

$N \equiv N$) and to other second row elements (e.g., $C=O$, $C=N$, $C \equiv N$, $N=O$). This type of π - bonding is not particularly strong for the heavier *p*-block elements. The heavier elements do form π bonds but this involves *d* orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the *d* orbitals are of higher energy than the *p* orbitals, they contribute less to the overall stability of molecules than does $p\pi - p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions: NO_3^- (three-coordination with π - bond involving one nitrogen *p*-orbital) and PO_4^{3-} (four-coordination involving *s*, *p* and *d* orbitals contributing to the π - bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

11.1 GROUP 13 ELEMENTS: THE BORON FAMILY

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium, thallium and nihonium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3) , borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $Al_2O_3 \cdot 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature. Nihonium has symbol Nh, atomic number 113, atomic mass 286 g mol^{-1} and electronic configuration $[Rn] 5f^{14} 6d^{10} 7s^2 7p^2$. So far it has been prepared in small amount and half life of its most stable

isotope is 20 seconds. Due to these reasons its chemistry has not been established.

Nihonium is a synthetically prepared radioactive element. Here atomic, physical and chemical properties of elements of this group leaving nihonium are discussed below.

11.1.1 Electronic Configuration

The outer electronic configuration of these elements is $ns^2 np^1$. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*-electrons plus 10 *d*-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

11.1.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

11.1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of *d*- and *f*-electrons, which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. The sum of the first three ionisation enthalpies for each of the

elements is very high. Effect of this will be apparent when you study their chemical properties.

11.1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally (Table 11.2). This is because of the discrepancies in atomic size of the elements.

11.1.5 Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

11.1.6 Chemical Properties

Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening *d* and *f* orbitals, the increased effective nuclear charge holds *ns* electrons tightly (responsible for *inert pair effect*) and thereby, restricting their participation in bonding. As a result of this, only *p*-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$. In thallium +1 oxidation state is predominant

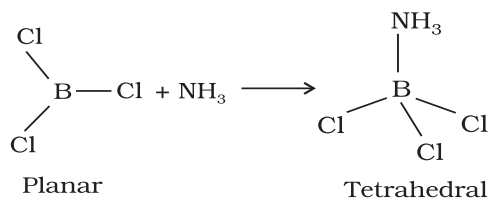
Table 11.2 Atomic and Physical Properties of Group 13 Elements

Property	Element					
	Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl	
Atomic number	5	13	31	49	81	
Atomic mass(g mol ⁻¹)	10.81	26.98	69.72	114.82	204.38	
Electronic Configuration	[He]2s ² 2p ¹	[Ne]3s ² 3p ¹	[Ar]3d ¹⁰ 4s ² 4p ¹	[Kr]4d ¹⁰ 5s ² 5p ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	
Atomic radius/pm ^a	(88)	143	135	167	170	
Ionic radius M ³⁺ /pm ^b	(27)	53.5	62.0	80.0	88.5	
Ionic radius M ⁺ /pm	-	-	120	140	150	
Ionization enthalpy (kJ mol ⁻¹)	$\Delta_i H_1$	801	577	579	558	589
	$\Delta_i H_2$	2427	1816	1979	1820	1971
	$\Delta_i H_3$	3659	2744	2962	2704	2877
Electronegativity ^c	2.0	1.5	1.6	1.7	1.8	
Density /g cm ⁻³ at 298 K	2.35	2.70	5.90	7.31	11.85	
Melting point / K	2453	933	303	430	576	
Boiling point / K	3923	2740	2676	2353	1730	
E [⊖] / V for (M ³⁺ /M)	-	-1.66	-0.56	-0.34	+1.26	
E [⊖] / V for (M ⁺ /M)	-	+0.55	-0.79(acid) -1.39(alkali)	-0.18	-0.34	

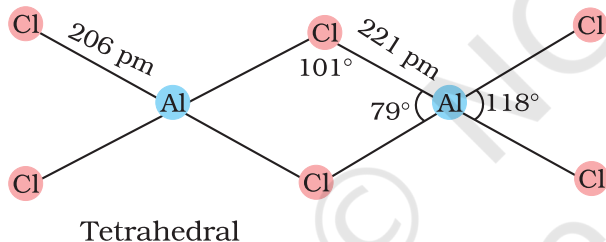
^aMetallic radius, ^b 6-coordination, ^c Pauling scale,

whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $\text{BCl}_3 \cdot \text{NH}_3$.



AlCl_3 achieves stability by forming a dimer



In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hydrolysis in water form tetrahedral $[\text{M}(\text{OH})_4]^-$ species; the hybridisation state of element M is sp^3 . Aluminium chloride in acidified aqueous solution forms octahedral $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion. In this complex ion, the $3d$ orbitals of Al are involved and the hybridisation state of Al is sp^3d^2 .

Problem 11.1

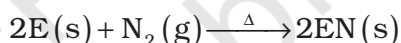
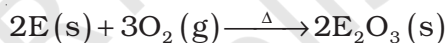
Standard electrode potential values, E^\ominus for Al^{3+}/Al is -1.66 V and that of Tl^{3+}/Tl is $+1.26 \text{ V}$. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution

Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make $\text{Al}^{3+}(\text{aq})$ ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^+ is more stable in solution than Tl^{3+} . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



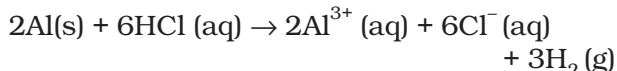
(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalis

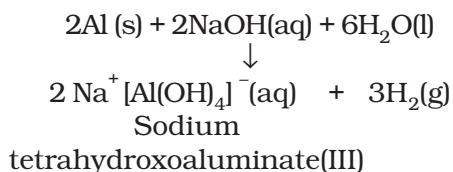
Boron does not react with acids and alkalis even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalis and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.



