combustion, methane oxidation, transportation, biomass burning, plant metabolism.	91	9
Nitrogen oxide (NO_x)	Fossil fuel burning, lightening, biomass burning, soil microbes.	40	60
Hydrocarbons (HC)	Fossil fuels, industrial processes, evaporation of organic solvents, agricultural burning, plant isoprenes and other biogenics.	84	16
Suspended Particulate Materials (SPM)	Biomass burning, dust, sea salt, biogenic aerosols, gas to particle conversion.	89	11

INTEXT QUESTIONS 32.3

1. What is atmospheric pollution?
2. Name two particulate pollutants.
3. Name two gaseous pollutants?
4. Name one source which causes pollution due to methane.
5. Name two air pollutants which form photochemical smog.

32.6 EFFECTS OF EXCESSIVE ATMOSPHERIC POLLUTANTS ON NATURE (OUTDOOR POLLUTION)

You are now familiar with the various atmospheric pollutants. Most of these are products of fuel combustion. These pollutants have been released into atmosphere ever since human first started burning wood and coal. Later on, pollutants are being released into air due to increased industrial activity. The nature has not been able to remove all these pollutants because much more pollutants are added than the nature can handle to maintain the balance. Therefore, pollutants have now accumulated in the atmosphere to a proportion whereby atmospheric composition of air has been significantly altered. It is the causes of physical phenomena such as photochemical smog, acid rain, ozone depletion, greenhouse effect and global warming. These are damaging to plants, animals and humans.

The figure Fig. 32.3 shows the four major effects of atmospheric pollutants. In the diagram, arrows from the pollutant depicts its involvement in the physical phenomenon. The sources of the pollutants are depicted below the names of the pollutants. The four major phenomena are subsequently discussed one by one. They are temperature inversion, photochemical smog, acid rain, greenhouse effect and ozone layer (shield) depletion.

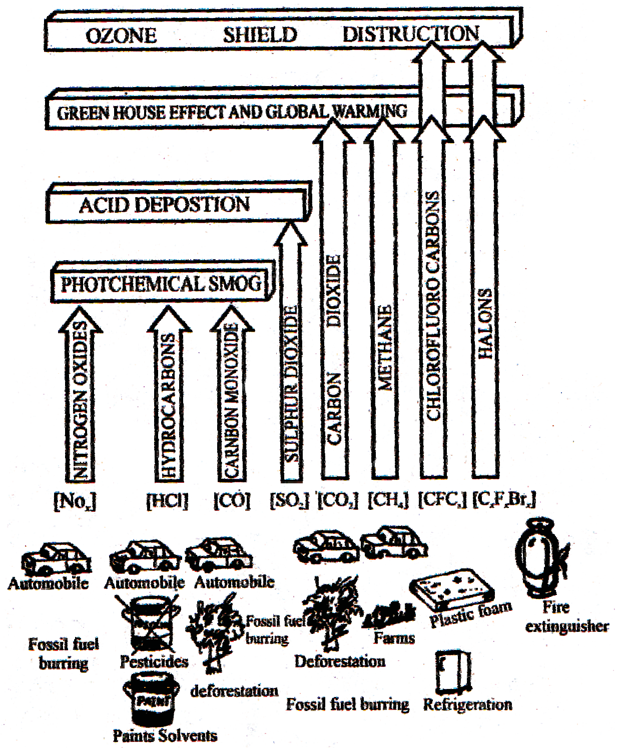


Fig. 32.3 : *Four Major Effects of Atmospheric Pollutants*

32.7 TEMPERATURE INVERSION AND PHOTO-CHEMICAL SMOG

Pollutants like sulphur dioxide which is released while burning sulphur containing fuels (fossil fuels) and particulate matter like soot present in stagnant air masses, get modified in sunlight and form a sheet called photochemical smog.

Smog is a combination of fog, smoke and fumes released by mills and factories, homes and automobiles.

When sunlight falls on stagnant air under low humid conditions in the presence of pollutants such as SO_2 soot, nitrogen oxides and hydrocarbons, photochemical smog is formed (photochemical: chemical reactions in the presence of light). Smog stays close to the ground and reduces visibility and causes irritation.

Photochemical smog is also called *PAN* ***smog*** due to the formation of peroxyacetyl nitrate or PAN and ozone which are formed from hydrocarbons and nitrogen oxides in the presence of solar radiation. PAN and ozone are called photochemical oxidants. Both of these are toxic irritants to human lungs.

Smog formation is accompanied by ***Temperature inversion or Thermal inversion,*** Temperature inversion causes smog to settle and remain near the ground till wind sweeps it away. Normally, warm air rises up into atmosphere. When a layer of cool air at the ground level is held there by an overlying layer of warm stagnant air. It is called **temperature** or **thermal inversion** (Fig.32.4).

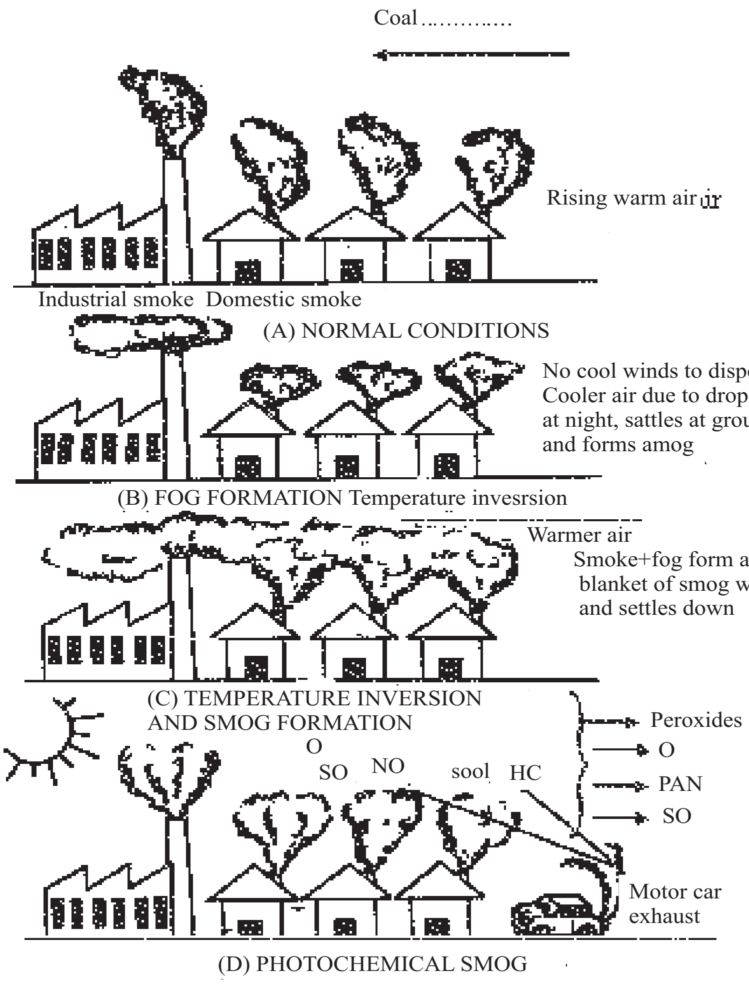


Fig. 32.4 : *Formation of Photochemical Smog and Temperature Inversion*

Exposure to smog causes respiratory problems, bronchitis, sore throat, cold, headache and irritation to eyes (red shot eyes). Smog also damages crops and reduces crop yield.

32.8 ACID RAIN

Coal and oil burned by power plants and other industries release SO_2 into air because coal and oil contain small amount of sulphur. Automobile exhausts add SO_2 and nitrogen oxides to the air. Both SO_2 and nitrogen oxides are converted into acids HNO_3 and H_2SO_4 when they combine with oxygen and water vapour in the atmosphere as per the following photo chemical reactions.

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

This reaction is promoted by O_3 in smog. The acids, so formed are washed down from air to earth during rain or snow fall. It is called acid rain or acid snow. The acids react with minerals present in soil to form sulphates and nitrates due to acid rain.

Rain water even in its purest form is slighlty acidic with pH 5.6 due to dissolved CO_2. But areas near coal and oil burning industries and where motor vehicles ply in large numbers, pH goes down to 2 and rain becomes strongly acidic. Mountain foot hills are the worst affected. There is moisture laden air rises to higher altitudes it condenses to fall as rain or snow, dropping its load of pollutants. In spring. snow melts and adds pollutants to lakes and other water bodies.

When the dissolved pollutants drop as rain or snow (wet deposition) it is termed acid precipitation. Deposition of dry gases and salts is dry deposition. Acid rain spreads over areas of several hundreds to several thousand kilometers.

32.8.1 Effects of Acid Rain

Some of the effects of acid rain are listed below:

(1) Excessive acid concentrations are phytotoxic (toxic to plants). There have been widespread death of trees in forests due to acid rain.

(2) Sea waters are rich in minerals and have great buffering capacity. But buffering capacity of fresh water bodies is low and acid deposits have a toxic effect on the fresh water ecosystems.

(3) Mature (capable of reproduction) fish survives in acid rain fed water bodies but fails to reproduce. So there are no young fish in such waters.

(4) Exposed surfaces of buildings, statues get corroded. Limestone or marble ($CaCO_3$) structures are specially damaged (Fig. 32.5).

The chemical reaction is like
$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O.$

The sulphates are leached out by rain water.

(5) Acidic sulphate when present in the atmosphere causes laziness. Acidic mist falling on the ground reduces visibility.

Fig. 32.5 : *A Stone statue showing corrosive effects of Acid Rain*

32.9 GREEN HOUSE EFFECT AND GLOBAL WARMING

The literal meaning and function of green house is to trap the heat. You must have seen delicate plants being grown in a glass chamber which is comparatively warmer inside than outside. Glass permits solar radiations to come in but restricts the outward movement of heat. The radiations get trapped inside the glass chamber and raises the temperature.

Gases such as CO_2, NO_2, CFCs (chloro fluorocarbons) allow sun rays to pass through them but then absorb and reradiate the heat back towards the earth. These are therefore termed as **green house gases**.

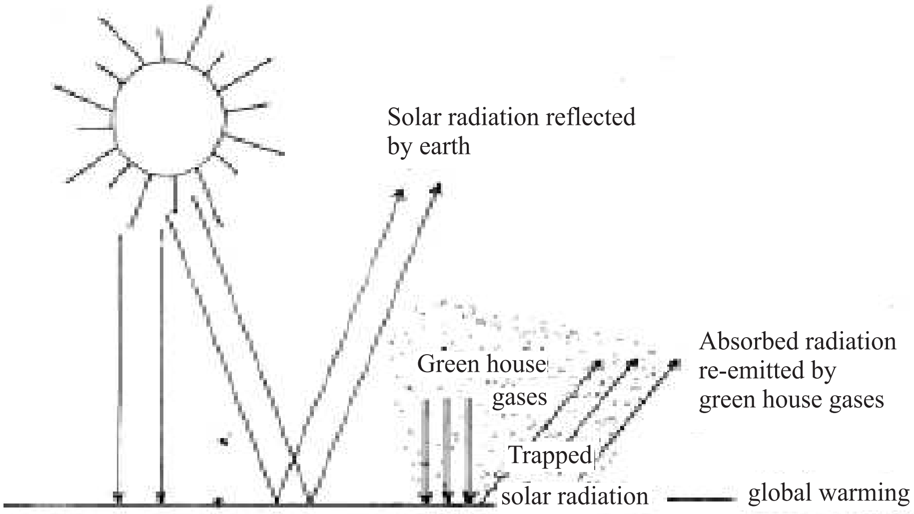


Fig. 32.6 : *Green House Effect*

32.9.1 Greenhouse Gases

The common green house gases and their sources of pollution are listed below:

(1) CO_2 - from fossil fuel burning.

(2) NO_2 - from fertilizer plants, automobile exhaust use and animal waste.

(3) CH_4 - from bacterial decomposition, biogas, flooded rice fields.

(4) CFCs - from freon, (a refrigerant), areosol sprays.

(5) HALONS (halocarbons) - from fire extinguishers.

32.9.2 How Does Earth's Atmosphere Trap Heat?

Radiations (ultra violet) from the sun penetrate the earth's atmosphere and reach earth. The surface of earth partially absorbs the radiations. The rest is re-radiated as infrared radiation from the earth's surface. In polluted air, molecules of CO_2, CH_4, CFCs, N_2O, O_3 and water vapours are present. These gases can absorb infrared radiations but cannot absorb the ultra violet radiations. Energy of these trapped radiations raise the temperature of earth and its atmosphere. Thus if proportion of green house gases increases in the atmosphere heat trapped by them will raise the temperature of the earth and will cause global warming.

Greenhouse effect leading to global warming shall have severe effects on rainfall, sea level, plant and animal growth..

Global warming is defined as the increase in the average global temperature of the atmosphere near earth's surface.

(1) **Rise in sea level:** It is estimated that by the turn of the century a rise of 5°C in global temperature will be due to effect of greenhouse gases if not checked now. Polar ice caps would melt because of rise in temperature and add more water to sea. Moreover water expands when it heats up. This will lead to rise of sea level. It will flood the low lying coastal area and many cities will get submerged in water.

(2) **Drought:** A 3° C warming will result in 10% decrease in precipitation (rain fall) and this will decrease rain fall causing drought conditions.

(3) **Effect on plant growth:** Drought will reduce photosynthesis in plants and lead to reduced growth of plants.

(4) **Effect on animals:** Warmer conditions will encourage growth of pests.

(5) **Water shortage:** Increase in temperature will lead to increased evaporation leading to shortage of water for agricultural, municipal and industrial use.

(6) **Climatic changes :** It has great effect on climate changes. For example, spring now occurs about a week earlier than normal time.

(7) **Increase in CO_2** Warmer conditions accelerate microbial degradation of organic matter and add more CO_2

(8) **Day and Night temperature :** Night temperatures have increased more than day temperature as green house gases prevent heat from escaping at night.

(9) **Formation of ozone hole :**

The atmosphere has two layers, the stratosphere and troposphere. Stratosphere lies 15 km to 50 km above the surface of earth. The energy of the sun splits some molecular O_2 in this layer to give individual (O) atoms which combine with intact molecular oxygen to give O_3. The layer of O_3 forms a shield as it absorbs UV rays and prevent them from striking the earth. If UV rays penetrate our atmosphere the life would not be possible as organisms cannot tolerate heavy doses of UV radiation. Troposphere is the atmospheric layer closest to the earth's surface whose compostion you have already studied. Chloro fluorocarbons and halons released into the atmosphere have destroyed the ozone shield and an **ozone hole** has been detected at the South Pole of Antartic and North Pole of Arctic.

32.10 DEPLETION OF OZONE LAYER

Ozone shield depletion is primarily caused due to the following reasons:

(a) Chlorofluorocarbons (CFCs) are the heat transfer agents used in refrigerators and air conditioners, and foaming agents in foam cups and cartons.

(b) Halons or halocarbons are anti fire agents used in fire extinguishers.

The ozone in the stratosphere is being depleted by the presence of mainly chlorofluorocarbons (CFCs) and halogen gas, particularly chlorine. The highly energetic ultra violet radiation splits up the CFCs, releasing chlorine. The released chlorine is responsible for convertion of the ozone into oxygen molecule consequently depletion of ozone layer occurs as per the following equations.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

It is believed that one molecule of CFC is capable of destroying 1,00,000 ozone molecules in the stratosphere. The area where the ozone is completely destroyed is known as **ozone hole.** The first ozone hole was observed over Antaractic Ocean.

The important function of ozone layer in the stratosphere in to protect us from dangerous ultra violet (UV) radiations from the sun by absorbing it.

32.10.1 Effects of Ozone Depletion

Ozone layer depletion will allow more UV rays to enter the troposphere and will cause a series of harmful effects such as :

(1) Plants and animals living on the surface will start dying.

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(2) UV radiation will fasten the formation of smog

(3) Temperature of the earth will increase leading to rise in sea level and flooding of low lying areas.

(4) More UV rays will directly fall on the skin of humans causing skin cancer.

(5) Leaves of plants will show chlorosis (loss of chlorophyll and yellowing),

32.11 EFFECTS OF AIR POLLUTION ON HUMANS

Air is mobile and impact of air pollution on ecosystems is reduced as wind blows away pollutants. But when winds are calm, air pollution becomes not only damaging but life threatening.

The damaging effects of atmospheric pollution have been described along with the account on pollutants. Long term exposure to moderate pollution causes more discase and death. Some adverse effects of air pollution on humans are summarised in table 32.4.

Table 32.4 : Effects of air pollutants on humans

Disease / Discomfort	Caused by
Emphysema. Bronchitis	CO, SO_2, PAN, O_3
Eye irritation, headache	SO_2, PAN, O_3
Silicosis. Asbestosis	Suspended particulate matter like silica, asbestos.
Coronary artery disease	Tobacco smoke
Anemia, kidney, liver damage	Pb
Fluorosis, Skin Cancer	Fluorides
Poisoning death	CO

32.12 CONTROL OF AIR POLLUTION

The alarming rate at which the atmosphere is being polluted, soon there will be more ailing human beings than healthy. The need of the hour is to put a quick check to atmospheric pollution.

Since most of air pollutants are emitted during combustion of fossil fuels, there are two practical approaches for air pollution control which are discussed below:

(i) One approach is control undesirable changes in the air we breathe by observing the following precaution :

(a) Limiting pollutants into air by using sulphur-free oil and coal, using catalytic convertors in automobiles and avoiding burning of waste material.

(b) Taking stringent measures against release of emissions from industries.

(ii) The other approach is to use sources of energy other than fossil fuels such as wind, water, solar power, etc. Use bicycles and battery powered cars rather than vehicles with internal combustion engines. Service vehicles should use lead free petrol.

Above all, it is necessary to educate the general public. Air pollution should become every human being's concern. Only then will the air become more congenial to healthy living.

INTEXT QUESTIONS 32.4

1. What is smog?
2. Name two photochemical oxidants.
3. Name two gases which form acid rain.
4. Mention any four greenhouse gases.
5. What are the sources of freons and halons in air?
6. What effect does acid rain have on marble statues ?
7. Mention one measure to control air pollution.

32.13 WATER POLLUTION – PARAMETERS

A large amount of water is discharged back after domestic and industrial usage. This is contaminated with domestic waste and industrial effluents. When this contamination reaches beyond certain allowed concentrations, it is called **pollution** and the contaminants are called the **pollutants**. **Water pollution** may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. If the concentration of substances naturally present in water increases then also the water is said to be polluted.

Water pollution may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. Industrialisation and population explosion are two important factors for water pollution.

Water may be called polluted when the following parameters stated below reach beyond a specified concentration in water.

(i) **Physical parameters**. Colour, odour, turbidity, taste, temperature and electrical conductivity constitute the physical parameters and are good indicators of contamination.

For instance, colour and turbidity are visible evidences of polluted water while an offensive odour or a bitter and difference than normal taste also makes water unfit for drinking.

(ii) **Chemical parameters**: These include the amount of carbonates, sulphates, chlorides, fluorides, nitrates, and metal ions. These chemicals form the total dissolved solids, present in water.

