

THE GROUP 13 ELEMENTS

Electronic Structures and Oxidation States:

Elements	Electronic Structures	Stable Oxidation States
B	[He] 2s ² 2p ¹	III
Al	[Ne] 3s ² 3p ¹	(I), III
Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹	I, III
In	[Kr] 4d ¹⁰ 5s ² 5p ¹	I, III
Tl	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	I, III

Most important oxidation states in bold

General Properties:

Boron is a non-metal, and always forms covalent bonds. Normally, it forms three covalent bonds at 120° using sp² hybrid orbitals. There is no tendency to form univalent compounds. All BX₃ compounds are electron deficient and may accept an electron pair forming co-ordinate bond.

The rest four elements, Al, Ga, In, Tl all form trivalent compounds. Tl shows inert pair effect and form univalent compounds dominantly. These four elements are more metallic, and more ionic than B. Many of their compounds are covalent when anhydrous but they form ions in solution.

Oxidation States and Type of Bonds:

The (+III) Oxidation State: The elements all have three outermost electrons. Excepting Tl they normally use these to form three bonds displaying an oxidation state (+III). Now the question is whether the compounds will be covalent or ionic?? The covalent characters of the compounds are suggested by the following facts:

- (i) Fajan's Rule: Small size and high charge (+3) favours covalent bonds
- (ii) The sum of three ionization energy is very high
- (iii) The electronegativity is greater than Gr-1 and Gr-2; thus, when reacting with other elements the difference will be less.

Boron is considerably smaller than the other elements and thus has higher ionization energy than others. The ionization energy is so high that boron is always covalent.

Many simple compounds of the remaining elements, such as, AlCl₃ and GaCl₃ are covalent when anhydrous. However, Al, Ga, In and Tl all form ions in solution. The type of bond is

determined by the energy factors involved. The transformation of covalent to ionic occurs, if the amount of hydration energy exceeds the ionization energy on hydration.

Let us consider the hydration of AlCl_3 .

The ionization energy for Al to Al^{3+} (i.e., $I_1 + I_2 + I_3$) is 5137 kJ/mole.

$$\Delta H_{\text{hydration}} \text{ for } \text{Al}^{3+} = -4665 \text{ kJ/mole}$$

$$\Delta H_{\text{hydration}} \text{ for } \text{Cl}^- = -381 \text{ kJ/mole}$$

$$\Delta H_{\text{hydration}} \text{ for } \text{AlCl}_3 = -4665 + (-381 \times 3) = -5808 \text{ kJ/mole}$$

Thus, $\Delta H_{\text{hydration}}$ for AlCl_3 exceeds the ionization energy for Al to Al^{3+} . So, AlCl_3 ionizes in water.

The (+I) Oxidation State: Inert Pair Effect:

In group 13, trivalence is expected owing to its electron configuration. But, there is an increasing tendency to form univalent compounds in moving down the group. Compounds with Ga(I) , In(I) , Tl(I) are known. With Ga and In the (+I) oxidation state is less stable than +III state. But, in case of Tl, thallic compounds (+I) are more stable than thallic compounds (+III).

Why such monovalency?

The atoms in this group possess general electronic configuration s^2p^1 . The monovalency is explained by the s-electrons remained as paired and cannot take part in bonding. This is called inert pair effect. If the energy required to unpair them exceeds the energy evolved during formation of bonds, the s electrons will remain paired. The strength of MX_3 bond decreases down the group.

Compounds	Mean Binding Energy (In kJ/mole)
GaCl_3	242
InCl_3	206
TlCl_3	153

Thus, the s-electrons prefer to remain as inert. The inert pair effect is not the explanation of why covalency occurs in group 13. It merely describes what happens, i.e., two electrons do not participate in bonding. The reason that they do not take part in bonding is energy.

The (+II) Oxidation State: Gallium is apparently divalent in few compounds, such as, GaCl_2 . However, Ga is not really divalent, as the structure of GaCl_2 has been shown to be $\text{Ga}^+[\text{GaCl}_4]^-$ which contains Ga(I) and Ga(III).

Melting Points, Boiling Points and Structures:

The melting points of group 13 elements don't show a regular trend. Boron and gallium have unusual crystal structure.

Elements	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)
B	2180	3650
Al	660	2467
Ga	30	2403
In	157	2080
Tl	303	1457

Boron has an unusual crystal structure which results in the melting point being very high. There are at least four different allotropic forms of boron. Boron has insufficient electrons to fill the valence shell even after forming bonds. Boron tries to solve this issue by forming different allotropes. The small size and high ionization energy of boron restricts its contribution towards metallic bonding. All four allotropic forms contain icosahedral units with boron atoms at all 12 corners.

The elements Al, In, and Tl all have close packed structure. Gallium has an unusual structure. Each metal atom has one close neighbor at a distance 2.43 \AA and size distant neighbours at distances between 2.70 \AA and 2.79 \AA . This remarkable structure favours discrete diatomic molecule rather than a metallic structure. This results in a remarkably low melting point of gallium $30\text{ }^{\circ}\text{C}$. Ga is also unusual because the liquid expands when it forms the solid, i.e., the solid is less dense than the liquid. This property is unique to Ga, Ge and Bi.

