CHAPTER

21

Chemistry of Beryllium, Radium and Their compounds and Portland Cement

Beryllium

Occurrence

Beryllium does not occur free in nature. In the combined state this metal is largely found as silicates. Its important minerals are : *beryl*, 3 $BeO.Al_2O_2.6SiO_2$ (containing 11–15% of BeO); *chryso beryl*, $BeO.Al_2O_3$ (containing 19% of BeO); and *phenacite*, $2BeO.SiO_2$ (containing 45% of BeO). The chief and the important mineral from which beryllium is extracted is beryl. In India it is found in Bihar, Orissa, Madras and Rajsthan.

Extraction.

Beryllium is obtained from beryl mineral by any of the following two methods:

1. Electrolysis Method. This method consists of the following two steps:

(a) Conversion of beryl into sodium beryllium fluoride, Na_2BeF_4. The finely powdered beryl is mixed with sodium fluosilicate, Na_2SiF_6 and a little sodium fluoride and then fused at a temperature of 800–900°C. As a result, beryllium and aluminium present in the mineral are converted into soluble sodium beryllium fluoride and sodium aluminium fluoride respectively.

$$3BeO.Al_2O_3.6SiO_2 + 6Na_2SiF_6 \xrightarrow[800-900^\circ C]{NaF} \underset{\substack{\text{Sodium}\\ \text{beryllium fluoride}\\ \text{(soluble)}}}{3Na_2BeF_4} + \underset{\substack{\text{Sodium aluminium}\\ \text{fluoride}\\ \text{(insoluble)}}}{2Na_2AlF_6} + 3SiF_4 + \underset{\text{Silica}}{9SiO_2} \downarrow$$

The added sodium fluoride reacts with silicon tetrafluoride so formed to give sodium fluosilicate again.

$$2NaF + SiF_4 \longrightarrow \underset{\substack{\text{Sodium}\\ \text{fluosilicate}}}{Na_2SiF_6}$$

The fused mass is boiled with water and filtered. The filterate contains sodium beryllium fluoride while the residue contains mostly sodium fluoride and silica.

(b) Electrolysis of sodium beryllium fluoride, Na_2BeF_4. The filtrate is evaporated to dryness and the residue obtained is mixed with sodium fluoride and barium fluoride. The fluorides of sodium and barium are added to increase the conductivity and to decrease the volatility of the fused mass at high temperatures. The mixture is fused at 1400°C and electrolysed in a graphite pot which itself acts as anode and a water cooled iron pipe dipping in the melt acts as cathode. The beryllium is deposited on the cathode. The fluorides of sodium and barium are added at intervals to maintain the concentration of beryllium constant in the electrolyte.

2. Electrolytic Reduction Method. This method also consists of the following two steps:

(*a*) ***Conversion of beryl into beryllium oxide (beryllia), BeO.*** The finely powdered beryl is fused with potassium carbonate at about 1500°C in an electric furnace and then evaporated with conc. H_2SO_4. The resulting mass is extracted with boiled water and filtered. The filtrate contains the sulphates of beryllium, potassium and aluminium while the residue contains mostly silica.

$$3BeO.Al_2O_3.6SiO_2 + 6K_2CO_3 \longrightarrow 3BeO + Al_2O_3 + 6K_2SiO_3 + 6CO_2$$

$$BeO + H_2SO_4 \longrightarrow \underset{\text{(Soluble)}}{BeSO_4} + H_2O$$

$$Al_2O_3 + 3H_2SO_4 \longrightarrow \underset{\text{(Soluble)}}{Al_2(SO_4)_3} + 3H_2O$$

$$K_2SiO_3 + H_2SO_4 \longrightarrow \underset{\text{(Soluble)}}{K_2SO_4} + H_2O + \underset{\text{Residue}}{SiO_2 \downarrow}$$

The filtrate is concentrated when most of the potassium and aluminium sulphates crystallize out as potash alum.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

The concentrated solution now contains beryllium sulphate along with some potassium and aluminium sulphates. This is added to a hot and concentrated solution of $(NH_4)_2CO_3$ when remaining aluminium is precipitated as its hydroxide.

$$Al_2(SO_4) + 3(NH_4)_2CO_3 + 3H_2O \longrightarrow \underset{\text{ppt.}}{2Al(OH)_3} + 3(NH_4)_2SO_4 + 3CO_2 \uparrow$$

The filterate on concentration deposits basic beryllium carbonate, $Be(OH)_2.BeCO_3$ which on ignition gives beryllium oxide.

$$Be(OH)_2.BeCO_3 \xrightarrow{\Delta} 2BeO + H_2O + CO_2 \uparrow$$

(*b*) ***Reduction of beryllium oxide, BeO to Be metal.*** The beryllium oxide is mixed with powdered coke and introduced into an alternating current arc furnace (Fig. 21.1). The furnace consists of a big carbon crucible provided with a tapping hole and is enclosed in the fire bricks. The crucible acts as one of the electrodes. The other carbon electrode dips in the charge and is held vertically. On striking the electric arc between the electrodes, beryllium oxide is reduced to beryllium which in the molten state is taken away through the tapping hole. CO escapes from the hole.

$$BeO + C \longrightarrow Be + CO \uparrow$$

Physical Properties.

Beryllium is silvery white in colour, malleable, easily forged and takes a high polish. It is a light metal (S.G. = 1.842) and possesses a high melting point (1280°). Its specific heat is probably the highest of all the known metals and this accounts for the non-metallic nature of the metal (*cf. Boron*).

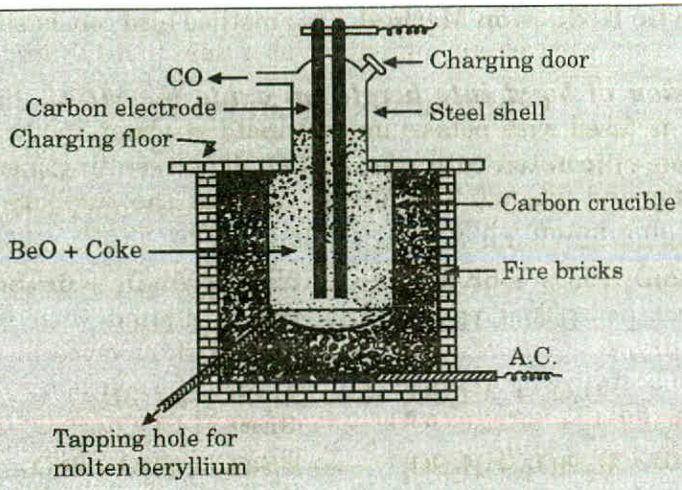

Fig. 21.1. Preparation of beryllium by the electrolytic reduction of beryllium oxide, BeO.

Chemical Properties.

(i) Action of air. The metal is more permanent in the air than magnesium, but is oxidised in the moist air. When heated to redness in oxygen, it forms a protective layer of the oxide round the metal. The metal powder, however, burns in air brilliantly forming the oxide, BeO.

(ii) Action of water. Water or steam is not decomposed even at red heat (compare with magnesium).

(iii) Combination with elements. It does not directly combine with sulphur but unites with halogens (difficultly with iodine, but with incandescence with chlorine and bromine). It unites directly with carbon and boron and gives alloys with metals.

(iv) Action of acids. It is easily acted upon by hydrochloric acid and dilute sulphuric acid, evolving hydrogen. It liberates sulphur dioxide with strong sulphuric acid.

$$Be + 2H_2SO_4 \longrightarrow BeSO_4 + SO_2 + 2H_2O$$

Cold concentrated nitric acid makes it passive while hot acid produces nitrogen peroxide.

$$Be + 4HNO_3 \longrightarrow Be(NO_3)_2 + 2H_2O + 2NO_2$$

(v) Action of alkalies. It is attacked readily by alkalies with the formation of *beryllates* and liberation of hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$

Uses

(i) In making alloys. *Beryllium bronzes*, which contain 2.5 to 2.25% of beryllium are hard and can be tempered just like steel. These are being used for making springs and slip-rings for high speed motors. *(ii)* Because of its high transparency to X-rays, it is used for making "windows" of X-ray tubes. *(iii)* It is also used for making electrodes of neon signs. *(iv) It is used as a moderator in nuclear reactors.* This use depends on the fact that beryllium absorbs fewer neutrons than any other known structural material. *(v)* Beryllium also finds special applications in

the fields of developing rockets, missiles and high speed air crafts. (*vi*) Recently beryllium has been used as an ingredient of a new textile fibre of rayon type.

Compounds of Beryllium

1. Basic beryllium acetate, $3Be(CH_3COO)_2.BeO$ *or* $Be_4O(CH_3COO)_6$.

It is a complex compound of beyllium with acetic acid, CH_3COOH. In this complex compound beryllium is *tetra-covalent*.

Preparation. It is prepared by dissolving beryllium hydroxide or carbonate in glacial acetic acid. The resulting solution is diluted with water and then evaporated to dryness. The residue is extracted with chloroform which dissolves basic beryllium acetate which can be obtained from the solution by crystallization.

$$4Be(OH)_2 + 6CH_3COOH \longrightarrow 3Be(CH_3COO)_2.BeO + 7H_2O$$

$$4BeCO_3 + 6CH_3COOH \longrightarrow 3Be(CH_3COO)_2.BeO + 3H_2O + 4CO_2 \uparrow$$

Properties. It is a colourless volatile crystalline solid with m.pt. = 283°C and b.pt. = 330°C, It is insoluble in water but soluble in the organic solvents such as glacial acetic acid, chloroform and ether. It is a covalent compound and is slowly hydrolysed by boiling water. It reacts with mineral acids to form the corresponding beryllium salt and acetic acid.

$$3Be(CH_3COO)_2.BeO + 8HCl \longrightarrow 4BeCl_2 + 6CH_3COOH + H_2O$$

$$3Be(CH_3COO)_2.BeO + 4H_2SO_4 \longrightarrow 4BeSO_4 + 6CH_3COOH + H_2O$$

Uses. (*i*) It is used as a starting source for the preparation of other beryllium compounds required for research work. (*ii*) It is also used as a means for purifying beryllium by solvent extraction.

Structure. X-ray diffraction studies have shown that the compound has a tetrahedral structure. The four beryllium atoms occupy the four corners of a regular tetrahedron and the oxygen atom lies at the centre. The six acetate groups are arranged along the six edges of the tetrahedron as shown in Figure 21.2.

Thus each Be-atom is attached to the central oxygen atom and three acetate-group-oxygen atoms. It may be noted that oxygen is the first short period element and hence its maximum covalency is 4 which is shown in this compound.

Fig. 21.2. Tetrahedral structure of basic beryllium acetate, $Be_4O\ (CH_3COO)_6$

2. Beryllium chloride, $BeCl_2$.

The *anhydrous* chloride is prepared: (*i*) by heating metallic beryllium in dry Cl_2 or HCl (*ii*) by passing CCl_4 or Cl_2 and SCl_2 vapour over heated BeO (*iii*) by the action of Cl_2 or HCl an heated Be_4C (*iv*) by heating a mixture of BeO and C in a current of Cl_2.

$$BeO + C + Cl_2 \xrightarrow{\Delta} BeCl_2 + CO$$

Properties. It forms snow-white fusible mass which sublimes readily. Melting and boiling points are 405° and 488°C respectively. It fumes strongly in moist air.

$$BeCl_2 + 2H_2O \rightleftarrows Be(OH)_2 + 2HCl$$

The fused salt is a poor conductor of electricity. It dissolves in water, evolving heat and crystallises out on drying in vacuum as tetrahydrate, $BeCl_2.4H_2O$. Anhydrous salt dissolves in alcohol and ether. With ether it forms an addition compound, $BeCl_2.2(C_2H_5)_2O]$. The sublimed chloride forms a tetraammoniate, $BeCl_2.4NH_3$ with NH_3.

Uses. It may be used in organic synthesis in place of anhydrous aluminium chloride though it is less efficient.

Uses. It is used (*i*) in surgery for plastering (*i.e.* setting) the fractured bones. (*ii*) in making casts for stalues, in dentistry, surgical instruments, toys etc. (*iii*) in making black board chalks.

Radium

Occurrence

Radium in minute quantities is found widely distributed throughout the earth's crust. It occurs in traces in almost all rocks and water of seas and oceans. All uranium minerals contain radium as it is a disintegration product in the uranium series. The two chief minerals of radium are: (*i*) *Pitchblende* or *uraninite*, U_3O_8. It contains barium, radium, arsenic, silicon, sulphur etc. This mineral occurs in Congo and Canada. (*ii*) *Carnotite*, $K(UO_2).(VO_4).4H_2O$. It is a potassium vanadate containing high percentage of radium and occurs in Katanga mines of Congo, U.S.A. and Russia.

Extraction of Radium from Pitchblende

The extraction of radium from pitchblende consists of the following two steps:

1. ***Preparation of*** $RaCl_2$**.** Preparation of $RaCl_2$ from pitchblende can be done by Curies' method. In this method pitchblende ore is roasted in a reverberatory furnace whereby As and S evaporate as their oxides. The residue is then fused with Na_2CO_3, washed with hot water, dissolved in dil. H_2SO_4 and filtered. Uranium passes into the solution as sodium uranate, Na_2UO_4 while Ra Ba and Si go into residue as $RaSO_4$, $BaSO_4$ and SiO_2 respectively. The residue containing $RaSO_4$ $BaSO_4$ and SiO_2 is again fused with Na_2CO_2 whereby $RaSO_4$ and $BaSO_4$ are converted into $RaCO_3$ and $BaCO_3$ while SiO_2 remains as such. The mass containing the carbonates and SiO_2 is treated with HCl and filtered. The filtrate contains $RaCl_2$ and $BaCl_2$ while SiO_2 is collected as residue. The solution containing $RaCl_2$ and $BaCl_2$ is concentrated and cooled when less soluble $RaCl_2$ crystallises out first, while more soluble $BaCl_2$ remains dissolved in mother liquor. This process of fractional crystallisation is repeated a number of times to get pure $RaCl_2$.

2. *Electrolysis of fused $RaCl_2$.* Radium metal is prepared by the electrolysis of fused $RaCl_2$, using a Pt–Ir anode and Hg cathode. The metal collects as an amalgam which is heated in an atmosphere of H_2 at 400–700°C whereby Hg distils over while radium is left behind as a white metal. The electrolytic cell used is shown in Fig. 21.3.

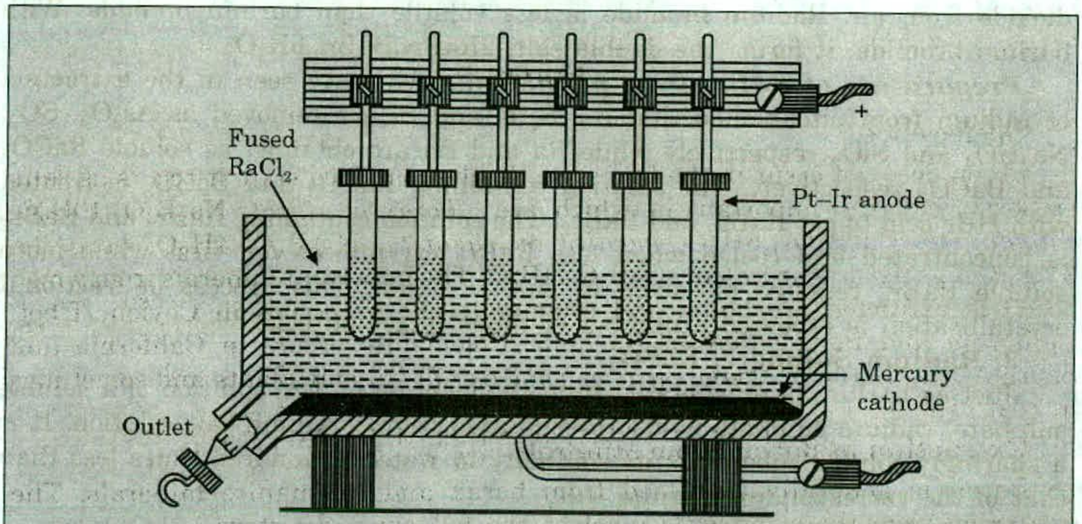

Fig. 21.3. Electrolytic cell used for the extraction of radium by the electrolysis of fused radium chloride.

Properties of Radium

Radium is a white metal which melts at 700°C, volatilises at 960°C and boils at 1140°C. When exposed to air, it blackens due to the formation of a nitride. It is luminescent and its blue luminescence becomes more pronounced when barium is present as impurity in it. It is acted upon by water, when its hydroxide is obtained. It is soluble in hydrochloric acid, forming the chloride. It gives out alpha, beta, and gamma rays. and this property of radio-activity remains unaffected between temperatures 2000°C and –250°C, and under other physical conditions. The radiations affect the photographic plate and discharge the electroscope. Radium salts give a caramine colour to the flame.

Compounds of Radium

Radium closely resembles barium in all its salts. Radium furnishes oxalate, phosphate, ferrocyanide, platinocyanide and other salts very much resembling the corresponding salts of barium. Its important compounds are discussed below:

1. Radium chloride, $RaCl_2.2H_2O$.

It is isomorphous with barium chloride, B $Cl_2.2H_2O$; both of them contain two molecules of water. The salt is prepared by dissolving radium carbonate in hydrochloric acid. When heated to 100° for many hours, it furnishes the anhydrous salt. It is less soluble in water than barium chloride. From the solution it can be precipitated by addition of alcohol, or by strong hydrochloric acid.

2. Radium Bromide, $RaBr_2.2H_2O$.

Like the chloride it also contains two molecules of water and is prepared by dissolving radium carbonate in hydrobromic acid. It is isomorphous with barium bromide, $BaBr_2. 2H_2O$. When exposed to air, it loses bromine and becomes alkaline after absorbing moisture, and then finally it becomes carbonate after taking carbon dioxide from air. Radium bromide is less volatile than barium bromide. With barium bromide, it forms the double salt, $2RaBr_2.BaBr_2.6H_2O$.

Preparation of $RaBr_2$ from pitchblende. We have seen in the extraction of radium from pitchblende that As, S, U and Si are removed as As_2O_3. SO_2, Na_2UO_4 and SiO_2 respectively while Ra and Ba are obtained as soluble $RaCO_3$ and $BaCO_3$ respectively. The solution containing $RaCO_3$ and $BaCO_3$ is treated with HBr acid to get $RaBr_2$ and $BaBr_2$. The solution containing $RaBr_2$ and $BaBr_2$ is concentrated and cooled when less $RaBr_2$ crystallises out first while more soluble $BaBr_2$ remains dissolved in mother liquor. This process of fractional crystallisation is repeated a number of times to get pure $RaBr_2$.

3. Radium Sulphate, $RaSO_4$.

Just as barium is precipitated from the solution on the addition of a soluble sulphate, radium sulphate is also precipitated from a radium salt solution. It is a sparingly soluble substance; its solubility in water is hundred times less than that of the corresponding barium salt.

Uses of radium salts.

(*i*) In the manufacture of *luminous prints* used for painting clock and watch dials, push buttons etc. The paint consists of a mixture of sulphides of Zn, Cu, Mn etc. containing a trace of radium bromide. (*ii*) In medicine in the treatment of cancer.

Portland Cement

What is Portland Cement ?

Cement is a very important building material which was first of all introduced in 1824 by Joseph Aspdin, a mason of Leeds, England. Be found that when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone like mass which resembled Portland rock which is a famous building stone of England. It is since then that the name *Portland cement* is given to a mixture of lime (obtained from lime stone), silica, iron oxide and alumina. Thus:

Cement is a dirty greenish heavy powder which contains lime in the form of aluminates and silicates. The various silicates and aluminates which constitute more than 90% of the cement are: *Tri-calcium silicate, $3CaO.SiO_2$; Dicalcium silicate, $2CaO.SiO_2$; Tricalcium aluminate, $3CaO.Al_2O_3$; Tetracalcium alumino ferrite, $4CaO.Al_2O_3$. Fe_2O_3.* Out of these, tricalcium silicate is the most important constituent of cement.

What is the Composition of Portland Cement ?

An average composition of a good simple of cement is: lime (CaO)—62%, silica (SiO_2)—22%, alumina (Al_2O_3)—7.5%, magnesia (MgO)—2.5%, iron oxide (Fe_2O_3)—

2.5%, sulphur trioxide (SO_3)—1.5%, sodium oxide (Na_2O)—1.0%, potassium oxide (K_2O)—1.0%. The essential constituents are lime (obtained from *lime stone*), silica and alumina (present in clay). For a good quality of cement the following ratios should be maintained;

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5 - 4.0, \quad \frac{\%CaO}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3} = 1.9 - 2.1.$$

Cement containing no iron is white but hard to burn. If less lime is present than given by the above ratio, the cement is low in strength and sets very soon. If more lime is there, the cement cracks. Excess of silica produces a slow-hardening cement while excess of alumina gives a quick-setting product.

Raw Materials Used in the Manufacture of Cement.

The important raw materials used in the manufacture of cement are.

1. *Lime stone, $CaCO_3$.* It provides lime, CaO. Chalk, marble and alkali waste can also be used, since these also supply CaO.

2. *Clay.* The composition of clay is $Al_2O_3.SiO_2.Fe_2O_3.2H_2O$. Clay supplies silica ($SiO_2$) and alumina ($Al_2O_3$) to the cement. Some of the clays do not contain Fe_2O_3 and the cement obtained in this case is white and hard to burn.

3. *Gypsum, $CaSO_4.2H_2O$.* The addition of gypsum decreases the setting time of cement.

Manufacture of Cement

The manufacture of cement consists of the following steps:

1. *Preparation of raw meal or slurry.* The raw materials *viz.* lime stone and clay are mixed in proper proportion by any of the following methods:

(*a*) *Dry process.* This process is employed when the raw materials *viz.* lime stone and clay are hard. In this process the lime stone is first broken into small pieces. It is then mixed with clay in the proper proportions and finally pulverised to such a fineness that 90–95% passes through a 100 mesh sieve. The mixture is made homogenous to produce what is known as **raw meal.**

(*b*) *Wet process.* This process is used when the raw materials *viz.* lime stone and clay are soft, the climate is fairly damp and the fuel is cheap. In this process, the lime stone is crushed to suitable size and the clay is washed with water in wash mills to remove foreign materials like flint. The powdered limestone is then mixed with the clay paste in the proper proportions (lime stone 75%, clay 25%) and the mixture is finely ground and made homogenous by means of a compressed air mixing arrangement. The resulting paste is known as **slurry.** The slurry contains about 40% water.

2. *Burning (calcination) of raw meal or slurry in rotary kiln: Preparation of cement clinker.* Raw meal or slurry prepared as above is introduced into the rotary kiln with the help of a screw conveyer. The rotary kiln consists of a long cylinder 6 to 8 feet in diameter and 100 to 250 feet in length. It is made of steel and is lined inside with fire bricks (Fig. 21.4). The kiln rotates on its axis at the rate of $\frac{1}{2}$ to 1 revolution per minute. As the kiln rotates, the charge slowly moves downwards due to the rotary motion of the kiln. Now the charge is heated by burning coal dust which enters at the lower end with the help of a blower. As the charge moves forward, it meets higher temperatures. When it reaches the lowest part of the kiln, the temperature is about 1500°C which is the maximum temperature in the kiln. The zone having this temperature is called *maximum temperature zone*. The charge takes 2-3 hours to cover the journey in the kiln.

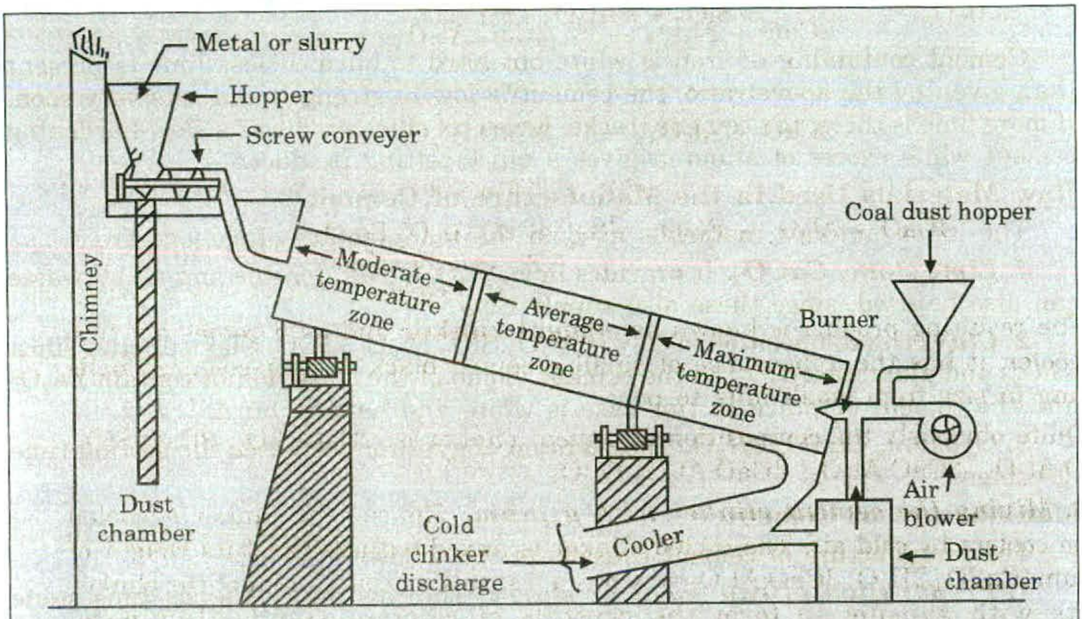

Fig. 21.4. Rotary kiln used for the manufacture of Portland cement.

Reactions Reactions taking place in the rotary kiln can be divided into the following three parts:

(i) Reactions taking place in moderate temperature zone. In this zone the temperature is upto 800°C. In this zone free moisture is removed and clay is broken into Al_2O_3, SiO_2 and Fe_2O_3.

$$\underbrace{Al_2O_3.2SiO_2.Fe_2O_3.2H_2O}_{\text{Clay}} \longrightarrow Al_2O_3 + 2SiO_2 + Fe_2O_3 + 2H_2O$$

(ii) Reactions taking place in average temperature zone. Here the temperature is 800–1000°C. In this zone lime stone ($CaCO_3$) decomposes into lime (CaO) and CO_2

$$\underset{\text{Lime stone}}{CaCO_3} \longrightarrow \underset{\text{Lime}}{CaO} + CO_2 \uparrow$$

(iii) Reactions taking place in maximum temperature zone. In this zone where the temperature is 1000–1500°C, the oxides *viz.* CaO, SiO_2, Al_2O_3 and Fe_2O_3 combine together and form calcium silicates *viz* $2CaO.SiO_2$, $3CaO.SiO_2$; calcium aluminates *viz.* $2CaO.Al_2O_3$; $3CaO.Al_2O_3$ and calcium ferrite *viz.* $4CaO.Al_2O_2.\ Fe_2O_3$.

$$2CaO + SiO_2 \longrightarrow \underset{\substack{\text{Dicalcium}\\ \text{silicate}}}{2CaO.SiO_2}$$

$$3CaO + SiO_2 \longrightarrow \underset{\substack{\text{Tricalcium}\\ \text{silicate}}}{3CaO.SiO_2}$$

$$2CaO + Al_2O_3 \longrightarrow \underset{\substack{\text{Dicalcium}\\ \text{aluminate}}}{2CaO.Al_2O_3}$$

$$2CaO + Al_2O_3 \longrightarrow \underset{\substack{\text{Tricalcium}\\ \text{aluminate}}}{3CaO.Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\substack{\text{Tetracalcium alumino}\\ \text{ferrite}}}{4CaO.Al_2O_3.Fe_2O_3}$$

The resulting product is known as **cement clinker** and as it comes out into the cooler, it has the appearance of small greenish black or grey-coloured balls varying in size from small nuts to peas.

Quite obviously the composition of cement clinker is: $2CaO.SiO_2$, $3CaO.SiO_2$, $2CaO.Al_2O_3$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$.

3. *Mixing the cement clinker with gypsum.* The cement clinker is cooled in the coolers by cold air. The cooled clinker is mixed with 2–3% of its weight of gypsum ($CaSO_4.2H_2O$).$3CaO.Al_2O_3$ which is a fast setting constituent of the clinker reacts with gypsum to form the crystals of calcium sulpho-aluminate, $3CaO.Al_2O_2.3CaSO_4.2H_2O$.

$$3CaO.Al_2O_3.\underset{\text{Gypsum}}{3(CaSO_4.2H_2O)} + 2H_2O \longrightarrow \underbrace{3CaO.Al_2O_3.3CaSO_4.2H_2O}_{\text{Calcium sulpho-aluminate.}} + 6H_2O$$

Thus we see that the addition of gypsum removes the fast setting $3CaO.Al_2O_3$ as $3CaO.Al_2O_3.3CaSO_4.2H_2O$ and hence the process of setting cement gets retarded and this results in better strength of the mass which sets.

Setting of Cement

The use of cement in the construction of buildings is based on its property of setting to a hard mass when its paste with water is allowed to stand for some time. When the cement is mixed with water, it absorbs water and the mass becomes hard and very resistant to pressure. This is known as the *setting of cement.* The reactions involved in the setting of cement are:

(i) Reactions taking place during first 24 hours. A short time after the cement is mixed with H_2O, the following reactions take place:

(*a*) $3CaO.Al_2O_3$ absorbs H_2O (hydration) and forms a colloidal gel of the composition, $3CaO.Al_2O_3.6H_2O$

$$3CaO.Al_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\substack{\text{Hydrated colloidal}\\ \text{gel of tricalcium}\\ \text{aluminate}}}{3CaO.Al_2O_3.6H_2O}$$

The gel of $3CaO.Al_2O_3.6H_2O$ so formed starts crystallising slowly.

(*b*) $3CaO.Al_2O_3$ which is a fast-setting material reacts with gypsum ($CaSO_4.2H_2O$) to form the crystals of calcium sulphoaluminate, $3CaO.Al_2O_3.3CaSO_4.2H_2O$.

$$3CaO.Al_2O_3 + \underset{\text{Gypsum}}{3(CaSO_4.2H_2O)} + 2H_2O \longrightarrow \underbrace{3CaO.Al_2O_3.3CaSO_4.2H_2O}_{\text{Calcium sulpho-aluminate}} + 6H_2O$$

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(ii) Reactions taking place between 1 and 7 days. $3CaO. SiO_2$ and $3CaO. Al_2O_3$ get hydrolysed (hydrolysis) according to the equations:

$$3CaO.SiO_2 + H_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{ppt.}}{Ca(OH)_2} + \underset{\text{(Amorphous)}}{2CaO.SiO_2}$$

$Ca(OH)_2$ formed starts changing into needle-shaped crystals which get studded in the colliodal gel, $2CaO.SiO_2$. formed as above and thus impart strength to it.

$$3CaO.Al_2O_3 + 6H_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{ppt.}}{3Ca(OH)_2} + \underset{\text{ppt.}}{2Al(OH)_3}$$

$Al(OH)_3$ so formed fills the interstices resulting in hardening the mass.

(iii) Reactions taking place between 7 and 28 days. $2CaO.SiO_2$ begins to hydrate (a very slow reaction) and forms the hydrated colloidal gel of the composition, $2CaO.SiO_2.xH_2O$.

$$2CaO.SiO_2 + xH_2O \xrightarrow{\text{Hydration}} \underset{\substack{\text{Hydrated colloidal gel}\\ \text{of dicalcium silicate}}}{2CaO.SiO_2.xH_2O}$$

Needles of $Ca(OH)_2$ formed in (*ii*) above get studded in the hydrated colloidal gel of $2CaO.SiO_2.xH_2O$ and thus impart strength to it.

$4CaO.Al_2O_3.Fe_2O_3$ also gets hydrated to form a colloidal gel of the composition, $3CaO.Al_2O_3.6H_2O$

$$4CaO.Al_2O_3.Fe_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\text{Hydrated colloidal gel}}{3CaO.Al_2O_3.6H_2O} + CaO.Fe_2O_3$$

The gel formed as above starts losing water partly by evaporation and partly by forming hydrates with the hydrated constituents. Thus cement sets to a hard mass.

Manufacture of Cement in India

In our country at present there are 56 factories in private as well as in public sectors which are manufacturing cement. Following are the important factories running in the country.