(iii) **Biological parameters**: The biological parameters include matter like algae, fungi, viruses, protozoa and bacteria. The life forms present in water are affected to a good extent by the presence of pollutants. The pollutants in water may cause a reduction in the population of both lower and higher plant and animal lives. Thus, the biological parameters give an indirect indication of the amount of pollution in water.

32.14 WATER POLLUTION – SOURCES

Water pollutants refer to the substances which are capable of making any physical, chemical or biological change in the water body. These have undesirable effect on living organisms. As mentioned earlier, the water used for domestic, agricultural and industrial purposes is discharged with some undesirable impurities in it. This contamination leads to the pollution of water, which is generally called the **fresh water pollution**. Fresh water pollution may be classified into two types: **surface water pollution** and **ground water pollution**.

32.14.1 Surface Water Pollution

When pollutants enter a stream, river or lake these gives rise to surface water pollution. The surface water pollution has a number of sources. These can categorised as:

- Point and Non-point Sources
- Natural and Anthropogenic Sources

(i) Point and Non-point Sources

The well-defined sources that emits pollutants or effluents directly into different water bodies of fresh water are called **point sources**. Domestic and industrial waste are examples of this type. The point sources of pollution can be effectively checked. On the other hand, the **non-point sources** of water pollution are scattered or spread over large areas. This type of sources deliver pollutants indirectly through environmental changes and account for majority of the contaminants in streams and lakes. For example, the contaminated water that runs off from agriculture farms, construction sites, abandoned mines, enters streams and lakes. It is quite difficult to control non-point sources.

(ii) Natural and Anthropogenic Sources

As mentioned earlier, an increase in the concentration of naturally occurring substances is also termed pollution. The sources of such an increase are called **natural sources**. **Siltation** (which includes soil, sand and mineral particles) is one such natural source. It is a common natural phenomenon, which occurs in most water bodies. Indiscriminate deforestation makes soil loose and flood waters bring silt from mountains into streams, rivers and lakes.

On the other hand, the human activities that result into the pollution of water are called **anthropogenic** or man made sources of water pollution**.** For example, domestic (sewage and waste water), industrial and agricultural wastes that goes into the rivers, lakes, streams and seas are anthropogenic sources. Certain materials that are leached from the land by run-off water and enter the various water bodies also belong to this category. The anthropogenic sources of water pollution are shown in Fig. 32.7.

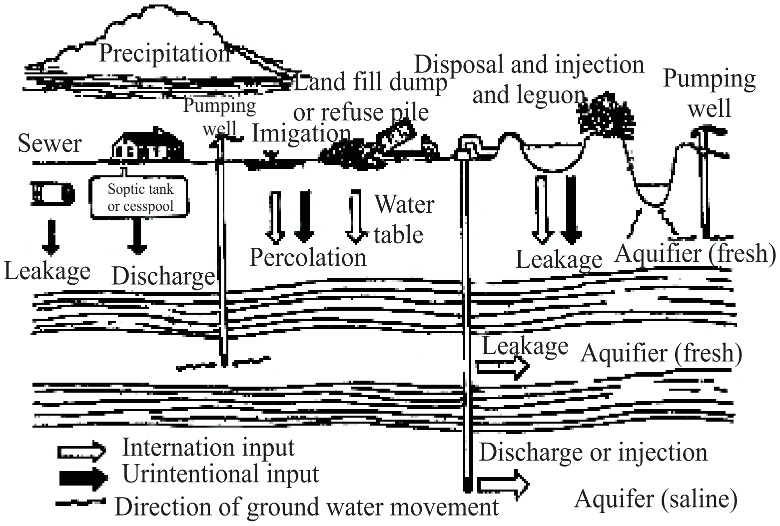

Fig. 32.7 : *Anthropogenic Sources of water pollution*

32.14.2 Ground Water Pollution

When the polluted water seeps into the ground and enters an aquifer it results into **ground water pollution**. The most of our villages and many townships, ground water is the only source of drinking water. Therefore, pollution of groundwater is a matter of serious concern. Groundwater gets polluted in a number of ways. The dumping of raw sewage on soil, seepage pits and septic tanks cause pollution of groundwater. Fig. 32.3. The porous layers of soil hold back solid particles while the liquid is allowed to pass through. The soluble pollutants are able to mix with the groundwater. In addition to these, the excessive use of nitrogenous fertilizers and unchecked release of toxic wastes and even carcionogenic substances by industrial units many ressult in slow trickling down

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through the earth's surface and mixing with the groundwater. This problem is very serious especially in areas where water table is high (i.e., where water is available near surface of earth).

The ground water can move over large distances by virtue of the large empty space available below the earth's surface. This way if some impurities seep into the ground water at one point, they may be observed at a different point far removed from the point of source. In such a case it is difficult to estimate the source of water pollution. However, suspended impurities and bacterial contaminants are removed in the process of seepage by the soil acting as an absorbent and filter, and water acting as a solvent.

Since the movement of groundwater through the porous rock is very slow, pollutants which get mixed with the groundwater are not readily diluted. Furthermore, groundwater does not have access to air (in contrast to surface water) therefore, oxidation of pollutants into harmless products in groundwater does not occur.

32.15 WATER POLLUTANTS

You have read the various sources from where pollutants enter the water bodies. Let us now learn about the various types of pollutants arising out of these sources. These can be broadly put under the following types.

(i) Sewage Pollutants (Domestic and Municipal Waste)

(ii) Industrial Pollutants

(iii) Agricultural Pollutants

(iv) Radioactive and Thermal Pollutants

(i) Domestic and Municipal Pollutants : The sewage contains garbage, soaps, detergents, waste food and human excreta and is the single largest sources of water pollution. Pathogenic (disease causing) microogranisms (baccteria, fungi, protozoa, algae) enter the water system through sewage making it infected. Typhoid, chloera, gastroenteritis and dysentery are commonly caused by drinking infected water. Water polluted by sewage may carry certain other bacteria and viruses cannot grow by themselves, but reproduce in the cells of host organisms. They cause a number of diseases, such as, polio, viral hepatitis and may be cancer which are resistant to like the organic matter are oxygen demanding substances. They are responsible for deoxygenation of water-bodies which is harmful for aquatic life.

Other ingedients which enter the various water bodies are the plant nutrients, i.e., nitrates and phosphates. They support growth of algae, commonly called **algal bloom** (blue-green species). This process is called **eutrophication** and is discussed in details in the next section.

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(ii) **Industrial Pollutants :** Many industries are located near rivers or fresh water streams. These are responsible for discharging their untreated effluents into rivers like highly toxic heavy metals such as chromium, arsenic, lead, mercury, etc. along with hazardous organic and inorganic wastes (e.g., acids, alkalies, cyanides, chlorides, etc.). River Ganges recives wastes from textile, sugar, paper and pulp mills, tanneries, rubber and pesticide industries. Most of these pollutants are resistant to breakdown by microorganisms (called nonbiodegradable), therefore damage the growth of crops and the polluted water is unsafe for drinking purposes.

Factories manufacturing plastic, caustic soda and some fungicides and pesticides release mercury (a heavy metal) along with other effluents in nearby water body. Mercury enters the food chain through bacteria, algae, fish and finally into the human body. The toxicity of mercury became evident by the Minamata Bay tragedy in Japan during the period 1953-60. Fish died due to mercury consumption and those who ate fish were affected by mercury poisoning and quite a few died. The milder symptoms of mercury poisoning are depression and irritability but acute toxic effects can cause paralysis, blindness, insanity, birth defects and even death. The high concentration of mercury in water and in fish tissues results from formation of soluble monomethylmercury ion, (CH_3, Hg^+) and volatile dimethylmercury $[(CH_3)_2 Hg]$ by anaerobic bacteria in sediments.

(iii) **Agricultural Waste:** Manure, fertilizers, pesticides, wastes form farms, slaughterhouse, poultry farms, salts and silt are drained as run-off from agricultural lands. The water body receiving large quantities of fertilizers (phosphates and nitrates or manures becomes rich in nutrients which leads to eutrophication and consequent depletion of dissolved oxygen. Consumption of water rich in nitrates is bad for human health especially for small children.

Pesticides (DDT, dieldrin, aldrin, malathion, carbaryl etc.) are used to kill insect and rodent pests. Toxic pesticide residues enter the human body through drinking water or through food chain (biomagnification). These compounds have low solubility in water but are highly soluble in fats. For example, the concentration of DDT in river water may be very low but some fish over a period of time accumulate so much of DDT that they become unfit for human consumption. The use of pesticides in our country is increasing very rapidly.

Some of these chemicals which are highly toxic become metabolised by animals that graze on fields. Therefore, these poisonous chemicals have been often observed in the humanfood chain. The presence of these chemicals in humans even in minute amounts can cause hormonal imbalance and may lead to cancer.

(iv) Physical Pollutants: Physical pollutants can be of different types. Some of them are discussed below :

(a) Radioactive Wastes : Radionucleides found in water are radium and potassium-40. These isotopes originate from natural sources due to leaching from minerals. Water bodies are also polluted by accidental leakage of waste material from uranium and thorium mines, nuclear power plants and industries, research laboratories and hospitals which use radioisotopes. Radioactive materials enter human body through water and food, and may be accumulated in blood and certain vital organs. They cause tumours and cancer.

(b) **Thermal Sources**: Various industries, nuclear power plants and thermal plants require water for cooling and the resultant hot water is often discharged into rivers or lakes. This results in thermal pollution and leads to the imbalance in the ecology of the water body. Higher temperature lowers the dissolved oxygen level (which is very essential for marine life) by decreasing the solubility of oxygen in water. Fish and other aquatic organism can get affected by a sudden change in water temperatures.

