21

p-BLOCK ELEMENTS AND THEIR COMPOUNDS – I

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

Objectives

After reading this lesson, you will be able to

- describe the methods of preparation of boric acid, borax, diborane and boron trifluoride;
- explain the structure of diborane,boric acid and boron trifluoride;
- list the uses of borax, boric acid and boron trifluoride;
- list examples of double salts;
- describe the preparation and uses of aluminium trichloride and potash alum;
- explain the structure of aluminium trichloride;
- list the allotropes of crystalline carbon;
- compare the structures of diamond and graphite;
- explain the structure and properties of carbon monoxide, carbon dioxide and silicon dioxide;
- compare hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride;
- describe preparation and uses of silicon carbide;
- explain the processes for manufacture of ammonia and nitric acid;
- list the properties and uses of ammonia and nitric acid;
- explain nitrogen fixation: natural and industrial and
- list a few nitrogenous, phosphatic and mixed fertilizers with their importance.

21.1 Boron and Aluminium

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

21.1.1 Boric Acid

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

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

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

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

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

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

In boric acid, $B(OH)_3$ units are linked by hydrogen bonds to give two dimensional sheets (Fig. 21.1). The sheets are held together by weak van der Waals forces which are responsible for the cleavage of solid structure into flakes.

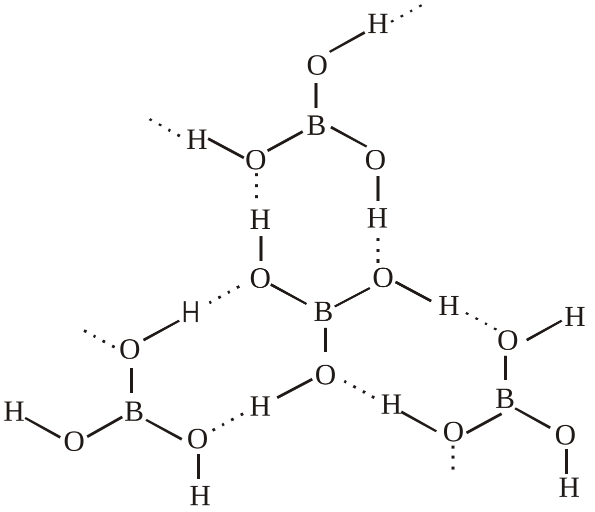


Fig. 21.1: *Structure of boric acid; the dotted lines represent hydrogen bonds*

Uses: Boric acid is used:

(i) as an antiseptic,

(ii) as a food preservative, and

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

21.1.2 Borax, $Na_2B_4O_7.10H_2O$

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

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

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

It is used:

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

(ii) as a preservative

(iii) in the manufacture of optical and borosilicate glasses

(iv) as a flux, and

(v) in making glazes for pottery and tiles.

21.1.3 Diborane, B_2H_6

Diborane is the most important hydride of boron.

Preparation:

It is prepared by the following methods:

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

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

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

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

Properties:

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

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

- It is readily hydrolysed by water

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

Structure : The molecular structure of diborane is shown below. The two boron atoms and the four terminal hydrogen atoms lie in one plane, the two bridging hydrogen atoms lie

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

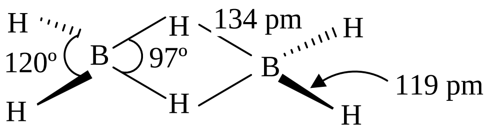


Fig.21.2 : *Structure of diborane, B_2H_6*

21.1.4 Boron Trifluoride

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

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

BF_3 hydrolyses according to the following equation

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

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

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

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

The structure of boron trifluoride is shown in Fig 21.3:

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

Note that in the resonating structures boron completes its octet.