1. Factories in public sector. The important factories of this type are: (*i*) *Cement Corporation of India.* This Corporation has set up the plants at Rajpur

(M.P.), Kurkunta (Mysore) and Bokajan (Assam). (*ii*) *Assam Cement Corporation of India Ltd., Cherpaunji (Assam).* (*iii*) *U.P. State Cement Corporation Ltd., Dalla (U.P.)* (*iv*) *T.N. industrial Development Corporation Ltd., Alangulam (Tamil Nadu).*

2. Factories in private sector. Important factories of this type are: (*i*) *Associated Cement Co. Ltd., Bombay.* It is the biggest manufacturing unit in India having 24 factories located in Madhya Pradesh (6), Gujarat (4), Bihar (3), Andhra Pradesh (3), Rajasthan (3), Mysore (2), Madras (1), Maharashtra (1) and Haryana (1). (*ii*) *Andhra Cement Co. Ltd., Vijayawada (Andhra Pradesh);* (*iii*) *Ashoka Cement Co. Ltd., Dalmianagar (Bihar);* (*iv*) *Bagalkot Udyog Co. Ltd., Bagalkot (Mysore);* (*v*) *Century Cement, Tilda (Madhya Pradesh);* (*vi*) *Dalmia Cement Ltd., Dalmiapuram (Tamil Nadu);* (*vii*) *J.K. Synthetics Ltd., Nimbahera (Rajsthan);* (*viii*) *Jaipur Udyog Ltd., Sawai Madhopur and Beawar (Rajsthan);* (*ix*) *Madras Cement Ltd., (Madras);* (*x*) *Mysore Cement Ltd., Bangalore;* (*xi*) *Orissa Cement Ltd., Sundergarh (Orissa);* (*xii*) *Punyam Cement and Minerals Industries Ltd., Cement Nagar (Andhra Pradesh);* (*xiii*) *Saurashtra Cement and Chemical Industries Ltd., Porbandar (Gujrat);* (*xiv*) *Shri Digvijay Cement Ltd., Digvijaygram, (Gujrat);* (*xv*) *Sone Valley Portland Cement Ltd., Japla (Bihar);* (*xvi*) *Travancore Cement Ltd., Kothayam (Kerala).*

Questions with Answers

Q.1 Explain the following, giving appropriate reason for your answer.

(*i*) Hydrated magnesium chloride cannot be dehydrated by heating.

or Dehydration of hydrated magnesium chloride is done in presence of HCl gas.

Ans : Formula of hydrated magnesium chloride is $MgCl_2.\ 6H_2O$. When heated, it gets hydrolysed by its own water of crystallisation to give MgO.

$$MgCl_2.\ 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$$

Therefore, the salt can be dehydrated by passing HCl gas through the hydrated salt at about 650 K.

$$\underset{\text{Hydrated}}{MgCl_2.\ 6H_2O} \xrightarrow[650K]{HCl\ (g)} \underset{\text{Anhydrous}}{MgCl_2} + 6H_2O$$

(*ii*) It is necessary to add gypsum in the final stages in the preparation of cement.

Ans : Gypsum ($CaSO_4.\ 2H_2O$) is added in the final stages of the preparation of cement in order to regulate the process of setting of cement. When water is added to cement, it sets into a hard mass. In the absence of gypsum, the setting will occur immediatly. The process is highly exothermic and as a result, cracks will appear after sometime. It is , therefore, necessary to control or regulate the time of setting.

(*iii*) Calcium is preferred over sodium to remove last traces of moisture from alcohol ?

Ans : Both Na and Ca react with water to form their respective hydroxides. However, Na is normally not preferred since it reacts with alcohol (C_2H_5OH) and evolves H_2

$$2\ C_2H_5OH + 2\ Na \rightarrow 2\ C1_2H_5OH\ \text{(Sod.ethoxide)} + H_2$$

On the other hand, calcium has no action with alcohol and is, therefore, preferred over sodium to remove water or moisture from alcohol.

(*iv*) Halides of Be dissolve in organic solvents while those of Ba do not.

Ans : Since Be^{2+} ion is the smallest in size and Ba^{2+} ion is the largest in size, among alkaline metal cations (M^{2+}), halides of Be^{2+} are covalent and those of Ba^{2+} are ionic. Due to covalent character, halides of Be^{2+} dissolve in organic solvents (non polar solvents) and due to ionic character, halides of Ba^{2+} donot dissolve.

(*v*) The solubility of calcium acetate in water decreases with rise in temperature while that of lead nitrate increases. (I.I.T. 2000)

Ans : The dissolution of calcium acetate in water is of exothermic nature while that of lead nitrate is of endothermic nature. Therefore, the solubility of lead acetate in water decreases with rise in temperature while that of lead nitrate increases.

(*vi*) $BeCl_2$ can be easily hydrolysed. (I.I.T. 1999)

Ans : Since Be^{2+} ions are small, they have high value of charge/size ratio and hence are easily hydrolysed. The hydrolysis occurs because Be–O bond is very strong.

(*vii*) $BeCl_2$ fumes in moist air but the chlorides of other alkaline earth metals donot.

or **Solution of $BeCl_2$ is acidic in nature.**

Ans : $BeCl_2$ reacts with the moisture present in air and produces the fumes of HCl gas. Thus $BeCl_2$ fumes in air.

$$BeCl_2 + 2\ H_2O\ \text{(moisture)} \longrightarrow \underset{\text{Fumes}}{2\ HCl} + Be\ (OH)_2$$

OR

Since $BeCl_2$ is a salt of weak base *viz* Be $(OH)_2$ and strong acid (HCl), it gives weak base and strong acid when dissolved in water.

$$BeCl_2 + 2H_2O \longrightarrow \underset{\text{Strong acid}}{2HCl} + \underset{\text{Weak base}}{Be\ (OH)_2}$$

Due to the production of strong acid, aqueous solution of $BeCl_2$ shows acidic character.

(*viii*) The reaction between marble and dil. H_2SO_4 is not used to prepare CO_2.

Ans : When marble ($CaCO_3$) reacts with dil. H_2SO_4, ppt. of $CaSO_4$ is obtained and CO_2 gas is evolved.

$$CaCO_3 + H_2SO_4 \longrightarrow \underset{\text{ppt.}}{CaSO_4} + H_2O + CO_2$$

The ppt. of $CaSO_4$ formed as above gets deposited on the surface of $CaCO_3$ and hence further reaction between $CaCO_3$ and dil. H_2SO_4 is prevented and the formaton of CO_2 ceases after some time.

(ix) Although Ba^{2+} ion is posinuous, yet it is safer to use $BaSO_4$ internally in patients prior to taking their stomach X-ray.

Ans : Since $BaSO_4$ is extremely insoluble, it does not pass from digestive system to circulatory system.

(x) Sodium and potassium can be obtained by the electrolysis of fused NaOH and KOH respectively but calcium cannot be obtained by electrolysing $Ca(OH)_2$.

Ans : This is because of the fact that $Ca(OH)_2$ decomposes into CaO (quick lime) which is diffcult to fuse.

Q.2 Give chemical equations involved in the isolation of $MgCl_2$ from sea water. **(I.I.T. 1993)**

Ans : Different steps involved in the isolation of Mg from sea water are :

(i) Sea water contains $MgCl_2$ and $MgSO_4$. Sea water is treated with Ca $(OH)_2$ so that ppt. of Mg $(OH)_2$ is abtained.

$$\text{Sea water containing } MgCl_2 \text{ and } MgSO_4 + Ca\,(OH)_2 \rightarrow \underset{\text{Percipitate}}{Mg\,(OH)_2} + CaCl_2 + MgSO_4$$

(ii) $Mg(OH)_2 + 4H_2O + 2HCl \longrightarrow MgCl_2.\ 6H_2O$

(iii) $MgCl_2.\ 6H_2O \xrightarrow{\Delta} MgCl_2 + 6H_2O$

Q.3 What happens when the following are heated ? (i) Hydrated magnesiam chloride (ii) Hydrated magnessium chloride in presence of NH_4Cl.

Ans : (i) MgO is obtained.

$$MgCl_2\ 6H_2O \xrightarrow[(-4H_2O)]{\Delta} MgCl_2.\ 2H_2O \xrightarrow{\Delta} \underset{\text{Mag. oxy chloride}}{Mg\,(OH).\ Cl} + HCl + H_2O$$

$$Mg\,(OH)\,Cl \xrightarrow{\Delta} MgO + HCl$$

(ii) Anhydrous magnesium chloride ($MgCl_2$) is obtained.

$$\begin{tikzcd}
MgCl_2.\ 6H_2O + NH_4Cl \arrow[r, "\Delta"] & \underset{\text{Double salt}}{MgCl_2.\ NH_4Cl.\ 6H_2O} \arrow[d, "\Delta\ (-6H_2O)"] \\
MgCl_2 + NH_4Cl & MgCl_2.\ NH_4Cl \arrow[l, "\Delta"']
\end{tikzcd}$$

Q.4 Complete the following :

(i) $Be_2C + H_2O \rightarrow$ ....

(ii) $BeCl_2 + LiAlH_4 \rightarrow$ ....

(iii) Be $(OH)_2$ + 2NaOH $\rightarrow$ ....

(iv) $CaSO_4.\ 2H_2O \xrightarrow{\Delta}$ ....

(v) Ca + $H_2O \rightarrow$ ....

(vi) BeO + NaOH $\rightarrow$ ....

(*vii*) $CaC_2 + H_2O \rightarrow$ ....

(*viii*) $CaC_2 + N_2 \rightarrow$ ....

(*ix*) $Ca\ (OH)_2 + Cl_2 \rightarrow$ ....

(*x*) $BaO_2 + H_2SO_4 \rightarrow$ ....

Ans : (*i*) $Be_2C + 2H_2O \rightarrow 2Be + CH_4$

(*ii*) $2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

(*iii*) $\underset{\text{Sod. beryllate}}{Be\ (OH)_2 + 2NaOH \rightarrow Na_2BeO_2} + 2H_2O$

(*iv*) $CaSO_4 . 2H_2O \xrightarrow{\Delta} \underset{\text{Plaster of Paris}}{CaSO_4 . \frac{1}{2} H_2O} + \frac{3}{2} H_2O$

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

(*vi*) $BeO + 2NaOH \rightarrow \underset{\text{sod. beryllate}}{Na_2BeO_2} + H_2O$

(*vii*) $CaC_2 + 2H_2O \rightarrow Ca\ (OH)_2 + HC \equiv CH$

(*viii*) $CaC_2 + N_2 \rightarrow \underset{\text{Cal. cyanamide}}{CaCN_2} + C$

(*ix*) $Ca\ (OH)_2 + Cl_2 \rightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$

(*x*) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

Q.5 What is the diffrence between milk of lime and lime water.

Ans : A suspension of slaked lime, *i.e*. Ca $(OH)_2$ in water is called milk of lime but a clear decanted solution of slaked lime in water is called lime water.

Q.6 On treatment with cold H_2O, an element (A) reacted with H_2O, liberating a colourless gas (B) and a solution (C). A reacted with (B) yielding a solid product (D) which reated with H_2O to give a basic solution due to the formation of (E). When CO_2 was bubbled through solution (C), initially a white ppt. (F) was formed but this ppt. redissolved forming solution (G) when more CO_2 was added. Precipitate (F) effervesced when moitered with conc. HCl. When (F) was heated with carbon at 1000 °C, a white compound (H) which when heated with carbon at 1000 °C gave a solid (I) of some commoercial importance. Identify the substances (A) to (I).

Ans : (A) is calcium metal which reacts with H_2O and evolves H_2 (B) and $Ca(OH)_2$ solution (C). Thus all the reactions can be written as :

$\underset{(A)}{Ca} + 2\ H_2O \longrightarrow \underset{\text{Solution (C)}}{Ca\ (OH)_2} + \underset{(B)}{H_2}$ (*Colourless and odourless gas*)

$\underset{(A)}{Ca} + \underset{(B)}{H_2} \longrightarrow \underset{(D)}{CaH_2}$ (*Solid product*)

$\underset{(D)}{CaH_2} + 2H_2O \longrightarrow \underset{\text{Basis solution (E)}}{Ca\ (OH)_2}$ (White ppt) + $2H_2$

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
Solution (F)
(C)

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$
(F) Soluble
(G)

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$
(F)

$CaCO_3 + C \xrightarrow{1000°C} CaO$ (*White product*) $+ 2CO$
(F) (H)

$CaO + 2C \xrightarrow{1000°C} CaC_2$ (*Solid*) $+ \frac{1}{2} O_2$.
(H) (I)

Thus the substances (A) to (I) are :

$A = Ca$, $B = H_2$, $C = Ca(OH)_2$, $D = CaH_2$,
$E = Ca(OH)_2$, $F = CaCO_3$, $G = Ca(HCO_3)_2$, $H = CaO$, $I = CaC_2$

Q.7 Element (A) burns in N_2 to give an ionic compound (B). Compound (B) with water gives (C) and (D). Solution of (C) becomes milky on bubbling CO_2 through it. Identity (A), (B), (C) and (D) and write the chemical equations for the reactions involved. (I.I.T. 1997)

Ans : Element $\xrightarrow{+N_2}$ Nitride of the element, A $\xrightarrow{+H_2O}$ (C) + (D)
(A) (B) $\downarrow +CO_2$
Milkiness.

Since (C) becomes milky on bubbling CO_2 through it, (C) should be $Ca(OH)_2$. Now we know that when a nitride reacts with H_2O, NH_3 is evolved. Thus (D) should be NH_3, nitride (B) should be Ca_3N_2 (an ionic compound) and hence the element (A) should be Ca.

Thus all the reactions involved can be written as :

$3Ca + N_2 \longrightarrow Ca_3N_2$
(A) (B)

$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$
(B) (C) (D)

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
(C) Milkiness

Q.8 Calcium burns in air to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identity the compounds A and B. (I.I.T. 1996)

Ans : Ca burns in air to form CaO and Ca_3N_2.

$$2\,Ca + O_2 \longrightarrow 2\,CaO$$
$$3\,Ca + N_2 \longrightarrow Ca_3N_2 \ \textit{(White powder)}$$

Calcium nitride on hydrolysis with H_2O gives ammonia, NH_3 (A)

$$Ca_3N_2 + 6\,H_2O \longrightarrow 3\,Ca\,(OH)_2\ \textit{(Gas)} + \underset{A}{2\,NH_3}\ \textit{(Alkaline solution)}$$

The alkaline solution of $Ca\,(OH)_2$ thus formed reacts with CO_2 present in the air to form $CaCO_3$ (B).

$$Ca\,(OH)_2 + CO_2 \longrightarrow \underset{B}{CaCO_3} + H_2O$$

Thus: $A = NH_3$ and $B = CaCO_3$

Q.9 Metal nitrate (A) on heating, decomposes to give a solid residue (B) which goes into solution with dil. HCl. The solution thus obtained gives a white ppt. (C) with $(NH_4)_2CO_3$. The ppt. (C) is dissolved in dil. HCl and treated with K_2CrO_4 solution to get yellow ppt. (D). Identity (A), (B), (C) and (D). Also give chemical equations.

Ans : The reactions can be shown as :

$$\underset{(A)}{\text{Metal nitrate}} \xrightarrow{\Delta} \underset{\text{Residue (B)}}{\text{Metal oxide}} \xrightarrow{+HCl} \underset{\text{Solution}}{\text{Metal chloride}}$$
$$\xrightarrow{+\,(NH_4)_2\,CO_3} \underset{\text{White ppt (C)}}{\text{Metal carbonate}} \xrightarrow{+HCl} \text{Metal chloride}$$
$$\xrightarrow{+\,K_2CrO_4} \underset{\text{Yellow ppt. (D)}}{\text{Metal chromate}}$$

Metal chromate may be either $PbCrO_4$ or $BaCrO_4$ and hence the metal nitrate may be either $Pb\,(NO_3)_2$ or $Ba\,(NO_3)_2$. Since $(NH_4)_2\,CO_3$ has been used in the above reactions, the metal nitrate is $Ba\,(NO_3)_2$. The reactions taking place at different steps can be written as :

$$\underset{(A)}{Ba\,(NO_3)_2} \xrightarrow{\Delta} \underset{\substack{\text{Solid residue}\\ \text{(B)}}}{BaO} + 2\,NO_2 + O_2$$

$$\underset{(B)}{BaO} + 2\,HCl\ \textit{(Dil)} \longrightarrow \underset{\text{Solution}}{BaCl_2} + H_2O$$

$$\underset{\text{Solution}}{BaCl_2} + (NH_4)_2\,CO_3 \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{(C)}}}{BaCO_3} + 2\,NH_4Cl$$

$$\underset{(C)}{BaCO_3} + 2\,HCl \longrightarrow BaCl_2 + H_2O + CO_2$$

$$BaCl_2 + K_2CrO_4 \longrightarrow \underset{\substack{\text{Yellow ppt.}\\ \text{(D)}}}{BaCrO_4} + 2\,KCl$$

Thus : $A = Ba(NO_3)_2$, $B = BaO$,
$C = BaCO_3$ and $D = BaCrO_4$

Q.10 Lime water becomes turbid on passing CO_2 through it, but becomes clear when more CO_2 is passed. Explain.

Ans : When CO_2 is passed through lime water [$Ca(OH)_2$], turbiditly due to the formation of insoluble $CaCO_3$ is obtained. This ppt. of $CaCO_3$ gets dissolved in excess of CO_2 due to the formation of soluble $Ca(HCO_3)_2$

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{ppt.}}{CaCO_3} + H_2O$$

$$\underset{\text{Soluble}}{Ca(HCO_3)_2} \xleftarrow{+CO_2}$$

University Questions

1. Give the preparation, properties, uses and structure of beryllium chloride. *(Agra 82, 83; Kanpur 81)*
2. Describe the preparation, properties, uses and structure of basic berryllium acetate. *(Meerut 80, 82, 84, 87, 88, 89; Agra 80, 81, 83; Kanpur 81)*
3. Describe the discovery, extraction and uses of radium. *(Madras 85)*
4. What is the role of gypsum in cement? *(Himachal Pradesh 99)*
5. How does beryllium occur in nature? Using flow sheet diagram give one method for its extraction. *(Gorakhpur 99)*
6. How will you obtain radium chloride from carnotite? *(Kumaon 2000)*
7. (*a*) Justify the position of radium in second group of periodic table. How it is obtained from pitchblende and how it is separated from Hg cathode?
   (*b*) How is beryllium obtained from beryl? Give anomalous behaviour and its diagonal relationship with aluminium. *(Lucknow 2000)*
8. Give line diagram of the extraction of beryllium from its important ore. *(Avadh 2000)*
9. Discuss the manufacture of Portland Cement *(Bangalore 2009)*

CHAPTER

22

General Characteristics of Group 13 (III A) Elements: Boron Group Elements

Group III A of the long form of the periodic table consists of *five* elements which are: *Boron* (B), *Aluminium* (Al), *Gallium* (Ga), *Indium* (In) and *Thallium* (Tl). These elements are collectively known as *boron group elements*.

Position of Boron Group Elements in the Periodic Table

The inclusion of boron group elements namely B, Al, Ga, In and Tl in the same sub-group of the periodic table is justified by the following general characteristics of these elements.

I. Electronic Configurations.

The electronic configurations of the atoms of boron group elements are: B ($Z = 5$) → 2, 3 ($2s^2p^1$); Al ($Z = 13$) → 2, 8, 3 ($3s^2p^1$); Ga($Z = 3$) → 2, 8, 18, 3 ($3d^{10}4s^2p^1$); In ($Z = 49$) → 2, 8, 18, 18, 3 ($4d^{10}5s^2p^1$); Tl ($Z = 81$) → 2, 8, 18, 32, 18, 3 ($4f^{14}5d^{10}6s^2p^1$). The configurations given in bracket are the valence-shell configurations. On the basis of the electronic configuration of the penultimate shell, these elements can be divided into two groups namely (*i*) 1*st* group of elements consists of B and Al elements whose penultimate shells have *inert gas type configuration* (s^2 or s^2p^6 configuration) (B has 2 electrons and Al has 8 electrons in their penultimate shell) (*ii*) 2*nd* group consists of Ga, In and Tl whose penultimate shells have *pseudo inert gas type configuration* ($s^2p^6d^{10}$ configuration). This difference in electronic configuration is responsible for the difference in properties of the elements of both the groups and also of boron and aluminium.

II. Similarities in Physical Properties and Gradation in Them.

Some of the physical properties of boron group elements are discussed below:

1. Atomic volume, atomic and ionic radii and density. Atomic volume, atomic and ionic radii (of M^{3+} ions) and density increase on moving from B to Tl.

2. Melting points, boiling points and heats of sublimation. Melting points *decrease* from B to Ga and then increase upto Tl. The low value of melting point of Ga is explained on the basis that its structure consists of Ga_2 molecules. Boiling points and heats of sublimation show a continuous *decrease*. The successive decrease in heat of sublimation indicates that the atoms of these elements are held less and less closely as we move from B to Tl.

3. Ionisation energies. First ionisation energies of these elements correspond to the removal of np^1-electron from ns^2p^1 configuration while the second and third ionisation energies correspond to the removal of ns^2-electrons in succession. Because of the increase in size of Al, the ionisation energy decreases from B to

Al. But in going from Al to Ga the value of ionisation energy increases. Thus increase in case of Ga is duo to the fact that the intervening *d*-electrons in Ga are not able to shield the nuclear charge effectively and hence the valence electrons in Ga are more firmly held to the nucleus and its ionisation energy increases.

Although the nuclear charge of these elements is *larger* and their size is *smaller* than that of the elements of Group II A, the first ionisation energies (*i.e.*, I_1 values) of these elements are lower than those of the elements of Group II A. This is due to the fact that the *p*-electrons (Group III A) are *less penetrating* and more shielded than *s*-electrons (Group II A), *i.e.*, *p*-electrons, being at a greater distance from the nucleus than the *s*-electrons, are held *less tightly* with the nucleus and hence can be removed more easily than the *s*-electrons.

The second and third ionisation energies (*i.e.*, I_2 and I_3 values) are considerably higher because the successive electron are to be removed from *s*-orbital.

In this group since the sum of I_1, I_2 and I_3 is very high for boron, boron is not able to exist as B^{3+} ion in its compounds. In fact the sum, $(I_1 + I_2 + I_3)$ for boron is the highest because of its extremely small size and because of the fact that its valence-electrons are not effectively shielded from the nuclear charge by the intervening electrons. However, as we move down the group, the total ionisation energies decrease but not in a regular order.

4. Oxidation states. Since boron atom has *small size* and *high ionisation energy*, it does not lose all its three valence-shell electrons (ns^2p^1 electrons) and hence does not give B^{3+} ion. It is for this reason that boron atom combines with other elements through covalent bonds, *i.e. boron atom gives mainly covalent compounds.* For convenience it is still preferred to treat boron atom in its compounds as B^{3+} ion. The small size and high charge of Al^{3+} ion give it high charge density. This charge density is responsible for the facts namely: (*a*) The compounds of Al in the gaseous state are *covalent*. (*b*) Due to *high hydration energy of Al^{3+}*, its compounds are *stabilised in solution*. (*c*) Its compounds in the solid state have *high lattice energy*.

Other elements namely Ga, In and Tl show +1 as well as +3 oxidation states, *i.e.* these elements form M^+ as well as M^{3+} cations. M^{3+} cations are obtained when all the three ns^2p^1 electrons are lost while M^+ cations are formed when only one np^1 electron is lost. In the formation of M^+ cations the electron pair in *ns* orbital remains inert. This is called **inert pair effect**. B and Al atoms do not show inert pair effect and hence do not form M^+ cations. Inert pair effect increases when we move from Ga to In to Tl. Thus Tl shows maximum inert pair effect and hence forms only Tl^+ cation which is the most stable ion in case of Tl element.

Relative stability of M^+ and M^{3+} cations. When we move down the group from B to Tl, the stability of +3 state *decreases* while that of +1 state *increases*, *i.e.* the stability of M^{3+} cations decreases from B^{3+} to Tl^{3+} while that of M^+ cations increases from B^+ to Tl^+ as shown below :

$$\boxed{\begin{array}{l} \mathbf{B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}} \\ \mathbf{B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}} \end{array}}$$

Thus when we compare the stability of the compounds formed by Ga^+, In^+ and Tl^+ ions, the compounds of Ga^+ are unstable, those of In^+ are moderately stable while those of Tl^+ are the most stable.

Compounds of Tl^+ are more stable than those of Tl^{3+} ($Tl^+ > Tl^{3+}$) and hence the compounds of Tl^{3+} get immediately changed (reduced) into those of Tl^+. In other words compounds of Tl^{3+} act as oxidising agents and those of Tl^+ act as reducing agents.

$$\underset{\text{Unstable (oxidising agent)}}{Tl^{3+}\text{ compounds}} \xrightarrow[(+2e^-)]{\text{Reduction}} \underset{\text{Stable (reducing agent)}}{Tl^{+}\text{ compounds}}$$

5. Nature of M^{3+} compounds. From the electronic configurations of these elements it is clear that all of them would be expected to form M^{3+} ions. The nature of the compounds of M^{3+} ions is decided by Fajan's rule according to which *the smaller the cation, the greater is its tendency to form covalent compounds.* Thus with the *increase* of the size of M^{3+} ions from B^{3+} to Tl^{3+}, the tendency of these ions to form covalent compounds *decreases*. Consequently the compounds of B^{3+} are predominantly covalent while Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+} give ionic compounds as well.

6. Electropositive (metallic) character. Electropositive (metallic) character of the elements *increases* as we move from B to Tl. This is indicated from the ionisation energies of these elements. Thus B is a *semi-metal i.e.*, it is closer to non-metals than to metals in its properties (its crystalline form is hard, inert and a poor conductor of electricity), while other elements are metallic and good conductors of electricity. Al, Ga, In and Ti have almost equal electropositive character as is evident from the fact that the ionisation energies of these elements do not differ much from each other.

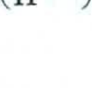
7. Oxidation potentials. With the exception of boron which does not form B^{3+} ion in aqueous solution due to large quantity of hydration energy associated with B^{3+} ion, the standard oxidation potentials of other elements corresponding to the reaction:

$$M\ (s) \longrightarrow M^{3+}\ (aq) + 3e^-$$

are quite high in spite of their large values of total ionisation energies. These high values of standard oxidation potential are due to *large heats of hydration* which result from the *high charges* and *small radii* of M^{3+} ions.

III. Similarities in Chemical Properties and Gradation in Them.

Some chemical properties of these elements and gradation in them are discussed below:

1. Formation of oxides and hydroxides. All the elements of this group form oxides and hydroxides. B^{3+} ion, being very small in size, has high (positive) charge density. Therefore, when this ion is placed in H_2O, it tends to pull off electrons from H_2O molecule towards itself sufficiently strongly by rupturing the O—H bond present in H_2O molecule . This results in a rapid hydrolysis of B^{3+} ion by H_2O to release H^+ ions. Hence $B(OH)_3$ and B_2O_3 are *acidic in character*. Al^{3+} and Ga^{3+} ions being relatively large than B^{3+} ion, have smaller ability to rupture the O—H bond in H_2O molecule by pulling off electrons. Thus Al^{3+} and Ga^{3+} ions are hydrolysed to a smaller extent than B^{3+} ion. This means that the oxides and hydroxides of Al^{3+} and Ga^{3+} are *amphoteric*. In^{3+} and Tl^{3+} ions are even larger than Al^{3+} and Ga^{3+} ions and hence their hydrolysis by H_2O is very low, *i.e.*, the O—H bond in water is hardly affected by In^{3+} and Tl^{3+} ions and this makes the oxides and hydroxides of In^{3+} and Tl^{3+} ions *distinctly basic*. Thus we see that *on moving down the group from boron to thallium, the oxides and hydroxides of these elements change from acidic through amphoteric to basic in character.* This trend is inconsistent with the change from *non-metallic to metallic character of these elements.* This trend shows that the oxides and hydroxides of B are *acidic*, those of Al and Ga are *amphoteric* while those of In and Ti are *basic*.

2. Formation of trihalides. All the elements of this group react with halogens to form the trihalides, MX_3.

Properties. (*i*) *Covalent and ionic character.* Boron trihalides are *covalent in character* due to the *small size* and *high charge density* on B^{3+} ion.

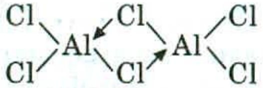
The fluorides of Al, Ga, In and Tl are *ionic* and have high melting points while the other halides of these elements are *covalent* when *anhydrous*. For example anhydrous $AlCl_3$ is covalent but in water it gets hydrolysed to give Al^{3+} (*aq*) ions. This change from a covalent compound in an aqueous solution is mainly due to the high hydration energy of Al^{3+} ions. However, BCl_3, on hydrolysis, does not give B^{3+} ions, because the ionisation energy of B^{3+} ion is very large.

(*ii*) *Geometry* (*i.e., shape*) *of trihalides*. The normal trihalides are *planar triangular* in shape which results from sp^2 hybridisation of the central atom. The central atom in these trihalides has a *vacant p*-orbital which remains *unhydridised*. As an example BF_3 can be considered. The shape of BF_3 molecule has already been discussed.

(*iii*) *Formation of $BX_3.L$ complexes*. The boron trihalides (BX_3) form complexes of $BX_3.L$ type where L is a *neutral* or *anionic donor* (*i.e.*, ligand). These complexes are *tetrahedral in shape* and in their formation the unhybridised vacant *p*-orbital accepts the lone pair of electrons denoted by the donor, L. Thus:

$$\underset{\substack{\text{Planar triangular} \\ (sp^2)}}{BX_3} + L \longrightarrow \underset{\substack{\text{Tetrahedral} \\ (sp^3)}}{BX_3.L}$$

(*iv*) *Formation of dimeric molecules.* Boron trihalides exist as *discrete species* (*i.e., monomeric moiecules*, BX_3) while the trihalides of other elements (*e.g.* $AlCl_3$, $AlBr_3$, $GaCl_3$, $InCl_3$, $InBr_3$ and InI_3) exist as *dimers* both in vapour sate and in non-polar solvents. In the formation of dimers the trihalides make use of the vacant *p*-orbital which remained unhybridised in the formation of MX_3 trihalides. In these dimeric molecules the halogen atoms are arranged *tetrahedrally* around the central atom (*i.e.*, each central atom is surrounded by four halogen atoms) and form halogen bridges between MX_2 units (M = central atom *viz.*, Al, Ga, In). Dimeric structure of aluminium trihalide, $(AlCl_3)_2$ is shown below:



In this structure the four terminal Cl atoms and two Al atoms lie in the same plane while the bridging Cl atoms are above and below this plane. Thus each Al atom is surrounded by halogen atoms. The arrows indicate the donation of an electron pair by the chloride ion to Al atom. This electron pair goes into the vacant *p*-orbital of Al atom. In the solid state $AlCl_3$ has a layer structure in which each Al atom is surrounded by *six* Cl atoms.

Here a question arises: *Why the trihalides of aluminium exist as dimers while the trihalides of boron exist as monomers*? This is explained on the basis of the *smaller size of boron atom relative to that of aluminium.* Owing to its small size, boron atom cannot coordinate to four larger halide ions and hence cannot form the dimeric molecules.

The dimeric structures are retained when the halides are dissolved in non-polar solvents like C_6H_6. But when the halides are dissolved in H_2O, due to heat of hydration, the dimeric structure, $(MX_3)_2$ splits into $[M(H_2O)_6]^{3+}$ and X^- ions which yield a conducting solution.

$$(MX_3)_2 + 12H_2O \longrightarrow 2\ [M(H_2O)_6]^{3+} + 6X^-$$

The covalent dimers may also be splited by reactions with donor molecules giving complexes of $R_3N.AlCl_3$ type.

(*v*) *Formation of complex halides*. Boron trihalides (*e.g.*, BF_3) also form complex halides of the type, $[BF_4]^-$ in which boron atom (central atom) has a co-ordination number equal to 4. It can not extend its co-ordination number beyond 4 due to the non-availability of *d*-orbitals in its configuration. However, the trihalides of other elements of this group form the complex halides of $[AlF_6]^{3-}$ $(GaCl_6]^{3-}$, $[InCl_6]^{3-}$ etc., type in which the central atom has co-ordination number of 6 which is because of the presence of *d*-orbitals in these central atoms.

(*vi*) *Electron-acceptor property: Formation of addition compounds.* The trihalides of all the elements of this group act as Lewis acids, *i.e.*, they react with donor molecules and form addition compounds. The Lewis acidity (*i.e.*, electron-acceptor ability) of the trihalides is in the order:

$$BX_3 > AlX_3 > GaX_3 > InX_3$$

The position of the halides of thallium is not clear.

3. Formation of hydrides. None of the elements of this group reacts directly with H_2 to form hydrides. However, hydrides of these elements have been prepared by indirect methods. Boron forms a large number of polymeric hydrides which are called *boranes*. Some examples are B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} etc. These hydrides are covalent in nature. Al forms only one high molecular weight polymeric hydride, $(AlH_3)_x$ which is an insoluble substance and, on heating, decomposes into its elements. X-ray and neutron diffraction studies have shown that this compound contains Al atoms surrounded octahedrally by six H-atoms. The structure consists of a network of AlH_2Al bridges. Ga gives GaH_4 which is called *gallane*. It is an unstable and volatile liquid. Indium gives polymerised solid hydride, $(InH_3)_x$. The hydrides given by Tl are extremely unstable. The elements of this group also form the *complex anionic hydrides* like $Li^+[BH_4]^-$, $Li^+[AlH_4]^-$,

$Li^+[GaH_4]^-$ etc. In the formation of these hydrides H^- ion acts as an electron pair donor while MH_3 hydride acts as an electron pair acceptor.