(c) **Sediments** : Soil particles carried to streams, lakes or oceans form the sediments. The sediment become polluting due to their large amount. Soil erosion defined as the soil carried by flood water from crop land, is responsible for sedimentation. The sediments may damage the water body by introducing a large amount of nutrient matter.

(v) Petroleum Products: Petroleum products are widely used for fuel, lubrication, plastics manufacturing, etc. and happen to be poisonous in nature. Crude oil and other related products generally get into water by accidental spillage from ships, tankers, pipelines etc. Besides these accidental spills, oil refineries, oil exploration sites and automobile service centres pollute different water bodies. Oil slick which floats on the water surface causes death of marine life and severely affects the ecosystem of the ocean.

A list of various types of water pollutants, their sources and effects have been summarised in Table 32.1.

Table 32.1: Types of water pollutants, their sources and effects

	Pollutant	Sources of Pollutants	Effects and Significance
1	Pathogens	Sewage, human and animal wastes, natural and urban runoff from land, industrial waste	Depletion of dissolved oxygen in water (foul odour) health effects (outbreaks of water borne diseases)

2	Organic pollutants ● Oil and grease	Automobile and machine waste, tanker spills, offshore oil leakage	Disruption of marine life, aesthetic damage
	● Pesticides and weedicides	Chemicals used for better yield from agriculture	Toxic effects (harmful for aquatic life), possible genetic defects and cancer; kills fish
	● Plastics	Industrial and household waste	
	● Detergents	Industrial and household waste	Eutrophication, aesthetics
3	Inorganic pollutants Fertilizers (phosphates and nitrates)	Agricultural runoff	Algal bloom and eutrophication, nitrates cause methemoglobenemia
	Acids and alkalies	Mine drainage, industrial wastes, natural and urban runoff	Kill fresh water organisms, unfit for drinking, irrigation and industrial use.
4	Radioactive materials	Natural sources, uranium mining and processing, hospitals and research laboratories using radioisotopes	Cancer and genetic defects
5	Heat	Cooling water for industrial, nuclear and thermal plants	Decreases solubility of oxygen in water, disrupts aquatic ecosystems
6	Sediments	Natural erosion, runoff from agricultural land and construction sites	Affects water quality, reduces fish population

INTEXT QUESTIONS 32.5

1. Define water pollution.
2. List any three anthropogenic sources of water pollution.
3. List the parameters indicating water pollution.

32.16 WATER POLLUTION AND SOME BIOLOGICAL EFFECTS

The natural source of water in the form of precipitation or rain is the purest form available in nature. However after reaching the surface and then underground it gets contaminated by a number of pollutants. There are some biological factors also mentioned earlier responsible for spoiling the quality of water. These include the lower plants like algae and bacteria which are the causes of nutrient accumulation in aquatic systems. This nutrient accumulation gives rise to a condition called eutrophication explained below.

32.16.1 Eutrophication

Eutrophication is a process by which a water body slowly becomes rich in plant nutrients such as nitrates and phosphates due to soil erosion and run off from the

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surrounding land. Let us try to understand this phenomenon. A water system like a lake or any reservoir may get a large inflow of organic matter from domestic wastes and run off from the surrounding land. Increasing human population, intensive agriculture and rapid industrial growth have led to an increasing release of domestic waste, agricultural residues, industrial wastes and land run-off into various water bodies. Nutrients are released from organic waste by aerobic (oxygen requiring) bacteria which start decomposing it. Dissolved oxygen is consumed in this process. As more and more organic matter enters a water body, more is the deoxygenation of the water body and larger is the production of nutrients. These nutrients fertilize an abnormal growth of algae and other large water plants such as duckweed. As more plants grow, some of them die also due to larger oxygen demand and therefore oxygen deficiency in the water body (i.e., deoxygenation of the water body). Such a water body is said to be **eutrophied** and the process is called **eutrophication**. The word eutrophication is derived from the Greek word which means well nourished as (eu:true, trophos:feeding)

Eutrophication of a water body results due to the release of large amount of nutrients by the action of aerobic bacteria on organic wastes entering a water body naturally or by human activity.

The above discussion leads us to a concept called biological oxygen demand (BOD). Let us try to understand by the description given below.

32.16.2 Biological Oxygen Demand (BOD)

The quality of oxygen used up by microorganisms at 27°C and in darkness during 3 days in breaking down organic wastes in a water body is called its **biological oxygen demand (BOD).**

It can be explained in the following manner.

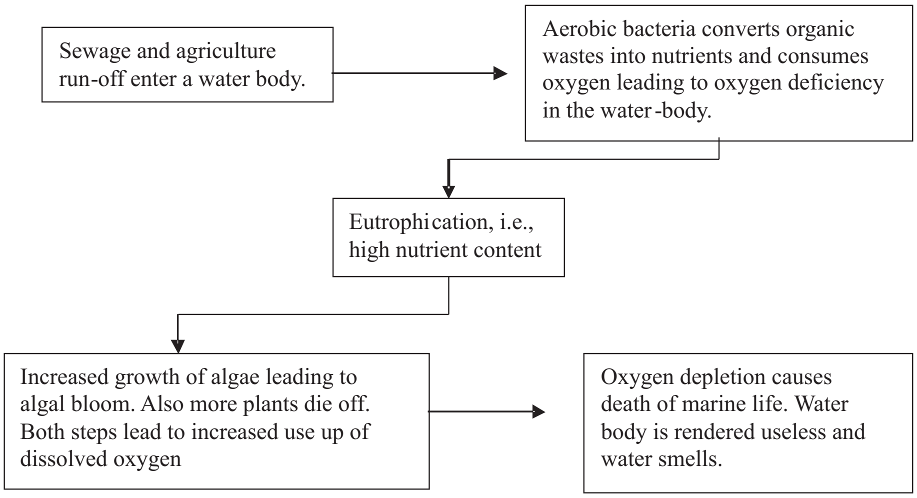
You know that there are many organic compounds or waste present in a water body. The microorganisms present in the system act upon this waste for their own consumption and growth. In the process the metabolic activity requires oxygen which is met by the dissolved oxygen present in water. It is this amount of oxygen which is defined as **biological oxygen demand (BOD).** The BOD value of an aquatic system depends upon:

- the type and amount of organic waste
- the organisms acting on it
- temperature and pH

The greater the amount of organic waste in the water body, the greater is the amount of oxygen required to break it down biologically and therefore higher is the BOD value of water. This value is a good measure in evaluating the degree of pollution in a water body. The less polluted water shows comparatively low value of BOD. Its value is used as a criterion for managing water pollution of a water body. An evaluation is made by determining oxygen concentration in water before and after incubation at 20º**C** in dark for 5 days.

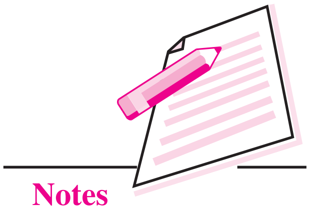
32.16.3 Biomagnification

A variety of toxic chemicals move through food chains. Toxic pesticides may be sprayed for controlling insect pests, fungi, herbs, but they concentrate in the food chain and harm to other (non target) organisms. For example, DDT was sprayed in the U.S. to control mosquitoes at a concentration expected to be harmless to non target organisms like fish and birds. DDT accumulated in the marshes and planktons. Planktons were eaten by fish and the fish had a higher concentration of DDT in its body. Further, when birds ate the fish, they accumulated still higher concentration. This increase in concentration of accumulated toxic chemicals as one goes higher in the food chain is termed **biomagnification.** Biomagnification has at times threatened the reproduction and survival of carnivores (secondary consumers) who occupy the highest level of the food chain.



32.17 WATER POLLUTION – SOME CONTROL MEASURES

Waste water generated by household activity, industries or garbage landfills is called **sewage** which is classified as the municipal water pollution. Sewage contains solid matters in the form of suspended colloidal and dissolved organic matter, detergent, mineral matter, nutrients and gases. Sewage is one of the major causes of water borne diseases and therefore the treatment of sewage is one of the important tasks. For a long time treatment of municipal waste in the form of sewage involved mainly of the removal of suspended solids, oxygen demanding materials and harmful bacteria. Now the disposal of the solid residue from sewage has been improved by applying municipal treatment processes.



The treatment of this waste water is carried out in the following three stages:

(i) Primary treatment

(ii) Secondary treatment, and

(iii) Tertiary treatment

Primary Treatment: When the waste water is to be dumped off into a river or flowing steam, the treatment is carried out by sedimentation, coagulation and filtration. This is known as primary treatment. If the water is required for drinking purposes, it has to undergo further treatment called secondary and tertiary treatments. The following steps are performed to do primary treatment of water:

(i) Sedimentation: This step is carried out in large tanks specially built for this purpose in sewage treatment plant. The polluted water is allowed to settle so that silt, clay and other matter settle to be bottom and water is slowly allowed to move out. Fine particles do not settle and are thus required to be removed in the next step.

(ii) Coagulation: Fine particles and colloidal suspension are combined into large particles by a process called coagulation. This step is carried out by the addition of special chemicals called coagulants (flocculants) such as potash alum. The large particles either settle to the bottom or are moved in the next step.

(iii) Filtration: Suspended particles, flocculants, bacteria and other organisms are filtered by passing the water through a bed of sand or finely divided coal or through some fibrous materials. The total impurities collected in these steps are called **sludge**. It is used as a valuable fertilizer. On composting (i.e. the action of anaerobic bacteria), it releases sludge gas. It consists mainly of methane gas which is used for cooking purposes.