The boiling point of B is very high, but the values decreases on descending down the group Al to Tl as expected. The Ga follow the usual trend like others as the unusual crystal structure no longer exists in the liquid phase.

Electropositive Character:

The electropositive or metallic character of the elements increases from B to Al, but then decreases from Al to Tl. This is shown by the standard electrode potential for the reaction:



Elements	M^{+}/M (volt)	M^{2+}/M (volt)
B	-0.87	
Al	-1.66	+0.55
Ga	-0.56	-0.79
In	-0.34	-0.18
Tl	+1.26	-0.34

The increase in metallic character from B to Al is usual trend on descending a group associated with increasing size. However, Ga, In and Tl do not continue the trend. The elements are less likely to lose electron because of the poor shielding by d electrons.

The standard electrode potentials E° for M^{3+}/M become less negative from Al to Ga to In and the potential become positive for Tl. Since, the ΔG° for $Al^{3+} + 3e^- \rightarrow Al$ will be positive. Thus, the reverse reaction will be spontaneous. The standard electrode potential becomes less negative on descending down the group; thus the (+III) oxidation state will be less stable in aqueous medium on descending down the group.

In a similar way, the E° values for M^{+}/M show that the stability of (+I) state increases on descending down the group. Thus, Tl (+I) is found to have greater stability.

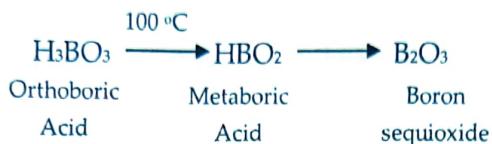
Ionization Energy:

The sum of the first three ionization energies for each of the elements is very high. Thus, boron has no tendency to form ions, and always form covalent bonds. The other elements normally form covalent bonds except in solution.

The ionization energy values do not decrease smoothly down the group. The decrease from B to Al is the usual trend on descending a group associated with increase in size. The poor shielding by d-electrons and the resulting d-block contraction affect the values of the later elements.

BORON SESQUIOXIDE AND THE BORATES:

Sesqui means one and a half, so the oxide should have a formula $MO_{\frac{3}{2}}$ or M_2O_3 . All the elements in the group form sesquioxides when heat with dioxygen. B_2O_3 is made more conveniently by dehydrating boric acid.



B_2O_3 is a typical non-metallic oxide and is acidic in properties. It is the anhydride of orthoboric acid and it reacts with basic (metallic) oxide forming salts called borates and metaborates. During borax beat test, borax or B_2O_3 is heated in a Bunsen burner flame with metal oxide on a loop of platinum wire. The mixture fuses to give a glass like metaborate beads. Metaborate beads of many transition metals have characteristic colours and so this reaction provides a means of identifying metals. The presence of cobalt in vitamin B12 is proved by this test.



However, it is possible to force B_2O_3 to behave as a basic oxide by reacting with very strongly acidic compounds. Thus, with P_2O_5 or As_2O_3 , boron phosphate or boron arsenate is formed.



Orthoboric acid H_3BO_3 is soluble in water, and behaves as a weak monobasic acid. It does not donate protons, rather it accepts HO^- . It is therefore a Lewis acid and is better to be written as $\text{B}(\text{OH})_3$.



Acidic Properties of H_3BO_3 :

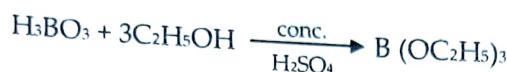
Since, $\text{B}(\text{OH})_3$ only partially reacts with water to form H_3O^+ , it behaves as a weak acid. Thus, $\text{B}(\text{OH})_3$ cannot be titrated satisfactorily with NaOH , as a sharp endpoint is not obtained. If certain polyhydroxy compounds, such as, glycerol, mannitol or sugars are added to the reaction mixture, then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid. It can now be titrated with NaOH , and the end point is detected using phenolphthalein as indicator.



The added compound must be cis-diol, to enhance the acidic properties in this way. The cis-diol forms very stable complexes with the $[B(OH)_4]^-$ formed by the forward reaction written above, thus effectively removing it from solution. The reaction is reversible. Thus, removal of one of the products at right hand side of the reaction upsets the balance, and the reaction proceeds completely to the right. Thus, all the $B(OH)_3$ reacts with NaOH: in effect it acts as a strong acid in the presence of cis-diol.

Reactions of H_3BO_3 :

When H_3BO_3 is heated with alcohol in the presence of conc. H_2SO_4 volatile esters are formed, and when ignited burns with a green flame.



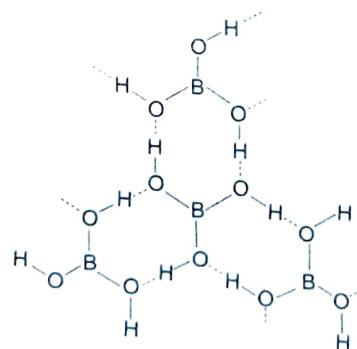
When H_3BO_3 is heated with CaF_2 in presence of conc. H_2SO_4 , BF_3 is produced. This is volatile and when ignited burns with a green flame.