Electron pair acceptor		***Electron pair donor***		***Complex hydride***
BH_3	+	H^-	$\longrightarrow$	$[BH_4]^{4-}$
AlH_3	+	H^-	$\longrightarrow$	$[AlH_4]^-$
GaH_3	+	H^-	$\longrightarrow$	$[GaH_4]^-$

The electron pair donated by H^- ion goes into the vacant *p*-orbital on the central atom. These complex hydrides are prepared as follows:

$$4LiH + AlCl_3 \xrightarrow{\text{Ether}} Li[AlH_4] + 3LiCl$$

The complex hydrides, particularly $Li[AlH_4]$ and $Na[AlH_4]$ are useful reducing agents. These are used to reduce the aldehydes and ketones to alcohols and nitrates to amines.

Anomalous Properties of Boron: Dissimilarities of Boron with Other Elements of Group III A.

In many properties boron differs from the other elements of its own subgroup. The main points of difference are:

(1) B has a very small atomic radius. The hypothetical B^{3+} ion has very small size, high charge and hence high charge density. This value is so high that B^{3+} ion does not exist. All the compounds of boron are, therefore, covalent.

(2) Boron has less than four valence-electrons and this gives it a great electron accepting power, *i.e.*, its compounds behave as strong Lewis acids and hence forms a large number of complex compounds exhibiting its tendency to acquire a stable octet.

(3) Boron shows a maximum covalency of four while all other elements show a covalency of six or more.

(4) It does not exihibit inert pair effect.

Comparison between Boron and Aluminium.

(A) Similarities. (*i*) *Electronic configuration.* Both have similar electronic configurations having three electrons in their outermost shells.

$$B(Z = 5) = 1s^2 2s^2 2p^1 \ (2, 3)$$
$$Al(Z = 13) = 1s^2 2s^2 2p^6 3s^2 3p^1 \ (2, 8, 3)$$

(*ii*) *Valency.* Both the elements are trivalent. They do not show variable valency because their penultimate shells are complete and stable. Both have generally no tendency to form B^{3+} and Al^{3+} ions and, therefore, form tri-covalent compounds. Aluminium, however, may also form electrovalent compounds with strong electron accepting atoms or groups.

(*iii*) *Oxidation state.* The common oxidation state of these elements is +3. Boron, however, also exhibits an oxidation state of –3 in the metal borides.

(*iv*) *Action of conc. H_2SO_4.* Both react with conc. H_2SO_4 to form SO_2.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2 \uparrow$$
$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O + 3SO_2 \uparrow$$

(*v*) *Action of alkalies.* They react with alkalies to form H_2.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2 \uparrow$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2 \uparrow$$

(*vi*) *Formation of oxides.* Both form oxides when heated with oxygen at high temperature.

$$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$$

$$4Al + 4O_2 \xrightarrow{800°C} 2Al_2O_3$$

These oxides are amphoteric and dissolve in acids as well as in alkalies to form salts.

$$B_2O_3 + 6HCl \longrightarrow 2BCl_3 + 3H_2O$$

$$B_2O_3 + 6NaOH \longrightarrow \underset{\substack{\text{Sodium}\\\text{borate}}}{2Na_3BO_3} + 3H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium meta-aluminate}}{2NaAlO_2 + H_2O}$$

(*vii*) *Formation of nitrides.* Both, when heated with nitrogen or ammonia, form nitrides.

$$2B + N_2 \longrightarrow 2BN$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$2B + 2NH_3 \longrightarrow 2BN + 3H_2$$

$$2Al + 2NH_3 \longrightarrow 2AlN + 3H_2$$

These nitrides are decomposed by steam to form ammonia.

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

(*viii*) *Formation of sulphides.* Both from sulphides on heating with sulphur at high temperatures. These are hydrolysed by water.

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

$$Al_2S_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2S$$

(*ix*) *Formation of chlorides.* They form trichlorides by direct combination with Cl_2 or by passing Cl_2 over heated mixture of their oxides and charcoal.

$$2B + 3Cl_2 \longrightarrow 2BCl_3$$

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

These trichlorides are covalent and are hydrolysed by water.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

(*x*) *Formation of alkyl compounds.* Both form similar types of alkyl compounds.

$$2BCl_3 + 3Zn(CH_3)_2 \longrightarrow 2B(CH_3)_3 + 3ZnCl_2$$
$$2Al + 3Hg(CH_3)_2 \longrightarrow 2Al(CH_3)_3 + 3Hg$$

(B) Dissimilarities. Although B and Al both belong to the same group of the periodic table, yet they show many dissimilarities. The difference in their properties is due to the big difference in their size and ionisation potential. The points showing dissimilarities between boron and aluminium are given in the following table.

Boron	Aluminium
1. There are two electrons in the penultimate shell (2, 3).	There are eight electrons in the penultimate shell (2, 8, 3).
2. It is a non-metal and is a bad conductor of heat and electricity.	It is a metal and is a good conductor of heat and electricity.
3. It has high melting point (2300°C).	It has low melting point (660°C).
4. It exhibits allotropy and is found in two forms *viz*. crystalline and amorphous.	It does not exhibit allotropy.
5. Its crystalline form is very hard.	It is sufficiently soft.
6. It forms covalent compounds only.	It forms both covalent and electrovalent compounds.
7. It reacts with hydrogen to form a number of hydrides like B_2H_6, B_5H_9, etc.	It does not form any stable hydride.
8. It does not decompose water or steam.	It decomposes steam to form hydrogen. $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$
9. It does not react with dil. acids.	It reacts with dil. acids to form hydrogen. $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2 \uparrow$
10. It is oxidised by conc. HNO_3 to form boric acid. $B + 3HNO_3 \rightarrow H_3BO_3 + 2NO_2$	It becomes passive with conc. HNO_3
11. It dissolves in fused alkalies to form hydrogen. $2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$	It dissolves in hot alkalies to form hydrogen. $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
12. Borates are very stable.	Aluminates are lese stable.
13. $B(OH)_3$, *i.e.*, H_3BO_3, is weakly acidic.	$Al(OH)_3$ is amphoteric.
14. BCl_3 is a fuming liquid.	$AlCl_3$ is a solid.
15. It combines with metals to form borides. $3Mg + 2B \rightarrow Mg_3B_2$	It combines with metals to form alloys.
16. Its maximum covalency is 4.	Its maximum covalency is 6.

Diagonal Relationship between B and Si: Similarities between B and Si.

Boron resembles silicon in many of its properties with which it is diagonally related. Some common properties showing the similarities between B and Si are given below:

1. Preparation. Both the elements can be prepared by reducing their oxides with Mg.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$
$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

2. Action of alkalies. Both the elements dissolve in alkalies (boron only in fused while silicon in fused as well as aqueous), forming *metaborate* (BO_2^-) and *metasilicate* (SiO_3^{2-}) end liberate H_2.

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2 \uparrow$$
$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_2 + 2H_2 \uparrow$$

3. Action of water and non-oxidising acids. None of the elements is attacked by water and non-oxidising acids.

4. Occurrence. None of these elements occurs in the free state. Both are found as oxy-compounds, *e.g. borates* and *silicates*.

5. Non-metallic character. Chemically both the elements are typical non-metals and are bad conductors of heat and electricity.

6. Allotropic forms. Both the elements exist in two allotropic forms *viz. amorphous* and *crystalline*. The crystalline form of both the elements is harder and less reactive than the amorphous form.

7. Density, electronegativity, ionisation potential and boiling points. Density, electronegativity, ionisation potential and boiling point of both the elements are almost the same.

8. Melting points. Both the elements have high melting points (B = 2300°C, Si = 1420°C).

9. Formation of covalent compounds. Both the elements form mainly covalent compounds like hydrides (*e.g.* B_2H_6, SiH_4), halides (*e.g.* BX_3, SiX_4), oxides (*e.g.* B_2O_3, SiO_2).

10. Reactivity. Both the elements are normally inert at ordinary temperature. For example they are not oxidised in air and do not react with other elements or with dil. acids. However, the reactivity can be increased by increasing the temperature. At high temperatures these elements react with a number of metals and non-metals.

11. Combination with metals. Both the elements combine with metals like Mg and form borides and silicides respectively.

$$2B + 3Mg \longrightarrow Mg_3B_2 \qquad (\textit{Boride})$$
$$Si + 2Mg \longrightarrow Mg_2Si \qquad (\textit{Silicide})$$

12. Oxides. *Preparation.* Boron and silicon combine with O_2 at elevated temperature to form the stable oxides *viz.* B_2O_3 and SiO_2.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$Si + O_2 \longrightarrow SiO_2$$

Properties. (*i*) These oxides are solids of high melting points and are acidic in nature, since they give salts (metaborates, BO_2^- and metasilicates, SiO_3^{2-} respectively) with strong alkalies.

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sod. meta-borate}}{2NaBO_2} + H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sod. meta-silicate}}{Na_2SiO_3} + H_2O$$

(*ii*) These oxides also react with fused metal oxides forming metaborate (BO_2^-) and meta silicate (SiO_3^{2-}).

$$B_2O_3 + MO \longrightarrow M(BO_2)_2$$

$$SiO_2 + MO \longrightarrow MSiO_3$$

(*iii*) Oxides also appear to have some *feeble basic character*, since they also react with HF.

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

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

These reactions have been used to prepare the fluorides of these elements.

(*iv*) Both the oxides have macro-molecular structure.

(*v*) When these oxides are reduced by Mg metal, elements are obtained in the free state.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

(*vi*) Oxides, in association with water, give the corresponding oxy acids *viz. boric acids* and *silicic acids.*

(*vii*) When heated with carbon in an electric furnace, carbides are obtained.

$$2B_2O_3 + 7C \longrightarrow B_4C + 6CO$$

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

13. Halides. *Preparation.* (*i*) BCl_3 and $SiCl_4$ can be prepared by passing dry Cl_2 over a heated mixture of the oxide (B_2O_3 or SiO_2) and carbon.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

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

(*ii*) BF_3 and SiF_4 can be prepared as follows:

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

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

(*iii*) Both the elements burn in the vapours of halogens and form their respective halides.

Properties. (*i*) Halides of both the elements are covalent compounds.

(*ii*) Chlorides (BCl_2 and $SiCl_4$) are liquids, fume in moist air end are readily hydrolysed by water to give *orthoboric acid*, H_3BO_3 and *orthosilicic acid*, H_4SiO_4.

$$BCl_3 + 3H_2O \longrightarrow \underset{\text{Orthoboric acid}}{H_3BO_2} + 3HCl$$

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Orthosilicic acid}}{H_4SiO_4} + 4HCl$$

(*iii*) Fluorides (BF_3 and SiF_4) are colourless fuming gases and are readily hydrolysed by water.

$$\begin{aligned} BF_3 + 3H_2O &\longrightarrow H_3BO_3 + 3HF \\ [BF_3 + HF] &\longrightarrow HBF_4] \times 3 \end{aligned}$$

On adding:

$$4BF_4 + 3H_2O \longrightarrow \underset{\text{Orthoboric acid}}{H_3BO_3} + \underset{\text{Hydro fluoboric acid}}{3HBF_4}$$

$$\begin{aligned} SiF_4 + 4H_2O &\longrightarrow H_4SiO_4 + 4HF \\ [SiF_4 + 2HF] &\longrightarrow H_2SiF_6] \times 2 \end{aligned}$$

On adding:

$$3SiF_4 + 4H_2O \longrightarrow \underset{\text{Orthosilicic acid}}{H_4SiO_4} + \underset{\text{Fluosilicic acid}}{2H_2SiF_6}$$

Both the acids *viz*. H_3BO_3 and H_4SiO_4 are weak acids.

(*iv*) Halides can act as *Lewis acids* towards suitable donor molecules to form *adducts*, *e.g.*

Halides		***Donor molecules***		***Adducts***
BX_3	+	py	⟶	$BX_3.py$
SiX_4	+	2py	⟶	$SiX_4.2py$

Here py = pyridine which is a donor molecule.

(*v*) When benzene solution of anhydrous chlorides is refluxed with alcohol, alkoxides (*i.e.*, esters) are obtained.

$$\begin{aligned} BCl_3 + 3C_2H_5OH &\longrightarrow (C_2H_5)_3\ BO_3 + 3HCl \\ SiCl_4 + 4C_2H_5OH &\longrightarrow (C_2H_5)_4SiO_4 + 4HCl \end{aligned}$$

(*vi*) Halides can be reduced by *lithium aluminium hydride*, $LiAlH_4$ to get the hydrides of B and Si *viz*. B_2H_6 and SiH_4.

$$\begin{aligned} 4BCl_3 + 3LiAlH_4 &\longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6 \\ SiCl_4 + LiAlH_4 &\longrightarrow LiCl + AlCl_3 + SiH_4 \end{aligned}$$

14. Non-existence of oxy salts. No oxy salts of boron and silicon containing cationic boron and silicon are known.

15. Hydrides. B and Si form similar hydrides known as *boranes* and *silanes* respectively.

Preparation. These can be prepared by their magnesium salts *e.g.*

$$\begin{aligned} Mg_3B_2 + 6HCl &\longrightarrow 3MgCl_2 + B_2H_6 + \text{Higher boranes} \\ Mg_2Si + 4HCl &\longrightarrow 2MgCl_2 + SiH_4 + \text{Higher silanes} \end{aligned}$$

(*ii*) B_2H_6 and SiH_4 can also be prepared by the reduction of their chlorides by *lithium aluminium hydride*, $LiAlH_4$

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

$$SiCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + SiH_4$$

Properties (*i*) All the hydrides are covalent compounds which are either volatile liquids or gases and possess a disagreeable smell.

(*ii*) They instantly catch fire on exposure to air, forming the oxides of the elements and H_2O.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 2H_2O$$

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

(*iii*) They can be hydrolysed by water

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

$$SiH_4 + 4H_2O \longrightarrow H_4SiO_4 + 4H_2$$

(*iv*) They are strong reducing agents *e.g.*

$$B_2H_6 + Cl_2 \longrightarrow B_2H_5Cl + HCl$$

$$SiH_4 + Cl_2 \longrightarrow SiH_3Cl + HCl$$

16. Sulphides. Both the elements combine with sulphur at elevated temperatures to form sulphides (B_2S_3 and SiS_2). These sulphides are attacked by water with the liberation of H_2S.

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

$$SiS_2 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2S$$

17. Nitrides. Nitrides (BN and Si_3N_4) can be obtained either by the direct combination of the elements with N_2 or by passing N_2 over heated mixture of the oxide and carbon. These nitrides decompose steam, liberating NH_3.

$$BN + 3H_2O\ (\textit{steam}) \longrightarrow H_3BO_3 + NH_3$$

$$Si_3N_4 + 12H_2O\ (\textit{steam}) \longrightarrow 3H_4SiO_4 + 4NH_3$$

18. Carbides. *Preparation.* The carbides *viz.* B_4C and SiC are obtained by heating the elements with carbon in an electric furnace. On a commercial scale these are obtained by heating their oxides with carbon in an electric furnace.

$$2B_2O_3 + 7C \longrightarrow B_4C + 6CO$$

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

Properties. These are covalent network solids. These are inert towards water. Both the carbides are hard substances and are used as abrasive.

19. Formation of complexes. Both the elements form complexes, *e.g. hydrofluoboric acid*, HBF_4 and *fluosilicic acid*, H_4SiF_6.

Comparison between Boron and Silicon

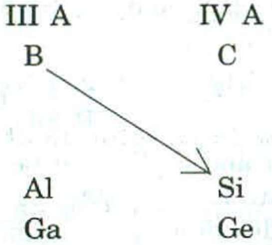
(A) Similarities. For this see "*Diagonal relationship between boron and silicon: Similarities between boron and silicon*".

(B) Dissimilarities. The following points show the dissimilarities between boron and silicon.

Boron	Silicon
1. Boron has three electrons in its valence-shell (2, 3)	Silicon has four electrons in its valence-shell (2, 8, 4)
2. Boron in the form of minerals constitutes only 0.001% of the earth's crust	Silicon is the second most abundant element and constitutes 26% of the earth's crust
3. Boron is tri-covalent in its compounds	Silicon is tetra-covalent in its compounds
4. Boron on heating with N_2 gives BN $2B + N_2 \longrightarrow 2BN$	Silicon does not combine with N_2
5. Boron is oxidiged by hot conc. H_2SO_4 or conc. HNO_3 to form H_3BO_3 $2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$ $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$	Silicon is attacked only by HF, forming hydrofluosilicic acid, H_2SiF_6 $Si + 6HF \longrightarrow H_2SiF_6 + 2H_2$
6. B_3O_3 is amphoteric in nature	SiO_2 is acidic in nature.

Position of Boron in the Periodic Table

We know hat boron is present in Group III A of the periodic table. The element lying below it is aluminium and the element which is diagonally related to boron is silicon which is present in Group IVA (period number = 3) as shown below :



Position of boron in the periodic table

Thus the position of boron in the periodic table is justified by discussing (1) *Similarities between B and Al,* and (2) *Similarities between B and Si.* These points have already been discussed in this chapter.

Questions with Answers

Q.1 BCl_3 is trigonal planar while $AlCl_3$ is tetrahedral in dimeric state. Explain.

Ans : Both BCl_3 and $AlCl_3$ are electron deficient molecules having six electrons in the valence shell of their respective central atoms. To complete their octets, the central atom in each case can accept a pair of electrons from the chlorine atom of another molecule froming dimeric structures. However, because of small size of B, it cannot accommodate four big sized Cl atoms around it. Therefore, *BCl_3 prefers to exist as monomeric planar molecule in which B atom is sp^2 hybridized.*

On the other hand, Al because of its bigger size can easily accommodate four Cl atoms around it. As a result, $AlCl_3$ exsts as a dimer. In this dimer, since the covalency of Al has increased to 4, *Al is sp^3-hybridized and the four Cl atoms are held tetrahedrally around it.*

Q.2 Aqueous solution of hydrous $AlCl_3$ is acidic in natuer. Explain.

Ans : Aqueous solution of $AlCl_3$ is acidic due to its hydrolysis.

$$AlCl_3 + 3H_2O \longrightarrow \underset{\text{weak base}}{Al\,(OH)_3} + \underset{\text{strong acid}}{3\,HCl}$$

or $$3Cl^- + 3H_2O \longrightarrow 3OH^- + 3HCl$$

Since the acid produced in the above reaction is a strong acid, the solution of $AlCl_3$ in water is acidic in nature.

Q.3 In non polar solvents $AlCl_3$ is covalent but in polar solvents this compound is electrovalent. Explain.

Ans : In non-polar solvents or organic solvents like benzene, $AlCl_3$ exists as a dimeric molecule, $(AlCl_3)_3$ or Al_2Cl_6 which has covalent bonds and hence is covalent in nature. On the other hand in polar solvents like water, $AlCl_3$ gets hydrated to form hydrated salt, $AlCl_3.\ 6H_2O$. In the formation of $AlCl_3.\ 6H_2O$, $AlCl_3$ gets hydrated by H_2O molecules and a large amount of hydration energy is also liberated. This hydration energy helps in the ionisation of hydrated salt, $AlCl_3.\ 6H_2O$ to produce $[Al(H_2O)_6]^{3+}$ (hydrated ion) and Cl^- ions. Due to the production of ions, $AlCl_3$ in polar solvents behaves as an electrovalent compound.

$$AlCl_3 + 6H_2O \longrightarrow AlCl_3.\ 6H_2O \longrightarrow \underset{\text{Hydrated ion}}{[Al\,(H_2O)_6]^{3+}} + 3Cl^- + \text{Hydration energy}$$

Q.4 When BF_3 is added to a solution of AlF_3 in KF, AlF_3 is precipitated. Explain.

Ans : Since KF is an ionic fluorid, it gives F^- ions which combine with AlF_3 to form AlF_6^- ion (complex ion)

$$\begin{array}{rcl} 3KF & \longrightarrow & 3K^+ + 3F^- \\ AlF_3 + 3F^- & \longrightarrow & [AlF_6]^{3-} \\ \hline 3KF + AlF_3 & \longrightarrow & 3K^+\,[AlF_6]^{3-} \text{ or } K_3\,[AlF_6] \end{array}$$

Now since B-atom has smaller size and higher electronegativity than Al atom, B-atom has higher tendency to form complexes.

Thus BF_3 will react with $K_3\,[AlF_3]$ formed as above and forms the complex, $K\,[BF_4]$. AlF_3 is obtained as precipitate.

$$K_3\,[AlF_6] + 3BF_3 \longrightarrow \underset{\substack{\text{Pot. tetra-}\\ \text{fluoro borate}}}{3K\,[BF_4]} + AlF_3\,(s)\downarrow$$

Q.5 AlF_3 dissolves in KF but not in anhydrous HF. Explain.

Ans : Anhydrous HF is a covalent compound and is strongly H-bonded. Therefore, it does give F^- ions and hence AlF_3 does not dissolve in HF. In contrast, KF contains F^- ions and hence combines with AlF_3 to form the soluble complex.

$$3KF \longrightarrow 3K^+ + 3F^-$$

$$AlF_3 + 3F^- \longrightarrow [AlF_6]^-$$

On adding : $3KF + AlF_3 \longrightarrow 3K^+ + [AlF_6]^{3-}$ or $K_3[AlF_6]$

Pot. hexafluoro
aluminate
(soluble complex)

Q.6 BF_3 and BCl_3 do not form dimeric molecules but BH_3 forms a dimer, B_2H_6. Explain.

Ans : Since F and Cl atoms are big in size, these atoms cannot be accomdated around small B-atom in the bridged position and hence BF_3 and BCl_3 donot form dimeric molecules. On the other hand, since H-atoms are small in size, these atoms can be accomdated round small B-atom in the bridged position and hence dimeric molecule, B_2H_6 is easily fromed.

Q.7 Boron trihaldes (excepting BF_3) and $AlCl_3$ fume in moist air. Explain. (Roorkee 1986)

Ans : All the given halides are hydrolysed by H_2O present in moist air and fumes of HCl are produced. (Also see the action of moist air on $BeCl_2$)

$$BX_3\ (X = Cl, Br, I) + 3H_2O \rightarrow B(OH)_3 + 3HX$$

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

BF_3 reacts with H_2O in the following way :

$$F_3B + :\ddot{O}H_2 \rightarrow F_3B \leftarrow OH_2 \text{ (Adduct)}$$

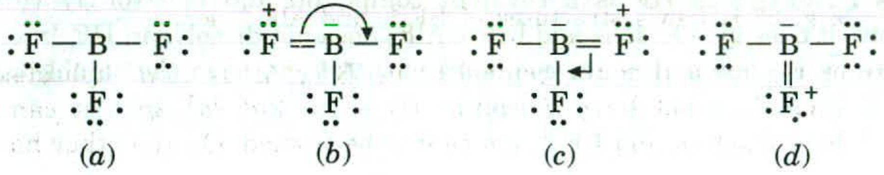
Q.8 Explain why B–F bond energy in BF_3 is 646 KJ/mole but that of N–F bond energy in NF_3 is only 280 KJ/mole.

***or* Explain why B–F bond energy in BF_3 molecule is higher than N–F bond energy in NF_3 molecule.**

Ans : We know that BF_3 molecule (sp^2 hydridisation of B-atom) has three B–F bonds each of which has double bond character due to the formation of an additional $[2p\ (F) \rightarrow 2p\ (B)]p$ bond which is a $(p\pi - p\pi)$ bond. This bond is formed by the donation of an electron pair from filled $2p$ orbital of F-atom to the vacant $2p$ orbital of B-atom. In case of NF_3 molecule (sp^3 hybridisation of N-atom), since there is no vacant $2p$ orbital on N-atom, there is no scope of the formation of a $[2p(F) \rightarrow 2p\ (N)]\pi$ bond in NF_3 molecule. Thus none of the three N–F bonds in NF_3 molecule has double bond character. Now since bond energy increases with the increase in double bond character, B–F bond energy in BF_3 molecule is higher than N–F bond energy in NF_3 molecule.

Q.9 Write all the possible octet structures for BF_3 molecule and say which of these structures are the most stable ?

Ans : For BF_3 molecule, the following octet structures can be written.

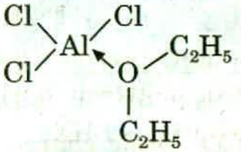


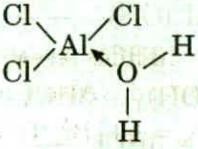
(a) (b) (c) (d)

Structure (*a*) is a covalent structure while structures (*b*), (*c*) and (*d*) are ionic structures. We know that greater is the number of B–F covalent bonds present in a contributing structure, greater is the stability of that structure. Now since each of the ionic structures has four B–F covalent bonds while covalent structure has only three B–F covalent bonds, ionic structures are more stable than covalent staructure. BF_3 molecule has 54% π-character.

Q.10 Anhydrous $AlCl_3$ is more soluble in diethyl ether than hydrous (hydrated) $AlCl_3$. Explain.

Ans : Higher solubility of anhydrous $AlCl_3$ in diethyl ether, $O(C_2H_5)_2$ as compared to that of hydrous $AlCl_3$ can be explained as follows on the basis of bonding. Anhydrous $AlCl_3$ is an electron-deficient compound while hydrated $AlCl_3$ is not. Therefore, Anhyd. $AlCl_3$ is more soluble in diethyl ether because the oxygen atom of ether donates a pair of electrons to the vacant *p*-orbital on the Al atom in $AlCl_3$ froming a coordinate bond.





Hydrated $AlCl_3$
($AlCl_3.H_2O$)

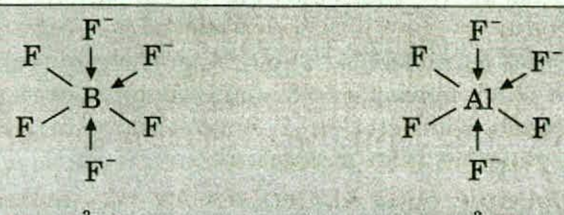
In case of hydrated $AlCl_3$ Al is not electron deficient since H_2O has already donated a pair of electrons to it.

Q.11 Aluminium forms AlF_6^{3-} ion but boron does not form BF_6^{3-} ion. Explain why? (Punjab 1995 April)

Ans : (*i*) Explanation based on steric hinderance.

Since B-atom is much smaller in size than Al-atom, this atom cannot accomdate six F^- ions around it and hence cannot form BF_6^{3-} ion. On the other hand, since Al is a bigger atom, it can easily accomdate six F^- ions and can from AlF_6^{3-} ion.

(*ii*) Explanation based on the presence/absence of *d*-orbitals. Lewis structures of the given ions are given in Fig. 22.1.



BF_6^{3-} ion
(wrong structure)

AlF_6^{3-} ion
(correct structure)

Fig. 22.1. Lewis structures of BF_6^{3-} and AlF_6^{3-} ions.

These structures show that the central atom (B or Al) is sp^3d^2 hybridised. Now since B-atom does not have *d*-orbitals (B = $2s^1\ 2p^1\ 2p^1\ 2p^\circ$), it cannot undergo sp^3d^2 hybridisation and BF_6^{3-} ion cannot be fromed. On the other hand, since Al has $3d$ orbitals ($Al = 3s^1\ 3p^1\ 3p^1\ 3p^\circ\ 3d^\circ\ 3d^\circ$), it can undergo sp^3d^2 hybridisation and can accept three electron pairs donated by three F^- ions to form $AlF_3{}^{3-}$ ion.

***(iii)* Explanation based on the rule of maximum covalency.**

In both Lewis structures, B and Al atoms show a covalency of six. Now since B is an element of *2nd* period, it cannot extend its covalency beyond four, *i.e.* B can form $BF_4{}^-$ but not $BF_6{}^{3-}$. On the other hand, since Al is an element of *3rd* period (higher period), it can achieve a covalency of six, *i.e.* it can from $AlF_6{}^{3-}$.

Q.12 Explain why Al $(OH)_3$ is amphoteric. (MLNR 1995)

Ans : Al $(OH)_3$ is an amphoteric compound since it reacts both with acids as well as with alkalies to form salt and water (solvent). With acids it behaves as a weak base, since it ionises to a slight extent to give OH^- ions which combine with H^+ ions obtained by the ionisation of the acid to form H_2O. Thus its reaction with HCl shows its basic character.

$$\begin{aligned} Al\,(OH)_3 &\longrightarrow Al^{3+} + 3OH^- \\ 3HCl &\longrightarrow 3H^+ + 3Cl^- \end{aligned}$$

On adding : $Al\,(OH)_3 + 3HCl \longrightarrow Al^{3+}\,[Cl^-]_3 + 3H^+ + 3OH^-$

or $\underset{}{Al\,(OH)_3 + 3HCl} \longrightarrow \underset{\text{Salt}}{AlCl_3} + \underset{\text{Solvent}}{3H_2O}$ (Basic character)

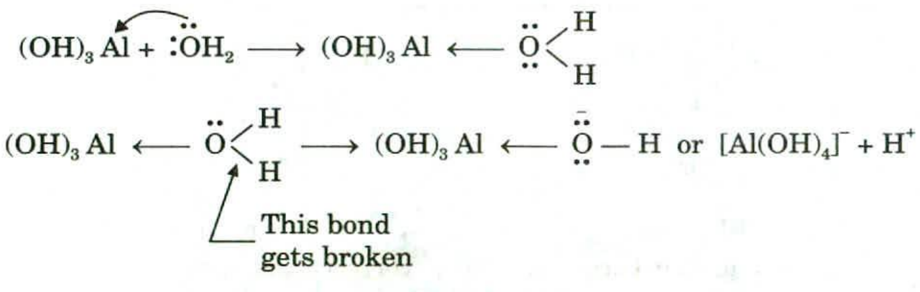
In presence of an alkali, Al $(OH)_3$ acts as an acid, since it gives metaborate ion ($AlO_2{}^-$) and H^+ ions. These H^+ ions combine with OH^- ions obtained by the ionisation of the alkali to form H_2O (solvent). Thus the reaction between Al $(OH)_3$ and NaOH shows the acidic character of Al $(OH)_3$.

$$\begin{aligned} Al\,(OH)_3 &\longrightarrow AlO_2{}^- + H_2O + H^+ \\ NaOH &\longrightarrow Na^+ + OH^- \end{aligned}$$

$$Al\,(OH)_3 + NaOH \longrightarrow Na^+\,[AlO_2]^- + H_2O + H^+ + OH^-$$

or $Al\,(OH)_3 + NaOH \longrightarrow \underset{\text{Salt}}{Na^+AlO_2{}^-} + \underset{\text{Solvent}}{2H_2O}$ (Acidic character)

The formation of $AlO_2{}^-$ ion takes place through the following steps :



$$[Al\,(OH)_4]^- \xrightarrow{\text{Dissociation}} AlO_2{}^- + 2H_2O$$

On adding : $Al\,(OH)_3 + H_2O \longrightarrow AlO_2{}^- + 2H_2O + H^+$

or $Al\,(OH)_3 \longrightarrow AlO_2{}^- + H_2O + H^+$

Q.13 Boron atom does not from B^{3+} ion Explain. (Punjab 1996 Oct)

Ans : In order to get B^{3+} ion, we will have to remove three electrons from the valence-shell of B-atom ($B = 2s^2\ 2p^1$). Obviously, energy required to remove three electrons is equal to the sum of IE_1, IE_2 and IE_3 of B-atom. Now since B-atom has very small size and the sum of IE_1, IE_2 and IE_3 is so high that lattice energy liberated in the interaction of B^{3+} ion with anions is not enough for the fromation of B^{3+} ion.

University Questions

1. Justify the inclusion of B, Al, Ga, In and Tl in the same group of the periodic table on the basis of the following properties : (*i*) ionisation energies (*ii*) oxidation states (*iii*) covalent character (*iv*) hydrated ions (*v*) size of atoms (*vi*) reactivity (*vii*) electropositive or metallic character. (*Jodhpur 83*)
2. Arrange BF_3, BCl_3 and BBr_3 in the increasing order of their Lewis acid strength. (*Delhi Hons. 86, 87*)
3. Explain the following: (*i*) Acceptor behaviour of boron halides (*ii*) B—X bond shortening in boron halides (*iii*) Lewis acid character of boron halides. (*Raj. 87, 87 S*)
4. Discuss the position of boron in the period table. (*Meerut 80 S, 82 S, 83 S, 84; Agra 83; Raj. 81; Utkal 86; Madras 86*)
5. Discuss the similarities and dissimilarities between boron and aluminium. (*Meerut 88, 89; Agra 88*)
6. Discuss the similarities and dissimilarities between boron and silicon. (*Meerut 80, 83; Jiwaji 80; Agra 83; Garhwal 81; Indore 81; Lucknow 81; Delhi 86*)

CHAPTER

23

Chemistry of Group 13 (III A) Elements, Their Compounds and Ceramics Industry

Boron

Occurrence.

Boron does not occur in the free state. In the combined state it occurs as salts of boric acid, the important of which are : *borax or tincal*, $Na_2B_4O_7.10H_2O$; *colemanite*, $Ca_2B_5O_{11}.5H_2O$; *kernite or razorite*, $Na_2B_4O_7.4H_2O$; *boracite*, $2Mg_3B_8O_{15}$, $MgCl_2$; *barocalcite*, $CaB_4O_7.4H_2O$. The important minerals from which boron is extracted are borax and colemanite. Borax occurs in Ceylon, Tibet, California and Puga valley in Kashmir. Colemanite occurs in California and South Africa. Boron is also present to some extent in some plants and sometimes in coal ash.