Secondary or Biological Treatment: The water after primary treatment is not fit for drinking purposes and has to undergo further treatment. This is done through secondary or biological treatment. A commonly used method is to allow polluted water to spread over a large bed of stones and gravel so that the growth of different microorganisms needing nutrients and oxygen is encouraged. Over a period of time a fast moving food chain is set up. For example, bacteria consume organic matter from the polluted water; protozoa live on bacteria. Every form of life including algae and fungi help in the cleaning up process. This is called secondary treatment of water. It involves the following processes

(i) Softening : By this treatment undesirable cations of calcium and magnesium are removed from hard waters. Either water is treated with lime and soda ash to precipitate Ca^{2+} ions as carbonates or it is passed through cation exchangers. This makes water soft.

(ii) Aeration: In this process, soft water is exposed to air by forcing air through it to add oxygen to water. This encourages bacterial decomposition of organic matter into harmless products such as carbon dioxide and water. The addition of oxygen reduces carbon dioxide. sulphide etc.. The water is as yet not fit for drinking purposes. The pathogenic and other microorganisms need to be killed. This is done in the next treatment.

Tertiary Treatment : The tertiary treatment is actually disinfecting water. Chlorine is the most commonly used disinfectant used for killing bacteria. However, chlorine also reacts with traces of organic matter present in water and forms undesirable chlorinated hydrocarbons (toxic and potentially carcinogenic). It is therefore desirable to reduce the organic matter in water before passing chlorine gas. Other methods of disinfection such as ultraviolet radiation, ozone gas treatment or reverse osmosis are preferred over chlorine treatment. But these methods are more expensive. Fig.32.8 gives a clear picture of the process of sewage treatment in total.

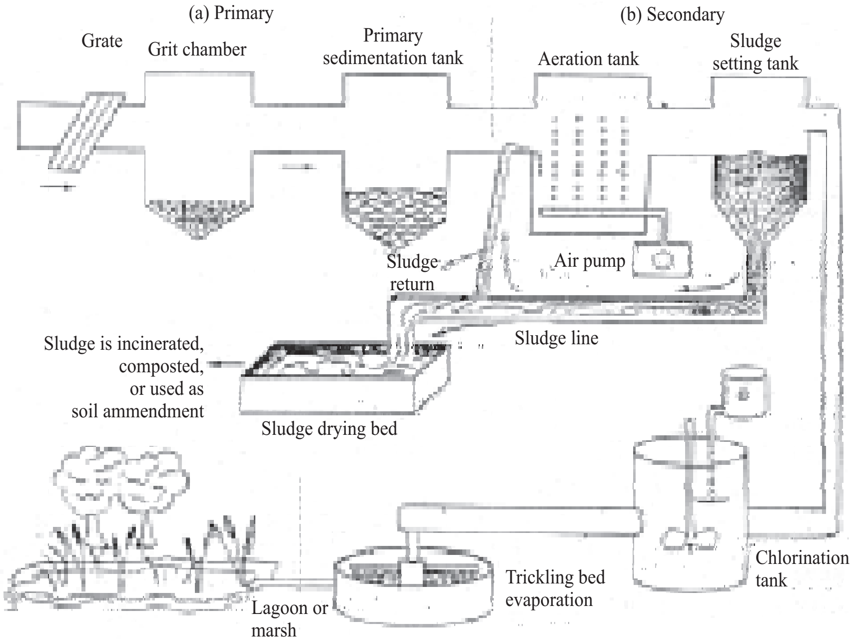


Fig. 32.8 : *Treatment process of sewage*

In a treatment plant, the waste is passed through a series of screens, chambers and chemical processes to reduce its bulk and toxicity. During primary treatment a large percentage of suspended solids and inorganic material is removed from sewage. The secondary stage reduces organic material by accelerating natural biological processes. Tertiary treatment is done when water is to be reused. Here 99% of solids are removed and various chemical processes are used to ensure that water is free from infecting materials.

INTEXT QUESTIONS 32.6

1. Define eutrophication.
2. Why does aquatic life get killed in an eutrophied pond?
3. What is the significance of BOD?
4. What is biomagnification?

32.18 SOIL POLLUTION

The adulteration of soil (land) by the addition of unwanted substances is known as soil pollution.

Sources of pollution

1. **Industrial waste:** The industrial wastes are the major cause of soil pollution because the wastes are toxic due to presence of cyanides, chromates, acids, alkalies, metal like nickel, cadmium, mercury and lead. Some industries like paper industries Sugar mills, textile mills and distilleries, chemical industries & cement industries are also responsible for soil pollution. The wastes of these industries are not bio-degradable.
2. **Urban and domestic waste:** The urban and domestic wastes referred as soil refuse, containing garbage, and rubbish, paper pieces, glass, plastics polythene bags, cans detergents and cakes. These substances emit gases, toxic hydrocarbons and pathogenic microbes cause to disease.
3. **Agricultural chemicals:** The fertilizers, pesticides, herbicides insecticides and fungicides are commonly used to save and increase the yield of crops but they have polluted the soil. Some time the entry of these chemicals in food chain has cause to adverse effects on health of consumers.
4. **Fertilizers:** The fertilizers increase the yield crop it has no doubt but the excessive use has adverse effects. It disturb the pH of soil, ionic balance and the presence of certain elements. So they have a number of health hazards. The nitrites cause to cancer in human body.
5. **Pesticides:** The chemicals are used to kill or to stop the growth of unwanted organisms and entry of these chemicals into food and water cause cause effect on the health of animals and human beings.
6. **Insecticides:** Some chemicals like DDT, BHC, aldrin, dieldrin are used to kill the insects, the use of DDT is banned by the Government because It is not biode gradable. It also effects the next crop in the field due to observed by the soil. Some bio degradable organ phosphates, carbonates may be used in place of insecticides.

7. **Herbicides:** The compounds used to control the growth of weeds, some inorganic compounds like sodium chlorate and sodium arsenite (Na_3AsO_3) were commonly used as herbicids. These one toxic in nature. So Now-a-days organic herbicide Triazines are preferred.
8. **Fungicides:** Fungicides are used to chock the growth of fungi. Fungi is one those plants in which chlorophyll is not present i.e. they can not make their food by the process photosynthesis. They live an dead organic matters as saprophytes. Organic compounds of mercury have been used as fungicides. Many people in Iraq resulted to death due to eating breads made from grains that been treated with methyl mercury fungicide. It's use have many disastrous consequences because these compounds breakdown in soil.

Control of soil Pollutions: The following steps have been suggested to control the soil pollutioins:

(i) The use of chemical fertilizers can be reduced by applying bio-fertilizers and manures.

(ii) Re cycling and recovery of materials appears to be a reasonable solution for reducing soil pollutions. Materials like papers, gas and some kinds of plastics can be recycled.

(iii) Control of land loss can be attempted through restoring forests and grass cover to check soil erosion and flood.

(iv) Proper methods should be adopted for the disposal of solid wastes.

INTEXT QUESTIONS 32.7

1. What is refuse?
2. Write the name of one insectide?
3. What is soil erosion?

32.19 GREEN CHEMISTRY AS AN ALTERNATIVE TOOL FOR REDUCING POLLUTION

We have discussed about hazards of environmental pollution in these units. The main reasons of this pollution is due to rapid industrialization, productions and use of toxic chemicals. An important initiative to protect the environment from chemical effluents and wastes is known as Green chemistry.

"Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances."

Green chemistry is environment friendly, linking the design of chemical products and processes with their impacts on human health and the environment.

Principles of Green Chemistry

(i) The use of starting materials, reagents and solvents which are less hazardous to man and his environment.

(ii) More efficient use of raw materials.

(iii) Utilisation of chemical reactions which completely incorporate the starting materials in to final products and last amount of by product.

(iv) Search new alternatives which are environmental friendly.

(v) It is better to prevent the waste than to treat or cleanup the waste after it has been created.

Achievements of Green chemistry

(i) Development of dense phase CO_2. Dense phase CO_2 has been recently developed chemical product with amazing characteristics. It has ability to clean everything. It can be used as recyclable solvent and finds number of applications in food industries.

(ii) Development of fuel cells of cellular phones which can last for the full life time of the phone.

(iii) Development of process involving use of CO_2 as a blowing agent for manufacture of poly styrene foam. This technology discard the use of chloro fluoro carbon.

(iv) H_2O_2 hydrogen peroxide gives better results and not harmful for bleaching of clothes in the laundary instead of tetrachloro ethene ($Cl_2C{=}CCl_2$). This compound is suspected to be carcinogenic and contiminated the ground water.

(v) Hydrogen peroxide (H_2O_2) is used with catalyst for bleaching papers, instead of toxic chlorine gas.

(vi) Ethanal (CH_3CHO) is now a days being prepared an a commercial scale by one step oxidation of ethane in presence of ionic catalyst in aqueous solution

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{in water}]{\text{Pd(II)Cu(II)}} CH_3CHO\ (90\%)$$

32.20 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTIONS

Environmental pollutions affects the plants, animals and human beings as well as materials. The production and improper disposal of waste are causes for the great deal of environmental pollution. In addition to the have hold waste

Notes

thesewage and municipal garbage, many toxic industrial wastes from manufacturing processes require treatment and safe disposal. The biodegradable and non-biodegradable waste like polythene bags plastics, metal scrap should be put in separate boxes. The biodegradable waste is deposited in the land fills.

Industrial wastes are also sorted as biodegradable and non-biodegradable, should be put in separate boxes. Fly ash, furnace stag mud and failings and gypsun like non-biodegradable wastes have produce great problem. Some chemical industries producing inflammable wastes and hazardous chemicals as by products.