Treatment of H_3BO_3 with Na_2O_2 gives sodium peroxoborate, $Na_2[B_2(O_2)_2(OH)_4]$, which is used as brightener in washing powder.

Structure of H_3BO_3 :

Crystal structure of H_3BO_3 shows a layer structure where $B(OH)_3$ units are H-bonded together into two dimensional sheets with almost hexagonal symmetry. The layers are quite large distance (3.18 \AA) apart and thus the structure breaks quite easily into fine particles



Uses of H_3BO_3 : It is used-

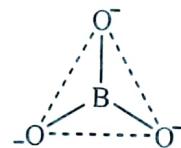
- ✓ As antiseptic in medicine
- ✓ In making enamels
- ✓ In tanning industry

Borates:

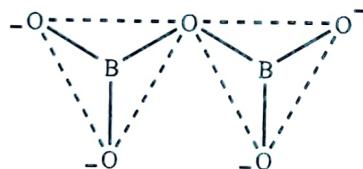
Borates are the name for a large number of boron-containing oxyanions. The anions in borates contain triangular BO_3 or tetrahedral BO_4 or combination of both. Polynuclear anions are formed by corner sharing oxygen atoms among boron oxygen triangles or tetrahedrals. The overall charge on a given borate is equal to the total number of terminal oxygen and tetrahedral boron atoms each contributing one unit negative charge.

Structure of Borates:

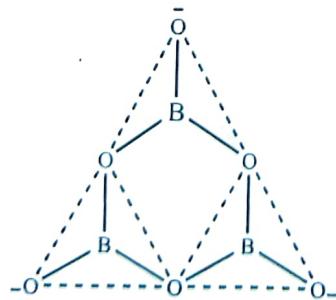
(i) Discrete BO_3^{3-} units:



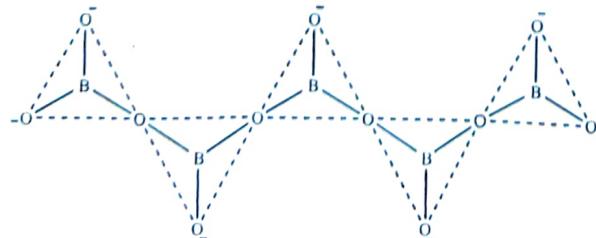
(ii) $\text{B}_2\text{O}_5^{4-}$ two BO_3 units join by sharing a corner



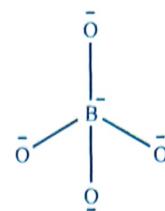
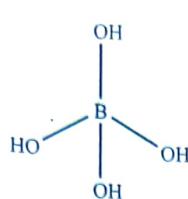
(iii) $\text{B}_3\text{O}_6^{3-}$



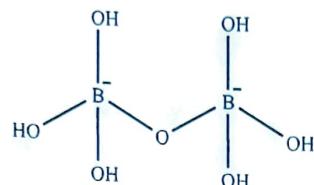
(iv) $(\text{BO}_2)_n^{n-}$ infinite chain of BO_3 units $[\text{Ca}(\text{BO}_2)]_n$



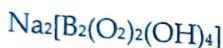
(v) $\text{B}(\text{OH})_4$ and BO_4^{5-} discrete unit



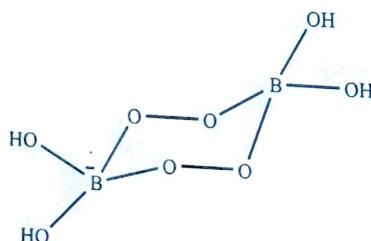
(vi) $[(\text{HO})_3\text{-B-O-B-(OH)}_3]^{2-}$



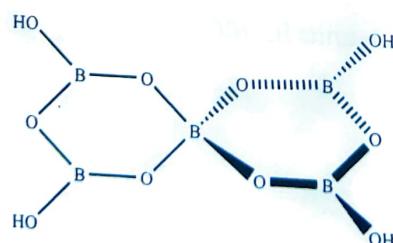
(vii) $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$

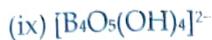


Sodium peroxoborate, sodium perborate

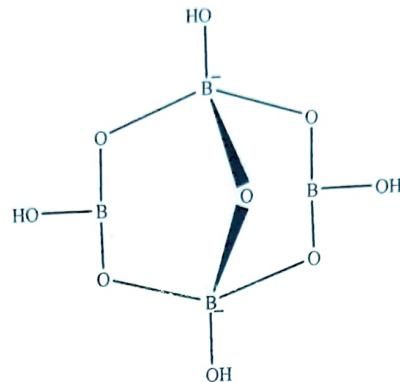


(viii) $[\text{B}_5\text{O}_6(\text{OH})_4]^-$





Two BO_3 and two BO_4 units form the closed anionic structure present in borax.