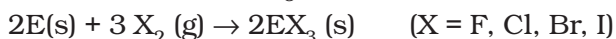
However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.

Aluminium also reacts with aqueous alkali and liberates dihydrogen.



(iii) Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI_3).

**Problem 11.2**

White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

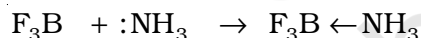
Solution

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

11.2 IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[\text{M}(\text{OH})_4]^-$ and octahedral $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.



It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (*e.g.*, AlCl_3) are dimerised through halogen bridging (*e.g.*, Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

Problem 11.3

Boron is unable to form BF_6^{3-} ion. Explain.

Solution

Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore,

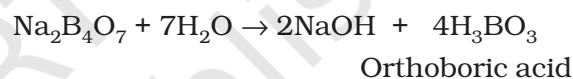
the maximum covalence of boron cannot exceed 4.

11.3 SOME IMPORTANT COMPOUNDS OF BORON

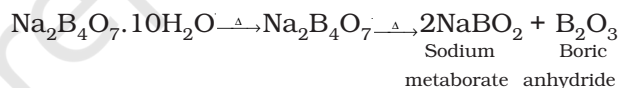
Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

11.3.1 Borax

It is the most important compound of boron. It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. Borax dissolves in water to give an alkaline solution.



On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.



The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ bead is formed.

11.3.2 Orthoboric acid

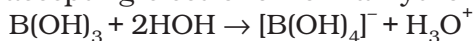
Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.



It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It has a

layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in Fig. 11.1.

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:



On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3 .

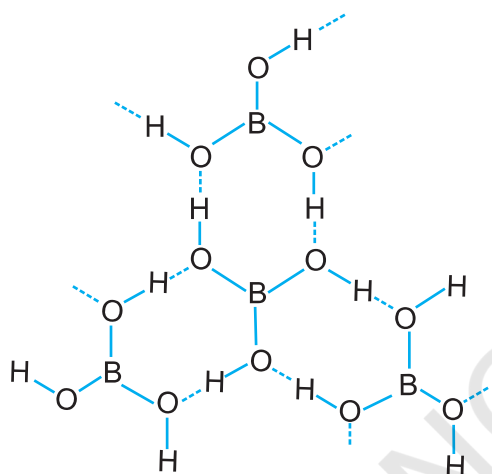


Fig. 11. 1 Structure of boric acid; the dotted lines represent hydrogen bonds

Problem 11.4

Why is boric acid considered as a weak acid?

Solution

Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

11.3.3 Diborane, B_2H_6

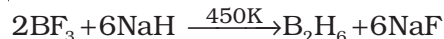
The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with LiAlH_4 in diethyl ether.



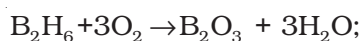
A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.



Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

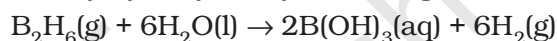


Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

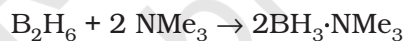


$$\Delta_c H^\ominus = -1976 \text{ kJ mol}^{-1}$$

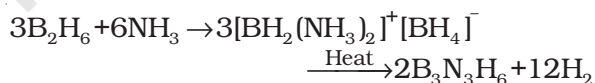
Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.



Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $\text{BH}_3 \cdot \text{L}$



Reaction of ammonia with diborane gives initially $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which is formulated as $[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$; further heating gives borazine, $\text{B}_3\text{N}_3\text{H}_6$ known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.



The structure of diborane is shown in Fig.11.2(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three

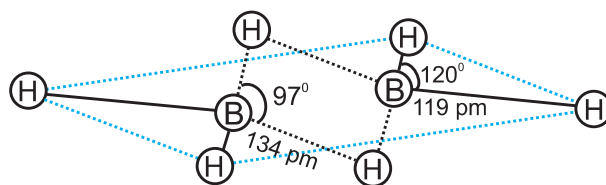


Fig.11.2(a) The structure of diborane, B_2H_6

centre–two electron bonds shown in Fig.11.2 (b).

Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[\text{BH}_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as **borohydrides**, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

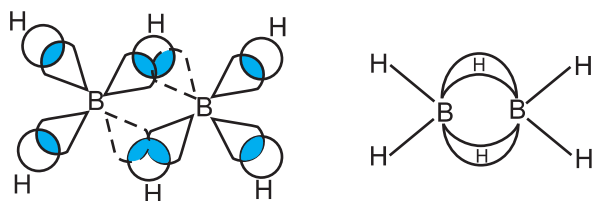


Fig.11.2(b) Bonding in diborane. Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

Both LiBH_4 and NaBH_4 are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

11.4 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods. The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps. An aqueous solution of

orthoboric acid is generally used as a mild antiseptic.

Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and everyday life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

11.5 GROUP 14 ELEMENTS: THE CARBON FAMILY

Carbon, silicon, germanium, tin lead and flerovium are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin