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The p -Block Elements

Such elements in which only outer most shell is incompletely filled and last electron enters in p-orbitals of the outer most shell are called p-block elements. In long form of periodic table these elements have been placed in extreme right from group 13 to 18.

The valence shell electronic configuration of p-block elements is ns^2, np^{1-6}. The inner core of the electronic configuration of these elements differ and this difference greatly influences the physical properties such as atomic and ionic radii, ionisation enthalpy, electron gain enthalpy etc. as well as the chemical properties of these elements. Hence, a lot of variation in properties of elements in a definite group has been observed.

The maximum oxidation state of a p-block element corresponds to the total number of valence electrons (i.e. the sum of the s and p-electrons) in respective element. Thus, the number of possible oxidation states increases on moving left to right in a period of the periodic table.

In addition to group oxidation state (G), due to inert pair effect heavier p-block elements also exhibit a lower oxidation state of (G-2), which is two unit lesser than the normal group oxidation state of respective group. In boron, carbon and nitrogen families, the group oxidation state (G) is the most stable state for the lighter elements, but lower oxidation state (G-2) becomes progressively more stable for the heavier elements in these group.

The general electronic configuration and important oxidation States of p-block elements are listed here-

Group	**13**	**14**	**15**	**16**	**17**	**18**
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2,-4	+3,-3	+4,+2,-2	+5,+3,+1,-1	+6,+4,+2

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The non-metals and metalloids exist only in the p-block of the periodic table. The non-metallic character of elements decreases down the group. In fact, the heaviest element of each group in p-block is the most metallic in nature. The change of non-metallic to metallic character in a group can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic (electrovalent) because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities.

Just like s-block, the first member of p-block elements differs from the remaining members of its group. It is because of smaller atomic size and absence of vacant d-orbitals in their valence shell.

The maximum covalence of first member of p-block elements (second period elements starting from boron) is restricted to four (using 2s and three 2p orbitals). On the other hand, the second member of p-block elements (the third period elements starting from aluminium) having the electronic configuration $3s^2$, $3p^{1-6}$ contain vacant 3d orbitals in their valence shell and therefore, they can expand their covalence beyond four. For example, boron forms only $[BF_4]^-$ while, aluminium forms $[AlF_6]^{3-}$ ion.

The first member of a group differs from the heavier members in its ability to form pπ – pπ multiple bonds with itself (e.g. C=C, C≡C, N≡N) and with other second row elements (e.g. C=O, C=N, C≡N, N=O). This type of π – bonding is not sufficiently strong for the heavier p-block elements. However, the heavier p-block elements form π bonds involving d-orbitals (dπ - pπ or dπ – dπ bonding). Since, d- orbitals have higher energy than the p-orbitals, dπ - pπ or dπ – dπ bondings give lesser contribution to the overall stability of molecules as compared to pπ – pπ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than that for the first member in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions- NO_3^- (coordination number =3, with π – bond involving one p-orbital of nitrogen atom) and PO_4^{3-} (coordination number = 4, involving s, p and d orbitals contributing to the π – bond).

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GROUP-13 ELEMENTS (BORON FAMILY)

Gr. 13 consists of in all five elements, namely Boron (B), Aluminium (Al), Gallium (Ga), Indium (In) and Thallium (Tl). This group shows a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to the boron. Gallium, indium and thallium are almost metallic in nature.

Boron is a fairly rare element. It 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 is found 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 ($Al_2O_3.2H_2O$) 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.

Electronic Configuration

The outer electronic configuration of these elements is ns^2np^1. Here, boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons while thallium has noble gas plus 14 f- electrons plus 10 d-electron cores. Thus, the electronic structures of these elements are relatively complex and it affects the properties and therefore, the chemistry of all the elements of this group.

Atomic Radius

On moving down the group, new shells are added one by one and therefore, the atomic radius in general goes on increasing. However, atomic radius of Ga (135 pm) is found to be exceptionally lesser than that of Al (143 pm). It is because of insufficient or poor screening effect of inner d-electrons in Ga.

Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases continuously.