Some methods are usually employed one given below

1. Recycling: When materials one recycled, there are several benefits, apart from savings on the cost of raw materials, waste disposal costs are reduced.
   - (i) the collections and recycling of glass.
   - (ii) Iron scrap can be used in manufacturing steel.
   - (iii) Polythene bags and plastics can also recycled.
   - (iv) The newspapers, used copies, and magazines can be used for making papers.

Sewage treatment

Sewage is the liquid waste which includes house hold wastes, Industrial wastes ground wastes, etc. which contains 99.9 water with inorganic, organic matters in dissolved, suspension and colloidal states. It involves the following stages.

(i) The removal of large solid particles. It can be done by screening and sedimentation. The solid wastes are deposited in land fillsites.

(ii) It is allowed to stand is tanks. Many solids settle down by the use of the chemicals like alums and ferrousulphate while oil, grease, float on the surace which can be shimmed off.

(iii) Next stage involve the biological oxidation of organic content of waste materials by microorganisms followed by filtration.

(iv) Finally some physical and chemical processes are applied to remove some chemicals like phosphates and adding chlorine to improve the quality of waste water.

(i) **Incineration:** It convert the organic and biogical wastes to carbon dioxide and water at higher temp 1273 k and excessive supply of oxygen. Exhaust gases must be filtered. The incomplete oxidation of Poly chlorinated biphynyls (PCBs) may convert to toxic polychlorobidenzodioxins (PCDDs). Main problem of this process is air pollution due to incomplete oxidations.

(ii) **Digestion:** In digestion, sluge is kept in a closed tank in the absence of air for a prolonged period whereby it goes anaerobic respirations, yields gases like carbon dioxide methane and ammonium sulphide. The methane gas can be used as fuel.

$$2(CH_2O) \longrightarrow CO_2 + CH_4$$

(iii) **Dumping:** Dumping of the sewage stage into sea has been very common. However dumping of the sluge into land is increasing now-a-days. Because it has nitrogen and phosphorous which act as fertilizers for the soil.

INTEXT QUESTIONS 328

1. Write the names of those wastes which can be recycled
2. Name the chemicals which are used in sedimentation of solid waste.
3. How the incrination cause to air pollutions?

WHAT YOU HAVE LEARNT

- Surroundings in which we live is our environment.
- There are two components of environment : physical or abiotic and living organisms or biotic
- Pollutants may be defined as substances added to natural surroundings.
- There are two major sources of pollutants - stationary and mobile.
- Pollutants have adverse effects on environment and living organisms.
- SO_2, CO_2, CO, smoke, Pb, Hg, CFC, etc. pollute air. Their sources and effects are varied.
- Pollution in simple words is the unhealthy and harmful condition for living organisms and non-living things.
- Pesticides, plastic, detergents, chlorine, mercury, etc. pollute water and endanger life of aquatic organisms.
- Unwanted sounds are termed as noise. Sounds is measured in decibels. Beyond 70 decibels noise has harmful effects on humans.
- The Government of India has set up various environmental laws and judiciary system to punish the polluters.
- Nature's balance has beeen upset by human activities releated to urbanisation, industrialisation and intensive agriculture.

- Atmosphere is made up of gases of which nitrogen - 78%, oxygen - 21%, carbondioxide - 0.1 to 0.3%, inert gases 1 %
- Increase of temperature with altitude is known as positive lapse rate where as decrease in temperature with increase of altitude is negative lapse rate of temperature.
- Air pollution is due to

  (i) particulate matter (soot, dust)

  (ii) aerosols composed of hydrocarbons

  (iii) gases like SO_2, NO_2 are mostly released by burning fossil fuels.
- NO_2 and hydrocarbons are modified by sunlight to form photochemical smog. Smog is a combination of smoke and fog. Automobile exhausts give out NO_2 and hydrocarbons. They form PAN (peroxyacetyl nitrate) which along with ozone and SO_2 forms photochemical smog.
- Smog cools and settles down near the earth and forms a blanket, while warmer air covers it. Thus there is a 'temperature inversion' with warm air above and cool air below unlike in the normal conditions.
- SO_2 and NO_2 form acids which drop as H_2SO_4 and HNO_3 on statues and spoil them. This is called acid precipitation. Acid rain kills trees, prevents reproduction in fish and causes poor visibility.
- Greenhouse gases are CO_2, NO_2, CH_4, chlorofluorocarbons and halons. They trap solar radiation and cause global warming.
- Global warming due to greenhouse effect leads to drought, rise in sea level, lack of rain and water shortage.
- There is a layer of ozone in stratosphere, which protects us from UV radiation by absorbing it.
- Chlorofluorocarbons which are used in refrigerators and foam cups as aerosols and halons used in fire extinguishers, when released into the air cause depletion of ozone shield which protects us from harmful effects of solar radiations. It is feared that ozone depletion will have damaging effects on humans such as causing skin cancer.
- Complete destruction of ozone layer over an area is termed as ozone hole.
- Air pollution causes respiratory diseases such as emphysema and bronchitis, eye irritation, fluoroisis, cancer and may even be fatal.
- Control measures include use of sulphur free oil and coal, use of alternative sources of energy such as wind and solar power, use bicycle and battery powered vehicles, stop burining waste indiscriminately, have stringent measures for release of emissions from industries and above all educate general public and caution them against releasing air pollutants.

- Water pollution refers to any physical, chemical or biological change that has an undesirable affect on living organisms.
- Sewage, industrial, agricultural pollution and physical pollutants are the various sources of water pollution. These sources may be limited to a point sources or spread over large areas (non-point sources).
- Sewage, fertilizers, detergents, toxic wasters released by industries are some of the sources of groundwater pollution.
- Phosphatic, and nitrogenous fertilizers cause algal bloom and severe oxygen depletion in water body. The water body is said to be eutrophied.
- The quantity of oxygen needed by micro-organisms in degrading organic wastes in a water body is defined in terms of its biological oxygen demand (BOD).
- Biological magnification of toxic materials released into water bodies poses a serious threat to aquatic life and eventually to human life.
- Polluted water may be made useful for human consumption by subjecting it to various treatments.
- Legislative measures have been enacted in our country to restrict the pollution of various water bodies.

TERMINAL EXERCISE

1. What is environment?
2. Explain the term anthropogenic pollutants.
3. Write four major pollutants of water, their sources and effects.
4. Differentiate between the Primary and Secondary Pollutants.
5. What are the damaging effects of SO_2 and NO_2 on plants and animals?
6. Write a note on carbon monoxide poisoning.
7. What is thermal inversion and how is it caused?
8. Enumerate the various effects of acid rain.
9. What is ozone hole? What are the effects of ozone depletion?
10. Why does sea level rise due to global warming?
11. How do greenhouse gases cause global warming.
12. Mention five disease/discomforts in humans caused by different air pollutants.
13. Enumerate the various measures of control of air pollution.
14. How the industrial wastes and domestic wastes are helpful in soil pollution?

15. What one fungicides.
16. How to control soil pollution?
17. Explain main effects of water pollutions.
18. What are the various types of water pollutants? State their consequences.
19. What are the effects of detergents on fresh water bodies?
20. What are the various sources of groundwater pollution?
21. How is the disease ‘methaemoglobinaemia’ caused?
22. How can domestic waste be used as manure?
23. What will be the problem arise due to abundance of phyto plankton?
24. Write in brief about sewage treatment.

ANSWERS TO INTEXT QUESTIONS

32.1

1. The air, water, earth and living beings in a joint form is called environment.
2. There are two components of environment namely biotic and abiotic.
3. Living organisms such as plants, animals, microbles, etc.
4. Causes holes in the ozone layer.
5. Atmosphere, biosphere, hydrosphere and lithosphere.

32.2

1. Any substance which is present in its excess concentration such as CO_2, CO, SO_2.
2. Volcenicerruptions and run-off from surface mines.
3. Secondary pollutants are the products of reaction between the primary pollutant and the normal environmental constituents.
4. Environmental pollution is the deterioration or unclean objectionable conditions in the quality of natural resources such as air water and soil because of the action or presence of unwanted substances in undesirable concentration.

32.3

1. undesirable level of undesirable and harmful substances in the atmosphere
2. soot, fluoride, Pb dust, NaCl (any two)
3. SO_2, CO_2, CO, NH_3, H_2S (any two)

4. methanogenic bacteria, ruminant stomach, fermentation in water logged paddy fields (any one).
5. PAN and O_3

32.4

1. fog and smoke
2. O_3 and PAN
3. SO_2 and NO
4. CO_2, NO_2, CH_4, CFC, Halons
5. refrigerants, fire extinguishers
6. corrode them
7. reducing use of fuel which releases air pollutants and use clean renewable fuels. Educate everyone about dangers of pollution.

32.5

1. Refer to section 32.2
2. Refer to section 32.3.1. (ii)
3. Refer to section 32.1

32.6

1. Refer to section 32.5.1
2. Refer to section 32.5.1
3. Refer to section 32.5.2
4. Refer to section 32.5.3

32.7

1. The urbon and domestic wastes referred as soil refuse containing.
2. DDT or BHC,
3. The loss of fertile layer (dipper layer) of soil is called soil erosion.

32.8

1. Glass, polythene, ion, paper etc.
2. Potash Alumns and ferrous sulphate.
3. The conversion of biological wastes to CO_2 and water at 1273 K. The incomplete oxidation PCBS are also causes to air pollutions.