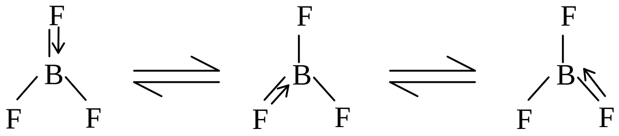


Fig 21.3 : *Resonatimg structures of boron trifluoride*

21.1.5 Aluminium trichloride

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

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

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

When pure, it is a white solid which sublimes at 453K. Aluminium has only three valence electrons. When these are used to form three covalent bonds, the atom has only six electrons in its valence shell. Since it is electron deficient it, therefore, exists as a dimer. The aluminium atoms complete their octets by dative bonding from two chlorine atoms. The arrangement of chlorine atoms about each aluminium atom is roughly tetrahedral. The structure of the dimer is shown in Fig. 21.4.

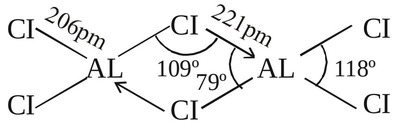


Fig.21.4 : *Structure of* $AlCl_3$

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

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

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

21.1.6 Double Salts: Alums and Potash Alum

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

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

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

Ammonium alum $(NH_4)\,Al\,(SO_4)_2 \cdot 12H_2O$

Chrome alum $KCr\,(SO_4)_2 \cdot 12H_2O$

Ammonium chrome alum $(NH_4)Cr\,(SO_4)_2 \cdot 12H_2O$

Ferric alum $K\,Fe\,(SO_4)_2 \cdot 12H_2O$

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

Intext Questions 21.1

1. Write the formula of the following:
   (i) Boric acid (ii) Borax

   ....

2. Write one reaction for the preparation of diborane.

   ....

3. What is the general formula of alums?

   ....

4. Write the formula of anhydrous solid aluminium trichloride and its structure.

   ....

5. Mention one use each of
   (i) borax (ii) boric acid (iii) boron trifluoride

   ....

21.2 Carbon and Silicon

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

21.2.1 Allotropic Forms of Carbon

Diamond and Graphite : Structures and Properties

Diamond and graphite, both are crystalline forms of carbon. But they are structurally different. Due to the difference in the arrangement of carbon atoms, they show different properties. In diamond, each carbon atom is sp^3 hybridized and is linked to four other carbon atoms by strong covalent bonds in a tetrahedral fashion. It gives rise to a three-dimensional arrangement (Fig.21.5). On the other hand, in graphite, the carbon atoms are arranged in layers. In each layer a particular carbon atom is sp^2 hybdridized and is linked to three other carbon atoms in a hexagonal arrangement. The fourth electron is free and does not participate in bonding. The different layers are held together by weak van der Waals forces (Fig 21.6).