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Atomic and Physical Properties of Group 13 Elements						
Property	**Element**					
	Boron B	**Aluminium Al**	**Gallium Ga**	**Indium In**		**Thallium Ti**
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)	(88)	143	135	167		170
Ionic radius M^{3+}(pm)	(27)	53.5	62.0	80.0		88.5
Ionic radius M^+ (pm)	-	-	120	140		150
Ionization enthalpy ($kJ\ mol^{-1}$)	Δ_iH_1	801	577	579	558	589
	Δ_iH_2	2427	1816	1979	1820	1971
	Δ_iH_3	3659	2744	2962	2704	2877
Electronegetivity	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
Boling point (K)	3923	2740	2676	2353		1730
E^0 (M^{3+}/M)	-	-1.66	-0.56	-0.34		+1.26
E^0 (M^{+}/M)	-	+0.55	-0.79(acid) -1.39(alkali)	-0.18		-0.34

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Ionization Enthalpy

The ionisation enthalpy does not decrease smoothly down the group. It decreases from B to Al due to increase in atomic size. From Al and Ga it exceptionally increases due to insufficient or poor screening effect of inner d-electrons in Ga. It again decreases from Ga to In and then exceptionally increases

from In to Tl due to insufficient or poor screening effect of inner d and f-electrons in Tl to compensate the increase in nuclear charge.

Here, the order of first three ionisation enthalpies is as under-

$$\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$$

The sum of first three ionisation enthalpies for these elements is very high.

Physical Properties

Metallic Nature-

Boron is non-metallic in nature. It is extremely hard and black coloured solid which exists in many allotropic forms. Due to very strong crystalline lattice, boron has exceptionally high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. Gallium having very 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.

Chemical Properties

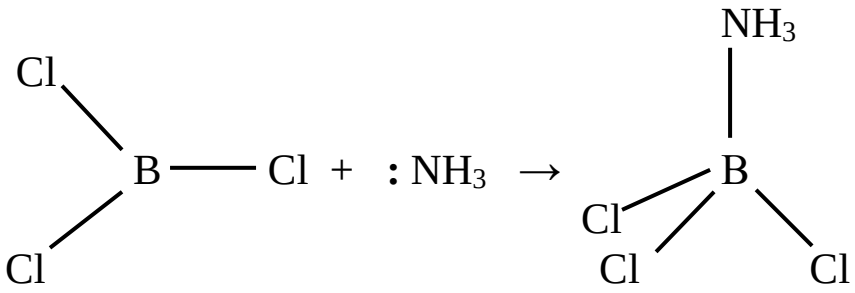
Oxidation state and trends in chemical reactivity

Due to small atomic size, the sum of first three ionization ethalpies of boron is very high. Hence, it does not form +3 ions and forms only covalent compounds. For aluminium, the sum of the first three ionisation enthalpies is considerably low. Hence, it is 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-

$$Al < Ga < In < Tl$$

In trivalent state, in the molecules of the compounds of these elements, the central atom (e.g., boron in BF_3) contains only six electrons. These electron deficient molecules have tendency to accept a lone pair of electrons from Lewis bases to achieve stable electronic configuration and therefore, they behave like Lewis acids. For example, BCl_3 easily accepts a lone pair of electrons from ammonia to form addition compound.

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The tendency to behave as Lewis acid decreases with the increase in the atomic size of central atom down the group.

In trivalent state most of the compounds being covalent are hydrolysed in water. For example, trichlorides on hyrolysis in water form tetrahedral $[M(OH)_4]^-$ ions where central atom M is sp^3 hybridized.

In acidified aqueous solution, Aluminium chloride forms octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex ion Al utilizes its vacant the 3d orbitals and is sp^3d^2 hybridized.

Ques.- Standard electrode potential values, (E^0) for Al^{3+}/Al is -1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.
Sol^n- More negative value of standard electrode potential for aluminium reveals that, Al has higher tendency to form $Al^{3+}(aq)$ ions and is more electropositive as compared to thallium.

On the other hand, due to inert pair effect, Tl^{3+} is not only unstable in solution as compared to Tl^+, but it is also a powerful oxidising agent. Thus, Tl^+ is more stable in solution than Tl^{3+}.

(i) Reactivity towards air

Crystalline form of boron is almost unreactive in air. Aluminium forms a very thin oxide layer over its surface which protects it from further attack of air. Amorphous boron and other members on heating in air form their oxides of type E_2O_3.

$$4B(s) + 3O_2(g) \rightarrow 2B_2O_3(s)$$
$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$
$$4Ga(s) + 3O_2(g) \rightarrow 2Ga_2O_3(s)$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and

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gallium oxides are amphoteric while, those of indium and thallium are basic in nature.