Extraction of Boron From Minerals.

Boron is generally extracted from borax and colemanite minerals. The extraction from these minerals involves the following two steps :

(i) Preparation of boric anhydride; B_2O_3. (a) From borax. The finely powdered mineral is boiled with conc. HCl or conc. H_2SO_4 when sparingly soluble boric acid separates out.

$$\underset{\text{Borax}}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

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

Boric acid on strong heating forms boric anhydride.

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

(b) From colemanite. The finely powdered mineral is dissolved in the boiling water and sulphur dioxide gas is passed through the solution. Calcium bisulphite being highly soluble remains in solution and the sparingly soluble boric acid separates on cooling.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 11H_2O + 4SO_2 \longrightarrow \underset{\substack{\text{Calcium bisulphite}\\ \text{(highly Soluble)}}}{2Ca(HSO_3)_2} + \underset{\text{(Insoluble)}}{6H_3BO_3}$$

Boric acid on strong heating forms boric anhydride.

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

Alternatively, the finely powdered colemanite mineral is boiled with calculated quantity of sodium carbonate solution.

$$2Ca_2B_6O_{11} + 2Na_2CO_2 + H_2O \longrightarrow 3Na_2B_4O_7 + 3CaCO_3 \downarrow + Ca(OH)_2$$

The precipitate of calcium carbonate is removed by filteration and borax is crystallized from the filtrate: From borax, boric anhydride may be obtained as above.

(ii) Reduction of boric anhydride. The boric anhydride so obtained is mixed with sodium, potassium or magnesium powder and heated in a covered crucible when it is reduced to boron.

$$B_2O_2 + 6K \longrightarrow 2B + 3K_2O$$
$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

The heated mass is stirred with an iron rod so as to oxidise the excess of sodium or potassium. The mass is now boiled with water, then with hydrochloric acid and finally with hydrofluoric acid, when dark brown powder of amorphous boron only remains as residue and rest everything is dissolved. This residue is now washed with water.

Crystalline form of boron is similarly obtained by the reduction of boric anhydride with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

The crystals are treated with NaOH solution to remove the impurity of aluminium.

Extraction of Boron by Electrolysis.

Now-a-days boron is obtained by the electrolysis of a fused mixture of boric anhydride, magnesium oxide and magnesium fluoride at 1100°C. The electrolysis is carried out in a carbon crucible which itself acts as anode and cathode is of iron which remains in the centre of the crucible. The magnesium obtained by electrolysis of its oxide reduces boric anhydride to boron which is deposited on the cathode.

$$2MgO \longrightarrow 2Mg + O_2$$
$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

Boron so obtained still contains a number of impurities. It is purified by heating it electrically in vacuum at 1100°C. At this temperature, the impurities are volatized off leaving behind pure boron.

Physical Properties

Boron exists in two allotropic forms *viz. crystalline or adamantine* and *amorphous boron.* Crystalline form can be obtained by the reduction of B_2O_3 or KBF_4 by Al.

$$B_2O_3 + 2Al \longrightarrow Al_2O_3 + 2B \text{ (\textit{crystalline boron})}$$
$$KBF_4 + Al \longrightarrow AlF_3 + KF + B \text{ (\textit{crystalline boron})}$$

Crystalline boron can also be prepared by dropping amorphous boron in molten Al at 1500° when it appears to dissolve. On cooling yellow coloured crystals deposit on this surface of Al. The mass is broken up and heated with HCl to dissolve away Al when very hard crystals are left behind. Boron obtained by this method is not pure since it contains some aluminium as impurity.

Crystalline boron is black and possesses metallic lustre. It is extremely inert. It is scarcely attacked by conc. HNO_3 or H_2SO_4 and not at all by boiling conc.

HCl or HF. It is, however, vigorously attacked by fused sodium peroxide and by fused oxidizing fusion mixture. Crystalline boron is very hard and is second to diamond in hardness. Its specific gravity is 3.3. Both needle-like and plate-like hexagonal crystals of crystalline boron are known. It is a bad conductor of electricity. Amorphous boron is brown powder of density 2.45. It is very hard to fuse. The m.pt. and b.pt. are 2300°C and 2550°C respectively.

Chemical Properties.

1. Action of air and O_2. Amorphous boron is very reactive. When it is heated at 700°C in air or O_2, it burns with a reddish flame forming a mixture of oxide and nitrate.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$2B + N_2 \longrightarrow 2BN$$

2. Action of acids. Halogen acids have no action on boron but it is attacked by oxidising acids like HNO_3 and H_2SO_4,

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$
$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

3. As reducing agent. Boron is powerful reducing agent, since it can replace carbon from CO_2, silicon from SiO_2 and N_2 from NO.

$$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$$
$$4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$$
$$4B + 6NO \longrightarrow 2B_2O_3 + 3N_2$$

4. Action of alkalies. It is vigorously attacked by fused alkalies or by fusion with oxidising fusion mixture.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2 \uparrow$$

5. Action of metals. Excepting with Cu, Ag and Au, boron combides with other metals at high temperatures to form borides. These borides are extremely hard substances. Mg_3B_2 and Be_3B_2 are attacked by acids with the formation of boron hydrides.

6. Action of non-metals. Boron also reacts with non-metals. For example : (*a*) Boron combines with N_2 at a temperature greater than 900° to form boron nitride, BN. (*b*) Boron forms boron sulphide B_2S_3 when heated with S. (*c*) On heating with carbon in an electric furnace an extremely hard substance namely boron carbide, B_4C is formed.

7. Action of steam. Boron reacts with steam at red heat liberating H_2.

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2 \uparrow$$

Uses of Boron

Boron is used (*i*) as a deoxidiser in the casting of copper, (*ii*) for making boron steels which are very hard and are used as control rods in atomic reactors. (*iii*) the traces of boron compounds are essential for plant metabolism and for the fertility of soil, (*iv*) as a catalytic agent, (*v*) in the manufacture of thermometers and thermoregulators, (*vi*) as scavanger to remove gaseous impurities from molten copper and as a semi-conducting material, (*vii*) the hydrides of boron are used as fuels for rockets because of their very high energy/weight ratio, (*viii*) metallic borides and boron carbide are used as abrasives.

Compounds of Boron

1. Boric Acid, H_3BO_3.

Several boric acids like *orthoboric acid* (H_3BO_3 or $\frac{1}{2}B_2O_3.\frac{3}{2}H_2O$ or $B(OH)_3$], *metaboric acid* (HBO_2 or $\frac{1}{2}B_2O_3.\frac{1}{2}H_2O$), *pyroboric acid* ($H_6B_4O_9$ or $2B_2O_3.3H_2O$) and *tetraboric acid* ($H_2B_4O_7$ or $2B_2O_3.H_2O$) are known. Out of these orthoboric acid which is generally referred to as **boric acid** is the most important and is stable both in the solid state and in solution. The remaining acids are stable in the solid state and gradually change into orthobaric acid in solution

$$\underset{\text{Metaboric acid}}{HBO_2} + H_2O \longrightarrow \underset{\text{Boric acid}}{H_3BO_3}$$

$$\underset{\text{Tetraboric acid}}{H_2B_4O_7} + 5H_2O \longrightarrow 4H_3BO_3$$

Occurrence : Small quantities of boric acid are present in the jets of steam called *soffioni* which is mixed with other gases in the volcanic district of Tuscany. Besides this, it is also found in many mineral waters. It is also present in traces of hops, in berries and fruits and often in wines.

Extraction : Boric acid can be extracted from borax and colemanite minerals as discussed under the extraction of boron.

Properties : (*i*) Boric acid forms colourless nacreous laminae which are soapy to the touch. It is slightly soluble in cold water, more so in hot and is volatile in steam. 100 grams of water dissolve 4.01 gms. at 12°C and 39.95 gms. at 100°C. The solution in water is a very weak acid.

(*ii*) *Acidic nature* : *Action of alkalies.* It is a weak acid and gives only a wine red colour with litmus. It reacts with alkalies to form salts

$$NaOH + H_3BO_3 \longrightarrow \underset{\text{Sod. metaborate}}{NaBO_2} + 2H_2O$$

$$2NaOH + 4H_3BO_3 \longrightarrow \underset{\text{Sod. tetraborate}}{Na_2B_4O_7} + 7H_2O$$

The end point during the titration of $B(OH)_3$ against NaOH is not sharp, since excessive hydrolysis of $Na^+BO_2^-$ occurs. However, if the titration is carried out in presence of polyhydroxy compounds like glycerol or sugar, $B(OH)_3$ behaves as a strong monobasic acid and the end point can be detected as easily as it can be done during the titration of strong acid with a strong alkali.

(*iii*) *Action of acetic anhydride.* When treated with acetic anhydride, boron acetate is formed.

$$2B(OH)_3 + \underset{\text{Acetic anhydride}}{5(CH_3CO)_2O} \longrightarrow (CH_3COO)_2BOB(OOCCH_3)_2.6CH_3COOH$$

(*iv*) *Action of Na_2O_2.* With Na_2O_2 it gives sod. metaborate peroxohydrate, $NaBO_2.H_2O_2.3H_2O$.

(*v*) It is a very weak acid and ionises mainly as monobasic acid and that too, to a very limited extent. It is not a proton donor but behaves as a *Lewis acid, i.e.* it can accept a lone pair of electrons from an OH^- ion.

$$H_2O \longrightarrow OH^- + H^+ \quad ...(i)$$

$$B(OH)_3 + OH^- \longrightarrow [B(OH)_4]^- \quad ...(ii)$$

On adding (*i*) and (*ii*), we get :

$$B(OH)_3 \text{ (or } H_3BO_3) + H_2O \rightleftarrows [B(HO)_4]^- + H^+$$

The above equilibrium lies to the left, showing that it is a weak acid.

(*vi*) *Action of heat.* It decomposes on heating to form metaboric acid at 100°C, tetraboric acid at 140°C and a glassy mass of boric anhydride at red heat.

$$4 \times [H_3BO_3 \xrightarrow{100°C} \underset{\text{Metaboric acid}}{HBO_2} + H_2O] \quad ...(i)$$

$$4HBO_2 \xrightarrow{140°C} \underset{\text{Tetraboric acid}}{H_2B_4O_7} + H_2O \quad ...(ii)$$

$$H_2B_4O_7 \xrightarrow{\text{Read heat}} \underset{\substack{\text{Boric}\\\text{anhydride}\\\text{(Glassy mass)}}}{2B_2O_3} + H_2O \quad ...(iii)$$

On adding (*i*), (*ii*) and (*iii*), we get

$$4H_3BO_3 \longrightarrow 2B_2O_3 + 6H_2O$$

$$\text{or } 2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

This equation represents that on strong heating H_3BO_3 gives B_2O_3

(*v*) *Action of C_2H_5OH.* When H_3BO_3 is heated with alcohol (C_2H_5OH) in presence of conc. H_2SO_4, volatile ester namely triethyl borate, $(C_2H_5)_3BO_3$ is formed. This ester burns with a green-edged flame.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} (C_2H_5)_3BO_3 + 3H_2O$$

(*vi*) *Action of CaF_2 and conc. H_2SO_4.* When H_3BO_3 is heated with CaF_2 and conc. H_2SO_4, BF_3 is obtained.

$$3CaF_2 + 3H_2SO_4 + 2H_3BO_3 \xrightarrow{\text{Heat}} 3CaSO_4 + 2BF_3 + 6H_2O$$

(*vii*) *Action of soda-ash, Na_2CO_3,* When H_3BO_3 is neutralised by Na_2CO_3, borax is obtained.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + 6H_2O + CO_2$$

(*viii*) *Action of alkali acid fluorides.* When an alkali acid fluoride (MHF_2) reacts with H_3BO_3, alkali fluoborate (MBF_4) is obtained. For example :

$$2NaHF_2 + H_3BO_3 \longrightarrow \underset{\text{Sod. fluoborate}}{NaBF_4} + NaOH + 2H_2O$$

Uses. Boric acid is used (*i*) in the manufacture of pottery glazes, glass and enamels, (*ii*) in medicine as an antiseptic and as an eye lotion (*iii*) as preservative in food industry, (*iv*) in tanning industry, (*v*) in candle industry to stiffen wicks, (*vi*) in the manufacture of borax and pigments.

Structure of BO_3^{3-} ion. This ion has *triangular planar shape* which results from sp^2 hybridisation of B-atom in the excited state (configuration of B-atom in the excited state is $2s^1.\ 2p^1.\ 2p^1.\ 2p^0$). How triangular planar shape is obtained from sp^2 hybridisation has already been explained.

Boric acid is covalent compound and contains planar triangular BO_3^{3-} units which are bonded together through *hydrogen bonds* into *two-dimensional* sheets as shown in Fig. 23.1.

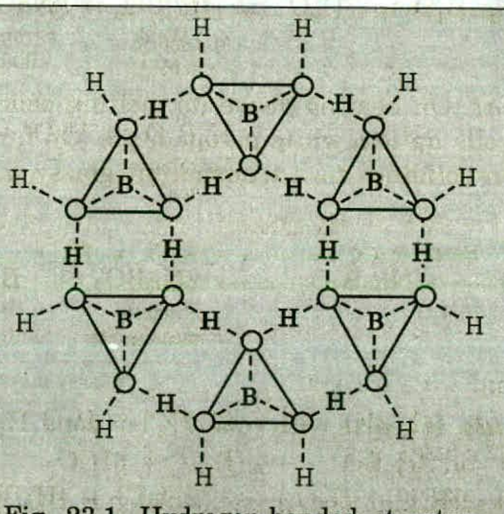


Fig. 23.1. Hydrogen-bonded structure of orthoboric acid, H_3BO_3.

It may be seen from the figure that each boron atom of each BO_3^{3-} unit is bonded to three oxygen atoms and each oxygen atom in this unit is bonded to a hydrogen atom through H-bonds. The H-atoms act as bridge between the two O-atoms of different BO_3^{3-} units.

2. Sodium Tetraborate or Borax, $Na_2B_4O_7.10H_2O$.

It is the sodium salt of tetraboric acid, $H_2B_4O_7$. It occurs naturally as *tincal* or *suhaga* in the dried-up lakes of Tibet, Ceylon, California (U.S.A.) and India. In India it is found in *Ladakh* and *Puga Valley of Kashmir.* Tincal contains about 55% of borax, $Na_2B_4O_7.10H_2O$. Borax can be obtained from colemanite (see the extraction of boron) and by the action of Na_2CO_3 on H_3BO_3. Some of the properties of borax are discussed below :

(i) Different forms of borax. Borax exists in three forms (*a*) *Ordinary* or *prismatic borax* which is *decahydrate* or *monoclinic*, $Na_2B_4O_7.10H_2O$. This is the common form of borax and is obtained when a solution of the salt is crystallised at room temperature (*i.e.* below 60°) (*b*) *Octahedral or Jeweller's borax* which is *pentahydrate*, $Na_2B_4O_7.5H_2O$ and is obtained when the solution is crystallised above 60° (*c*) *Borax glass* which is the *anhydrous* form, $Na_2B_4O_7$ and is obtained by heating the ordinary borax above its melting point until all the water of crystallisation is given off. It is a colourless glassy mass (density = 2.37), absorbs moisture from air and is gradually converted into decahydrate form.

(ii) Basic nature. It is sparingly soluble in cold water and fairly soluble in hot water. The solution is alkaline in reaction because borax is hydrolysed and it forms a mixture of sodium hydroxide (a strong base) and boric acid (a weak acid).

$$\begin{array}{r}
Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3 \\
NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3] \times 2 \\
\hline
Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Weak acid}}{4H_3BO_3} + \underset{\text{Strong alkali}}{2NaOH}
\end{array}$$

(iii) Action of heat. On heating above its melting point, it loses its water of crystallization and swells up to a white porous mass. On further heating, it melts to a liquid which then solidifies to a transparent glassy mass which consists of $NaBO_2$ and B_2O_3.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\text{Heat}} Na_2B_4O_7 \longrightarrow \underbrace{\underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Glassy mass}}$$

(iv) Action of acids. It reacts with conc. HCl or conc. H_2SO_4 to form sparingly soluble boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

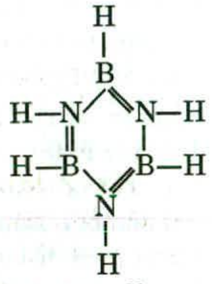
(v) Action of NH_4Cl. When heated with NH_4Cl, it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + \underset{\text{Boron nitride}}{2BN} + B_2O_3 + 4H_2O$$

Uses. Borax is used : (*i*) In borax bead test for the detection of basic radicals. (*ii*) In the manufacture of enamels and glazes for pottery. (*iii*) In making optical glass and borosilicate glassware. (*iv*) As a flux in metallurgy. (*v*) As a preservative for food. (*vi*) In the manufacture of washing powders and soaps. (*vii*) In leather and match industries.

3. Borazine or Borazole, $B_3N_3H_6$.

This compound is iso-electronic with benzene and hence has been called *Inorganic Benzene* by Weberg. In our discussion we shall represent this compound by the structure given in the margin.



Structure of borazine, $B_3N_3H_6$

The suffix *ole* added with the name of this compound indicates the presence of OH group in the compound, but the fact is that the compound does not contain any OH group. It is, therefore, wrong to call this compound borazole. The word borazone has been derived from the older name *benzol* that was used for benzene with which borazine is iso-electronic.

Preparation. Borazine can be prepared by the following methods :

(i) By Stocks' method. In this method diborane (B_2H_6) and NH_3 are heated in 1 : 2 molar ratio at low temperature (= – 120°C) to get diammoniate of diborane (B_2H_6. $2NH_3$) which is an addition compound. This compound, on being heated at 200°C, gives borazine.

$$\underset{\text{(Ratio = 1 : 2)}}{B_2H_6 + 2NH_3} \xrightarrow{-120^\circ C} \underset{\substack{\text{Diammoniate}\\ \text{of diborane}}}{B_2H_6.2NH_3}$$

$$2(B_2H_6.2NH_3) \xrightarrow{200^\circ C} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

This method gives 40% yield of $B_3N_3H_6$.

(ii) By heating BCl_3 with NH_4Cl. When BCl_3 is heated with NH_4Cl in chlorobenzene (C_6H_5Cl) in the presence of Fe, Ni or Co (used as catalyst) at about 140°C, B, B, B-trichloroborazine (chloro groups attached with B-atoms) is formed. This derivative of borazine, on being reduced by lithium borohydride ($LiBH_4$) in polyether gives borazine, $B_3N_3H_6$

$$3NH_4Cl + 3BCl_3 \xrightarrow[C_6H_5Cl\ (\text{Fe, } 140^\circ C)]{\text{Heat in presence of}} \underset{\substack{\text{B, B, B-trichloro-}\\ \text{borazine}}}{Cl_3B_3N_3H_3} + 9HCl$$

$$3Cl_3B_3N_3H_3 + 6LiBH_4 \xrightarrow{\text{Reduction}} \underset{\text{Borazine}}{2B_3N_3H_6} + 6LiCl + 3B_2H_6$$

The yield of borazine obtained by this method is about 50–60%.

(iii) By heating a mixture of $LiBH_4$ and NH_4Cl.

$$3LiBH_4 + 3NH_4Cl \xrightarrow{275^\circ C} \underset{\text{Borazine}}{B_3N_3H_6} + 3LiCl + 9H_2$$

Properties (*i*) Physical properties. Borazine is a colourless, mobile volatile liquid. It freezes at –58°C. Its boiling and melting points are 63°C and –58°C respectively.

(ii) Addition reactions. (*a*) One molecule of $B_3N_3H_6$ adds three molecules of H_2O, CH_3OH, CH_3I, HCl or HBr in the cold without a catalyst. The more negative group of these molecules is generally attached with boron, since boron atom is less electronegative than nitrogen atom in B—N bond. When hydrogen chloride derivative is heated at 50–100°C, it loses three H_2 molecules to give B-*trichloroborazine*.

$$\underset{\text{Borazine}}{B_3N_3H_6} \xrightarrow{+\,3HCl} \underset{\substack{\text{Hydrogen}\\ \text{chloride}\\ \text{derivative}}}{B_3N_3H_9Cl_3} \xrightarrow[50\text{–}100^\circ]{-\,3H_2} \underset{\substack{\text{B-trichloro-}\\ \text{borazine}}}{B_3N_3H_3Cl_3}$$

Addition reaction shown above for borazine is not shown by benzene, *i.e.* C_6H_6 does not add HCl.

(*b*) One molecule of borazine also adds three molecules of Br_2 at 0°C and gives *B-tribromo-N-tribromoborazine* which, on being heated at 60°C, loses three molecules of HBr and forms B-tribromo-borazine.

$$\underset{\text{Borazine}}{B_3N_3H_6} \xrightarrow[0^\circ]{+\,3Br_2} \underset{\substack{\text{B-tribromo-}\\ \text{N-tribromo-}\\ \text{borazine}}}{B_3N_3H_6Br_6} \xrightarrow[60^\circ]{-\,3HBr} \underset{\substack{\text{B-tribromo}\\ \text{borazine}}}{B_3N_3H_3Br_3}$$

This reaction can be compared with that shown by benzene where substitution takes place

$$C_6H_6 \xrightarrow[\substack{\text{In presence of}\\ FeBr_3}]{+\,Br_2} \underset{\substack{\text{Bromo}\\ \text{benzene}}}{C_6N_5Br} + HBr$$

(iii) Hydrolysis. (*a*) Borazine gets slowly hydrolysed by water to produce H_2, boric acid [$B(OH)_3$ or H_3BO_3] and NH_3. Hydrolysis is favoured by the increase in temperature.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 \text{ or } 3H_3BO_3 + 3NH_3 + 3H_2$$

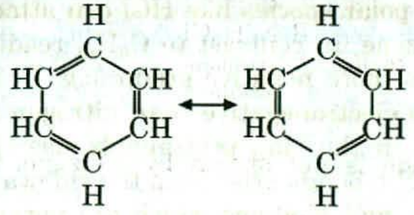
(*b*) It is also reported that under proper conditions, borazine reacts with three molecules of water to produce *B-trihydroxyl borazine*, $(OH)_3B_3N_3H_3$ in which OH groups are attached with boron atoms.

$$\underset{\text{Borazine}}{B_3N_3H_6} + 3H_2O \longrightarrow \underset{\substack{\text{B-trihydroxyl}\\ \text{borazine}}}{B_3N_3H_3\,(OH)_3} + 3H_2$$

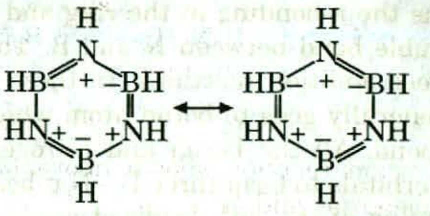
(iv) Hydrogenation. Benzene can be hydrogenated to produce saturated *cyclohexane*, C_6H_{12}. Borazine can also be converted into *cyclotriborazane*, $B_3N_3H_{12}$ by special techniques as shown below :

$$\underset{\text{Borazine}}{B_3N_3H_6} \xrightarrow{+\,3HCl} \underset{\substack{\text{Hydrogen}\\ \text{derivative}}}{B_3N_3H_9Cl_3} \xrightarrow[\text{chloride}]{+\,3NaBH_4} \underset{\substack{\text{Cyclotri-}\\ \text{borazane}}}{B_3N_3H_{12}} + \tfrac{3}{2}B_2H_6 + 3NaCl$$

Structure. Various chemical reactions and electron diffraction studies of borazine have shown that this compound is iso-electronic with benzene and hence its structure is similar to that of benzene. Thus, like benzene, borazine also has a *planar hexagonal structure* containing six-membered ring in which B and N atoms alternate.

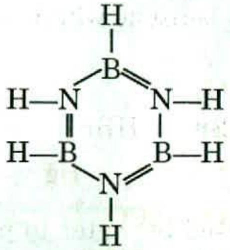


Benzene (C_6H_6)

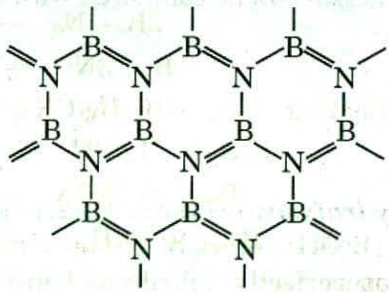


Borazine ($B_3N_3H_6$)

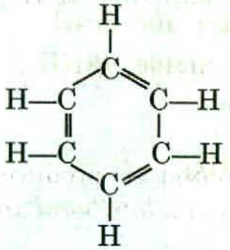
In the structure of borazine each of the B—N distances is equal to 1.44A° which is between the calculated single B—N (= 1.54 A°) and double B = N (= 1.36 A°) bond distances. The angles are equal to 120°. The ring structure of borazine is related to the layer lattice structure of boron nitride in the same way in which the ring structure of benzene is related to the layer lattice structure of graphite (*see* below)



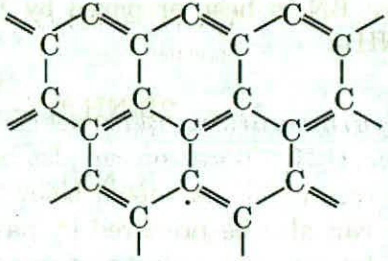
Borazine ($B_3N_3H_6$)



Boron nitride $[(BN)_n]$



Benzene (C_6H_6)



Graphite (C_n)

Since borazine is isoelectronic with benzene, both the compounds have aromatic π-clouds of electron density which is delocalised over the atoms of the ring. In C_6H_6, C = C bonds are non-polar while in case of $B_3N_3H_6$, due to the difference in electronegativity between B and N atoms, B—N bond is polar ($B^{\delta+} - N^{\delta-}$) and hence π cloud in $B_3N_3H_6$ is more lumpy with more electron density localised on N atom. This partial localisation of electron density on N atom weakens the π-bonding in the ring and as such polar species like HCl can attack this double bond between N and B. Thus borazene, in contrast to C_6H_6, readily undergoes addition reactions. In these reactions more negative group (*e.g.* Cl in HCl) generally goes to boron atom which is less electronegative than nitrogen in B—N bond. All the boron and nitrogen atoms in the ring presumably use sp^2 hybrid orbitals to form three B—N σ-bonds. B—N π-bonds arise from the sideways overlapping of the unhybridised *p*-orbitals of B- and N-atoms which are normal to the plane of the ring. Unlike in benzene, the π-electrons are not derived from all the six atoms of the ring but from the three N-atoms. Molecular orbital calculations indicate that the π-electrons are partially delocalised. These calculations also have shown that N—B π-electron drift is largely counterbalanced by the B—N σ drift.

4. Boron Nitride, BN.

Preparation. It is formed (*i*) by heating boron to a white heat in an atmosphere of nitrogen or NO

$$2B + N_2 \longrightarrow 2BN$$

$$5B + 3NO \longrightarrow 3BN + B_2O_3$$

(*ii*) by heating B_2O_3 with $Hg(CN)_2$, KCN or NH_4Cl.

$$B_2O_3 + Hg(CN)_2 \longrightarrow 2BN + CO + CO_2 + Hg$$

$$B_2O_3 + 2KCN \longrightarrow 2BN + K_2O + 2CO$$

$$B_2O_3 + 2NH_4Cl \longrightarrow 2BN + 3H_2O + 2HCl$$

(*iii*) when perfectly anhydrous borax ($Na_2B_4O_7$) is heated with dry NH_4Cl to a red heat in a platinum crucible.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2BN + 2NaCl + B_2O_3 + 4H_2O$$

The resulted mass is treated with dil. HCl which dissolves B_2O_3 and NaCl, leaving behind BN. It is repeatedly washed with water and dried.

(*iv*) *Pure* BN is best prepared by heating boron amide, $B(NH_2)_3$ or boron imide, $B_2(NH)_3$.

$$2B(NH_2)_3 \xrightarrow{\Delta} 2BN + 4NH_3$$

$$B_2(NH)_3 \xrightarrow{\Delta} 2BN + NH_3$$

(*v*) BN can also be prepared by passing N_2 gas through a mixture of B_2O_3 and carbon heated in an electric furnace.

$$B_2O_3 + 3C + N_2 \longrightarrow 2BN + 3CO \uparrow$$

Properties. (*i*) Boron nitride is a white powder of density 2.34. It melts under pressure at 3000°C. It is very stable and unreactive substance. It remains unaffected by mineral acids, solutions of alkalies and Cl_2 at red heat.

(*ii*) *Decomposition.* (*a*) It gets decomposed when heated in steam, evolving NH_3.

$$BN + 3H_2O \longrightarrow B(OH)_3 \text{ or } H_3BO_3 + NH_3$$

(*b*) It is decomposed, but slowly, by HF, forming ammonium borofluoride, NH_4BF_4

$$BN + 4HF \longrightarrow NH_4BF_4$$

(*c*) It is also decomposed when fused with KOH.

$$BN + 3KOH \longrightarrow K_3BO_3 + NH_3 \uparrow$$

(*iii*) *Reaction with K_2CO_3.* When BN is fused with K_2CO_3, potassium cyanate (KCNO) and potassium metaborate (KBO_2) are obtained.

$$BN + K_2CO_3 \longrightarrow KCNO + KBO_2$$

Uses. BN possesses same hardness as diamond and can withstand temperature of more than 300°C. Due to this property it is used for coating crucible linings.

Structure. Boron nitride has a layered lattice structure. Each layer consists of a hexagonal arrangement of B and N atoms (Fig. 23.2). This structure of BN resembles that of graphite. The layer gets superimposed on one another so that B and N-atoms are alternately above one another. The inter-atomic distances are 1.45 A° and the distance between the layers is 8.33 A°. BN, like graphite, is able to act as host; it is able to occlude oxides, sulphides, oxyhalides and chlorides in the same way as graphite does. BN, when heated to 3000°C at 70,000 atmospheric pressure yields a cubic form with a diamond structure.

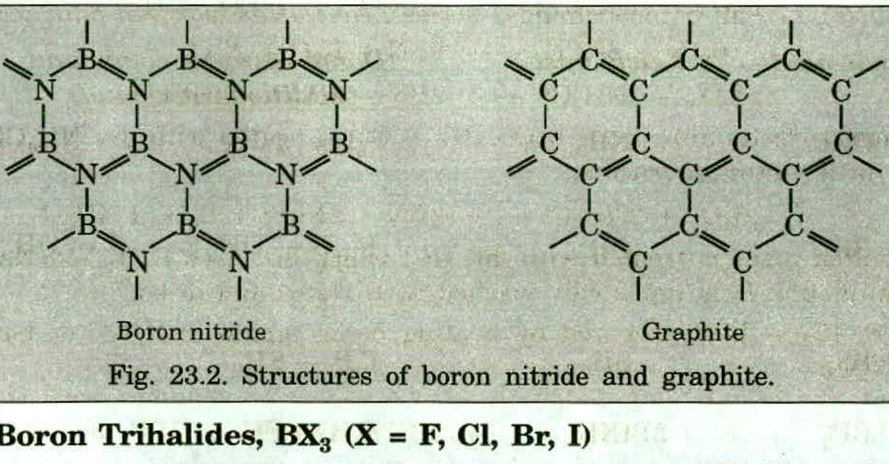


Fig. 23.2. Structures of boron nitride and graphite.

5. Boron Trihalides, BX_3 (X = F, Cl, Br, I)

Boron reacts with halogens and forms all the trihalides, BX_3 (X = F, Cl, Br, I).

Preparation. All the trihalides of boron, with the exception of BF_3, can be prepared by the treatment of a mixture of B_2O_3 and carbon on appropriate halogen at higher temperature.

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO$$
$$(X = Cl, Br, I)$$

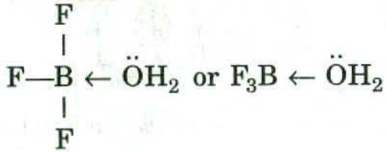
Properties. (*i*) ***Physical state.*** BF_3 and BCl_3 are gases, BBr_3 is a liquid and BI_3 is a solid at room temperature.

(ii) Covalent character. Boron trihalides are covalent in character due to the *small size* and *high charge density* on B^{3+} ion. Some other points in favour of the covalent character of boron trihalides are : (*a*) As liquids they do not conduct electricity *i.e.*, they are *non-electrolytes*. (*b*) Their boiling points are very low as compared to the halides of the elements of group IA and IIA. (*c*) They exist as discrete molecular species (*i.e.*, monomeric molecules) in all the states. (*d*) The boiling points of boron halides *increase as the atomic number of the halogen atoms increases.* This behaviour is very similar to that shown by covalent halogen compounds of carbon.

(iii) Geometry. Boron trihalides have planar triangular geometry which results from sp^2 hybridisation of B-atom (central atom). B-atom has a vacant $2p$-orbital which remains unhybridised. As an example the geometry of BF_3 can be considered.

(iv) Formation of complex halides. Boron trihalides (*e.g.* BF_3) also form complex halides of the type $[BF_4]^-$ in which boron atom (central atom) has a coordination number equal to 4. Boron cannot extend its coordination number beyond 4 due to the non-availability of *d*-orbitals in its configuration.