Uses of Borates:

Borates are used in-

- ✓ Fabrication of heat resistant glasses (e.g., pyrex), glass wool, fibre glass
- ✓ Detergents, soaps and cleaners
- ✓ Porcelain enamels

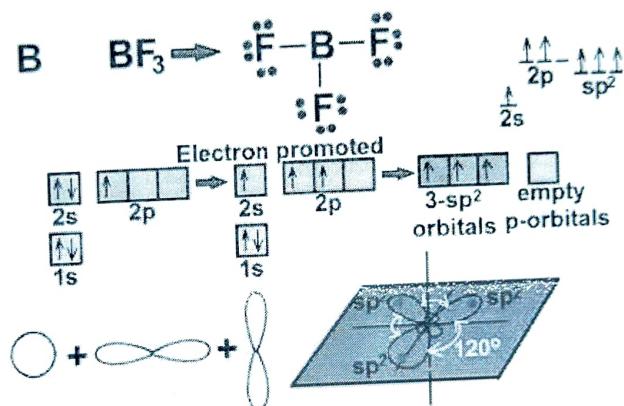
A point to note: The uses of borates in glass and ceramic industries reflect the diagonal relationship between boron and silicon and the similarity between various borate and silicate networks.

TRIHALIDES:

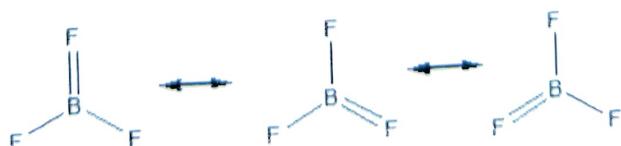
All the elements form Trihalides. The boron halides are covalent. BF_3 is gaseous, BCl_3 liquid and BI_3 is solid. BF_3 is colourless gas and can be obtained in larger quantities by the following reaction.



The shape of BF_3 molecule is planar triangle with $\angle \text{F-B-F}$ bond angle $\approx 120^\circ$. This is predicted by VSEPR as three pair around the B atom favor this as most stable shape. The VBT predicted hybridization between 2s and 2p orbital resulting sp^2 ; one pure p orbital remains as also predict electron promoted between 2s and 2p orbital resulting sp^2 ; one pure p orbital remains as vacant. The six electrons in the outer shell results the compound as electron deficient.

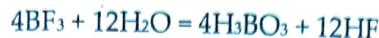


The bond length in BF_3 are 1.30 \AA and are significantly lower than the sum of the covalent radii ($\text{B}=0.8 \text{ \AA}$, $\text{F}=0.72 \text{ \AA}$). The bond energy is very high: 646 kJ/mole , which is higher than any single bond. The shortness and strength of the bonds is interpreted in terms of $\text{p}\pi-\text{p}\pi$ interaction, that is the bond possesses some double bond character. The empty unhybridized pure p-orbital may accept electron pair from a full p_z orbital on any one of the three fluorine atoms. Thus, a dative bond is formed, and the B atom attains octet of electrons. The identical bond lengths in the BF_3 can be explained in terms of the resonance between three structures.



The empty 2p_z orbital on the B atom in BF₃ can also be filled by a lone pair of electrons from donor molecules such as, Et₂O, NH₃, (CH₃)₃N or by ions such as F⁻ when this occurs a tetrahedral molecule or ion is formed.

The boron halides are all hydrolyzed by water. BF₃ hydrolyses incompletely and form fluoroborates.

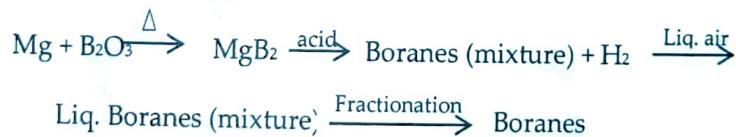


The other halides hydrolyze completely, giving boric acid.



BORANES:

None of the group 13 elements react directly with hydrogen, but several interesting hydrides are known. The boron hydrides are called boranes by analogy with alkanes. The study of boranes was initiated by Alfred Stock (1912 – 1936), who prepared and characterized several boron hydrides. He heated Mg and B to obtain magnesium boride (MgB₂), which on acidification leads to the formation of a mixture of boranes.



Many of these boranes are sensitive to air and moisture. Stock thus prepared vacuum technique for their study.

The naming of neutral boranes is illustrated by the following examples, where the Greek prefix shows the number of boron atoms and the number of hydrogen atoms is in brackets:

B₅H₉ pentaborane(9)

B₆H₁₂ hexaborane(12)

B₅H₁₁ pentaborane(11)

The naming of anions is illustrated by the following, where the hydrogen count is specified first followed by the boron count, and finally the overall charge in brackets:

B₅H₈⁻ octahydropentaborate(1-)

DIBORANE (B_2H_6):

Diborane is the simplest and most studied boron hydrides. It is used to prepare the higher boranes. Diborane is an important reagent in the synthetic organic chemistry. Diborane is a powerful reducing agent for certain functional groups. It attacks site with high electron density.