With dinitrogen at high temperature both boron and aluminium form their nitrides.

$$2B(s) + N_2(g) \xrightarrow[\Delta]{\Delta} 2BN(s)$$

$$2Al(s) + N_2(g) \rightarrow 2AlN(s)$$

(ii) Reactivity towards acids and alkalies

Boron being highly unreactive, does not react with acids and alkalies even at moderate temperature.

Aluminium reacts with both acids and alkalies and therefore, shows amphoteric behaviour. It dissolves in dilute HCl to liberates dihydrogen.

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$$

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).

$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s)$$

Where, X = F, Cl, Br, I

Ques. Give the reason-

White fumes appear around the bottle of anhydrous aluminium chloride.

Sol^{n}-

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

Important Trends and Anomalous Behaviour of Boron

(1) The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water.

(2) Tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$ ions except for boron exist in aqueous medium.

(3) The monomeric trihalides being electron deficient behave like strong Lewis acids. For example, Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$H_3N: + BF_3 \rightarrow H_3N \rightarrow BF_3$$

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(4) Due to the absence of vacant d orbitals in valence shell, the maximum covalence of B is 4. On the other hand, due to availability of vacant d-orbitals in valence shell Al and other elements can expand their covalence beyond 4.
(5) $AlCl_3$ undergoes dimerization through halogen bridging to form its dimer Al_2Cl_6. Here, metal completes its octet by accepting a lone pair of electrons from bridge halogen.

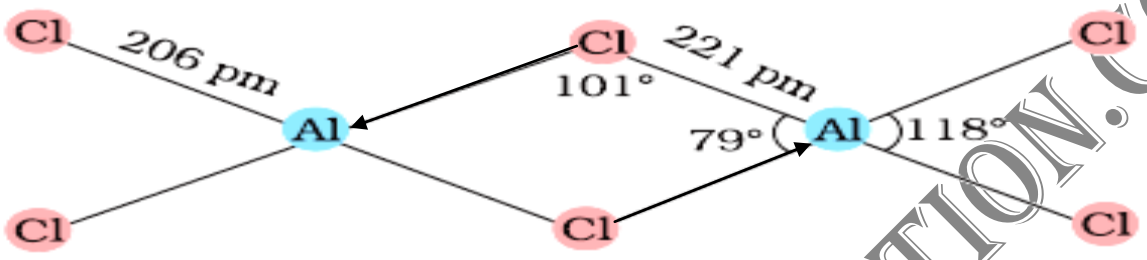


Fig.- Dimer of $AlCl_3$

Ques.-Boron is unable to form BF_6^{3-} ion. Explain.
Sol^n- Due to non-availability of d-orbitals in valence shell (2^{nd} shell), boron is unable to expand its covalence beyond 4. Thus, the maximum covalence of boron cannot exceed 4.

Some Important Compounds of Boron

(1) Borax ($Na_2B_4O_7.10H_2O$)

(i) It is the most important compound of boron.
(ii) It is a white coloured crystalline solid of formula $Na_2B_4O_7.10H_2O$. In fact, it contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and therefore, its correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$.
(iii) Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + \underset{\text{Orthoboric acid}}{4H_3BO_3}$$

(iv) Effect of Heat- On heating, borax first loses water crystallization and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

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The metaborates of many transition metals have characteristic colours and therefore, this reacton forms the basis of borax bead test for their identification in the laboratory.

For example, when a mixture of CoO and borax is heated in a Bunsen flame on a loop of platinum wire, a blue coloured bead of $Co(BO_2)_2$ is formed.

(2) Orthoboric acid (H_3BO_3)

(i) Orthoboric acid, H_3BO_3 is a white coloured crystalline solid with a soapy touch.

(ii) It is sparingly soluble in water but highly soluble in hot water.

(iii) It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

(iv) It can also be prepared by the hydrolysis (reaction with water or dilute acid) of most of the boron compounds such as halides, hydrides etc.

(5) It has a layer structure in which planar BO_3 units remain joined by intermolecular hydrogen bonds.