(v) Electron-acceptor property : Formation of addition compounds. The structure of BX_3 molecule consisting of three B—X bonds indicates that boron atom is surrounded by a sextent (*i.e.* six electrons), *i.e. there are two electrons short of an octet.* Hence B-atom (central atom) in BX_3 molecule can accept an electron pair from the donor atoms like N, P, O, S, F etc. in NH_3, PH_3, H_2O, H_2S, HF, F^- etc. respectively to form *donor-acceptor compounds* (*addition compounds or adducts*), *i.e.*, all boron trihalides act as *Lewis acids* (*electron-pair acceptors*).

Lewis acid		***Lewis base***		***Donor-acceptor compound (Addition compound)***
BF_3	+	$:NH_3$	→	$F_3B \leftarrow NH_3$
BF_3	+	$:\ddot{O}H_2$	→	 $F-\underset{\underset{F}{\mid}}{\overset{\overset{F}{\mid}}{B}} \leftarrow \ddot{O}H_2$ or $F_3B \leftarrow \ddot{O}H_2$
BF_3	+	$:\ddot{S}H_2$	→	$F_3B \leftarrow \ddot{S}H_2$
BF_3	+	$:\underset{..}{\ddot{F}}H$	→	$F_3B \leftarrow \ddot{F}H$ *or* HBF_4 *or* $H^+[BF_4]^-$
BF_3	+	$:\underset{..}{\ddot{F}}^-$	→	$[F_3B \leftarrow \underset{..}{\ddot{F}}:]^-$ or $[BF_4]^-$

The tendency of donor atoms like N, P, O and S to coordinate to BF_3 molecule makes this compound an extremely useful catalyst for Friedel-Crafts reactions like alkylations and acylations, esterifications and polymerisation of olefins.

The addition compounds like $F_3B \leftarrow NH_3$, $F_3B \leftarrow OH_2$ have tetrahedral shape and in their formation the unhybridised *p*-orbital accepts the lone pair of electrons donated by the donor atom.

Relative order of electron-acceptor ability of boron trihalides. Since F atom has the highest electron-attracting power (*i.e.* highest electronegativity), it should create the greatest positive charge on B-atom which would enhance its capacity for accepting the electrons from a donor atom. Thus the order of electron-acceptor ability of boron trihalides should be as follows :

$$\boxed{\mathbf{BF_3 > BCl_3 > BBr_3 > BI_3}}$$

But the measurement of the molar heats of formation of solutions of boron trihalides in nitrobenzene and dipole moments of their adducts with pyridine has shown that the electron-acceptor power of boron trihalides is opposite to that shown above, *i.e.* the observed order is :

$$\boxed{\mathbf{BF_3 < BCl_3 < BBr_3 < BI_3.}}$$

This anomaly has been explained as follows :

We have seen that in BF_3 molecule boron atom (configuration of boron atom in the excited state is $2s^1.2p^1.2p^1.2p^0$) is sp^2 hybridised. All the three sp^2 hybrid orbitals on boron atom overlap with three singly filled $2p$-orbitals of three F atoms ($F \rightarrow 2s^2, 2p^2\ 2p^2\ 2p^1$) to form three sp^2 (B)—$2p$ (F) σ-bonds. Since filled $2p$-orbital on F-atom and vacant $2p$-orbital on B-atom are of *the same energy*, they overlap *laterally* with each other to form a p(B)—p(F) π bond (or more correctly $p\pi$ (B)—$p\pi$ (F) π-bond) and as a result of this overlap $2p$-electrons of F atom are transferred into the vacant $2p$-orbital of B-atom (see Fig 23.3) and the B—F bond acquires some double bond character.

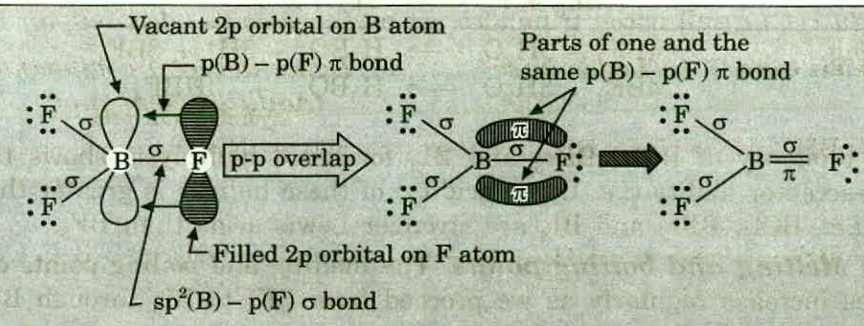
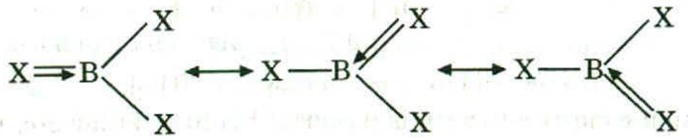


Fig. 23.3. Formation sp^2 (B)—p (F) σ bond and p (B)—p (F) π bonds in BF_3 molecule.

This type of bond formation is known as *dative* or *back bonding.* The effect of back bonding from F atom to B-atom is that positive charge on B-atom is reduced, *i.e.* the electron deficiency of B-atom is compensated and as such electron-acceptor property (*i.e.* Lewis acidity) of BF_3 is *decreased*. The overlapping of $2p$-orbital of B-atom with filled $2p$-orbital of F-atom is maximum in case of BF_3, because both the $2p$-orbitals are at a nearer distance from each other and of equivalent energy. Thus the tendency of $p\pi$—$p\pi$ back bonding in BF_3 is maximum and *decreases* as we move to BCl_3 and BBr_3, because of the increasing distance and energy difference between $2p$-orbital of B-atom and $3p$ and $4p$-orbitals of Cl and Br atoms respectively. Hence BBr_3 would give more stable adducts than BCl_3 and BCl_3 more stable than BF_3. In other words the electron-acceptor ability of boron trihalides is in the order :

$$\boxed{\mathbf{BF_3 < BCl_3 < BBr_3 < BI_3}}$$

In order to explain the equality of all the three observed B—X bond lengths in BX_3, resonance between the three equivalent structures has been suggested.



(vi) Hydrolysis. We have seen that B-atom BX_3 molecule has a hunger for two electrons to fill its vacant 2*p*-orbital. This hunger initiates the hydrolysis of BX_3 molecule by H_2O whose oxygen atom can easily donate its electron pair to B-atom. Thus BX_3 halides (X = Cl, Br and I) are easily hydrolysed to boric acid (H_3BO_3) and corresponding halogen acids (HX).

$$\underset{(X\,=\,Cl,\ Br,\ I)}{BX_3} + 3H_2O \longrightarrow H_3BO_3 + 3HX$$

BF_3, however, gives hydrofluoboric acid, HBF_4 (also called fluoboric acid) which is produced by the combination of H^+ and BF_4^- ions.

$$\begin{array}{lrcl}
 & BF_3 + 3H_2O & \longrightarrow & H_3BO_3 + 3HF \\
 & [HF & \longrightarrow & H^+ + F^-] \times 3 \\
 & [BF_3 + F^- & \longrightarrow & BF_4^-] \times 3 \\
\hline
\textit{On adding} & 4BF_3 + 3H_2O & \longrightarrow & H_3BO_3 + 3H^+ + 3BF_4^- \\
\text{or} & 4BF_3 + 3H_2O & \longrightarrow & H_3BO_3 + \underset{\text{Hydrofluoboric acid}}{3HBF_4}
\end{array}$$

The tendency of BCl_3, BBr_3 and BI_3 for rapid hydrolysis shows that the electron-acceptor ability (*i.e.* Lewis acidity) of these halides is greater than that of BF_3, *i.e.*, BCl_3, BBr_3 and BI_3 are stronger Lewis acids than BF_3.

(vii) Melting and boiling points. The melting and boiling points of boron trihalides increase regularly as we proceed from BF_3 to BI_3 through BCl_3 and BBr_3.

(viii) Solvolytic reactions. While BF_3 forms addition compounds with certain donor molecules containing labile hydrogen, the other trihalides of boron undergo solvolytic reactions with such donor molecules. The extent of solvolysis depends on the *concentration of the donor molecules and temperature.* Some solvolytic reactions of BCl_3 are shown below :

$$BCl_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3HCl$$

$$BCl_3 + 4NH_3 \longrightarrow BN + 3NH_4Cl$$

$$BCl_3 + 3N_2H_4 \longrightarrow B(N_2H) + 3N_2H_5Cl$$

$$BCl_3 + 6C_6H_5NH_2 \textit{ (in benzene)} \longrightarrow B(NHC_6H_5) + 3C_6H_5NH_2.HCl$$

6. Boron Trifluoride, BF_3

Among the boron trihalides **boron trifluoride** is the most important. It is prepared by heating a mixture of CaF_2, B_2O_3 and conc. H_2SO_4.

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

The gas is collected over mercury since it is exceedingly soluble in H_2O. *Pure* BF_3 is best prepared by the action of potassium fluoborate, KBF_4 on B_2O_3

$$KBF_4 + 2B_2O_3 \longrightarrow BF_3 + K[B_4O_6F]$$

Boron trifluoride is a colourless gas (density 2.37) with a suffocating odour, m.pt. = – 127°C, *b.pt.* = – 101°C. It is not combustible. It fumes strongly in moist air and is readily decomposed by water into boric acid and fluoboric acid (HBF_4)

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

It forms addition compounds with NH_3, PH_3, alcohols, ether etc. which act as electron pair donors and thus behave as a *Lewis acids* (electron pair acceptors)

$$H_3N : + BF_3 \longrightarrow H_3N \longrightarrow BF_3$$

$$R_2O : + BF_3 \longrightarrow R_2O \longrightarrow BF_3$$

It is used as a catalyst in organic chemistry.

7. Fluoboric Acid (HBF_4) and its Salts.

Preparation. Fluoboric acid is prepared by dissolving BF_3 in water or by dissolving H_3BO_3 in conc. HF.

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

$$H_3BO_3 + 4HF \longrightarrow HBF_4 + 3H_2O$$

Properties. HBF_4 is a strong acid, stronger than HF. It is decomposed when heated. The salts given by this acid are *fluoborates* or *borofluorides.* These salts are prepared by dissolving the corresponding metallic oxides, hydroxides or corbonates in aqueous hydrofluoboric acid. Fluoborates are also obtained in solution by treating alkali acid fluorides with H_3BO_3.

$$2NaHF_2 + H_3BO_3 \longrightarrow NaBF_4 + NaOH + 2H_2O$$

Excepting KBF_4, the fluoborates are crystalline solids and fairly soluble in water. They decompose on heating, evolving BF_3.

$$KBF_4 \xrightarrow{\Delta} KF + BF_3$$

Here it may be noted that in acid as well as in its salts, boron is *tetracovalent.*

Uses. (*i*) HBF_4 is used as a catalyst in organic chemistry (*ii*) HBF_4 is used in the preparation of fluoborates. (*iii*) The acid and its salts are used in electroplating. (*iv*) KBF_4 is now used for the extraction of boron from its minerals.

Aluminium

Occurrence of Aluminium.

Aluminium does not occur free in nature. It is a constituent of clay, slate and many types of silicate rocks and forms 7.28% of the earth crust. It occurs : (*i*) *As oxides, e.g.* (*a*) *Corundum, Ruby Sapphire, Emerald,* Al_2O_3 (*b*) *Bauxite* which is the hydrated oxide, $Al_2O_3.2H_2O$ and is the chief ore of aluminium. (*c*) *Gibbsite,* $Al_2O_3.3H_2O$, and (*d*) *Diaspore*, $Al_2O_3.H_2O$. Usually all hydrated oxide ores containing 50 to 70% of Al_2O_3, about 25–30% of water with varying amounts of ferric oxide, titanic oxide and silica are called bauxite ores. Bauxite is the chief mineral used for the extraction of Al and is found in Kashmir, Bihar, Maharashtra, Madhya Pradesh and Tamil Nadu. (*ii*) *As fluoride, e.g. Cryolite,* Na_3AlF_5. (*iii*) *As silicates e.g.* (*a*) *Felspar,* $K_2O.Al_2O_3$. $6SiO_2$ or $KAlSi_3O_8$. (*b*) *Koalin, porcelain,* *mica, china clay, slate* etc., $Al_2O_3.2SiO_2.2H_2O$. (*iv*) *As basic phosphate e.g. Turquoise* which is a hydrated basic phosphate, $AlPO_4.Al(OH)_3.H_2O$, coloured blue with copper phosphate, (*v*) *As basic sulphate e.g. alumite* or *alum stone*, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.

Extraction of Aluminium from Bauxite.

The extraction of aluminium from bauxite consists of the following *three* steps:

1. Purification of bauxite and preparation of $Al(OH)_3$. Bauxite is associated with silica, SiO_2 and ferric oxide, Fe_2O_3 (*red bauxite*) and these impurities must be completely removed in order to get good quality of aluminium. A number of processess have been suggested for this purpose.

(a) Baeyer's process. It is especially used for red bauxite containing ferric oxide as chief impurity. It is first roasted at a low temperature to convert any ferrous oxide to ferric oxide and then digested at 150°C with a concentrated solution of caustic soda in an autoclave. The aluminium oxide present in bauxite dissolves in caustic soda forming soluble sodium meta-aluminate, $NaAlO_2$, while the impurities are left behind.

$$Al_2O_3.2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered and agitated with some freshly precipitated $Al(OH)_3$ when the whole of aluminium present in solution in the form of sodium meta-aluminate precipitates in the form of $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + \underset{\text{ppt.}}{Al(OH)_3}$$

(b) Hall's process. (*Dry* or *fusion process*). In this process, ore is fused with sodium carbonate when the aluminium oxide present is converted into soluble sodium meta-aluminate. The silica and ferric oxide are left as insoluble residue when the fused mass is extracted with water.

$$Al_2O_3.2H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2\ (\textit{soluble}) + CO_2 + 2H_2O$$

The filtrate is warmed at a temperature of 50–60°C and a current of carbon dioxide is passed through it when aluminium hydroxide is precipitated.

$$2NaAlO_2 + 3H_2O + CO_2 \longrightarrow \underset{\text{ppt.}}{2Al(OH)_3} + Na_2CO_3$$

(c) Serpek's process. This is used chiefly for ores containing silica as the chief impurity. The ore is mixed with carbon and nitrogen gas passed over the mixture heated to 1800°C when aluminium nitride is formed. It is hydrolysed to get aluminium hydroxide. Silica (SiO_2) is reduced to silicon

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

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

2. Conversion of $Al(OH)_3$ into Al_2O_3. The precipitate of $Al(OH)_3$ obtained by any of the above methods is washed, dried and ignited to get Al_2O_3.

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

3. Recovery of Al from Al_2O_3 by Hall's electrolytic process. Al is obtained from Al_2O_3 by electrolysing it. This method was discovered by American chemist, Charless Martin Hall in 1886. Hence the name *Hall's electrolytic process.*

In this method a solution of Al_2O_3 in fused cryolite, Na_3AlF_6 is taken in an electrolytic cell in which it is electrolysed. The cell consists of a cast iron box, measuring 6' × 3' × 3' (Fig. 23.4). This box is lined with a refractory material which acts as a thermal insulation. Within this lining there is a layer of carbon (carbon lining) which acts as cathode. A number of carbon rods are suspended from a copper bus bar and can be raised and lowered, as desired. These carbon rods act as anodes (carbon anodes). These rods are immersed in the electrolyte (solution of Al_2O_3 in fused crysolite, Na_3AlF_6). The bath containing the electrolyte is maintained at a temperature of 875–950°C. A glow lamp (control lamp) is connected in parallels with the electrolyte cell. This lamp begins to glow when the quantity of Al_2O_3 gets exhausted. Now more quantity of Al_2O_3 as added. Thus it is a continuous process. When electric current is passed, AlF_3 [from cryolite, Na_3AlF_6 or $3NaCl.AlF_3$)] ionises as :

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al is liberated at the cathode and F_2 goes to anode where it reacts with Al_2O_3 to from AlF_3 and O_2 is liberated. The oxygen liberated at anode reacts with carbon anodes to form CO and CO_2.

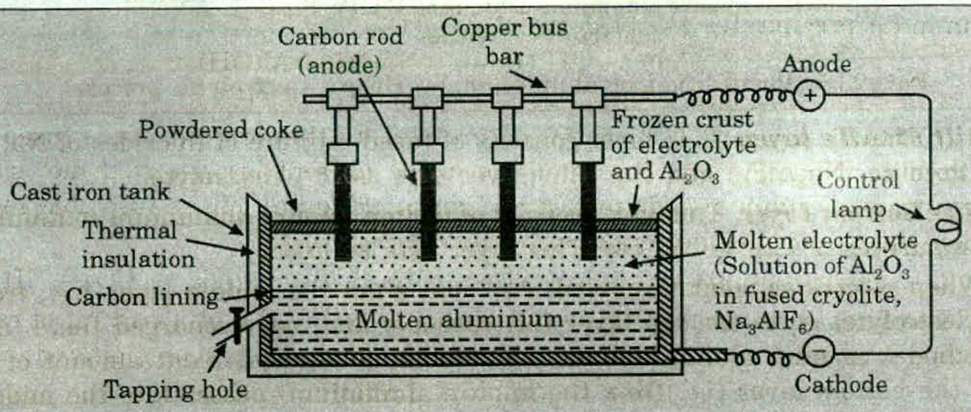


Fig. 23.4. Recovery of aluminium by the electrolysis of molten Al_2O_3 (Hall's electrolytic process).

At cathode : $$Al^{3+} + 3e^- \longrightarrow Al$$

At anode : $$3F^- \longrightarrow 3F + 3e^-$$

$$3F + 3F \longrightarrow 3F_2$$

$$2Al_2O_3 + 6F_2 \longrightarrow 4AlF_3 + 3O_2$$

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

$$C + O_2 \longrightarrow CO_2$$

Molten aluminium collects at the bottom of the cell from where it is withdrawn periodically through the tapping hole. The formation of CO and CO_2 by the reaction between O_2 and carbon anodes causes a serious consumption of the anodes and hence these have to be replaced frequently. The electrolyte is covered with a layer of powdered coke to avoid the loss of heat by radiation.

4. Purification of aluminium by Hoop's electrolytic process. Aluminium obtained as above is not perfectly pure, since it contains the impurities of Cu, Si, Fe etc. Aluminium obtained as above is, therefore, purified. The purification is done by *Hoop's electrolytic process.* The cell used consists of a carbon-lined iron tank (Fig. 23.5). This tank contains the following three liquid layers one over the other of different specific gravity.

(i) Top layer. This layer consists of pure molten aluminium. This layer acts as cathode.

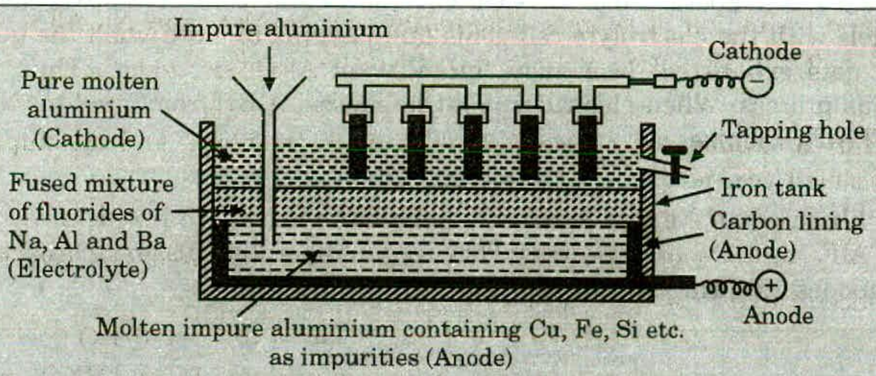


Fig. 23.5. Purification of aluminium by Hoop's electrolytic process.

(ii) Middle layer. This layer consists of fused mixture of fluorides of Na, Al (*i.e.*, cryolite, Na_3AlF_6) and Ba. This layer acts as the electrolyte.

(iii) Bottom layer. This layer consist of molten impure aluminium containing the impurities of Cu, Fe, Si etc. This layer acts as anode.

When electric current is passed, Al^{3+} ions from the middle layer (*i.e.*, from the electrolyte) go to the top layer (*i.e.* cathode) and are discharged there (*i.e.*, at cathode) as pure aluminium. At the same time an equivalent amount of Al from the bottom layer (*i.e.* from the impure aluminium) passes into the middle layer (*i.e.*, into the electrolyte), while the impurities of Cu etc. present in the bottom layer do not pass, but remain below *i.e.* they do not dissolve into the electrolyte. Al obtained in this way is 99.99% pure. It is periodically removed from the tapping hole.

Impure Al containing the impurities of Cu, Fe, Si etc., are introduced into the bottom layer as shown in the figure.

Physical Properties of Aluminium.

Aluminium shows a bluish white lustre which is destroyed on long exposure to air due to the formation of a layer of oxide on it. It is a light metal (density 2.7), malleable and ductile at 100—150°C but brittle below its melting point which is 651°C. It is a good conductor of heat and electricity.

Chemical Properties of Aluminium :

1. Action of air. Aluminium is not affected in dry air but in moist air a thin film of oxide is formed over its surface. It burns in oxygen producing brilliant light.

$$4Al + 3O_2 \longrightarrow Al_2O_3 + 772{,}000 \text{ cals.}$$

2. Action of water. Aluminium, if pure, is not affected by pure water but is corroded by water containing salts if some impurities are present in the metal. It decomposes boiling water. Aluminium-mercury couple is used as a reducing agent because it decomposes water evolving hydrogen.

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2$$

3. Action of alkalies. Aluminium dissolves in alkalies with the evolution of hydrogen and formation of soluble aluminates viz. $NaAlO_2$ and Na_3AlO_3

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$
$$2Al + 6NaOH \longrightarrow 2Na_3AlO_3 + 3H_2$$

4. Action of acids. Aluminium dissolves in hydrochloric and dil sulphuric acid producing hydrogen

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$
$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2 \text{ (\textit{Reaction very slow})}.$$

Hot concentrated sulphuric acid produces sulphur dioxide

$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Concentrated nitric acid has no action on aluminium. Dilute HNO_3 reacts only slowly on impure Al to produce $Al(NO_3)_3$

$$8Al + 30HNO_3 \longrightarrow Al(NO_3)_3 + 3NH_4NO_3 + 9H_2O$$

5. Action of halogens. Finely powered heated aluminium combines with halogens, if the latter are passed over it.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

6. Action of nitrogen. Aluminium combines with nitrogen forming aluminium nitride.

$$2Al + N_2 \longrightarrow 2AlN$$

7. Action of carbon monoxide and carbon dioxide. Red hot aluminium is attacked by both carbon monoxide and carbon dioxide.

$$6Al + 3CO \longrightarrow Al_2O_3 + \underset{\text{Aluminium carbide}}{Al_4C_3}$$

$$4Al + 3CO_2 \longrightarrow 2Al_2O_3 + 3C$$

8. Reducing properties. Aluminium metal is a good reducing agent and reduces oxides of iron, chromium and manganese etc. to corresponding metals.

$$2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3 + \text{heat}$$
$$2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3 + \text{heat}$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn + \text{heat}$$

This property is made use of in the extraction of chromium, manganese etc. by *Gold Schmidt's aluminothermic process.*

Uses of Aluminium.

(*i*) Because of its lightness, good conductivity and resistance to corrosion, aluminium is used for making *alloys* which find extensive application in industries and arts (*ii*) For making utensils, frames, coils for motors and wire for electrical transmission. (*iii*) *Aluminium foil* is used for wrapping confectionary, cigarettes etc. (*iv*) Aluminium powder is used in making silvery paints, in fireworks, flashlight powders and in thermit welding. (*v*) In the extraction of chromium and manganese. (*vi*) As a deoxidiser and for preventing blow holes in metallurgy. (*vii*) It is used for the manufacture of electric cables. (*viii*) Aluminium amalgam is used as a reducing agent. (*ix*) It is also used for making alloys. Some of its important alloys are given in the table below :

Alloy	Approx. composition	Uses
Magnalium	Al = 94.5%, Mg = 5.5%	Scientific apparatus, machined articles.
Duralumin	Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%	Aircraft parts, railroad cars, boat machinery.
Nickeloy	Al = 95%, Cu = 4%, Ni = 1%	Aircraft part.
Y-alloy	Al = 93%, Cu = 4%, Ni = 2%, Mg = 1%	Pistons and machinery parts.
Alnico	Steel = 50%, Ni = 2%, Al = 20%, Co = 1%	For making permanent magnets.

Compounds of Aluminium

1. Aluminium Chloride, $AlCl_3$ or Al_2Cl_6.

Preparation. When aluminium metal or $Al(OH)_3$ is treated with HCl, solution of *hydrated* aluminium chloride, $AlCl_3.6H_2O$ is obtained.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

On evaporating the solution, the crystals of $AlCl_3.6H_2O$ are obtained. On heating these crystals, anhydrous aluminium chloride cannot be obtained because of the formation of Al_2O_3.

$$2(AlCl_3.6H_2O) \xrightarrow{\text{Heat}} Al_2O_3 + 6HCl + 9H_2O$$

The anhydrous aluminium chloride is, however, prepared :

(*i*) By passing dry chlorine or hydrochloric acid gas over heated aluminium powder. The vapour of aluminium chloride is condensed in the receiver as shown in Fig. 23.6.

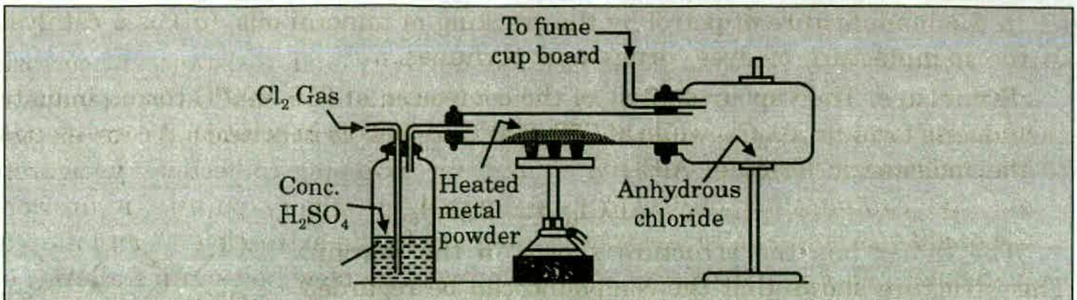


Fig. 23.6. Preparation of anhydrous aluminium chloride.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$
$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

(*ii*) By heating a mixture of alumina and coke in a current of chlorine (*Mac Affe process*),

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

(*iii*) By heating alumina (Al_2O_3) in a current of carbonyl chloride ($COCl_2$).

$$Al_2O_3 + 3COCl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

(*iv*) By heating alumina in a current of S_2Cl_2 vapour and Cl_2. (*Commercial preparation*)

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 \longrightarrow 8AlCl_3 + 6SO_2$$

Properties. (*i*) Anhydrous salt is a white crystalline solid. It is hygrocopic and fumes in moist air. It sublimes at 180°C. (*m.pt.* = 193°C at 2 atom, pressure).

(*ii*) It is a typical covalent compound as is shown by its volability, solubility in organic solvents like C_2H_6, CS_2 etc. and poor conductivity of the fused state.

(*iii*) An aqueous solution of the salt is acidic in nature because in water it undergoes hydrolysis and forms HCl.

$$AlCl_3 + 3H_2O \rightleftarrows Al(OH)_3 + 3HCl$$

With moist air, the salt gives the fumes of HCl. The equation representing the reaction is the same as given above.

(*iv*) When NH_4OH is added to $AlCl_3$ solution, white precipitate of $Al(OH)_3$ is obtained.

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{\substack{\text{White}\\\text{ppt.}}}{Al(OH)_3} + 3NH_4Cl$$

(*v*) With excess of NaOH, the salt solution gives sodium meta-aluminate, $NaAlO_2$ (soluble)

$$AlCl_3 + 4NaOH\ (\textit{excess}) \longrightarrow \underset{\text{(soluble)}}{NaAlO_2} + 2H_2O + 3NaCl$$

(*vi*) It forms addition compounds with a number of donor molecules like NH_3, PH_3, $COCl_2$ etc.

$$AlCl_3 + 6NH_3 \longrightarrow AlCl_3.6NH_3 \quad \textit{(Addition compound)}.$$

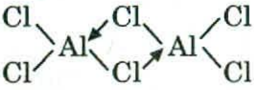
Uses. It is used : (*i*) in organic chemistry for introducing alkyl radicals originally linked with halogen into benzene nucleus (*Friedel Craft's reaction*).

(*ii*) in the manufacture of petrol by the cracking of mineral oils, (*iii*) as a catalyst in the manufacture of dyes, drugs and perfumes.

Structure. The vapour density of the compound at 350–400°C corresponds to the dimeric formula, Al_2Cl_6 while at 750–800°C as well as in solution it corresponds to the monomeric formula, $AlCl_3$.

$$Al_2Cl_6 \rightleftarrows 2AlCl_3.$$

The dimer has the structure shown in the margin. This structure shows that the compound can be regarded as an auto-complex, $Al(AlCl_6)$. In this structure, the halogen atoms are tetra-hedrally arranged about each aluminium atom. The dimeric formula is retained when it is dissolved in non-polar solvents such as benzene, but because of higher heat of hydration, the covalent dimer is broken into $[Al.6H_2O)^{3+}$ or $[Al\ (H_2O)_6]^{3+}$ and $3Cl^-$ ions on dissolution in water.



2. Aluminium Nitride, AlN.

Preparation. (*i*) By heating strongly aluminium powder in an atmosphere of nitrogen or ammonia.

$$2Al + N_2 \xrightarrow{800^\circ} 2AlN$$

(*ii*) By heating alumina mixed with coke in a current of nitrogen.

$$Al_2O_3 + 3C + N_2 \xrightarrow{1800^\circ} 2AlN + 3CO$$

Properties. It is a colourless crystalline solid which is decomposed by water or alkalies.

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

It is thermally stable upto 800°C. When heated with HCl at 900°C and with Cl_2 at 300°, it gives $AlCl_3$.

$$AlN + 3HCl \xrightarrow{900^\circ C} AlCl_3 + NH_3$$

$$AlN + 3Cl_2 \xrightarrow{300^\circ C} 2AlCl_3 + N_2$$

Uses. Its formation during purification of bauxite by Serpeck's process is utilised for the manufacture of ammonia.

Structure. Crystalline AlN has wurtzite structure.

3. Aluminium Sulphate, $Al_2(SO_4)_3.18H_2O$.

This compound occurs as *hair salt* or *feather alum*.

Preparation. Commercially it is prepared from bauxite ore, $Al_2O_3.2H_2O$. Bauxite is treated with conc. H_2SO_4 and the resulting solution is cooled and the product is recrystallised from water containing alcohol when lustrous crystals of $Al_2(SO_4)_3.18H_2O$ are obtained.

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 5H_2O$$

Properties. Anhydrous salt is a white powder (density 2.71) while hydrated salt forms colourless crystals (density 1.62) having a sour astringent taste. It is soluble in H_2O and the solution is acidic in nature due to hydrolysis.

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

On heating, crystals of the salt lose water of crystallisation leaving anhydrous salt which decomposes at 100°C into Al_2O_3 and SO_3.

$$\underset{\text{Hydrated}}{Al_2(SO_4)_3.18H_2O} \xrightarrow[(-\,18H_2O)]{\text{Heat}} \underset{\text{Anhydrous}}{Al_2(SO_4)_3} \xrightarrow{800°C} Al_2O_3 + 3SO_3$$

With sulphates of alkali metals it forms double sulphates called *alums* having the composition $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R stands for univalent basic radical like Na, Rb, Cs, NH_4^+ etc., and M is a trivalent metal like Al, Cr, or Fe.

Uses. It is used : (*i*) in the purification of sewage and water, since it possesses remarkable power of precipitating collides (*ii*) as a mordant in dyeing (*iii*) in sizing of paper (*iv*) in foam fire-extinguishers (*v*) in the tanning of kid-leather (*vi*) as a starting material in the preparation of other aluminium salts (*vii*) in the preparation of alums.

4. Alums.

Originally the name alum was given to the double salt, potassium aluminium sulphate, $K_2SO_4.Al_2(SO_4)_3.24H_2O$. But now this name is used for all the double salts having the composition : $M_2^I\ SO_4\ M_2^{III}(SO_4)_3.24H_2O$, where M^I stands for univalent basic radical like Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Tl^+ and M^{III} is a trivalent metal Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+} etc. The crystals of alums are made up of $[M^I(H_2O)_6]^+$, $[M^{III}(H_2O)_6]^{3+}$ and two SO_4^{2-} ions. Some common examples of alums are (*i*) *Potash alum,* (or *common alum*)—$K_2SO_4.Al_2(SO_4)_3.24H_2O$; (*ii*) *Sodium alum*—$Na_2SO_4.Al_2(SO_4)_3.24H_2O$; (*iii*) *Ammonium alum* $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$; (*iv*) *Chrome alum*, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ etc. The crystals of alums are generally obtained when hot solutions of equimolecular quantities of their constituent sulphates are mixed and the resulting solution is cooled. All the alums are isomorphous, form mixed crystals in all proportions and also layer-crystals. They are usually much more soluble in hot water than in cold water. In solution they give the ions of the component salts.