Preparation:

Precautions:

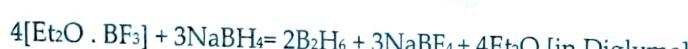
- ✓ The B_2H_6 gas is highly toxic and gets decomposed to H_3BO_3 and H_2 in contact with water
- ✓ Its mixture with O_2/air are inflammable and explosive
- ✓ Diborane also reacts with stopcock grease

Hence, diborane should be prepared using all glass vacuum apparatus using vacuum line techniques.

(1) Reduction of etherate complex of boron halides with $LiAlH_4$



Similar reduction can be obtained using $NaBH_4$ in diglyme



(2) Reaction of $NaBH_4$ with I_2 in diglyme forms B_2H_6 . [Diglyme is a polyether $CH_3OCH_2CH_2OCH_2CH_2OCH_3$]



(3) Reaction of $NaBH_4$ with 85 % phosphoric acid or, anh. Sulphuric acid leads B_2H_6



(4) Industrially BF_3 gas can be directly reduced by sodium hydride at $180^\circ C$



A point to note: Although BH_3 exists in the form of Lewis acid base adduct and as a presumable intermediate in reactions of diborane, only trace quantities of free BH_3 has been detected. The equilibrium constant of dimerization is approximately 10^5



Properties:

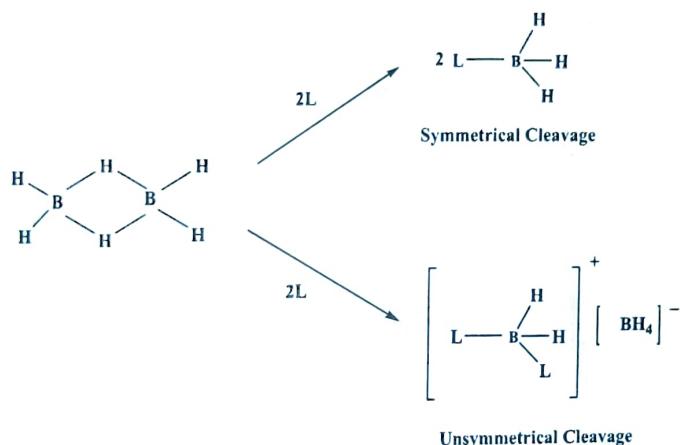
1. B_2H_6 is a colourless diamagnetic gas. It reacts spontaneously and vigorously with air; the heat of combustion is very high.



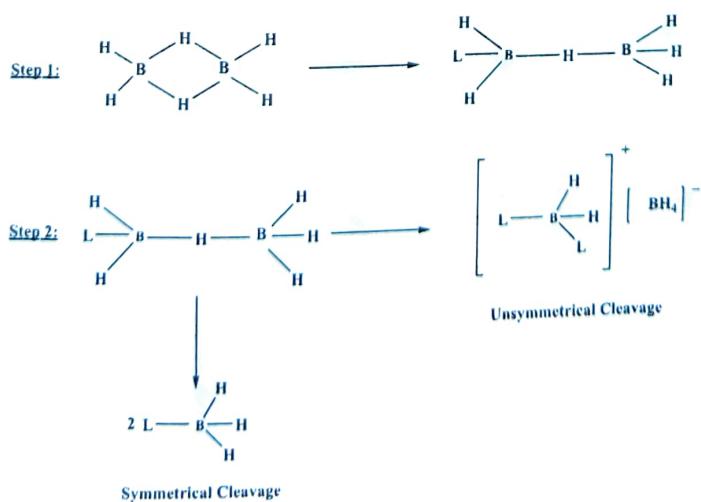
2. Diborane readily hydrolysed by water, which coordinates to B-centre as Lewis base



3. The hydrolysis of B_2H_6 reveals its Lewis acid character. The water molecule acts as Lewis base and splits the B_2H_6 into two symmetrical fragments. This is termed as symmetrical homolytic cleavage. During unsymmetrical cleavage of B_2H_6 ionic products are obtained.



Unsymmetrical cleavage of this kind is observed when diborane reacts with strong bases having no steric crowding (such as, NH_3 , MeNH_2).



Symmetrical or Unsymmetrical??

Most of the donor atoms are sufficiently electronegative. The B atom containing L, thus suffers from electron deficiency (partial positive charge is developed) and favours the attack of second L. This leads to unsymmetrical cleavage.

However, if the attack by second L suffers from steric congestion, the second L is expected to attack preferably to the other B centre, causing symmetrical cleavage.

4. Hydroboration reaction:

The hydroboration reaction involves the addition of diborane to alkenes or alkynes in ether solvent at room temperature in N₂ atmosphere. If the organic molecule is not symmetrical, the reaction follows the anti-Markonikoff's rule, i.e., B attaches to least substituted C-atom.



The extent of substitution depends on the substitution in alkenes. R₃B may form when the alkene is unhindered. The alkyl borane is not isolated and may be utilized to obtain alkanes, alcohols, carboxylic acids by using proper reagent.