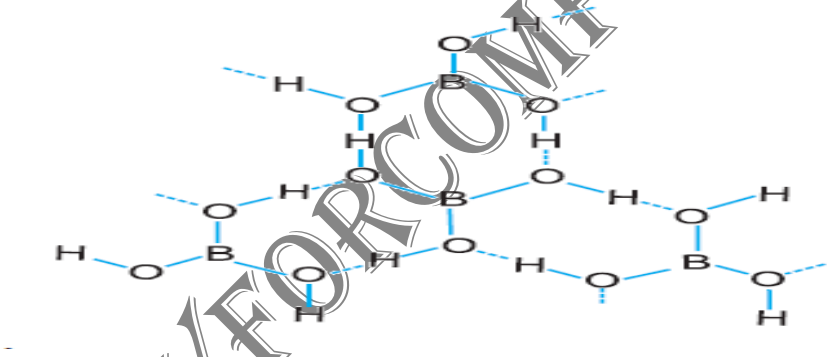


Fig.- Layer structure of Boric acid

(6) 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.

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

(7) Effect of Heat-On heating above 370K, orthoboric acid forms metaboric acid, HBO_2, which on further heating yields boric oxide (B_2O_3).

$$H_3BO_3 \xrightarrow[-H_2O]{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

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Q.- Why is boric acid considered as a weak acid ?
Ans.- Boric acid is not able to release H^+ ions on its own. In fact, it takes OH^- ions from water molecule and releases H^+ ions for some extent. Hence, it is considered to be a weak acid.

Diborane (B_2H_6)

The simplest boron hydride is known as diborane.

Preparation Methods-

(1) Diborane is usually prepared by treating boron trifluoride with $LiAlH_4$ dissolved in diethyl ether.

$$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

(2) Laboratory method- In laboratory diborane is prepared by oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

(3) Industrial Preparation- On industrial scale, diborane is produced by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Properties-

(1) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.

(2) On exposure to air it catches fire easily and burns to releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O;\ \Delta_cH^0 = -1976\ kJ\ mol^{-1}$$

Most of the higher boranes are also inflammable in air.

(3) Boranes are readily hydrolysed by water to give boric acid and releases hydrogen.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

(4) Diborane undergoes cleavage reactions with Lewis bases to form borane adducts.

$$B_2H_6 + 2NMe_3 \rightarrow 2Me_3N.BH_3$$
$$B_2H_6 + 2\ CO \rightarrow 2OC.BH_3$$

(5) Diborane reacts with ammonia to form adduct $B_2H_6.2NH_3$, which is formulated as $[BH_2(NH_3)_2]^+[BH_4]^-$. On further heating, it gives borazine, $B_3N_3H_6$. It has ring structure with alternate BH and NH groups and is also called inorganic benzene.

$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2\ B_3N_3H_6 + 12H_2$$

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Structure of diborane

Diborane is an electron deficient compound which does not contain sufficient number of valence electrons for normal covalent bonding. For ethane like bonding it requires in all 14 electrons but it contains only 12 valence electrons for bonding. Hence, it fulfils its bonding requirement by multicentred bonding called 3-centred-2-electron bonds (3c-2e bonds). Here, all the four terminal hydrogen atoms and the two boron atoms lie in one plane. There are two bridging hydrogen atoms above and below this plane. The four terminal B-H bonds are regular two centre-two electron bonds, while the two bridge (B-H-B) bonds are three centre-two electron bonds.

In fact, in diborane both the boron atoms are sp3 hybridized, where three sp^3 hybridized orbitals are half filled while, the rest one is vacant. Half filled sp^3 hybridized orbital of one boron atom, vacant sp^3 hybridized orbital of other boron atom and half filled 1s orbital of bridge hydrogen atom overlap together to form 3c-2e bonds. These bonds usually distort to take banana shape and therefore, they are also called banana bonds.

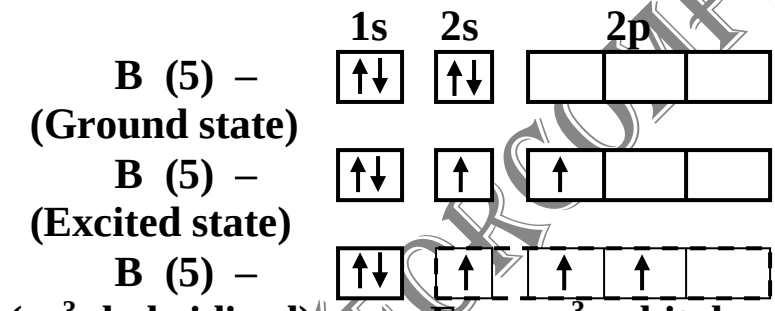


Fig.- sp^3 hybridization in Boron (schematic)

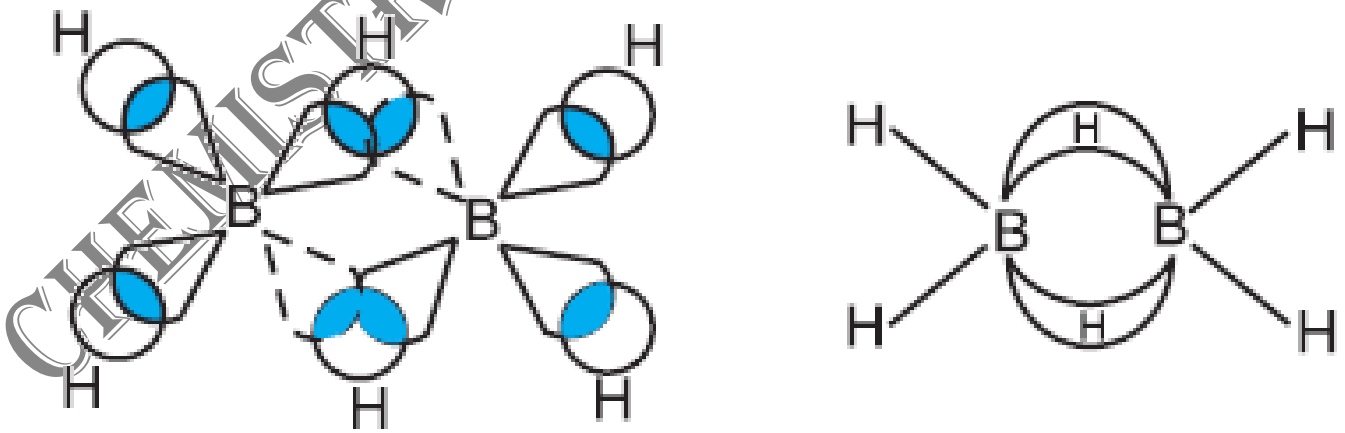


Fig.- 3-Centre-2-Electron Bonding in Diborane

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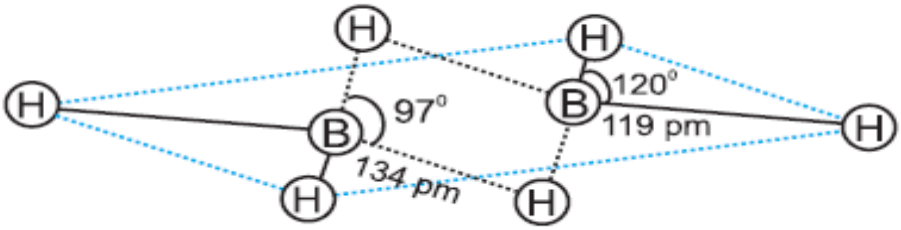


Fig.- Geometry of Diborane

Boron also forms a series of hydridoborates. The most important one of them is tetrahedral $[BH_4]^-$ 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.

$$2MH + B_2H_6 \rightarrow 2M^+[BH_4]^- \text{ (M = Li or Na)}$$

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

Uses of Boron and its Compounds

Boron being extremely hard and refractory solid. It has high melting point, low density and very low electrical conductivity. The common applications of boron and its compounds are as under-

(1) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.

(2) Boron-10 (^{10}B) isotope has high ability to absorb neutrons and therefore, metal borides are used in nuclear reactors for making protective shields and control rods.

(3) Borax and boric acid are used in manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibre glass.

(4) 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.

(5) An aqueous solution of orthoboric acid is used as a mild antiseptic.

Uses of Aluminium and its Compounds

Aluminium is a bright silvery-white metal, with high tensile strength. It has very high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. The common use of aluminium and its compounds are as under-

(1) Aluminium is extensively used in industry and every day life.

(2) It forms alloys with Cu, Mn, Mg, Si and Zn.

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(3) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates, foils etc. and therefore, they are used in packing, making utensils, construction of aeroplane and in transportation industry.

- The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

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