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

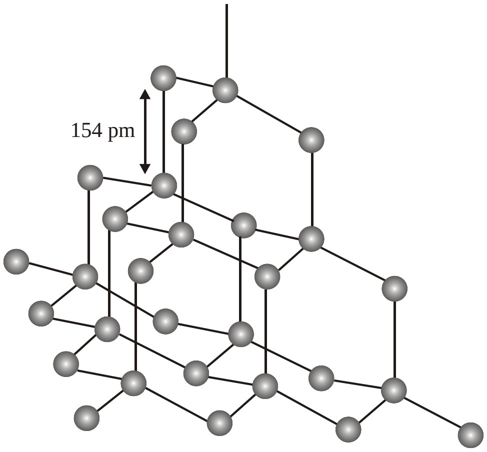


Fig.21.5 : *Structure of diamond*

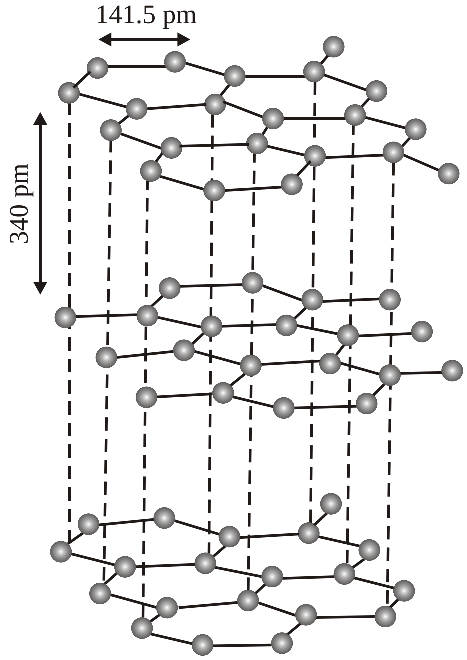


Fig. 21.6 : *Structure of graphite*

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

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

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

Fullerenes

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

21.2.2 Oxides of Carbon and Silicon

Structure

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

$$:C \, \vdots\vdots \, O: \qquad \text{or} \qquad :C \overset{\leftarrow}{\equiv} O:$$

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

$$O = C = O$$

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

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

Properties

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

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

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

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

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

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

21.2.3 Halides of Carbon and Silicon

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

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

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

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

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

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

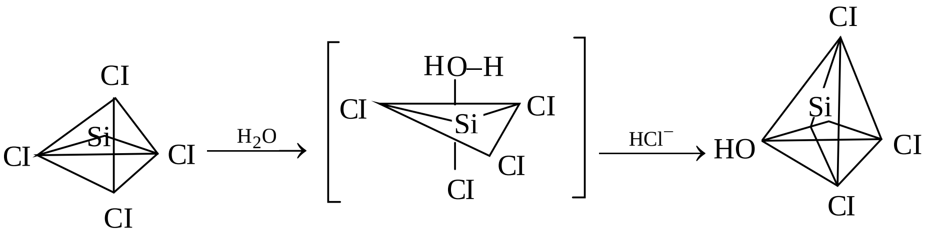
$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

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

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

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

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



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

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

21.2.4 Silicon Carbide, SiC

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

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

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

Intext Questions 21.2

1. Write two properties of diamond which are not exhibited by graphite.

   ....

2. What is the state of hybridization of carbon in (i) diamond (ii) graphite?

   ....

3. What is the nature of bond in carborundum?

   ....

4. Write the state of hybridization of carbon in CCl_4

   ....

5. Which one is affected by water and why; CCl_4 or $SiCl_4$?

   ....

6. Which is an acidic oxide, CO or CO_2?

   ....

7. What happens when SiO_2 is attacked by F_2?

   ....

21.3 Nitrogen and Phosphorus

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

21.3.1 Ammonia

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

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

or

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

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

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

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

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

In the actual process the hydrogen required is obtained from water gas and the nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (1 : 3 by volume) is compressed to 200-300 atm and then passed into the catalytic tubes packed with the catalyst. The catalyst in made by fusing Fe_3O_4 with KOH and Al_2O_3. The temperature of the catalytic tubes is maintained at 673 –773K by heating them electrically. The issuing gas containing about 10 per cent ammonia is cooled and the liquid ammonia condenses. The unconverted mixture of hydrogen and nitrogen is returned to the inlet and passed again over the catalyst. A typical plant might be arranged as shown in Fig.21.7