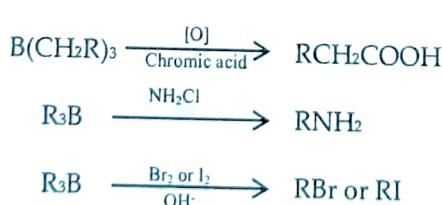
(a) *Alkanes*: Protonolysis by refluxing with an anh. carboxylic acid leads alkane.



(b) *Alcohol*: Alcohol is obtained by oxidative hydrolysis with alkaline H₂O₂



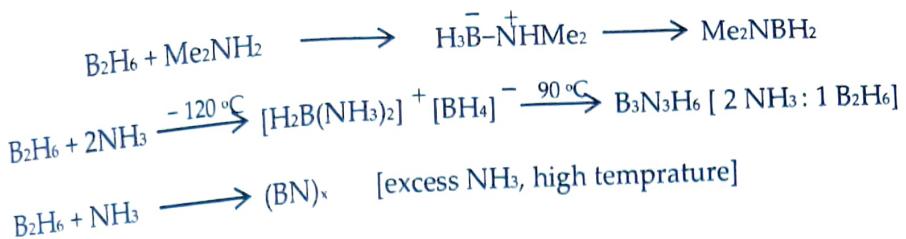
(c) *Carboxylic acid/Amine/Halide*: Oxidation by chromic acid forms carboxylic acid. Amine and alkyl halide are obtained by using NH₂Cl and alkaline X₂



5. Reaction with ammonia:

All the boranes act as Lewis acids and can accept electron pair from amines forming adducts. They also react with NH₃, but the final product depends on the reaction condition.





6. Other reactions:



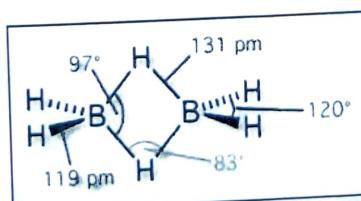
Structure of diborane:

The hydrides of boron differ from other hydrides. There are not enough valence electrons to form conventional 2c-2e bond, and so these compounds are termed as electron deficient. Electron diffraction and other physical studies reveal that, in B_2H_6 the two B atoms are joined by two B-H-B bridges in a plane perpendicular to that of the plane containing terminal B-H bonds. The bridge bonds are somewhat longer than the terminal B-H bonds.

The difference in environment between 'bridging -H' and 'terminal -H' has been confirmed by-

(a) Raman spectroscopy

(b) During methylation B_2H_6 can be methylated upto $\text{Me}_4\text{B}_2\text{H}_2$



Bonding in Diborane:

The bonding in diborane has been most satisfactorily explained by the concept of multicenter M.O.s. Longuet Higgins first considered 3c-2e B-H-B bridge bond to explain the bonding of diborane. The concept was also extended to explain the bonding in higher boranes.

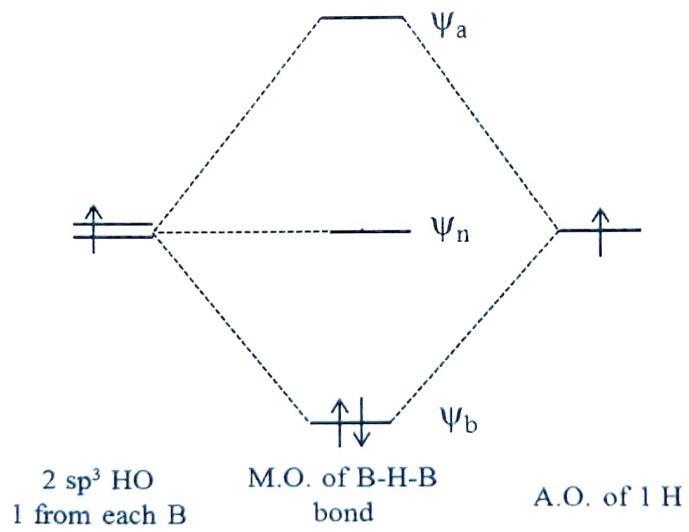
➤ The M.O. description starts with four roughly sp^3 hybrid orbitals on each boron and the 1s atomic orbital on the H atoms

➤ Two orbitals on each boron overlaps with 1s atomic orbitals of two hydrogen atoms to give the terminal 2c-2e bonds. These corresponding to four bonding and four anti-bonding M.O.s formed by four hybrid orbital on B and four 1s orbital of H. Eight electrons (four from two B + four from four H) occupy the bonding M.O.s.

➤ We are now left with two hybrid A.O.s and one valence electron in each BH_2 unit. If the two BH_2 units are brought close keeping all the B and H atoms in plane the unused hybrid orbitals on each B atoms will point to each other in an approximately perpendicular plane. The 1s orbital of the two remaining hydrogens can now suitably overlap with these orbitals forming two sets of B-H-B bridge bonds.