QUESTION PAPER DESIGN

Subject : Chemistry **Class : Senior Secondary** **Duration : 3 hours**

Paper : Theory **Marks : 80**

1. Weightage by Objectives

Objective	Knowledge	Understanding	Application
Percentage of marks	25%	45%	30%

2. Weightage to Questions

Total number of question	30			
Form of questions	E	SA (I)	SA(II)	MCQ
Marks	6	4	2	1

3. Distribution of Marks (80 marks Theory paper and 20 marks Practical)

MCQ	1 × 10	=	10
SA II	2 × 9	=	18
SA I	4 × 7	=	28
E	6 × 4	=	24
	30		80

E (6 marks)	60
SA I (4 marks)	60
SA II (2 marks)	25
MCQ (1 marks)	15
Reading & revision	20
Total time	**180 minutes**

4. Weightage by Content

Module	**Marks**
1. Some Basic Concepts of Chemistry	04
2. Atomic Structure and Chemical Bonding	10
3. States of Matter	08
4. Chemical Energetics	06
5. Chemical Dynamics	12
6. Chemistry of Elements	18
7. Chemistry of Organic Compounds	18
8. Chemistry in Everyday Life	04
Total	**80**

SAMPLE QUESTION PAPER

CHEMISTRY

(313)

Time : 3 hr. **Maximum Marks : 80**

Note:

(i) Attempt all questions .

(ii) All questions are compulsory.

(iii) Marks for each question is indicated against it.

(iv) Use log tables if necessary

1. Maximum number of electrons in a subshell with $l = 3$ and $n = 4$ is 1

A. 10 B. 12 C. 14 D. 16

2. Bond order of 1.5 is shown by 1

A. O_2^{2-} B. O_2 C. O_2^+ D. O_2^-

3. What is the molarity of the solution which contains 32.0 g of methyl alcohol (CH3OH) in 200 mL solution 1

A. 3M B. 2M C. 7.5M D. 5M

4. Which of the following is incorrect for lyophilic sols? 1

A. They are rreversible

B. They are formed by inorganic substances

C. They are readily coagulated by addition of electrolytes

D. They are self stabilized

5. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + heat.

What is the effect of the increase of temperature on the equilibrium of the reaction? 1

A. equilibrium is shifted to the left

B. equilibrium is shifted to the right

C. equilibrium is unaltered

D. reaction rate does not change

6. Given $E^{\circ}_{Cr^{+}/Cr} = -0.72V$, $E^{\circ}_{Fe^{2+}/Fe} = -0.42V$

The potential for the cell 1

Cr/Cr^{3+} (0.01 M) || Fe^{2+} (0.01 M) | Fe is

A. –0.26 V B. 1.14 V C. 0.339 V D. –0.339 V

7. In which of the following compounds, nitrogen exhibits highest oxidation state? 1

A. NO_2 B. NH_2OH C. N_2H_4 D. NH_3

8. The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence: 1

A. $BCl_3 > BF_3 > BBr_3$ B. $BF_3 > BCl_3 > BBr_3$

C. $BBr_3 > BF_3 > BCl_3$ D. $BBr_3 > BCl_3 > BF_3$

9. Clemmensen reduction of a ketone is carried out in the presence of which of the following? 1

A. H_2 and Pt as catalyst B. Glycol with KOH

C. Zn-Hg with HCl D. $LiAlH_4$

10. Which polymers occur naturally**?** 1

A. Starch and Nylon B. Starch and Cellulose

C. Proteins and Nylon D. Proteins and PVC

11. Calculate the molar masses of NH_3 and $CaCO_3$? 2

12. A sample of nitrogen gas consists of 4.22×10^{23} molecules of nitrogen. How many moles of nitrogen gas are there? 2

13. Why BF_3 has less dipole moment as compare to NH_3 ? Explain 2

14. What is Aufbau principle? What are ($n+l$) rules? 2

15. Calculate the pressure (atm) required to compress 500 mL of gas at 0.20 atm into a volume of 10 mL. 2

16. Calculate the standard enthalpy of the reaction 2

$$2H_2S(g) + SO_2(g) \longrightarrow 3S\ (s) + 2H_2O\ (l)$$

given that

$\Delta_f H_0(H_2S) = -20.6$ kJ mol^{-1}

$\Delta_f\ H_0\ (SO_2) = -\ 296.9$ kJ mol^{-1}

$\Delta_f\ H_0\ (H_2O) = -\ 289.9$ kJ mol–

17. Write the IUPAC names of the following complexes: 2

(i) $K_4[Fe(CN)_6]$ (ii) $[Cr(en)_3]Cl_3$

18. What is the polar part (hydrophilic) and oil-soluble (hydrophobic) part in a synthetic detergent molecule? 2

19. Write the names of monomers of terylene? 2

20. How does colloidal solution differ from true solution? 4

21. For the reaction at 298 K, 4

    $1/2\ N_2(g) + 3/2\ H_2\ (g) \longrightarrow NH_3(g);\ \Delta H = -46$ kJ

    (a) What is the value of Δn_g ?

    (b) Calculate the value of ΔU at 298 K?

22. Calculate the solubility product for Ag_2SO_4 if $[SO_4^{2-}] = 2.5 \times 10^{-2}$ M. 4

23. Calculate the standard Gibb's energy ΔG_0 for the reaction occurring in Daniell cell 4

    $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

    at 298 K. The E_0 cell at this temperature is 1.1V. Is the reaction spontaneous?

24. Calculate in B.M., magnetic moments expected for the following ions: 4

    V^{4+} and Ni^{3+}

25. Explain the following giving suitable reasons: 4

    (i) BF_3 is a weaker Lewis acid as compared to BCl_3.

    (ii) CCl_4 does not hydrolyse but $SiCl_4$ does.

    (iii) N_2 is inert at room temperature.

    (iv) H_2S is gas but H_2O is liquid at room temperature.

26. Write short notes on the following reactions 4

    (i) Reimer Tiemann reaction.

    (ii) Aldol condensation

27. (i) Aryl halides are extremely less reactive towards nucleophilic substitution reactions. Why? 2

    (ii) How would you convert nitrobenzene to aniline ? 2

    (iii) Explain why phenol is a stronger acid than ethanol . 2

28. (a) Identify A and B in the following reaction 3

    $CH_3CHO \xrightarrow{NaOH} A \xrightarrow{\Delta} B$

    (b) 1. Although haloalkanes are polar in nature, they are immiscible in water. Explain. 3

    2. Which one of the following isomers has the higher boiling point and why? (i) *o*-dichlorobenzene (ii) *p*-dichlorobenzene

29. (i) Calculate the bond orders for Li_2 and Be2molecules using the molecular orbital diagrams. 6.

    (ii) Predict the magnetic behaviour of O_2.

    (iii) Give the significance of the azimuthal and magnetic quantum numbers?

30. Compound [A] of chromium when treated with sodium carbonate in the presence of atmospheric oxygen gave a yellow colored compound [B]. Compound [B] on treatment with acid gave an orange colored compound [C]. [B] can also be obtained by treatment of [C] with alkali. Identify the compound A, B, C and write the chemical equations. 6

MARKING SCHEME

CHEMISTRY

(313)

Question No.	Expected value points	Distribution of Marks
1.	(C)	1
2.	(C)	1
3.	(D)	1
4.	(A)	1
5.	(A)	1
6.	(B)	1
7.	(A)	1
8.	(D)	1
9.	(C)	1
10.	(B)	1

11. Molecular mass of NH_3 = (Atomic mass of N) + 3 (Atomic mass of H) 2

$= [14 + (3 \times 1)]$ amu

$= 17$ amu

Molar mass of K_2SO_4 = (2 × molar mass of K^+) + (molar mass of SO_4^{2-}) 2

= (2 × molar mass of K+) + (molar mass of S + 4 x molar mass of O)

$= [(2 \times 39 \text{ x}1) + (32 \times 1 + 4 \times 16)] \text{ g mol}^{-1}]$

$= (78.2 + 32.1 + 64) \text{ g mol}^{-1} = 174.3 \text{ g mol}^{-1}$

12. Moles of N_2 gas $= \dfrac{4.22 \times 10^{23} \text{ molecules}}{6.022\ 10 \text{ molecules mol}^{-1}} = 0.70$ mol 2

13. The dipole moment for BF_3 is less due to its symmetrical planar structure although the B–F bonds are polar. But NH_3 has a pyramidal structure which makes the arrangement of three N–H bonds unsymmetrical. In addition to three N–H bonds, nitrogen atom has a lone pair of electrons. which also has an orbital dipole moment in which the electron pair is the negative centre. Hence, NH_3 has high dipole moment than BF_3. 2

Marking Scheme

14. Aufbau principle states that the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules. 1

    There are two ($n+l$) rules. These are an orbital with a lower value for $(n + l)$ is filled first. 1/2

    If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first 1/2

15. Boyle Law equation is

    $p_1V_1 = p_2V_2$ 1/2

    (.20 atm) (500 mL) = $p2$ (10 mL)

    $$p_2 = \frac{(0.20 \text{ atm})\ (500 \text{ ml})}{10 \text{ ml}} \qquad 1$$

    $$p_2 = 10 \text{ atm.} \qquad 1/2$$

16. $\Delta_rH_0 = 2\Delta_fH_0(H_2O) - 2\Delta_fH_0\ (H_2S) - \Delta_fH_0\ (SO_2)$ 2

    $= -\ 241.7$ kJ

17. (i) Potassium-hexacyano ferrate(II) 1

    (ii) Tris (ethylenediamine) chromium(III) chloride 1

18. Carboxylate anion (hydrophilic) and oil-soluble (hydrophobic) part long normal alkyl chain.2

19. Ethylene glycol and terphthalic acid. 2

20.