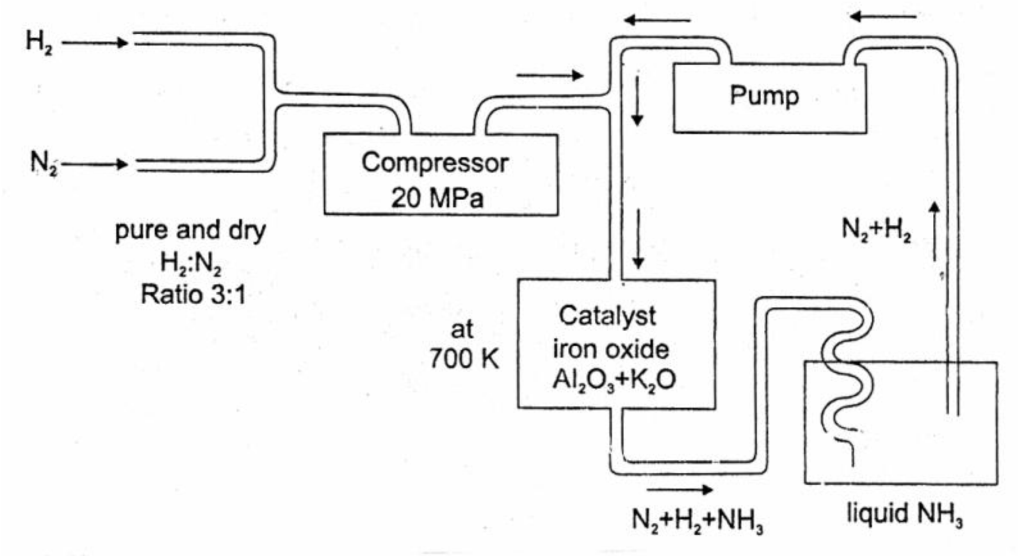


Fig.21.7 : *The Haber process for the manufacture of ammonia*

Properties

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

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

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

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

Chemical reactions

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Uses :

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

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

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

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

(iv) Liquid ammonia is used in refrigerators.

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

Structure : Ammonia molecule is trigonal pyramid with the nitrogen at the apex. The nitrogen atom is sp^3 hybridized in which a lone pair of electrons occupies one of the tetrahedral positions. The angle $H\hat{N}H$ becomes 107^0 instead of 109^0 (in CH_4) due to lone pair-bond pair repulsion (Fig. 21.8).

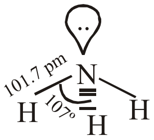


Fig. 21.8 : *Structure of ammonia*

21.3.2 Oxoacids of Nitrogen

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

Nitric Acid, HNO_3

Preparation

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

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

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

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

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

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

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

Properties

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

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

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

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

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

(c) On heating it gives NO_2

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

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

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

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

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

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

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

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

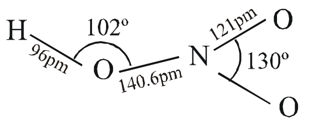
(vi) $4Zn + \underset{\textbf{dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

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

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

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

Structure : In the gaseous state HNO_3 exists as a planar molecule with the structure: (Fig. 21.9):



Fig, 21.9 : *Structure of nitric acid molecule*

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

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

21.3.3 Nitrogen Fixation

Any process by which atmospheric nitrogen is converted into a useful nitrogen compound is referred to as a method of *Nitrogen Fixation*.

The importance of fixation of atmospheric nitrogen is to make up for the loss of nitrogen from soil, created by cultivation. The chief sources of making up this loss of nitrogen are:

(a) Natural fixation

(b) Artificial fixation

(a) Natural fixation of nitrogen : The natural agencies which bring about the fixation are as following:

(i) *Lightning storms:* The nitric oxide produced in the lightning is oxidised to nitrogen dioxide.

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO$$

$$2NO + O_2 \xrightarrow{\text{air}} 2NO_2$$

The dioxide dissolves in rain water to give nitric acid which is carried to the soil and used by plants in the form of nitrates.

(ii) *Symbiotic bacteria :* The other natural agency is nitrogen fixing bacteria, **symbiotic bacteria.** These bacteria appear to live as ‘guests’ on the rootlets of leguminous plants, ‘the hosts’. The bacteria convert atmospheric nitrogen into a form available as food for the plant on which they live. It is thus a cooperative affair; the plants furnish home and food for the bacteria and the bacteria in turn furnish nitrogen drawn from air as an essential food to the plants.