Alums are often used for the removal of colloidal impurities from water (as coagulants).

5. Potash Alum or Common Alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ *or* $KAl(SO_4)_2.12H_2O$.

Preparation. Commercially it is prepared as follows from alunite or alumstone mineral, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.

The mineral alunite is calcined and treated with H_2SO_4 when $Al(OH)_3$ component is converted into $Al_2(SO_4)_3$. Now calculated quantity of K_2SO_4 is added to the solution which is then crystallised for alum. Finally it is purified by recrystallisation.

$$\underset{\text{Alunite mineral}}{K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3} + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Properties. Potash alum is a white crystalline solid, soluble in water but insoluble in alcohol. The aqueous solution is acidic due to the hydrolysis of aluminium sulphate. When heated, it melts at 92°C and on further heating loses the whole of its water of crystallisation and swells up. The swollen mass so produced is called *burnt alum (phul phatkiri)*.

Uses. It is used in purification of water, water proofing of textiles and in dyeing and paper industry. It is also employed as a styptic to arrest bleeding.

Thallium

Occurrence.

Thallium is one of the rare elements which constitutes only 10^{-5} per cent of the earth's crust. It is present in traces in Cu, Zn and Fe blendes and pyrites. It is also found in mica, carnallite, alluminite etc. Flue dust obtained from the roasting of thalliferrous pyrites contains about 0.25% or more of thallium and it is probably the best source of thallium.

Extraction from Flue Dust.

Flue dust contains Tl_2O and the oxides of other elements like Cu, Pb, As, Bi, Fe etc. Flue dust is dissolved in aqua regia and the resulted solution contains TlCl, $CuCl_2$, $PbCl_4$, $AsCl_3$, $BiCl_3$ and $FeCl_3$. This solution is evaporated to drive away HNO_3 and then heated with H_2S. By this operation $CuCl_2$, $PbCl_4$, $AsCl_3$ and $BiCl_3$ are precipitated as sulphides while TlCl and $FeCl_3$ go into the solution. The solution which contains TlCl and $FeCl_3$ is heated with NH_4OH to get the precipitate of $Fe(OH)_3$ and the filtrate which contains TlOH is treated with KI to get the precipitate of TlI. The precipitate of TlI is treated with hot conc. H_2SO_4 to get Tl_2SO_4. Tl_2SO_4, on electrolysis, gives Tl metal which is collected at the cathode. Alternatively Tl_2SO_4, on being treated with Zn metal gives the Tl metal. The essential reactions are shown below :

$$Fe_2O_3\ (\textit{From flue dust}) + 6HCl\ (\textit{From aqua regia}) \rightarrow 2FeCl_3 + 3H_2O$$

$$Tl_2O\ (\textit{From flue dust}) + 2HCl\ (\textit{From aqua regia}) \rightarrow 2TlCl + H_2O$$

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{ppt.}}{Fe(OH)_3} + 3NH_4Cl$$

$$TlCl + NH_4OH \longrightarrow \underset{\text{(In solution)}}{TlOH} + NH_4Cl$$

$$TlOH + KI \longrightarrow \underset{\text{ppt.}}{TlI} + KOH$$

$$2TlI + H_2SO_4\ (\textit{hot and concentrated}) \longrightarrow Tl_2SO_4 + 2HCl$$

$$Tl_2SO_4 \xrightarrow{\text{Electrolysis}} \text{Tl is collected at cathode}$$

$$Tl_2SO_4 + Zn \longrightarrow 2Tl + ZnSO_4$$

Physical Properties.

Thallium is a soft grey metal. Its melting and boiling points are 303° and 1457°C. It is so soft that it can be scratched even by finger nails. It is malleable but not ductile. It exists in two allotropic forms, namely, α, and β forms. It alloys with a number of metals like Cu, Ag, Au, Zn, Cd, etc.

Chemical Properties.

Tl is more reactive than In and Ga due to its tendency to form unipositive ion, Tl^+. It oxidises in moist air and decomposes steam at red heat. It dissolves readily in dil. mineral acids except HCl, giving Tl (I) compounds. It does not dissolve readily in HCl because TlCl is insoluble. It combines with halogens at ordinary temperature and with S, Se and Te on heating. It does not combine with B, C, N_2 and H_2 even on heating.

Similarities between Thallium and Other Elements Outside its Group.

(*a*) Similarities with alkali metals. Some of Tl (I) compounds are similar to the corresponding compounds of alkali metals. This similarity is due to the fact that Tl^+ ion has the same charge and approximately the same size as the ions derived from the heavier alkali metals. Some points showing the similarity are : (*i*) Tl (+ 1) cyanide, perchlorate, sulphate, phosphate and carbonate are stable salts and are isomorphous with alkali salts. For example, Tl_2SO_4, $TlClO_4$ and Tl_2PtCl_6 are isomorphous with K_2SO_4, $KClO_4$ and K_2PtCl_6 respectively. (*ii*) TlOH is soluble in water giving strong alkaline solution which is very similar in behaviour to NaOH. (*iii*) The aqueous solution of Tl_2CO_3 is strongly alkaline like that of Na_2CO_3. (*iv*) TlF has distorted NaCl type structure while other Tl (+ 1) halides crystallise with CsCl crystal.

(*b*) Similarities with lead. The cause of similarity between Tl (I) and Pb (II) is that Tl^+ and Pb^{2+} ions are isoelectronic, *i.e.* these ions have identical electronic configuration. Some points showing the similarity are: (*i*) Thallium and lead both are white metals with a bluish type. (*ii*) Both the metals are so soft that they can be cut with a knife and scratched with a finger's nail. (*iii*) Both the metals mark the paper and have low melting points. (*iv*) The halides, chromates and sulphides of both the elements are formed by the same method. These salts have the same appearance and are sparingly soluble in H_2O. TlCl, like $PbCl_2$, is soluble in hot water.

(*c*) Similarities with silver. (*i*) Chlorides, bromides and iodides of Tl(I) and Ag(I) have similar colour and are sparingly soluble in H_2O. (*iii*) Like AgCl, TlCl turns violet on exposure to light.

Uses of Thallium.

Thallium does not have any worthwhile application as a metal. However, its salts are very useful. Some uses of its salts are : (*i*) Thallium salts are toxic and hence are used as fungicide, germicide, and for killing rats and destroying vermin. (*ii*) Thallium salts have been used in ointments for the treatment of ring worms. (*iii*) Thallium compounds have unusually high refractive index and are, therefore, used for the preparation of optical glasses like Crooke's glasses. (*iv*) Tl_2CO_3 has been recommended as a standard in acidimetry. (*v*) Thallium oxysulphide is used in thallosulphide photoelectric cells. (*vi*) Certain thallium salts have been used as depilatories. (*vii*) Alloys of Tl with Ag are lustrous and remain unattacked in air. An alloy containing Tl = 10%, Al = 10% and Ag = 80% is resistant to the action of H_2S.

Ceramics Industry

The art of making the articles from china clay or kaoline (*e.g.* chinaware, earthware stoneware etc.) comes under ceramics industry.

Raw Materials Required for the Manufacture of Whiteware.

Following are the raw materials which are required for the manufacture of whiteware.

1. Clay. It is *hydrated aluminium silicate.* Some common clays are : (*i*) *Kaolin*, $Al_2O_3.2SiO_2.2H_2O$ (*ii*) *Beidellite*, $Al_2O_3.2SiO_2$. H_2O (*iii*) *Halloysite*, $Al_2O_3.2SiO_2$. $3H_2O$. Clay is used for the manufacture of whiteware due to its following properties : (*i*) It is plastic and can be moulded when it is wet. (*ii*) It retains its shape when dried. (*iii*) When mould mass is heated to a high temperature, it sinters together forming a hard, coherent mass without losing its original colour.

2. Felspar or spar. It is double silicate of K or Ca with Al. Some common felspars are : (*i*) *Potash felspar*, $K_2O.Al_2O_3.6SiO_2$ (*ii*) *Soda felspar*, $Na_2O.Al_2O_3$. $6SiO_2$ (*iii*) *Lime felspar*, $CaO.Al_2O_3.6SiO_2$. Felspar is fusible and serves as a flux as well as a binder for the clay particles. It is not present in the naturally occurring clays and hence is added from outside.

3. Sand or flint. Sand (SiO_2) or flint is used as an opener for reducing the shrinkage of the clay.

4. Fluxes. Fluxes are easily fusible materials. Borax, boric acid, soda ash, pearl ash (K_2CO_3), fluourspar (CaF_2), cryolite (Na_3 AlF_6), iron oxide, lead oxides etc. are used as fluxes.

5. Refractories. These are substances which can withstand high temperature (at least 600°) in the furnaces without melting. Al_2O_3, FeO, Cr_2O_3, $MgCO_3$, TiO_2, SiC, ZrO_2 etc. are the important examples of refractories.

Manufacture of Whiteware.

The manufacture of whiteware consists of the following steps :

1. Preparation of slip. Clay, felspar, sand etc. are mixed with H_2O and stirred in a revolving *blunger* to get a cream-like paste which is known as *slip*. The slip so prepared is filtered through vibrating screen to remove the coarse materials (*e.g.* bits of wood, metals, coal etc.) present in it.

2. Filtering and aging. The slip obtained as above is passed through the filter paper so that almost all water is removed and a moist cake is obtained. This moist cake contains only 10–30% water. The moist cake is stored in dampt cellars for a few weeks. This is called *aging of the slip*. This process increases the plasticity of the clay.

3. Shaping of the articles. The shaping of the articles is done by hand moulding, by potter wheel or by die pressing. When cast is required, Na_2CO_3 or K_2CO_3 or water glass is added to the clay.

4. Drying the articles. The articles are now dried in air or chambers through which warm air circulates.

5. Firing. The dried articles are placed in clay boxes called *saggers* which are placed in the furnace called *hovel oven* so that the articles may not coins in direct contact of the flames. During the process of firing the following changes occur : (*i*) At 150°–600°C water is completely removed. (*ii*) At 800–900°C lime stone ($CaCO_3$), if any, gets decomposed. ($CaCO_3 \rightarrow CaO + CO_2 \uparrow$). (*iii*) At 350–900°C, oxidation of ferrous salts and organic matter present in the raw materials takes place. (*iv*) At 1200–1300°C, silicates of different metals may be formed by the combination of metallic oxides with silica (SiO_2).

The article obtained after it has been fired is porous like a biscuit and hence is called *biscuit*.

6. Glazing of the biscuit. In order to make the earthware impervious to liquids, glazes are applied on it. *Dipping* or *immersion, pouring, spraying, dusting, volatilization* etc. are the various methods of applying the glazes on the articles. The biscuit is again fired in a furnace at a temperature 700–990°C. During the firing, the article becomes smooth and shining in appearance. SiO_2, Al_2O_3, lead oxide, ceric oxide etc. are the examples of the glazes. The glazes contain at least one alkaline earth metal.

7. Colouring of the articles. The colouring agent is sometimes mixed in clay, felspar, sand etc. or in glaze components. The materials used as colouring agents are cobalt oxide (blue), copper oxide (green or red), chromium (green or red), iron oxide (yellow, orange or red), gold chloride (pink), MnO_2 (violet), TiO_2 (faint yellow) etc. The colours imparted by them are given in brackets.

Questions with Answers

Q.1 Explain the following with reasons :

(*i*) Al metal cannot be obtained by carbon reduction method.

Ans : In carbon reduction method pure alumina (Al_2O_3) obtained from bauxite ore ($Al_2O_3 . 2H_2O$) is heated with carbon. In this reaction Al_2O_3 is not reduced to Al by carbon. Instead Al_4C_3 is formed.

$Al_2O_3 + 3C \xrightarrow{\Delta} 2Al + 3CO$ (*This reaction does not take place*)

$2Al_2O_3 + 9C \xrightarrow{\Delta} Al_4C_3 + 6CO$

(*ii*) Aqueous solution of anhydrous $AlCl_3$ is a good conductor of electricity.

Ans : We know that anhydrous $AlCl_3$ exists as a dimer, Al_2Cl_6. When it is dissolved in water, dimeric structure gets broken into $[Al(H_2O)_6]^{3+}$ and Cl^- ions. Due to the production of these ions, the aqueous solution of dimer acts as a good conductor of electricity.

$Al_2Cl_6 + 12H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$

(*iii*) Aluminium forms AlF_6^{3-} ion but boron does not form BF_6^{3-} ion.
(Punjab 1995 April)

Ans : Since AlF_6^{3-} ion has octahedral geometry, in the formation of this ion Al-atom in its excited state ($Al = 3s^{10}\ 3p^1\ 3p^1\ 3p^{\circ}\ 3d^{\circ}\ 3d^{\circ}$) undergoes sp^3d^2 hybridisation. Further since Al-atom has *d*-orbitals in its valence shell, the occurrence of sp^3d^2 hybridisation of Al-atom in AlF_6^{3-} ion is possible. On the other hand, since B-atom does not have *d*-orbitals, the occurrence of sp^3d^2 hybridisation of B-atom in BF_6^{3-} ion is not possible and hence BF_6^{3-} ion is not formed.

(*iv*) Like Na, Al cannot be obtained by the electrolysis of fused $AlCl_3$.

Ans : We know that Na can be obtained by the electrolysis of fused NaCl containing $CaCl_2$ and KF, but Al cannot be obtained by electrolysing fused $AlCl_3$, since $AlCl_3$ is a covalent solid and hence sublimes at 453K.

Q.2 What happens when :

(*i*) Borax is heated strongly. (Roorkee 1986)

(*ii*) A mixture of borax and CaO is heated in a falme. (Roorkee 1984)

Ans : (*i*) A glass transparent mass of boric anhydride (B_2O_3) is formed.

$$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow[(-10H_2O)]{\Delta} \underset{\substack{\text{Anhydrous}\\ \text{borax (white}\\ \text{porous mass)}}}{Na_2B_4O_7} \xrightarrow{\Delta} 2NaBO_2 + \underset{\substack{\text{Boric}\\ \text{anhydride}}}{B_2O_3}$$

(*ii*) Blue bead of cobalt metaborate $Co(BO_2)_2$ is formed

$$CaO + Na_2B_4O_7.10H_2O \rightarrow 2NaBO_2 + 10H_2O + \underset{\substack{\text{Cobalt}\\ \text{metaborate}\\ \text{(blue bead)}}}{Co(BO_2)_2}$$

Actually the above reaction takes place through the following steps :

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} 2NaBO_2 + 10H_2O + \underset{\text{Glassy bead}}{B_2O_3}$$

$$CoO + B_2O_3 \rightarrow CoO.B_2O_3 \text{ or } Co(BO_2)_2$$

$$Na_2B_4O_7.10H_2O + CoO \rightarrow 2NaBO_2 + 10H_2O + \underset{\text{Blue bead}}{Co(BO_2)_2}$$

Q.3 Starting from borax, how would you obtain the following (*i*) boric acid (*ii*) boron trioxide (*iii*) boron (*iv*) boron intride (*v*) boron trichloride.

Ans : The preparation of the given compounds from borax can be shown in the flow sheet given in Fig. 23.7.

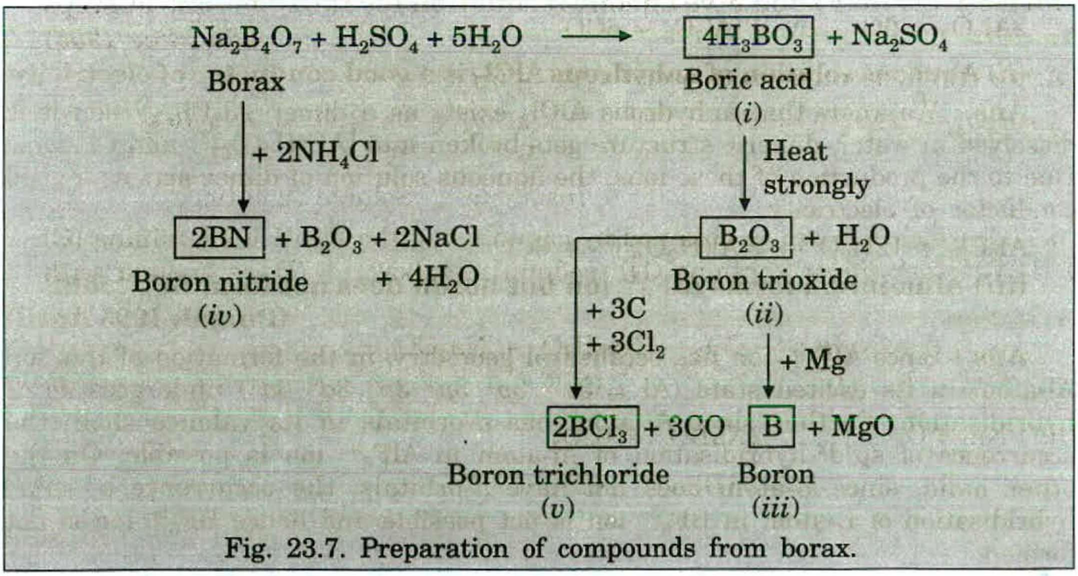


Fig. 23.7. Preparation of compounds from borax.

Q.4 A certain salt, X gives the following tests :

(*i*) Its aqueous solution is alkaline to litmus.

(*ii*) On strongly heating, it swells to give a glassy bead.

(*iii*) When conc. H_2SO_4 is added to a hot concentrated solution of X, white crystals of a weak acid separates out.

Identity X and write down the chemical equation for reactions at (*i*) (*ii*) and (*iii*). (Roorkee 1992)

Ans : (*i*) X is borax, $Na_2B_4O_7 .10H_2O$

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\substack{\text{(strong}\\ \text{alkali)}}}{2NaOH} + \underset{\substack{\text{(weak}\\ \text{acid)}}}{4H_3BO_3}$$

Due to the presence of strong alkali *viz* NaOH, aqueous solution of $Na_2B_4O_7$ is alkaline to litmus.

(*ii*) $$Na_2B_4O_7.10H_2O \xrightarrow[(-10H_2O)]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + \underset{\text{Glassy bead}}{B_2O_3}$$

(*iii*) $$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow \underset{\substack{\text{White crystals}\\ \text{(Weak acid)}}}{4H_3BO_3} + Na_2SO_4$$

Q.5 (*i*) A white ppt. (B) is formed when a mineral (A) is bolied with Na_2CO_3 sloution.

(*ii*) The ppt. is filltered and the filtrate contains two compounds (C) and (D). The compound (C) is removed by crystalisation and when CO_2 is passed through the mother liquor left, (D) changes to (C).

(*iii*) The compound (C), on strong heating, gives two compounds (D) and (E).

(*iv*) (E), on heating with CoO, producess blue coloured substance (F).

Identity (A) to (F) and give chemical equation for the reactions at steps (*i*) to (*iv*) *(Roorkee 1995)*

Ans : (*i*) (A) is colemanite ore, $Ca_2B_6O_{11}.5H_2O$

$$\underset{(A)}{Ca_2B_6O_{11}} + 2Na_2CO_3(aq) \xrightarrow{\text{Boil}} \underset{\substack{(B)\\ \text{Insoluble}}}{2CaCO_3} + \underbrace{\underset{(C)}{Na_2B_4O_7} + \underset{(D)}{2Na_2BO_2}}_{\text{Soluble (Solution)}}$$

(*ii*) (C) which is borax is obtained by crystallising the solution containing (C) and (D). Mother liquor contains (D) (sodium metaborate). (D) is treated with CO_2.

$$\underset{(D)}{4NaBO_2} + CO_2 \rightarrow \underset{(C)}{Na_2B_4O_7} + Na_2CO_3$$

(*iii*) $$\underset{(C)}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{(D)}{2NaBO_2} + \underset{(E)}{B_2O_3}$$

(*iv*) $\underset{\text{(E)}}{B_2O_3} + CoO \xrightarrow{\Delta} \underset{\text{(F)}}{Co\,(BO_2)_2}$

(Blue coloured
cobalt metaborate)

Above discussion shows that : A = $Ca_2B_6O_{11}.5H_2O$, B = $CaCO_3$, C = $Na_2B_4O_7$, D = $NaBO_2$, E = B_2O_3, F = $Co\,(BO_2)_2$.

Q.6 Identity A and B in the following reactions :

Colemanite ore + A $\longrightarrow$ $Na_2B_4O_7$ + ...

$Na_2B_4O_7$ + B $\rightarrow$ H_3BO_3 + ... (Roorkee 1989)

Ans : A is sodium carbonate, Na_2CO_3

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$$

B is either conc. H_2SO_4 or HCl

$$Na_2B_4O_7 + \underset{\text{(B)}}{H_2SO_4} + 5H_2O \longrightarrow Na_2BO_4 + 4H_3BO_3$$

$$Na_2B_4O_7 + \underset{\text{(B)}}{2HCl} + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

Q.7 How will you convert $AlCl_3$ into $AlBr_3$.

Ans : Reaction are given below :

(*i*) $AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{ppt}}{\boxed{Al\,(OH)_3}} + 3NH_4Cl$

$Al\,(OH)_3 + 3HBr \longrightarrow \boxed{AlBr_3} + 3H_2O$

(*ii*) $AlCl_3 + 3NH_4OH \longrightarrow \boxed{Al\,(OH)_3} + 3NH_4Cl$

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

$Al_2O_3 + 3C + 3Br_2 \longrightarrow \boxed{2AlBr_3} + 3CO$

University Questions

1. How does boron occur in nature? How is boron extracted from its minerals? Describe the properties and uses of boron. (*Meerut 82 S, 83 S, 84, 85 S*)
2. Give the method for the preparation and uses of borax. (*R.E.E. 81*)
3. How will you get the following from borax : boron, BN, boric acids, BCl_3, BF_3, B_2H_6, B_2O_3, B_2H_6 and inorganic benzene? (*Meerut 1982, 82 S, 84, 85, 87; Agra 81, 82*)
4. Give the preparation, properties and uses of boric acid. (*Meerut 83, 89; Rohilkhand 84; Kanpur 81; Allahabad 87; R.E.E. 74*)
5. Explain the following giving appropriate reasons :
   (*i*) Although H_3BO_3 has negligible tendency to give protons, even then it behaves as a weak monobasic acid in solution. (*Raj. 86; Gorakhpur*)

(*ii*) On addition of glycerol or ethyl glycol, the acidity of boric acid increases. (*Allahabad 87*)

(*iii*) The pH of orthoboric acid solution decreases in presence of ethylene glycol.

6. Write a note on "Borazine". (*Delhi 89*)

7. Explain the following, giving appropriate reasons :

(*i*) Borazine is more reactive than benzene. (*Delhi 80; Delhi Hons. 86*)

(*ii*) Borazine is called inorganic benzene. (*Madras 86; Delhi Hons. 87; Madurai 86*)

8. Name the four important ores of Al. Describe the extraction of Al from bauxite. (*Raj. 86, 87; Meerut 85*)

9. Explain why : (*i*) in the electrolytic manufacture of Al-metal, carbon anodes are consumed. (*ii*) pure alumina cannot be electrolysed for the extraction of Al-metal. (*R.E.E. 80*)

10. Draw the structure of borazine. (*Delhi 99*)

11. How is boric acid produced? Give its two chemical properties, uses and chemical equations. (*Delhi 99*)

12. (*a*) How will you prepare boric acid ? Discuss its (*i*) acidic nature (*ii*) action of heat.

(*b*) Discuss the structure of borazine. Why it undergoes addition reactions readily in contrast to benzene ? Explain giving two reactions.

(*c*) Explain in brief "back bonding" and its effect on reactivity of the substance. (*Himachal Pradesh 99*)

13. (*a*) Explain why orthoboric acid is strongly acidic in presence of glycerol.

(*b*) Describe the method of preparation and uses of borazole. (*Allahabad 99*)

14. (*a*) What is back bonding? Explain why does it occur in boron halides and not in aluminium halides.

(*b*) Discuss the structure of diborane.

(*c*) Draw the structure of orthoboric acid. Why is it a weak acid but in the presence of ethylene glycol, it acts as a strong acid? (*Himachal Pradesh 2000*)

15. Compare the properties of Ga and Tl pair. (*Kanpur 2000*)

16. Give preparation, properties and applications of borax. (*Lucknow 2000*)

CHAPTER

24

Hydrides of Boron : Boranes

Boron does not combine directly with hydrogen to form its hydrides. Nevertheless a number of interesting hydrides of boron are known. The hydrides of boron are also called **boranes** to establish an analogy with alkanes.

Although the trivalency of boron suggests that a hydride of the molecular formula, BH_3 should also exist. This hydride, due to its unstable nature at room temperature, does not exist in the free condition, although the boric radical (BH_3) is found in several compounds like $OC.BH_3$ (borine carbonyl), $(CH_3)_3N.BH_3$. A systematic investigation of boranes was made by Stock in 1914.

The boranes are named as *di-, tri-, tetra-, penta-, hexa-boranes* and so on according to the number of boron atoms followed by the numeral which indicates the number of hydrogen atoms. For example B_5H_9 is called penta borane-9. Here penta indicates the number of boron atoms and 9 indicates the number of H-atoms.

The boranes have been grouped into two classes namely B_nH_{n+4} (n = 2, 5, 6, 8, 10 and 18) and B_nH_{n+6} (n = 4, 5, 6, 9 and 10). The boranes of the former type are quite stable and have high m. pts. while those of the latter type are unstable and have low m. pts. Different members of both the types are : (*i*) B_nH_{n+4} *type, e.g.* diborane, B_2H_6; pentaborane–9, B_5H_9; hexaborane–10, B_6H_{10}; octaborane–12, B_8H_{12}; decaborane–14, $B_{10}H_{14}$ etc. (*ii*) B_nH_{n+6} *type e.g.*, tetraborane, B_4H_{12}; pentaborane–11, B_5H_{11}; hexaborane–12, B_6H_{12}; enneaborane–15, B_9H_{15}; decaborane–16, $B_{10}H_{16}$ etc.

Boranes are the examples of electron-deficient compounds. Electron-deficient compounds are those in which the total number of atomic orbitals available on all the atoms of the compound is more than the total number of valence-electrons.

Diborane, B_2H_6

Preparation of Diborane.

B_2H_6 is prepared :

1. *By the action of ionic hydrides like NaH, CaH_2 etc. on BCl_3*

$$6NaH + 2BCl_3 \longrightarrow 6NaCl + B_2H_6$$
$$3CaH_2 + 2BCl_3 \longrightarrow 3CaCl_2 + B_2H_6$$

2. *By the action of boron trifluoride ether complex, $(C_2H_5)_2O.BF_3$ on metallic hydrides like LiH, $Li[BH_4]$, $Na[BH_4]$ etc.*

(*i*) $6LiH + 8(C_2H_5)_2O.BF_3 \longrightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$

(*ii*) $3Li[BH_4] + (C_2H_5)_2O.BF_3 \longrightarrow 2B_2H_6 + 3LiF + (C_2H_5)_2O$

(*iii*) $3Na[BH_4] + 4(C_2H_5)_2O.BF_3 \longrightarrow 2B_2H_6 + 3NaBF_4 + 4(C_2H)_2O$

Reaction (*i*) is used for the manufacture of B_2H_6 in U.S.A.

3. *By reducing BF_3 with LiH, Li[BH_4] or Na[BH_4].*

(*a*) $8BF_3 + 6LiH \longrightarrow 6LiBF_4 + B_2H_6$

(*b*) $BF_3 + 3Li[BH_4] \xrightarrow{\text{Ether}} 3LiF + 2B_2H_6$

(*c*) $BF_3 + 3Na[BF_4] \longrightarrow 3NaF + 2B_2H_6$

B_2H_6 is generally produced *in situ* in reactions (*b*) and (*c*).

4. *By reducing BCl_3 with Li[AlH_4].*

$$4BCl_3 + Li[AlH_4] \longrightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$$

5. *By reducing vapours of BCl_3 by molecular hydrogen.*

$$2BCl_3\ (\textit{vapours}) + 6H_2 \longrightarrow B_2H_6 + 6HCl$$

6. *By treating an alkali metal borohydride with HCl.*

$$2Li[BH_4] + 2HCl \longrightarrow B_2H_6 + 2LiCl + 2H_2\uparrow$$

$$2Na[BH_4] + 2HCl \longrightarrow B_2H_6 + 2NaCl + 2H_2\uparrow$$

Properties of Diborane.

1. It is an inflammable colourless gas with a sticky sweet odour and is extremely toxic. It is an extremely reactive gas and hence should be handled in a special apparatus so that it comes in contact only with glass and mercury.

2. Decomposition. (*a*) *By heat.* It is stable at low temperatures only in the absence of moisture. At higher temperatures B_2H_6 gets decomposed into a number of higher boranes. For example :

$$5B_2H_6 \xrightarrow{\text{115°C (U-tube)}} 2B_5H_{11} + 4H_2$$

$$2B_2H_6 \xrightarrow{-78\text{ to }100°\text{C}} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow{\text{100°C (sealed bulb)}} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow[\text{(tube)}]{\text{250°C, 120 mm.}} B_5H_9 + B_5H_{11} + 5H_2$$

$$5B_2H_6 \xrightarrow{\text{200–250°C}} 2B_5H_9 + 6H_2$$

(*b*) *By water* (*Hydrolysis*). It is readily decomposed by water into boric acid and H_2.

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

(*c*) *By aqueous alkalies* (*Hydrolysis*). When B_2H_6 is passed into a *concentrated* aqueous solution of KOH at 0°C, reaction occurs and the solution obtained on evaporation in vacuo deposits potassium hypoborate, $K(BH_2OH.BH_2OH)$ or $K_2(B_2H_6O_2)$.

$$B_2H_6 + 2KOH \xrightarrow{0°C} \underset{\text{Potassium hypoborate}}{K_2(B_2H_6O_2)}$$

If KOH solution is *diluted*, then potassium hypoborate, $K_2(B_2H_6O_2)$ is converted into potassium metaborate, KBO_2.

$$K_2(B_2H_6O_2) + 2H_2O \longrightarrow 2KBO_2 + 5H_2$$

The evolution of H_2 by the action of aqueous alkalies makes B_2H_6 as a useful reducing agent.

3. Action of lithium ethyl (LiC_2H_5) and alkali metal hydrides. LiC_2H_5 and alkali metal hydrides suspended in ether react with B_2H_6 and produce alkali metal borohydrides, MBH_4

$$2B_2H_6 + 2LiC_2H_5 \longrightarrow 3LiBH_4 + B(C_2H_5)_3$$
$$B_2H_6 + 2LiH \longrightarrow 2LiBH_4$$
$$B_2H_6 + 2NaH \longrightarrow 3NaBH_4$$

4. Reaction with trimethyl aluminium, $Al(CH_3)_3$. Aluminium borohydride, $Al(BH_4)_3$ is produced

$$Al(CH_3)_3 + 2B_2H_6 \longrightarrow B(CH_3)_3 + Al(BH_4)_3$$

5. Action of O_2 (Ignition or combustion). Pure B_2H_6 undergoes no change when mixed with dry air or O_2 at room temperature, but it may ignite (*i.e.* burn), if impure. In this reaction a large amount of energy is produced.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 480 \text{ Kcal}$$

The production of large amount of heat in the above reaction makes B_2H_6 a useful rocket fuel.

6. Action of halogens. It reacts with halogens (not iodine) under different conditions to give different products.

$$B_2H_6 + 6Cl_2 \xrightarrow{25°C} 2BCl_3 + 6HCl \quad (\textit{Vigorous reaction})$$

$$B_2H_6 + Br_2 \xrightarrow{100°C} B_2H_5Br + HBr \quad (\textit{Slow reaction})$$

7. Action of halogen acids. B_2H_6 reacts readily with HCl acid in presence of $AlCl_3$ as catalyst to form chlorodiborane (B_2H_5Cl). With HBr it reacts at 90°C in presence of $AlBr_3$ to give B_2H_5Br while with HI at 50°C in the absence of a catalyst to give B_2H_5I.

$$B_2H_6 + HX\ (X = Cl, Br, I) \longrightarrow B_2H_5X + H_2$$

8. Action of sodium or potassium amalgam. When B_2H_6 is treated with sodium or potassium amalgam (*reducing agents*) in cold, crystalline product of the composition, $B_2H_6.2Na$ or $B_2H_6.2K$ is formed.