True solution	Colloidal solution	2+2=4
(1) Size of solute in less than 1 nm.	(1) Particle size (1–100) nm.	
(2) Form transparent solution and allows light to pass through them.	(2) Path of light becomes visible.	

21. (a) $\Delta n = 1 - ½ - 3/2 = -1$ 1

    (b) $\Delta U = \Delta H - \Delta n$ RT 1

    $= 46000\ (\text{J mol}^{-1}) - (-\ 1)\ (8.314 \text{ Jk}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$ 2

    $= -\ 46000\ (\text{J mol}^{-1}) + 2247.6\ (\text{J mol}^{-1})$

    $= -\ 43.5 \text{ kJ mol}^{-1}$

22. Let the solubility of Ag_2SO_4 be 's' mol dm^{-3}. The concentrations of the Ag+ and the SO_4^{-2} would be '2s' mol dm^{-3} and 's' mol dm^{-3} respectively, and $K_{sp} = [Ag^+]_2[SO4^{-2}]_4$

    Given $[SO_4^{-2}] = 2.5 \times 10^{-2}M \longrightarrow [Ag^+] = 2 \times 2.5 \times 10^{-2}M = 5 \times 10^{-2}M$

    Substituting the values in the expression of K_{sp} we get,

    $K_{sp} = [5 \times 10^{-2}]2 \times [2.5 \times 10^{-2}] = 6.25 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$

23. For Daniell cell,

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ (oxidation) 1/2

$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$ (Reduction) 1/2

$n = 2$ 1/2

$\Delta G^0 = -nFE^0$, $\Delta G^0 = -2 \times 96500 \times 1.1$ 2

$= -212{,}300J$

$= -212.3KJ$ 1/2

Since ΔE^0 is –ve, the cell reaction is spontaneous

24. V^{4+} $3d^1$ n = 1, $\sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ B.M., 2

Ni^{3+} $3d^7$ n = 3, $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M 2

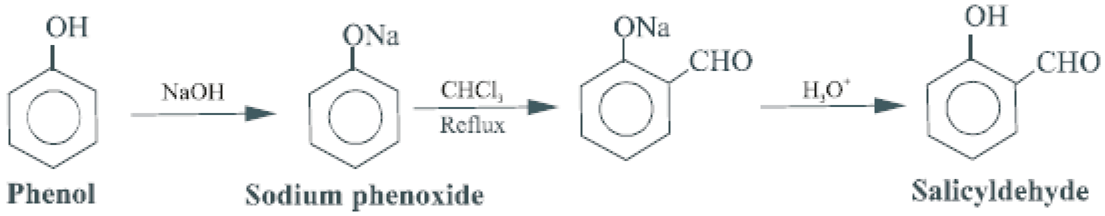
25. (i) Due to smaller B-F bond length, it forms pπ- pπ back bond. Due to this bonding electron deficiency of boron is compensated. But in case of BCl_3, due to bigger B-Cl bond length it can not form pπ-pπ back bond and it remain electron deficient. Hence, BCl_3 is more acidic than BF_3.

(ii) Due to absence of vacant d orbital in C in CCl_4 it can't be hydrolysed. But in $SiCl_4$, Si has vacant d orbital. Hence, $SiCl_4$ is hydrolysed. 1× 4 = 4

(iii) Due to formation of multiple pπ- pπ bonding between two N atom, it has very high bond dissociation enthalpy. Hence, it is inert at room temperature.

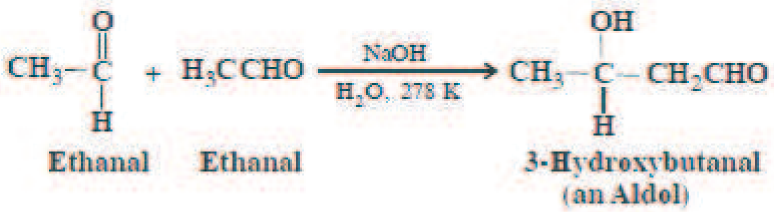
(iv) Due to formation of H-band between H_2O molecules it is liquid at room temperature. This type of bonding is not possible in H_2S. Hence it is gas at room temperature.

26. (i) Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes. For example when phenol reacts with chloroform in the presence of sodium hydroxide, it gives salicylaldehyde. This reaction is known as Reimer Tiemann Reaction**.** 2

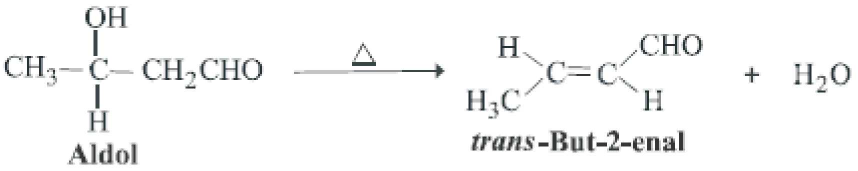


(ii) Aldehydes having α hydrogen atom on reaction with dil. NaOH give *aldols*. The reaction is illustrated below by using ethanal as the example. 2

Marking Scheme

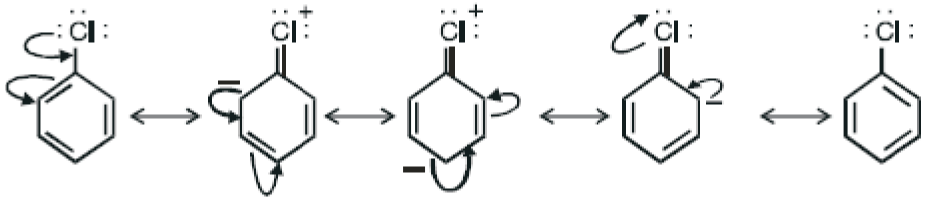


The product contains both the *aldehyde* and the *alcohol* functional groups and therefore, it is called an *aldol*. The aldol addition product on heating undergoes dehydration to give an α β-unsaturated aldehyde which is a condensation product.

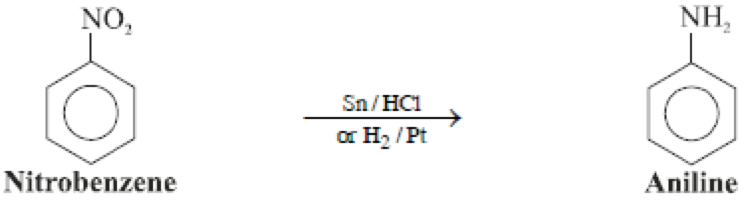


This complete sequence of reactions is called ***aldol condensation***

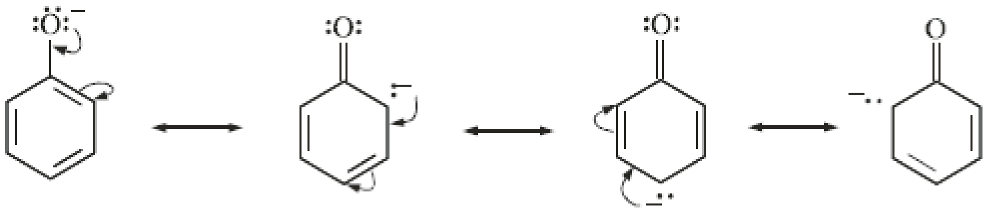
27. (i) This is due to the existernce of the phenomenon of resonance which cause carbon–halogen bond to acquire double bond character in haloarenes. Due to attainment of double bond character C-X bond dissociation energy becomes high. Hence, haloarenes are less reactive towards nucleophilic substitution reaction. The resonating structures of chlorobenzene are shown below : 2



(ii) By reduction of nitro group using hydrochloric acid and a metal such as Sn or Fe nitrobenzene can be converted to aniline. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. 2

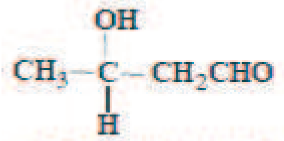


(iii) The greater acidity of phenols is due to the resonance stablisation of the phenoxide ion. The resonance structures of pheoxide ion can be represented as 2



The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of ethoxide ions.Hence phenol are more acidic than ethyl alcohol.

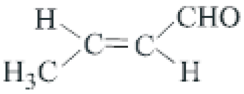
28. (a) A = 1+1/2



$CH_3-CH(OH)-CH_2CHO$

3-Hydroxybutanal
(an Aldol)

B = 1+1/2

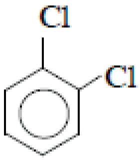


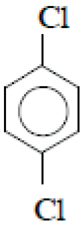
trans-But-2-enal

(b) Due to their inability to form hydrogen bonds with water molecule. Also, bigger halogen atom causes steric hindrance in the formation of H-band. 1+1/2

(ii) Para dichlorobenzene; due to greater symmetry and hence a better packing.

Due to this strong packing *Para* dichlorobenzene has high M.P and B.P 1+1/2





29. (i) Bond order = b.o. = ½(n_b - n_a)

for Li_2; Bond order = ½ [4-2] = ½[2] = 1 1

for Be_2; Bond order = ½ [4-4] = ½ [0] = 0 1

Marking Scheme

(ii) MO configuration of O_2 is s $2\sigma_2$, s* $2\sigma_2$, s$2pz_2$, p$2px_2$ = p $2py_2p^*$ $2p_1x$ = p* $2p_1y$ Due to 2 unpaired electrons O_2 molecule is paramagnetic. 2

(iii) The quantum number *l* is related to the geometrical shape of the orbital and the quantum, number, *ml* describes the orientation of the orbital in space. 2

30. A = $FeO.Cr_2O_3$ 1

B = Na_2CrO_4 1

C = $K_2Cr_2O_7$ 1

$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$ 1

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ 1

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ 1