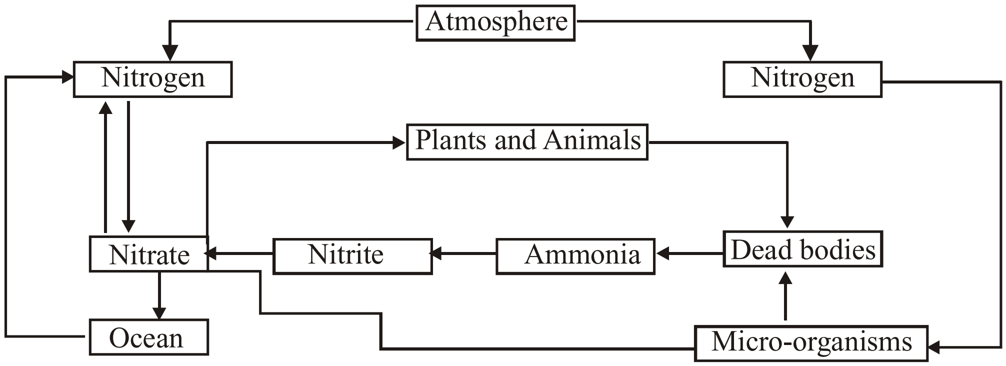


Fig. 21.10 : *Fixation of Nitrogen*

(b) **Artificial Fixation of Nitrogen :** The important artificial methods of fixing nitrogen are as follows :

(i) *Conversion to ammonia by Haber's process :* This is by far the most important method of fixing atmospheric nitrogen.

Ammonia is supplied to the soil as its salts, e.g. $(NH_4)_2\,SO_4$. It may also be oxidised to nitric acid and nitrate salts (e.g. KNO_3) which may be used for the purpose.

(ii) *Conversion into calcium cyanamide:* When calcium carbide is heated to 1373K in a stream of nitrogen the following reaction occurs

$$CaC_2 + N_2 \xrightarrow{1373K} \underset{\textbf{calcium cyanamide (nitrolim)}}{CaNCN} + C$$

The mixture of calcium cyanamide and carbon is directly used as a fertilizer under the name *nitrolim*

(iii) *Conversion into nitric acid:* In Birkeland and Eyde process nitrogen is made to combine with oxygen at a very high temperature (~ 3000K). The nitric oxide formed is converted into the dioxide

$$N_2 + O_2 \xrightarrow{3300\ K} 2NO$$

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

The dioxide is dissolved in water in the presence of air to form nitric acid. In this method electric sparking is used to generate that high temperature, so the method is good only where electricity is cheap.

(iv) *Conversion into nitride*. Certain metal oxides, e.g. Al_2O_3, MgO and BaO when heated with coke to ~1800K in a current of atmospheric nitrogen, give metal nitrides

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

The heated mass is reacted with water when the nitride is hydrolysed to produce ammonia

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

Ammonia may be supplied to the soil in the form of ammonium salts.

21.3.4 Fertilizers

Chemical compounds directly supplying the elements of primary importance, i.e. nitrogen, phosphorus and potassium to soil are known as fertilizers. A chemical compound acting as fertilizer may supply one or more than one of these elements. Thus the following broad classification of fertilizers emerges

(1) Nitrogenous fertilizers

(2) Phosphatic fertilizers

(3) Potassium fertilizers

(4) Mixed fertilizers

(1) Nitrogenous fertilizers: The chief compounds which act as nitrogenous fertilizers include

(i) ammonium sulphate, (ii) urea and (iii) calcium cyanamide

(i) **Ammonium sulphate** is one of the best nitrogenous fertilizers. It is prepared either by the action of sulphuric acid on ammonia (obtained from destructive distillation of coal)

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

or from gypsum by the action of aqueous ammonia and carbon dioxide

$$2NH_3 + H_2O + CO_2 + CaSO_4 \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

Ammonium sulphate is manufactured in our country at Sindri (Bihar) and Alwaye (Kerala).

(ii) **Urea:** It is usually made by the action of carbon dioxide and liquid ammonia at 453K under a pressure of 200 atm. The reaction occurs in two steps

$$2NH_3 + CO_2 \longrightarrow \underset{\textbf{ammonium carbamate}}{NH_2COONH_4}$$

$$NH_2COONH_4 \xrightarrow{\text{heat}} \underset{\textbf{urea}}{NH_2CONH_2} + H_2O$$

Large quantities of urea are manufactured at Nangal (Punjab) in our country. Of all the nitrogenous fertilizers urea has the maximum nitrogen content hence it is widely used.