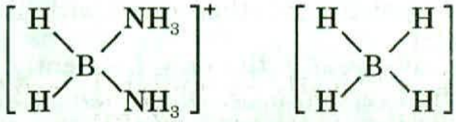
$$2Na\ (\textit{in the form of amalgam}) + B_2H_6 \rightarrow B_2H_6.2Na$$
$$2K\ (\textit{in the form of amalgam}) + B_2H_6 \rightarrow B_2H_6.2K$$

9. Reaction with NH_3. Diborane reacts with NH_3 giving various products depending on the experimental conditions. For example :

(*a*) When B_2H_6 reacts with *excess of NH_3 at low temperature* (–120°C), it forms an addition compound called *diammoniate of diborane*, $B_2H_6.2NH_3$ which forms a conducting solution in liquid ammonia.

$$B_2H_6 + 2NH_3\ (\textit{Excess}) \xrightarrow{\text{Low tempt. (–120°C)}} \underset{\substack{\text{Diammoniate}\\ \text{of diborane}}}{B_2H_6.2NH_3}$$

$B_2H_6.2NH_3$ is a white non-volatile solid and is soluble in water. It is an ionic compound and hence is represented, as $[BH_2(NH_3)_2]^+.\ [BH_4]^-$ or as follows :



The formation of $B_2H_6.2NH_3$ represents the only case of non-symmetrical cleavage of B_2H_6 by consecutive substitution.

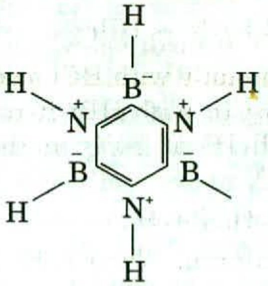
(*b*) With *excess* of NH_3 and at *high temperature*, boron nitride, $(BN)_x$ is formed.

$$xB_2H_6 + 2xNH_3\ (\textit{Excess}) \xrightarrow{\text{High temp.}} \underset{\text{Boron nitride}}{2(BN)_x} + 6xH_2$$

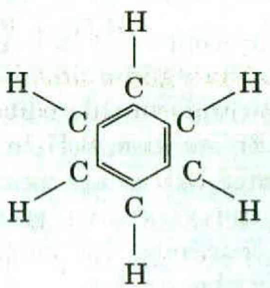
(*c*) When B_2H_6 and NH_3 are treated at high temperature in 1 : 2 ratio, *borazole* (also called *borazine*), $B_3N_3H_6$ is formed.

$$3B_2H_6 + 6NH_3 \xrightarrow{\text{High temp.}} \underset{\text{Borazole}}{2B_3N_3H_6} + 12H_2$$

Borazole has a flat hexagonal ring structure containing —BH— and —NH groups alternately. Thus it has an analogous electronic structure to that of C_6H_6 and is, therefore called *inorganic benzene*.



Borazine
($B_3N_3H_6$)



Benzene
(C_6H_6)

10. Formation of adducts. Because of its electron-deficient nature, B_2H_6 reacts with a number of molecules, having lone pairs of electrons [*e.g.*, $(CH_3)_2O$, $(CH_3)_2S$, CO, PF_3, $N(CH_3)_3$ etc.] (Lewis bases) to form adducts or addition compounds. Thus in these reactions B_2H_6 acts as an acceptor (Lewis acid) and the molecules like $(CH_3)_2O$, $(CH_3)_2S$ etc. act as donors (Lewis bases).

Acceptor (Lewis acid)		***Donor (Lewis base)***		***Adducts or addition compounds***
$\frac{1}{2}\ B_2H_6$	+	$(CH_3)_2O$ Ether	→	$(CH_3)_2O \rightarrow BH_3$ Dimethyl ether borane
$\frac{1}{2}\ B_2H_6$	+	$(CH_3)_2S$ Thioether	→	$(CH_3)_2S \rightarrow BH_3$
$\frac{1}{2}\ B_2H_6$	+	CO	$\xrightarrow[\text{20 atom.}]{200^\circ C}$	$CO \rightarrow BH_3$ Carbonyl borine

Uses of Diborane.

Among the boranes, diborane is the only frequently used borane, although other boranes may also find certain uses. Diborane is used : (*i*) as rocket fuel for supersonic bombers, (*ii*) for the preparation of high energy fuels and propellents, (*iii*) for the preparation of higher boranes, organic boron compounds and metal boron hydrides like $LiBH_4$, $NaBH_4$ etc. (*iv*) as a reducing agent in organic reactions, (*v*) as a catalyst in polymerisation reactions (*vi*) for welding torches.

Hydrogen-bridge Structure of Diborane.

Electron diffraction and infra-red spectroscopic studies of this molecule have shown that B_2H_6 has *hydrogen-bridge structure* shown in Fig. 24.1.

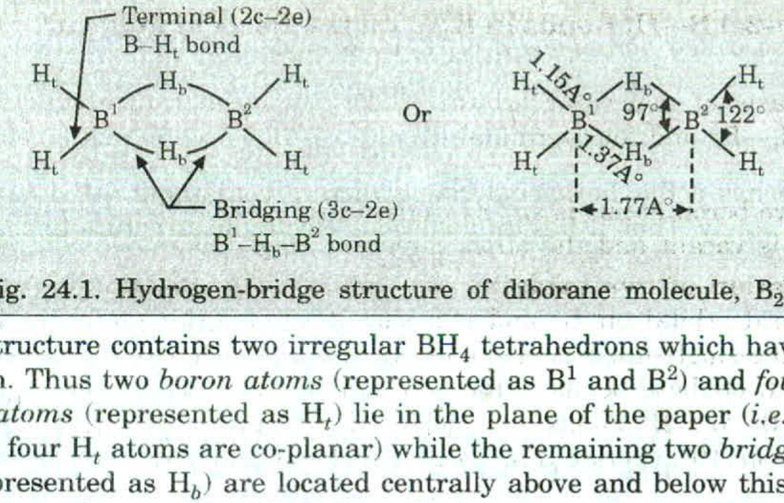


Fig. 24.1. Hydrogen-bridge structure of diborane molecule, B_2H_6

This structure contains two irregular BH_4 tetrahedrons which have one edge in common. Thus two *boron atoms* (represented as B^1 and B^2) and *four terminal hydrogen atoms* (represented as H_t) lie in the plane of the paper (*i.e.* two boron atoms and four H_t atoms are co-planar) while the remaining two *bridge hydrogen atoms* (represented as H_b) are located centrally above and below this plane and thus prevent the rotation between the two boron atoms. Specific heat measurements also show that rotation is hindered. Thus we see that the plane containing the two boron atoms and four terminal hydrogen atoms is perpendicular to that containing the two bridging hydrogen atoms. The following points may be noted from the hydrogen-bridge structure :

(*i*) B^1—H_t bond length = B^2—H_t bond length = 1.19A°. This bond length is almost equal to that expected for a single bond given by the sum of the single-bond normal covalent radii of boron and hydrogen. *i.e.* $r_B + r_H = 0.85 + 0.30 = 1.15A^\circ \simeq 1.19A^\circ$.

(*ii*) B^1—H_b bond length = B^2—H_b bond length = 1.37A° which is greater than $r_B + r_H$ (= 1.15A°).

(*iii*) B^1—B^2 bond length = 1.77A°.

(*iv*) $H_tB^1H_t$ bond angle = $H_tB^2H_t$ bond angle = 122° while $H_bB^1H_b$ bond angle = $H_bB^2H_b$ bond angle = 97°.

(*v*) B_2H_6 molecule has two types of bonds discussed below :

(*a*) *Four terminal (2c–2e)B—H_t bonds.* Each of these bonds is formed by the sharing of two electrons between two atoms (or nuclei) namely B and terminal H-atom (*i.e.* H_t atoms). This bond as called *terminal two-centre-two-electron* B—H_t bond and is denoted as (2*c*—2*e*) B—H_t bond. It is a normal σ-covalent bond.

(*b*) *Two bridging* (3c–2*e*) B^1—H_b—B^2 *bonds.* Each of these bonds is formed by the sharing of two electrons between three atoms (or nuclei) namely B^1, B^2 and bridging H (H_b) atoms. This bond is called bridging *three-centre-two-electron* B^1—H_b—B^2 *bond* and is denoted as (3*c*—2*e*) B—H_b—B bond. This bond makes a bridge between two B-atoms and is also called *bannana bond.*

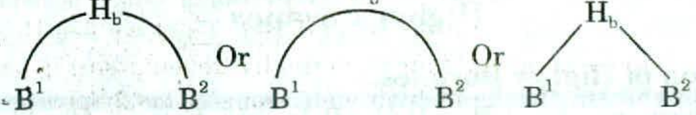
The above discussion makes it evident that the terminal (2*c*—2*e*) B—H_t bond holds two atoms together while the bridging (3*c*—2*e*) B^1—H_b—B^2 bond holds three atoms (B^1, B^2 and H_b) together.

Explanation of the Formation of Bridging (3c-2e) B^1—H_b—B^2 and Terminal (2c-2e) B—H_t Bonds in B_2H_6 on the Basis of Molecular Orbital Theory.

On the basis of molecular orbital theory the formation of two bridging (3*c*–2*e*) B^1—H_b—B^2 and four terminal (2*c*–2*e*) B—H_t bonds can be explained as follows :

Each of two boron atoms is sp^3 hybridised and gives four sp^3 hybrid orbitals one of which is vacant and the other three are singly filled.

(*a*) Formation of two bridging (3*c*—2*e*) B^1—H_b—B^2 bonds. One singly-filled sp^3 hybrid orbital on B^1 and one vacant sp^3 hybrid orbital on B^2 atom overlap with the singly-filled 1*s* orbital on H_b atom to form two (3*c*–2*e*) B^1—H_b—B^2 bonds. Each of these bonds contains a pair of electrons and forms a bridge between two B^1 and B^2 atoms. Obviously each of the bonds results from sp^3 (B^1)—1*s* (H_b)—sp^3 (B^2) overlap (Fig. 24.2). This bond is generally represented as :



(*b*) Formation of four terminal (2*c*—2*e*) B—H_t bonds. We have seen that two of the four sp^3 hybrid orbitals on each boron atom are consumed in the formation of one bridging (3*c*–2*e*) B^1—H_b—B^2 bond while the remaining two sp^3 hybrid orbitals on each boron atom are left with us. Each of these hybrid orbitals is singly-filled. Each of these two singly-filled sp^3 hybrid orbitals of each boron atom overlaps with singly-filled 1*s* orbital of H_t atom to form terminal (2*c*–2*e*) B—H_t bond (Fig. 24.2). This bond is a normal σ-bond and results from sp^3 (B)—1*s* (H_t) overlap. Thus we see that B_2H_6 has four terminal (2*c*–2*e*) B—H_t bonds.

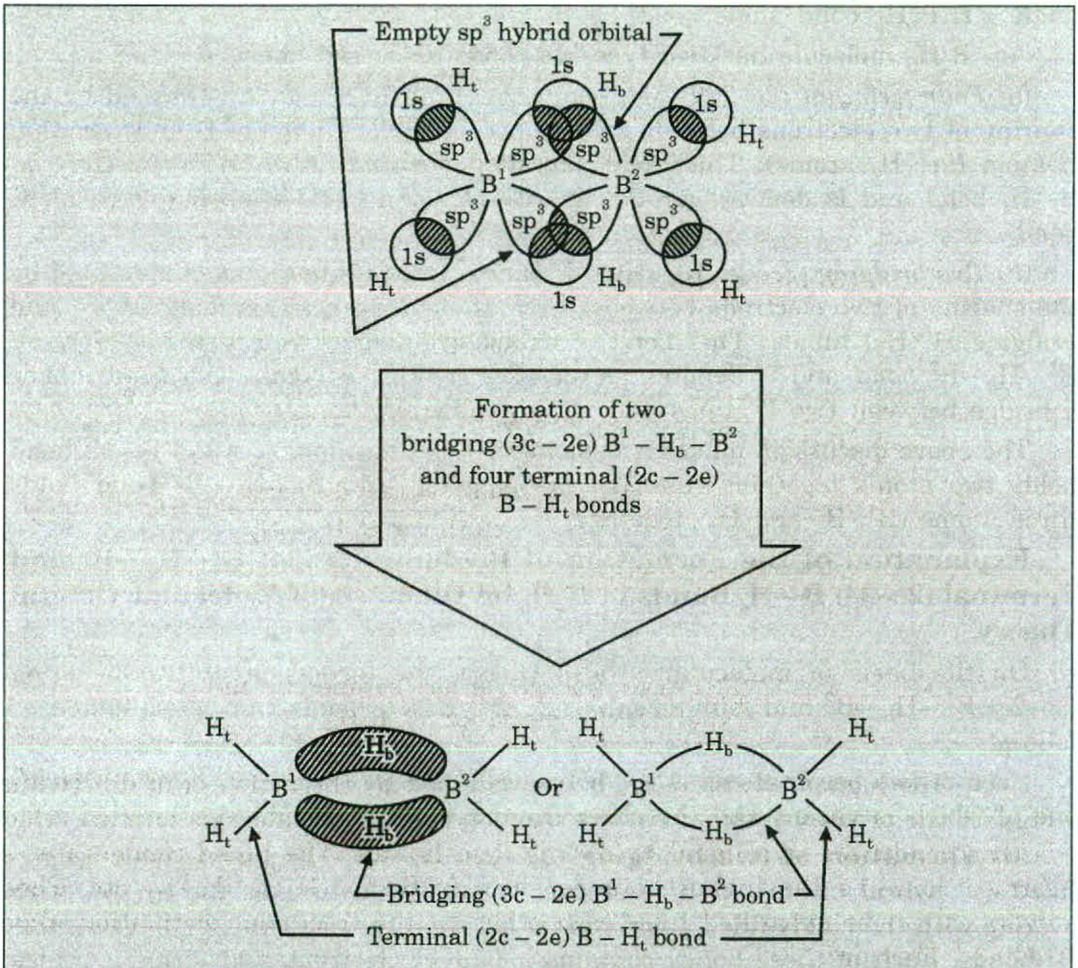


Fig. 24.2 Formation of two bridging (3*c*–2*e*) B^1—H_b—B^2 and four terminal (2*c*–2*e*) B—H_t Bonds in B_2H_6 molecule.

Higher Boranes

Preparation of Higher Boranes.

(*i*) Higher boranes like B_4H_{10}, B_5H_9, B_5H_{11}, $B_{10}H_{14}$ can be obtained : (*a*) by the thermal decompositian of B_2H_6 at different temperatures and (*b*) by the conversion of one higher borane into the other by heating it. Both these methods have been shown in Fig. 24.3.

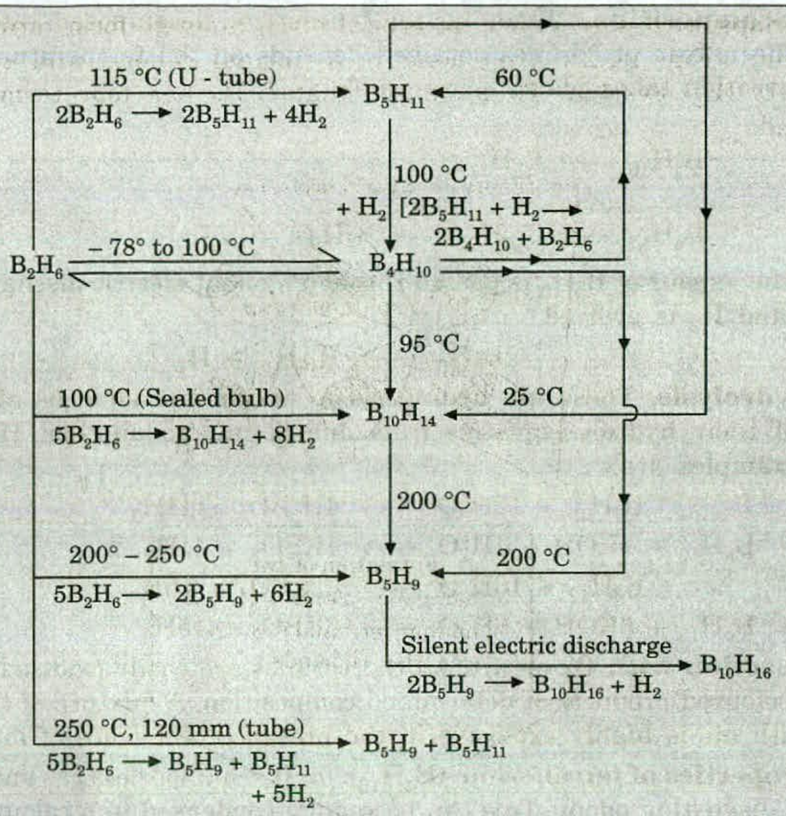


Fig. 24.3. Preparation of various boranes by the thermal decomposition of B_2H_6.

(*ii*) The higher boranes can also be obtained by the action of of dil. HCl on Mg_3N_2. The product obtained by this reaction is a volatile gaseous mixture which is then condensed to a liquid by cooling it in liq. air. The liquid condensates so formed contains the higher boranes such as B_4H_{10}, H_5H_9, H_5H_{11} etc. These hydrides can be separated from each other by the fractional distillation under reduced pressure.

(*iii*) **Wurtz-type synthesis.** This method has been used to prepare B_4H_{10}.

$$2B_2H_5I + 2Na(Hg) \longrightarrow B_4H_{10} + 2NaI$$

Properties of Higher Boranes.

(*i*) Physical state. All the higher boranes are volatile gases, liquids or solids.

(*ii*) Melting and boiling points. These are given as follows :

Borane	***m.pt.* (°C)**	***b.pt.* (°C)**	***Borane***	***m.pt.* (°C)**	***b.pt.* (°C)**
B_4H_{10}	–120	18	B_6H_{10}	–62.3	108
B_5H_9	–46.6	48	B_6H_{12}	–82.3	80–90
B_5H_{11}	–123	63	$B_{10}H_{14}$	–92.7	213

***(iii)* Decomposition.** When heated, these are decomposed into different boranes. The nature of boranes obtained depends on the temperature at which the decomposition takes place. For example :

$$B_4H_{10} \xrightarrow{60°C} B_5H_{11}$$

$$B_4H_{10} \xrightarrow{95°C} B_{10}H_{14} \xrightarrow{200°C} B_4H_9$$

When the vapour of B_5H_9 is passed through a silent electric discharge, $B_{10}H_{16}$ is formed and H_2 is evolved.

$$2B_5H_9 \longrightarrow B_{10}H_{16} + H_2 \uparrow$$

***(iv)* Hydrolysis.** These are hydrolysed by water and aqueous alkalies, but the rate of their hydrolysis varies from one borane to another. Hydrogen is evolved. Examples are :

$$\begin{aligned} B_4H_{10} + 12H_2O &\longrightarrow 4H_3BO_3 + 11H_2 \\ B_4H_{10} + 4KOH + 4H_2O &\longrightarrow 4KBO_2 + 11H_2 \\ B_6H_{12} + 16H_2O &\longrightarrow 6H_3BO_3 + 15H_2 \\ B_6H_{12} + 6KOH + 6H_2O &\longrightarrow 6KBO_2 + 15H_2 \end{aligned}$$

***(v)* Reaction with O_2 or air.** All the boranes are easily oxidised by O_2 and give dark coloured products of determined composition. A mixture of the gaseous boranes with air is highly explosive in the presence of a trace of moisture.

***(vi)* Properties of tetraborane (B_4H_{10}).** *(a)* It is a colourless gas and poisonous gas with a disgusting odour. This can be readily condensed to a colourless liquid with m.pt. = –120°C and b.pt. = 18°C.

(b) It is soluble in dry benzene but slightly so in cold water.

(c) Decomposition. It is stable in the absence of air and moisture. It decomposes at ordinary temperature, giving H_2 and lower boranes.

(d) Action of HCl. With HCl, H_2 is liberated

$$B_4H_{10} + HCl \longrightarrow B_4H_9Cl + H_2$$

(e) Reaction with CO. B_4H_{10} reacts with CO at 120°C in a hot-cold flow reactor and gives the carbonyl adduct, B_4H_8CO :

$$B_4H_{10} + CO \longrightarrow B_4H_8CO + H_2$$

***(vii)* Properties of pentaborane—9 (B_5H_9).** Some of the reactions shown by B_5B_9 are :

$$B_5H_9 + C_2H_4 \xrightarrow{AlCl_3} B_5H_8C_2H_5$$

$$B_5H_9 + 2LiH \xrightarrow{\text{Diethyl ether}} Li_2B_5H_{11}$$

$$B_5H_9 + 2Na(Hg) \xrightarrow{\text{Ether}} Na_2B_5H_9 \xrightarrow{\text{Vacuum}} B_5H_9$$

$$B_5H_9 + 2Li \xrightarrow{\text{Liq. } NH_3} Li_2B_5H_9$$

(*viii*) Properties of pentaborane—11 (B_5H_{11}). In presence of weak Lewis bases like ethers, amines etc., B_5H_{11} gives B_6H_{10} and B_2H_6

$$2B_5H_{11} \xrightarrow[\text{a Lewis base}]{\text{In presence of}} B_6H_{10} + 2B_2B_6$$

B_5H_{11} reacts with CO in a hot-cold flow reactor and gives the carbonyl adduct, B_4H_8CO.

$$B_5H_{11} + 2CO \longrightarrow B_4H_8CO + BH_3CO$$

When heated with H_2 at 100°C, it gives B_4H_{10}.

(*ix*) Properties of decaborane—l4 ($B_{10}H_{14}$). Some reactions shown by this hydride are :

$$B_{10}H_{14} + NaH \xrightarrow{(C_2H_5)_2O} NaB_{10}H_{13}.(C_2H_5)_2O + H_2$$

$$B_{10}H_{14} \xrightarrow[\text{liq. } NH_3]{2Na^+ \text{ in}} (Na^+)_2\ [B_{10}H_{14}]^{2-}$$

$$B_{10}H_{14} + 2L\ (L = CH_3CN, R_3N, R_3P) \xrightarrow{\Delta} B_{10}H_{12}L_2 + H_2$$

L is the weakly basic liquid.

$$B_{10}H_{14} + CH_3MgI \longrightarrow B_{10}H_{13}MgI + CH_4$$

Question with Answers

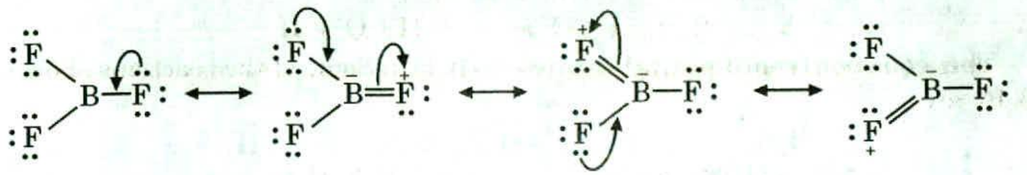
Q.1 Explain the following, giving appropriate reasons for your answer.

(*i*) BF_3 exists but BH_3 does not.

(*ii*) B–F bond length in BF_3 is shorter than that in BF_4^-.

(*iii*) Borazine or borazole ($B_3N_3H_6$) is called inorganic benzene.

Ans : (*i*) Due to pπ – pπ back bonding, the lone pair of electrons of F is denoted to the B-atom. This delocalization reduces the deficiency of electrons on B, thereby increasing the stability of BF_3 molecule.



Due to absence of lone pair of electrons on H-atom, this compensation does not occur in BH_3. In other words, electron deficiency of B stays and hence to reduce its electron deficiency, BH_3 dimerises to form B_2H_6.

(*ii*) Because of double bond character of B–F bonds in BF_3, it has a shorter B–F bond length than in BF_4^-.

(*iii*) Borazine is called inorganic benzene because the structure of borazine is similar to that of benzene. It is also isoelctronic and isosteric with benzene. Like C-atom in C_6H_6, both N^+ and B^- in $B_3N_3H_6$ are sp^2 hybridised.

Q.2 How is B_2H_6 converted into borazine ($B_3N_3H_6$) ?

Ans : At low temperature, diborane combines with ammonia to form an addition compound.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{Low temp.}} B_2H_6.2NH_3 \text{ (Addition Compound)}$$

When this addition compound is heated to 473K, it decomposes to form a volatile compound called borazine.

$$3[B_2H_6.\ 2NH_3] \xrightarrow{473K} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

Q.3 Compound X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen along with other products. The compound Y reacts with air explosively resulting in boron trioxide. Identity X and Y. Give balanced equations involved in the formation of Y and its reaction with air. Draw the structure of Y.

Step 1. *To determine the molecular formula and structure of compound* **Y**.

(*i*) Since the hydride **Y** reacts with air forming boron trioxide, **Y** *must be hydride of boron.*

(*ii*) %H = 21.72% (*Given*)

$\therefore$ %B = 100 − 21.72 = 78.28%

$$\text{Now B : H} = \frac{78.28}{11} : \frac{21.72}{1} = 7.12 : 21.72 = 1 : 3$$

$\therefore$ E.F of **Y** = BH_3

Since boron froms two types of hydrides, *i.e.* B_nH_{n+4} (nidoboranes) and B_nH_{n+6} (arachnoboranes), **Y** must be a nidoborane with $n = 2$. Thus, M.F. of **Y** = B_2H_6. If **Y** is B_2H_6 (diborane), then its structure must be as follows :

Bridges B.....H = 134 pm Terminal B − H = 119 pm

Step 2. *To detrmine the structure of the compound* **X**.

Since compound **Y** *i.e.*, B_2H_6 is formed by reduction of compound **X** with $LiAlH_4$, **X** must either BCl_3 or BF_3.

$$\underset{\mathbf{X}}{4BF_3} + 3LiAlH_4 \xrightarrow{\text{ether}} \underset{\mathbf{Y}}{2B_2H_6} + 3LiAlF_4$$

The equation representing the reaction of **Y** with O_2 may be written as follows.

$$\underset{\text{Diborane (Y)}}{B_2H_6} + 3O_2 \longrightarrow \underset{\text{Boron trioxide}}{B_2O_3} + 3H_2O$$

Thus **X** = BF_3 and **Y** = B_2H_6.

University Questions

1. Describe the hydrides of boron. *(Meerut B.Sc. 86; Punjab 82)*

2. Give the preparation, properties and uses of boron hydrides. *(Lucknow 80)*

3. Discuss the preparation of B_2H_6. *(Delhi Hons 87)*
Allahabad 87, 88; Delhi 88; Agra 88)

4. How does diborane react with water, ammonia and NaH. *(Delhi 82)*

5. Discuss the structure and bonding of B_2H_6.
(Raj 87; Meerut 83, 84, 85, 88;
Delhi Hons. 87; Utkal 85; Madras 86; Gorakhpur 82;
Allahabad 87, 88; Delhi 88; Bundelkhand 88)

6. Complete and balance the equation :
$B_2H_6 + LiAlH_4 \rightarrow$ ...... *(Meerut 83)*

7. Explain why : BF_3 is monomeric while BH_3 is dimeric. *(Delhi 99)*

8. Discuss the structure and constitution of diborane. *(Allahabad 99)*

9. Write note on "Hydrides of boron." *(Kanpur 2000)*

10. Describe the preparation, properties and constitution of diborane. *(Avadh 2000)*

11. (*i*) Explain why diborane is electron deficient compound.
(*ii*) Discuss the structure of B_2H_6 molecule. *(Lucknow 2001)*

12. Write the formula and structure of diborane. *(Meerut 2009)*

CHAPTER

25

General Characteristics of Group 14 (IV A) Elements : Carbon Group Elements

Group IV A of the long form periodic table consists of *five element viz.* Carbon (C), *Silicon* (Si), *Germanium* (Ge), *Tin* (Sn) and *Lead* (Pb). Carbon is an essential constituent of all organic matter while silicon is the main constituent of inorganic matter.

Position of Carbon Group Elements in the Periodic Table

The inclusion of carbon group elements in the same sub-group of the periodic table is justified by the following general characteristics of these elements.

I. Electronic Configurations.

The electronic configurations of these elements are : C(Z = 6) → 2, 4 ($2s^2p^2$); Si (Z = 14) → 2, 8 4($3s^2p^2$); Ge(Z = 32) → 2, 8, 18, 4 ($4s^2p^2$); Sn (Z = 50) → 2, 8, 18, 18, 4($5s^2p^2$); Pb(Z = 82) → 2, 8, 18, 32, 18, 4 ($6s^2p^2$). These configurations show that these elements have four electrons in their ultimate (valence) shell, two of which are in *s*-orbital while the remaining two are in *p*-orbitals. Hence these elements possess s^2p^2 configuration in the valence shell. The penultimate shell of C contains s^2 electrons (saturated), of Si contains s^2p^6 electrons (saturated), of Ge contains $s^2p^6d^{10}$ electrons (saturated) while of Sn and Pb contain $s^2p^6d^{10}$ electrons (unsaturated). This shows why C differs from Si and these two (*i.e.*, C and Si) from the other members of this sub-group.

II. Physical Properties and Gradation in Them.

Some of the physical properties of these elements are discussed below :

1. Occurrence. Carbon is the only element of this group which occurs in the *free state* as *diamond, graphite* and *coal.* In the combined state it occurs as *hydrocarbons, carbohydrates* and *carbon dioxide* in the atmosphere. Silicon is found as a major constituent in rocks either in the form of *silica* or *silicates.* Germanium is a *rare element.* Tin is mainly found in the form of *tinstone*, SnO_2 while lead occurs as mineral *galena*, PbS.

2. Allotropy. Excepting Pb, all other elements of this group show *allotrophy*, *i.e.* these elements exist in different allotropic forms. For example : (*i*) Carbon exists into the following two allotropic forms. (*a*) Crystalline forms: diamond and graphite. (*b*) Amorphous forms which are microcrystalline forms, *e.g.*, coal, coke, charcoal etc. (*ii*) silicon exists into two forms. (*a*) Crystalline form. (*b*) Amorphous form. It is the common variety of silicon. (*iii*) Germanium exists into two crystalline forms. (*iv*) Tin exists into three allotropic forms. (*a*) White tin (*b*) Grey tin (*c*) Rhombic tin.

3. Atomic volumes. These increase on moving down the group from C to Pb.

4. Density. Density of these elements shows a regular increase from C to Pb.

5. Atomic and ionic radii. Like atomic volumes, these values also increase from C to Pb.

6. Metallic and non-metallic character. The change from non-metallic to metallic character with the increase in atomic number is best illustrated by the elements of this group. The first two elements viz., C and Si are distinctly *non-metals,* although electrical properties of Si are like those of a semi-metal (*i.e.*, a *metalloid*); the third element *viz.*, Ge is partly a metal and partly a non-metal (*i.e.*, it is a *metalloid*) while the last two elements *viz.*, Sn and Pb are distinctly *metals.* Thus :

$$\underbrace{C,\ Si}_{Non\text{-}metals} \qquad \underset{Metalloid}{Ge} \qquad \underbrace{Sn,\ Pb}_{Metals}$$

$$\text{—— } Metallic\ character\ increases \longrightarrow$$

The change from non-metallic to metallic character with the increase in atomic number is due to the *reduction* in *effective nuclear charge* and *increase in the number of available orbitals* with the increase in the size of the atoms.

7. Melting and boiling points. As we move down the group from C to Pb, the melting points as well as boiling points *generally decrease*, although the decrease is not in a regular order. This decrease in melting points as well as in boiling points indicates that interatomic forces also decrease in the same direction. The melting and boiling points of C and Si are notably *high* because of the tendencies of these elements to form *giant molecules*.

8. Ionisation energies. The ionisation energy values decrease on moving down the group from C to Pb, although the decrease does not occur in a regular order. The irregularity in the decrease of these values is due to the filling of intervening *d*-orbitals in case of Ge and Sn end *f*-orbitals in case of Pb which are not able to screen the valence-electrons *effectively* in the elements following them.

9. Electronegativity. Carbon is the most electronegative element of this sub-group and the electronegativities decrease with the rise of atomic number but not in a regular manner. This is probably due to the filling of the *d*-orbitals in case of Ge and Sn and *f*-orbitals in case of Pb.

10. Valency. The elements are all tetracovalent. Their ionization potentials being very high, the existence of simple M^{4+} ions is unlikely. On account of their low electronegativity values M^{4-} ions also do not normally exist. Carbon does form C_2^{2-} ions in salt-like carbides, *e.g.*, calcium carbide, $Ca^{2+}\ C_2^{2-}$. C and Si do not form M^{4+} or M^{2+} ions. The rest of the elements, on the other hand, apart from showing *tetracovalency*, exhibit *bielectrovalency* also. Thus Ge, Sn and Pb give stable bivalent ions *viz.*, Ge^{2+}, Sn^{2+} and Pb^{2+}.

11. Oxidation states. (*a*) positive oxidation states and inert pair effect. Carbon and silicon show + 4 oxidation states while Ge, Sn and Pb show + 2 as well as + 4 oxidation states. The occurrence of + 2 and + 4 oxidation states in case of Ge, Sn and Pb is explained as follows : when only two *np* electrons from the ns^2p^2 configuration are lost, we get the elements in + 2 oxidation state *i.e.* M^{2+} cations are obtained. In this case the two ms^2 electrons remain inert and hence are not lost in the formation of M^{2+} cations. This pair of ns^2 electrons is called inert pair of electrons. Since the stability of inert pair of *ns* electrons increases on moving down the group, the stability of + 2 oxidation state also increases in the same direction, *i.e.* the stability of M^{2+} cations inreases from Ge^{2+} to Pb^{2+}, *i.e.* $Ge^{2+} < Sn^{2+} < Pb^{2+}$.

When all the four ns^2p^2 electrons are lost, we get the elements in + 4 oxidation state, *i.e.* M^{4+} cations are formed. On descending the group stability of + 4 oxidation state decreases, *i.e.* the stability of M^{4+} cations decreases from Ge^{4+} to Pb^{4+}, *i.e.* $Ge^{4+} > Sn^{4+} > Pb^{4+}$.

Compounds of Ge^{2+} are less stable than those of Ge^{4+} ($Ge^{2+} < Ge^{4+}$) and hence the compounds of Ge^{2+} are readily changed (oxidised) into those of Ge^{4+}. In other words compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidising agents.

$$\underset{\substack{\text{Less stable}\\\text{(Reducing agent)}}}{\text{Ge}^{2+}\text{ compounds}} \xrightarrow[(-2e^-)]{\text{Oxidation}} \underset{\substack{\text{More stable}\\\text{(Oxidising agent)}}}{\text{Ge}^{4+}\text{ compounds}}$$

On similar grounds it can be shown that the compounds of Sn^{2+} (*e.g.* $SnCl_2$) are *less stable* than those of Sn^{4+} (*e.g.* $SnCl_4$) ($Sn^{2+} < Sn^{4+}$) and hence the compounds of Sn^{2+} are readily changed (oxidised) into those of Sn^{4+}. In other words, compounds of Sn^{4+} act as strong reducing agents while those of Sn^{4+} act as oxidising agents.

$$\underset{\substack{\text{Less stable}\\\text{(Reducing agent)}}}{\text{Sn}^{2+}\text{ compounds (\textit{e.g.} SnCl}_2)} \xrightarrow[(-2e^-)]{\text{Oxidation}} \underset{\substack{\text{More stable}\\\text{(Oxidising agent)}}}{\text{Sn}^{4+}\text{ compounds (\textit{e.g.} SnCl}_4)}$$

When we compare the stability of the compounds of Pb^{2+} and Pb^{4+} ions, we find that Pb^{2+} compounds (*e.g.* $PbCl_2$) are *more stable* than those of Pb^{4+} (*e.g.* $PbCl_4$) ($Pb^{2+} > Pb^{4+}$) and hence the compounds of Pb^{4+} are readily changed (reduced) into those of Pb^{2+}. In other words compounds of Pb^{4+} act as strong oxidising agents while those of Pb^{2+} act as reducing agent.

$$\underset{\substack{\text{Less stable}\\\text{(Oxidising agent)}}}{\text{Pb}^{4+}\text{ compounds (\textit{e.g.} PbCl}_4)} \xrightarrow[(+2e^-)]{\text{Reduction}} \underset{\substack{\text{More stable}\\\text{(Reducing agent)}}}{\text{Pb}^{2+}\text{ compounds (\textit{e.g.} PbCl}_2)}$$

Thus when we compare the stability of M^{2+} and M^{4+} cations of Ge, Sn and Pb, we find that their stability is in the order $Ge^{2+} < Ge^{4+}$; $Sn^{2+} < Sn^{4+}$; $Pb^{2+} > Pb^{4+}$.

***(b)* Negative oxidation states.** Since the electronegativities of these elements are low, they do not have much tendency to form the negative ions. However, carbon forms C^{4+} and C_2^{2-} ions in certain compounds, *e.g.* $Be_4^{2+}\ C_2^{4-}$ or Be_2C(Be^{2+} and C^{-4} ions), $Al_4^{3+}\ C_3^{4-}$ (Al^{3+} and C^{4-} ions), $Na^+\ CH_3^+$ (Na^+, C^{-4} and H^+ ions), $Na_2^+\ C_2^{2-}$ (Na^+ and C_2^{2-} ions), $Ca^{2+}\ C_2^{2-}$ (Ca^{2+} and C_2^{2-} ions).

12. Nature of M^{2+} and M^{4+} compounds. The nature of the compounds of M^{2+} and M^{4+} cations can be predicted by *Fajan's rule* which states that *the smaller the cation, the greater is the amount of covalent character in its compounds.* Since Sn^{4+} ion is smaller than Sn^{2+}, the compounds of Sn^{4+} are *covalent in nature* while those of Sn^{2+} are *ionic.* Similarly Pb^{4+} compounds are covalent and those of Pb^{2+} are ionic. In general the compounds of M^{4+} are covalent and those of M^{2+} are ionic. As we move down the group, the tendency of given cations to form ionic compounds increases.

13. *sp*^{3} hybridisation and cavalency of 4. The valence shell electronic configuration of these elements *viz.* $ns^2\, np_x^{\,1}\, np_y^{\,1}\, np_z^{\,0}$ shows that these elements have two unpaired electrons and, therefore, should be bi-covalent. But, in fact, all these elements show a covalency of 4. This is explained as due to the excitation of the atom which causes the promotion of one of the paired *ns-electrons* to the vacant *np* level in the same shell. In this way four half-filled orbitals become available in the excited state of the atom which mix together to give four sp^3 hybrid orbitals (sp^3 hybridisation) resulting in a tetrahedral structure and each having one unpaired electron.

14. Tendency of the elements to form homo chains (M—M chains) : catenation or self-linkage. All the elements of this group have a tendency to link with each other and thus form long chains of identical atoms. Such long chains of identical atoms are called *homo chains.* This type of linking of identical atoms with each other is called *catenation* or *self-linkage.* This property decreases on moving down the group from C to Pb. Thus carbon has the *maximum* property of catenation, silicon has much *lesser* tendency, germanium has still *lesser tendency* whereas tin and lead *hardly* show this property. The maximum tendency of catenation associated with carbon forms the basis of the multiplicity of carbon compounds in the field of organic chemistry.

It has been observed that the tendency of catenation of these elements *decreases* with the *decrease* of energy of M—M bond. Thus the M—M bond energy values (in KJ/mole) are : C—C, 348; Si—Si, 222; Ge—Ge, 167; Sn—Sn, 155. These values show that these tendency of these elements towards catenation is in the order : C > Si > Ge > Sn > Pb.

Thus it is easy to prepare compounds containing C—C chains upto twenty carbon atoms, while for Si and Ge it is not possible to extend Si—Si or Ge—Ge chains beyond six units. For Sn and Pb it is not possible to extend the Sn—Sn or Pb—Pb chain even beyond two units.

III. Chemical Properties and Gradation in Them.

Some of the properties shown by these elements and gradation in them are discussed below :

1. Formation of hydrides. All the elements of group IV A form the hydrides which are covalent in nature. Hydrides of MH_4 type are in the gaseous state. The volatility of these hydrides decreases with the increasing atomic number of the central atom. Thermal stability of these hydrides decreases steadily from CH_4 to PbH_4 as is evident from their decomposition temperatures given as CH_4 = 800°C,

SH_4 = 450°C, GeH_4 = 285°C, SnH_4 = 150°C, PbH_4 = 0°C. The decrease in stability from CH_4 to PbH_4 is due to the decrease in M—H bond (M = C, Si, Ge, Sn, Pb) energy in going from C to Pb. This order also shows that the hydrides of the heavier elements of this group are thermally unstable.

2. Formation of oxides. Elements of group IV A. form the oxides which are of three types *viz.* (*i*) Monoxides (MO type oxides) (*ii*) Dioxides (MO_2 type oxides), and (*iii*) other oxides like C_3O_2, Pb_3O_4, Pb_2O, Pb_2O_3 etc.

3. Formation of halides. All the elements of this group form halides like MX_4, MHX_3 (*e.g.* $CHCl_3$, $SiHF_3$ etc), MX_2 (*e.g.* $SiCl_2$, Si_2I_2 etc.) and catenated halides (*e.g.* $Si_{14}F_3$, $Si_{10}Cl_{22}$ etc.). The tetrahalides may be prepared either by heating the element with the appropriate halogen or by passing dry halogen over a heat-mixture of the dioxide and carbon.

$$M + 2X_2 \longrightarrow MX_4$$

$$\underset{(M = C,\ Si\ etc.)}{MO_2} + 2C + \underset{(X = Halogen)}{2X_2} \longrightarrow MX_4 + 2CO$$

The thermal stability of tetrahalides *decreases* from CX_4 to PbX_4. Thus : $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$. Thermal stability and volatality of the tetrahalides of the same element *decreases* from F^- to I^-. Thus $MF_4 > MCl_4 > MBr_4 > MI_4$.

The fluorides of carbon (fluoro.carbons) are, therefore, the *most, stable* and *inert*.

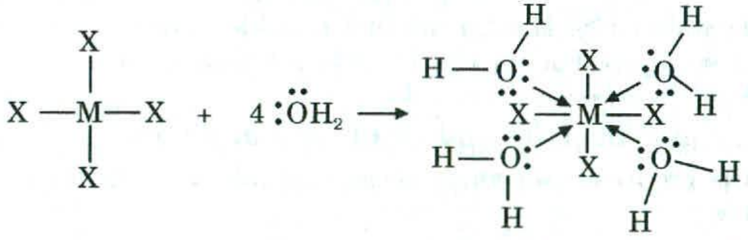
The tetrahalides of C are not hydrolysed by water while those of Si, Ge and Sn *get readily hydrolysed.* Thus :

$$CX_4 + H_2O \longrightarrow \text{No action}$$

$$\underset{\substack{(M = Si,\ Ge,\ Sn;\\ X = Halogen\ atom)}}{MX_4} + 4H_2O \longrightarrow M(OH)_4 + 4HX$$

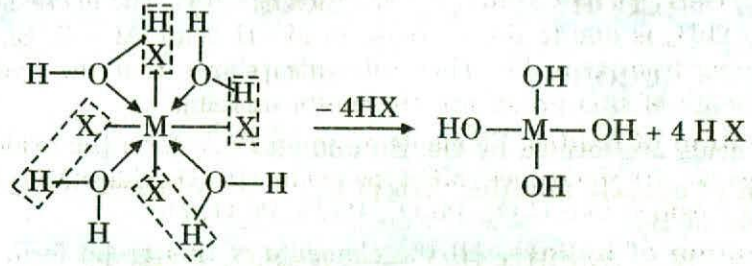
Actually the hydrolysis of tetrahalides takes place through the following two steps :

1st step. In this step oxygen atom of H_2O which acts as a *donor* attacks the central atom of the halide to form a coordinate bond with it and thus produces an *unstable intermediate compound*, $MX_4.4H_2O$.



Unstable intermediate compound ($MX_4.4H_2O$)

2nd step. In this step four HX molecules are eliminated from the unstable intermediate compound and hydroxide of the central element is formed. Thus X atoms of MX_4 molecule are replaced by OH^- ions.



Unstable intermediate compound
($MX_4.4H_2O$)

Why the tetrahalides of C are not hydrolysed while those of Si, Ge and Sn get readily hydrolysed can be explained as follows :

We know that C atom, being a member of 2nd period of the periodic table, has *no d*-orbitals in its valence shell and hence is unable to accommodate the lone pair donated by the donor oxygen atom of H_2O molecule to form an unstable intermediate compound. Thus the tetrahalides of C are not hydrolysed. On the other hand Si, Ge and Sn have vacant *d*-orbitals which can accept the lone pair and thus their tetrahalides get readily hydrolysed.

The ease with which the tetrahalides are hydrolysed by H_2O decreases from Si to Sn as the metallic character of the central atom increases in this order. Thus GeX_4 and SnX_4 tetrahalides are *less readily* hydrolysed than SiX_4 tetrahalides.

It may be mentioned here that empty orbitals are always available with any atom and they can be utilised, if sufficient energy is provided for the reaction to occur, *e.g.*, CCl_4 undergoes hydrolysis when superheated steam is used.

$$CCl_4 + H_2O\ (\textit{superheated steam}) \longrightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

Hydrolysis of tetrahalides of Pb follows essentially the same pattern, but due to the instability of tetravalent compounds of Pb, some decomposition of $PbCl_4$ to $PbCl_2$ also takes place.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

$PbCl_4$ is hydrolysed by H_2O as follows :

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

Excepting the tetrahalides of C, those of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ions like $[SiF_6]^{2-}$, $[GeX_6]^{2-}$ (X = F, Cl), $[SnX_6]^{2-}$ (X = F, Cl, Br I) and $[PbCl_6]^{2-}$ For example :

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

4. Formation of acids. (*a*) All the elements give acids of H_2MO_3 type, *e.g.*, H_2CO_3 (carbonic acid) and H_2SiO_3 (silicic acid), H_2GeO_3, (germanic acid), H_2SnO_3 (meta stannic acid) and H_2PbO_3 (meta plumbic acid). Sodium salts of these acids are stable.

(*b*) Carbon and silicon also form acids of the $(MOOH)_2$ type as shown below :

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid

$$\begin{array}{c} SiOOH \\ | \\ SiOOH \end{array}$$

Silicon oxalic acid

No such acids are formed by Ge, Sn and Pb.

5. Action of caustic alkalies. Except C, all are attacked by caustic alkalies with evolution of H_2.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2 \uparrow$$
$$Ge + 2NaOH + H_2O \longrightarrow K_2GeO_3 + 2H_2 \uparrow$$
$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2 \uparrow$$
$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + H_2 \uparrow$$

Differences of Carbon and Silicon From Other Elements of Group IVA.

Carbon and silicon differ from the remaining members of group IVA in the following respects :

1. Electronic configuration. Both carbon and silicon have respectively 2 and 8 electrons (configuration of inert gas) in their penultimate shell while the other elements of this group possess 18 electrons in their penultimate shell.

2. Metallic and non-metallic character. Both carbon and silicon are non-metals while Ge is a metalloid and Sn and Pb are metals.

3. Valency. Both C and Si show tetra-valency and do not give tetravalent or bivalent ions M^{4+} or M^{2+} ions). On the other hand Ge, Sn and Pb show tetra-covalency as well as form bivalent ions *viz.* Ge^{2+}, Sn^{2+} and Pb^{2+}.

4. Oxidation states. Both C and Si show an oxidation state of + 4 only while Ge, Sn and Pb show two types of oxidation states which are + 2 and + 4.

5. Catenation. Carbon and, to some extent, silicon have a tendency for catenation while other elements do not have this property to a great extent.

6. Nature of dioxide. CO_2 and SiO_2 are acidic while other dioxides (GeO_2, SnO_2 and PbO_2) are amphoteric.

7. Formation of acids. Carbon and silicon form the acids of the type.

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid

$$\begin{array}{c} SiOOH \\ | \\ SiOOH \end{array}$$

Silicon oxalic acid

while other elements do not give the acids of this type.

Comparison between Carbon and Silicon.

(A) Similarities. Both these elements belong to the same sub-group (group IVA) of the periodic table and have the same number of electrons (= 4) in their valence shell. It is for this reason that these elements have many similarities as discussed below :

(i) Electronic configuration. Both the elements have 4 electrons in their valence-shell as shown :

$$C\ (Z = 6) \longrightarrow 2,\ 4;\ Si\ (Z = 14) \longrightarrow 2,\ 8,\ 4$$

(ii) Occurrence. Both are widely distributed in nature. Carbon is an essential constituent of vegetable and animal kingdom, *i.e.*, of the organic compounds. Silicon is an essential constituent of mineral kingdom, *i.e.*, of the inorganic compounds.

(iii) Valency. Both are tetravalent. These elements show a covalency of four and form compounds by sharing of electrons.

(iv) Allotropy. Both show allotropy, *i.e.*, they exist in more than one form. Thus, carbon. occurs in two crystalline forms namely diamond and graphite and a number of amorphous forms such as coal, coke, charcoal etc. Silicon exists in two forms *viz.*, crystalline and amorphous.

(v) Formation of oxides. Both burn in oxygen to form acidic oxides.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

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

(vi) Formation of hydrides. Both form a number of covalent hydrides.

CH_4	C_2H_6	C_3H_8	C_4H_{10}
SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}

These are all colourless gases and burn in air to form oxides.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

Both CH_4 and SiH_4 can be prepared by similar methods, *i.e.*, by the action of water or acids on carbides and silicides, respectively.

$$Be_2C + 4HCl \longrightarrow 2BCl_2 + CH_4$$

$$Mg_2Si + 4HCl \longrightarrow 2BeCl_2 + SiH_4$$

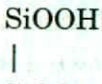
(vii) Formation of halides. Both form similar types of covalent halides.

CF_4	CCl_4	CBr_4	$CHCl_3$
SiF_4	$SiCl_4$	$SiBr_4$	$SiHCl_3$

(viii) Formation of acids. Both form similar types of acids, *e.g.*,

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

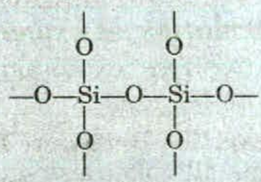
Oxalic acid



$$\begin{array}{c} SiOOH \\ | \\ SiOOH \end{array}$$

Silicon oxalic acid

(B) Dissimilarities. In some properties these elements differ from each other. The dissimilarity is due to the difference in the number of electrons in the penultimate shell (carbon has 2 electrons while silicon has 8 electrons). The points showing dissimilarity between these elements are given in the following table.

Carbon	Silicon
1. It has two electrons in the penultimate shell.	It has eight electrons in the penultimimate shell.
2. It is a black solid, melting point 3500°C.	It is a reddish brown solid, melting point 1410°C.
3. Some varieties of carbon, *i.e.*, graphite are good conductors of heat and electricity.	Bad conductor of heat and electricity.
4. It has a tendency to form long chains of identical atoms	It has a lesser tendency to form such chains.
5. No action with alkalies.	It reacts with fused alkalies to form H_2 $Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$
6. CO_2 is a gas. It has a linear structure. The carbon atom is attached to two oxygen atoms by double covalent bond. $O = C = O$	SiO_2 is a solid. It has a giant structure. The silicon atom is attached with oxygen atoms by single covalent bonds. 
7. The lower oxide (CO) is known.	The lower oxide SiO is unknown.
8. It forms a large number of stable hydrates known as hydrocarbons.	It forms lesser number of hydrides which are unstable.
9. It does not react with Cl_2 or Br_2 directly.	It reacts with Cl_2 or Br_2 at 500°C. $Si + 2Cl_2 \xrightarrow{500°C} SiCl_4$
10. CCl_4 is quite stable and is not hydrolysed by water.	$SiCl_4$ is less stable and hence is hydrolysed by water. $SiCl_4 + 3H_2O \longrightarrow \underset{\text{Silicic acid}}{H_2SiO_3} + 4HCl$
11. The oxy-acid H_2CO_3 is unstable.	The oxy-acid H_2SiO_3 is stable.
12. It does not form complex compounds.	It forms a number of complex compounds because of availability of *d*-orbital in the valency shell.

Comparison between Silicon and Tin.

(A) Similarities. The following similarities are important.

(i) Allotropy. Both tin and silicon show allotropy.

(ii) Oxides. Oxides of both (SiO_2 and SnO_2) are acidic.

(iii) Hydrides. Both form hydrides which are gases. Tin gives a hydride SnH_4 by the action of HCl on an alloy of tin and magnesium. The hydride of silicon, SiH_4 is, however, more stable.

(iv) Halides. Both give similar halides. Their chlorides are colourless, volatile liquids which are easily hydrolysed. The fluorides of both, SiF_4 and SnF_4 are known to form similar silicofluorides, K_2SiF_6 and stannifluorides, K_2SnF_6.

(v) Action of alkalies. Both of them react with hot alkalies solution and liberate hydrogen.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$

(*vi*) A similarity also exists between the silicates and meta-stannates.

B. Dissimilarities. The following dissimilarities may be noted :

(i) Metallic character. Tin is a metalloid whereas silicon is a non-metal.

(ii) Melting point. Tin metals at 232°C whereas the melting point of silicon is very high.

(iii) Action of dilute acids. Tin reacts with dilute acids to liberate hydrogen whereas silicon has no such action.

(iv) Salts. Nitrates, sulphates and other salts of tin are known but such compounds are rare in the case of silicon. Many varieties of silicon are found in nature (olivine Mg_2SiO_4) and can also be prepared but orthostannates are almost unknown (with the exception of cobalt stannate Co_2SnO_4). Most of the stannates are meta as Na_2SnO_3.

Similarities between Tin and Lead.

The following points show the similarities between the two elements.

(*i*) Although both the elements have electro-positive character, yet, being in the middle of the periodic table, they also show feeble electronegative character in some of its compounds like halides, metastannates, metaplumbates etc.

(*ii*) Both the elements form highly unstable hydrides.

(*iii*) They form quite stable halides. The formation of such halides indicates that these elements have feeble electronegative character.

(*iv*) Both the elements form similar complexes namely stannates and plumbates respectively.

(*v*) When caustic alkali is added to a Sn + 2) salt solution in the absence of air, $Sn(OH)_2$ is first precipitated which dissolves in the excess of alkali, forming stannite (SnO_2^{2-}). Similarly a plumbite (PbO_2^{2-}) is formed by the addition of an excess of an alkali to a Pb(+2) salt solution.

$$Sn^{2+} + 2NaOH \longrightarrow \underset{\text{ppt.}}{Sn(OH)_2} + 2Na^+$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sod. stannite}}{Na_2SiO_2} + 2H_2O$$

$$Pb^{2+} + 2NaOH \longrightarrow \underset{\text{ppt.}}{Pb(OH)_2} + 2Na^+$$

$$Pb(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sod. plumbite}}{Na_2PbO_2} + 2H_2O$$

(*vi*) Metastannates (*e.g.* Na_2SiO_3) and metaplumbates (*e.g.* Na_2PbO_3) are stable and well-defined compounds.

Question with Answers

Q.1 Elemental silicon does not form graphite-like structure as carbon does. Explain.

Ans : The crystal structure of graphite consists of hexagonal layers (sheets) of C-atoms. These layers are linked together by weak vander Waals forces. In each hexagonal layer each C-atom is linked with other C-atoms by C–C covalent bond (sp^2 hybridisation of C-atom) and one electron of C-atom is thus left unsused in $2p$ orbital of each C-atom. The singly-filled $2p$ orbital on one C-atom overlaps with the singly-fulled $2p$ orbital on the other C-atom and forms $p\pi - p\pi$ bond. Thus many $p\pi - p\pi$ bonds are formed. This results in that an extended delocalised π – bonding system encompasing the entire layer is produced. Thus graphite has a two-dimentional sheet-like structure. Si-atom, on the other hand, is not able to form graphite-like structure due to the following reasons :

(*a*) Since Si-atom is bigger in size than C-atom (Si = 117 pm, C = 77 pm), it has no tendency to undergo sp^2 hybridisation (It only undergoes sp^3 hybridisation) and does not form Si–Si bonds. Due to the bigger size of $3p$ orbitals of Si-atom than $2p$ orbitals of C-atom, $p\pi - \mathrm{p}\pi$ bond cannot be formed by the overlap of singly filled $3p$ orbitals on two Si-atoms.

(*b*) Silicon has much lesses tendency for catenation (self-linking of atoms) than carbon because Si–Si bonds are much weaker (bond energy of Si–Si bond = 200 $\mathrm{KJmol^{-1}}$) than C–C bonds (bond energy of C–C bond = 355 $\mathrm{KJmol^{-1}}$).

Above discussion shows that Si does not form an analogue of carbon since neither it has a tendency to undergo sp^2 hybridisation nor to form Si–Si bonds.

Q.2 Diamond is extremely hard while graphite is very soft. Explain.

Ans : In diamond each C-atom is covalenty bonded to four additional C-atoms in a rigid three-dimentional network solid. This makes diamond very hard. On the other hand, graphite is a two-dimentional covalent network solid consisting of hexagonal carbon atoms sheets (layers) which are linked together by weak vander Waals forces and hence can slide over each other. This sliding property of graphite makes it soft.

Q.3 Explain the following : (*i*) $PbCl_2$ is more stable than $PbCl_4$ (*ii*) $PbCl_4$ is less stable than $SnCl_4$ but $PbCl_2$ is more stable than $SnCl_2$.

Ans : (*i*) Due to inert pair effect, + 2 oxidation state of Pb is more stable than its + 4 oxidation state., *i.e.* Pb^{2+} ion is more stable than Pb^{4+} ion. Thus since $PbCl_2$ has Pb^{2+} ion and $PbCl_4$ has Pb^{4+} ion, $PbCl_2$ is more stable than $PbCl_4$.

(*ii*) Since the inert pair effect increases on moving down the group 4A elements, the tendency of ns^2 electron pair to participate in bond formation decreases and hence the stability of + 4 oxidation state decreases and that of + 2 oxidation state increases. Consequently $PbCl_4$ is less stable than $SnCl_4$ and $PbCl_2$ is more stable than $SnCl_2$.

Q.4 CO_2 is a gas while SiO_2 is a soild of high melting point. Explain why ?
(Punjab 1994 ; Kurukshetra 1994 ; Delhi 1995)

Ans : We know that since the forces of attraction existing between CO_2 molecules are weak vander Walls forces, CO_2 exists as a monomeric (discrete) linear molecule ($O = C = O$). Due to weak forces, CO_2 exists as a gas at ordinary temperature.

On the other hand, since silicon dioxide has three-dimentional polymeric structure containg many Si–O bonds, there are no discrete SiO_2 molecules. SiO_2 is extremely stable, since considerable amount of energy is required to break Si–O bonds present in the structure of SiO_2. Due to extreme stability associated with the polymeric structure, silica exsist as a solid with high melting point.

Q.5 Structure of SiO_2 is similar to that of diamond but different from that of graphite. Explain.

Ans : In the crystal structuer of SiO_2 each Si-atom is linked tetrahedrally with four O-atoms and hence all the valence shell four electrons of Si-atom are consumed in forming four Si–O bonds. Thus Si-atom in SiO_2 has no free electrons. In the structure of diamond, each C-atom is linked tetrahedrally with four C-atoms placed at the four corners of a tetrahedron. Thus C-atom in diamond has no free (mobile) electrons. Thus SiO_2 and diamond both have similar structure.

In graphite, hexagonal layers are attached with each other by weak vander Waal's forces. Each C-atom in each hexagonal layer is linked with three C-atoms by C–C bond. Thus each C-atom is left with a free (mobile) electron and hence graphite has different structure from SiO_2.

Q.6 Explain the following, giving appropriate reasons for your answer.

(*i*) $SnCl_2$ has higher melting point (is a solid) while $SnCl_4$ has lower melting point (is a volatile liquid).

(*ii*) PbF_4 is an ionic solid but $PbCl_4$ is a covalent liquid.

Ans : (*i*) In $SnCl_2$, Sn has a charge = + 2 and in $SnCl_4$ this atom has charge = + 4. Due to higher charge on Sn in $SnCl_4$, $SnCl_4$ is covalent and $SnCl_2$ is ionic (Fajan's rules). Being ionic, $SnCl_2$ exists as a solid and has high melting point. On the other hand, since $SnCl_4$ is covalent it exists as a liquid and has low melting point.

(*ii*) Since F^- ion is smaller than Cl^- ion, F^- ion gets polarised by Pb^{4+} ion in PbF_4 molecule to smaller extent than Cl^- ion is polarised by Pb^{4+} ion in $PbCl_4$. Due to smallar polarisation of F^- ion than Cl^- ion, PbF_4 is ionic and $PbCl_4$ is covalent. Being ionic, PbF_4 exists as a solid. On the other hand since $PbCl_4$ is covalent,it exists as a liquid at room temperature.

Q.7 Explain the following, giving appropriate reasons for your answer.

(*i*) Lead (II) chloride does not react with Cl_2 to give $PbCl_4$

(*ii*) Lead (IV) chloride is highly unstable towards heat.

Ans : (*i*) Due to inert pair effect, Pb is more stable in + 2 oxidation state than in + 4 oxidation state. Therefore, lead (II) chloride is more stable than lead (IV) chloride and hence lead (II) chloride does not react with Cl_2 to form lead (IV) chloride

$$\begin{array}{llll} PbCl_2(s) & + \; Cl_2(g) & \not\longrightarrow & PbCl_4(l) \\ (Pb = +2) & & & (Pb = +4) \\ \text{More stable} & & & \text{Less stable} \end{array}$$

(*ii*) Due to inert pair effect, Pb is less stable in + 4 oxidation state than in +2 oxidation state. Thus $PbCl_4$ is less stable than $PbCl_2$ and hence decomposes, on heating, to give more stable $PbCl_2$.

$$\underset{\substack{(Pb\,=\,+\,4)\\ \text{(Less stable)}}}{PbCl_4(l)} \xrightarrow{\Delta} \underset{\substack{(Pb\,=\,+\,2)\\ \text{(More satble)}}}{PbCl_2(s) + Cl_2(g)}$$

Q.8 Explain which of the following tetraiodides is the least stable and has doubtful existence ? CI_4, GeI_4, SnI_4 and PbI_4.

Ans : *PbI_4 is the least stable and hence has doubtful existance.*

Explanation. All the given tetraiodides have C^{4+}, Ge^{4+}, Sn^{4+} and Pb^{4+} cations. Since C-atom does not show inert pair effect, this element is the most stable in its group oxidation state (= + 4). Hence CI_4 is the most stable tetraiodide. Ge, Sn and Pb (heavier elements) exhibit inert pair effect. As we move down the group from Ge to Pb, inert pair effect becomes more and more prominant and hence stability of + 2 oxidation state of these elements increases as $Ge^{2+} < Sn^{2+} < Pb^{2+}$ and that of + 4 oxiadtion state decreases as $Ge^{4+} > Sn^{4+} > Pb^{4+}$. The decreasing order of stability of + 4 O.S. shows that Pb^{4+} ion is the least stable. Consequently PbI_4 is the least stable and hence has doubtful existence.

University Questions

1. Compare the properties of carbon with those of silicon. (*M.D Rohtak 82, 85, 87*)
2. Compare the properties of silicon and tin. (*Delhi 86*)
3. Compare between tin and lead. (*Delhi Hons. 86*)
4. Explain the following giving appropriate reasons :
   (1) $SnCl_2$ is a solid while $SnCl_4$ is a liquid.
   (2) Carbon and silicon are always tetravalent but Ge, Sn and Pb show divalency.
   (3) CCl_4 is resistant to hydrolysis but $SiCl_4$ is readily hydrolysed. (*Raj. 87; Allahabad 87; Delhi Hons. 87; Jodhpur 86; Meerut 88*)
   (4) Si—Cl bond is stronger than C—Cl bond, still $SiCl_4$ is hydrolysed easily bit CCl_4 is not. (*Jodhpur 83; Delhi Hons. 82, 86*)
   (5) CCl_4 does not act as a Lewis acid while $SiCl_4$ and $SnCl_4$ do so.
   (6) $[CF_6]^{2-}$ ion does not exist while $[SiF_6]^{2-}$ ion exists.
   (7) Saturated carbon compounds are not reactive whereas the corresponding silicon compounds are reactive. (*Agra 85; Raj. 85*)
   (8) All the tetrahalides of lead are known, except PbI_4. (*Allahabad 88*)
   (9) $PbCl_4$ exists while $PbBr_4$ and PbI_4 do not.
   (10) The boiling point of CCl_4 is greater than that of $SiCl_4$.
   (11) $[SiF_6]^{2-}$ ion is known but $[SiCl_6]^{2-}$ ion is not known.

OR

$SiCl_4$ does not react with Cl^- ions to form $[SiCl_6]^{2-}$ while SiF_4 reacts with F^- ions to give $[SiF_6]^{-2}$. *(Punjab Hons. 86)*

(12) Silicon has much less tendency to catenation than carbon. *(Delhi 88)*

(13) The elements *viz.* Si, Ge, Sn and Ph do not show the property of catenation to that extent to which carbon shows.

(14) Carbon possesses greater catenation property than other members of its group. *(Meerut 88)*

(15) The tendency for catenation decreases with the increasing atomic number in the carbon family. *(Agra 89)*

(16) Carbon frequently forms double bond with another carbon atom in its compounds while silicon atom does not do so. *(Gorakhpur 84)*

(17) Tin forms a large number of salts like sulphates, nitrates etc. While the corresponding compounds of silicon are unknown.

(18) Silicon does not form multiple bonds like carbon.

(19) Si—O bond is stronger than C —O bond. *(Jodhpur 86)*

(20) Properties of CO_2 are different from those of SiO_2. *(Delhi Hons. 86)*

(21) CO_2 is a gas while SiO_2 is a solid of high m.pt. *(Meerut 84, 88; Allahabad 88; Raj. 87S; Delhi 86; Punjab 83)*

(22) Solid CO_2 is known as dry ice.

5. Explain the following giving appropriate reasons for your answer : Tetrahalides of carbon are not hydrolysed whereas other members of the group are readily hydrolysed. *(Delhi 1999)*

6. Explain the following :

(*i*) Carbon shows catenation. *(Himachal Pradesh 1999)*

(*ii*) SiO_2 is solid while CO_2 is a gas at room temperature. *(Allahabad 99, Himachal Pradesh 2000)*

7. Give a comparative account of the chemistry of the following elements : C, Si, Ge, Sn, Pb. *(Allahabad 99)*

8. Compare the properties of Ge and Sn pair. *(Kanpur 2000)*

9. $SiCl_4$ is hydrolysed but CCl_4 is not. Explain. *(Lucknow 2000)*

10. Explain the following :

(*i*) CO_2 is a gas while SiO_2 is a solid.

(*ii*) Graphite conducts electricity whereas diamond is a bad conductor of electricity. *(Avadh 2000)*