(iii) **Calcium cyanamide, Ca (NCN):** It is manufactured by heating calcium carbide in nitrogen at 1373 K

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

It is used in the commercial name of nitrolim. When supplied to the soil it hydrolyses to ammonia which gets oxidised to nitrate and is used up by plants.

$$CaNCN + 3HOH \longrightarrow CaCO_3 + 2NH_3$$

(2) **Phosphatic fertilizers**: Calcium phosphate, $Ca_3(PO_4)_2$ is converted into superphosphate, Ca $(H_2PO_4)_2$, by the action of sulphuric acid.

$$Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

The product containing superphosphate and calcium sulphate is used in the name of *superphosphate of lime.*

(3) **Potassium fertilizers.** The chief compound serving as potassium fertilizer is potassium chloride.

(4) **Mixed fertilizers :** These are also known as NPK fertilizers. The important mixed fertilizers are $(NH_4)_3PO_4$, KNO_3, and ammonium super phosphate, $(NH_4)H_2PO_4$.

Rating of fertilizers. The rating of fertilizers is done on the basis of the percentage of N_2, P_2O_5 and K_2O in them. For example a fertilizer containing 2% N_2, 8% P_2O_5 and 2% K_2O has a rating of 2, 8, 2. For different crops different ratings are required. For example, some crops and required ratings are

Potato : 4, 8, 10; wheat: 2, 12, 6; sugar: 4, 12, 6.

Intext Questions 21.3

1. Does 'NH_4OH' exist as a molecule?

   ....

2. What is the bond angle in NH_3 molecule?

   ....

3. What is the state of hybridization of N in NH_3?

   ....

4. Name three elements which are essential to plant growth.

   ....

5. Write the formula of superphosphate of lime.

   ....

6. Name two compounds which are considered as nitrogenous fertilizers.

   ....

What You Have Learnt

- Method of preparation of boric acid. The acidic nature and structure of boric acid.
- Method of preparation and uses of borax.
- Methods of preparation and uses of boron trifluoride and diborane.
- The Lewis character and use of boron trifluoride.
- Preparation of aluminium trichloride and its structure
- Method of preparation of alums and uses
- The comparison of diamond and graphite.
- The structure and properties of carbon monoxide, carbon dioxide and silicon dioxide.
- Comparison of the hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride.
- Preparation and uses of silicon carbide (carborundum)
- The methods of preparation, properties and uses of ammonia and nitric acid.

- The salient features of nitrogen fixation.
- Fertilizers : nitrogenous, phosphatic, potassium and mixed. Their methods of preparation and their importance.

Terminal Questions

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

   (i) Nitrolim (ii) Urea (iii) Superphosphate of lime

Answers to Intext Questions

21.1

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

   Where N = monovalent large cation like K^+ or NH_4^+ and M = trivalent cation like Al^{3+}, Fe^{3+}, Cr^{3+}
4. Al_2Cl_6
5. (i) as a flux, for glazing pottery and tiles : in the manufacture of optical and borosilicate glasses.

   (ii) as an antiseptic, as a food preservative, for making enamels

   (iii) as a catalyst in Friedel-Crafts reaction.

21.2

1. Hardness and conducting nature. Diamond : hard, non conducting; graphite : soft, conducting.

2. sp^3 in diamond and sp^2 in graphite.
3. Covalent
4. sp^3
5. $SiCl_4$, as silicon can accept electron pair in its d-orbitals from water molecule.
6. CO_2
7. $SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$

21.3

1. No. Nitrogen cannot increase its covalency beyond 4.
2. 107^0.
3. sp^3
4. N, P and K
5. $Ca(H_2PO_4)_2$ along with $CaSO_4$ is known as superphosphate of lime.
6. Ammonium sulphate, Urea.