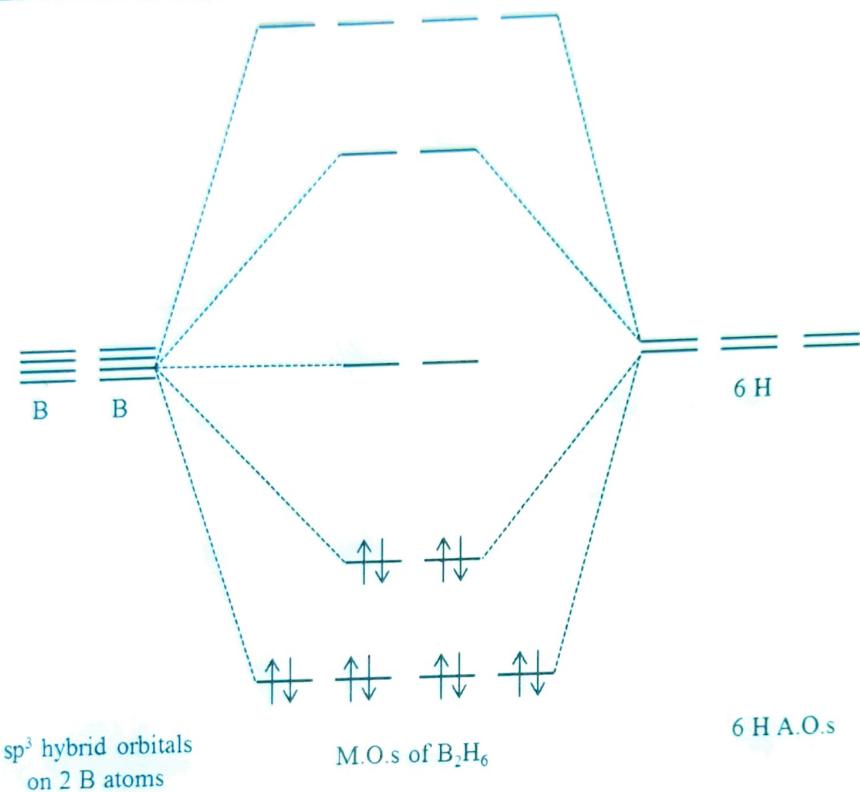
➤ For each B-H-B unit we have three orbitals: two from the B atoms (one from each BH_2 unit) and one from the H-atom. These three atomic orbitals give rise to one bonding, one non-bonding and one anti-bonding M.O. Two electrons, one from either of the two B atoms and one from H atom occupy the lowest energy bonding M.O. Each B-H-B unit thus form a three centre system held by two electrons, 3c-2e bond.

M.O. description of B-H-B unit:



Since, the bonding electron pair operates over three centres, the bond order is <1 and thus the strength of 3c-2e bond is considerably lower than the 2c-2e bond. This is also consistent with longer B-H distances in the bridges.

M.O. description of the bonding of Diborane:



BORAZINES:

The most important ring system in organic chemistry is the benzene ring either as a separate entity or polynuclear fused form, such as naphthalene, anthracene, phenanthrene. Inorganic chemistry has two well known analogues of benzene: borazine ($\text{B}_3\text{N}_3\text{R}_6$) and trimeric cyclo-phosphazene compounds ($\text{P}_3\text{N}_3\text{X}_6$).

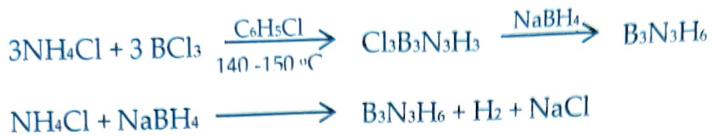
Borazine has been known since the pioneering work by Alfred Stock in this century. Stock's work was important in two regards:

- (i) He was the first to study compounds, such as, boranes, silanes and other similar non-metal compounds
- (ii) He developed vacuum line techniques for handling air and moisture sensitive compounds

Stock's synthesis:



Other more efficient synthetic routes are:



N or B substituted borazines may be prepared by appropriate substitution on the starting material prior to the synthesis of the ring

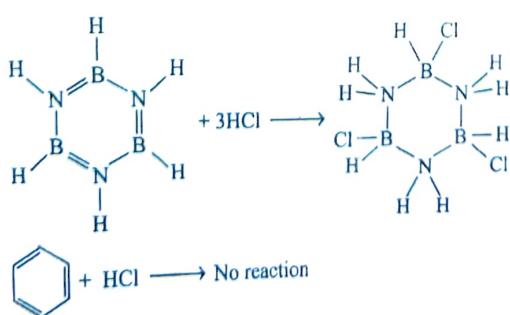


Properties:

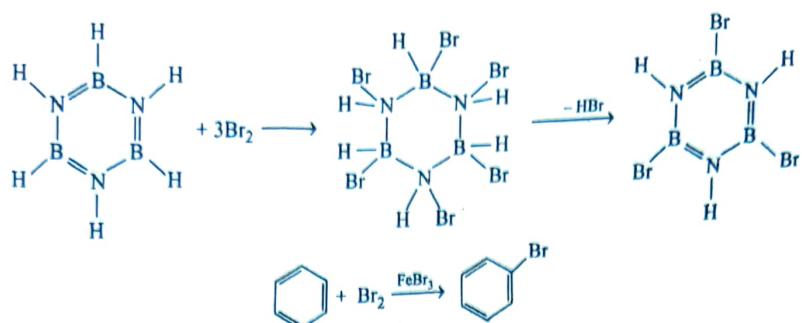
Borazine is isoelectronic with benzene, as $\text{B}=\text{N}$ with $\text{C}=\text{C}$. The physical properties of borazine are close enough to that of benzene. The similarity in the physical properties of the alkyl substituted benzene and borazine is even more remarkable. For example, the ratio of boiling points of the substituted borazines to those of the similarly substituted benzene is constant. This similarity in physical properties led to the labeling of borazine as 'Inorganic benzene'. This is a misnomer, as the chemical properties of borazine and benzene are quite different.

Both compounds have aromatic π -cloud of electron density delocalized over the ring atoms. Due to the difference in electronegativity between boron and nitrogen, the electron cloud in borazine is lumpy because more electron density is localized on nitrogen atoms. This partial localization weakens the π -bonding in the ring. Each nitrogen atom receives more σ -electron density from neighbouring boron than it gives away as π -donor. In addition, nitrogen retains its basicity and boron its acidity.

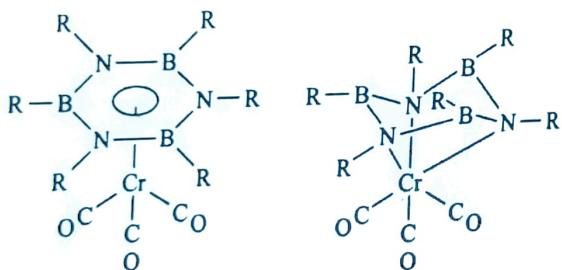
Polar species, such as, HCl can therefore attack double bond between B and N. Thus in contrast to benzene borazine readily undergoes addition reaction.



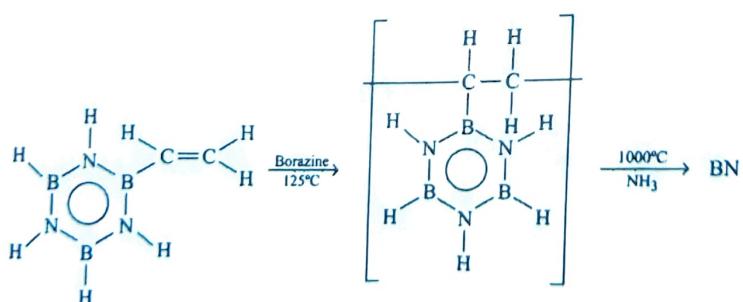
With Br_2 borazine undergoes addition reaction, while benzene undergoes substitution reaction.



The electronic difference between benzene and borazine is further supported by the properties of compounds of the type $(\text{R}_6\text{B}_3\text{N}_3)\text{Cr}(\text{CO})_3$. Although these are formally analogous to $(\eta^6\text{-C}_6\text{R}_6)\text{Cr}(\text{CO})_3$, the bonding is not so strong in borazine complex. Its ring-metal dissociation energy is about half to that of the arene complex. Additionally, there are considerable evidences that the borazine molecule is puckered in these complexes. The actual structure is intermediate between a true π -complex and the extreme σ -only model.



Inorganic analogue of styrene $(\text{CH}_2=\text{CH})\text{B}_3\text{N}_3\text{H}_5$ has been polymerized and decomposed to produce BN.



Benzene may be hydrogenated to produce the saturated compound, cyclohexane. Hydrogenation of borazine results in polymeric materials of indefinite composition. The saturated borazine can be prepared by the reduction of chloro derivative.

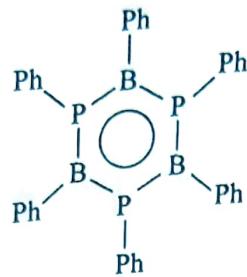


Analogous species of borazine:

Boroxine: $\text{H}_3\text{B}_3\text{O}_3$

- Can be prepared by the explosive oxidation of B_2H_6 or B_5H_9
- Boroxine is planer, but the π -delocalization is less than borazine
- Decomposes to give diborane and boron oxide

A B-P analogue of borazine has also been synthesized recently.

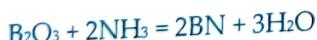


Lumazenes: Al-N analogue of borazine.

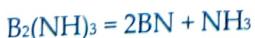
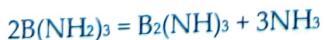
BORON NITRIDE (BN):

Preparation:

1. Boron reacts with nitrogen or ammonia at 1000°C to form boron nitride.
2. It may be prepared in small scale by fusing borax with ammonium chloride.



3. Thermal decomposition of boron amide gives boron nitride via the imide. Boron amide is obtained by reacting BCl_3 with NH_3 .



Properties:

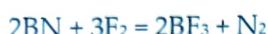
1. Boron nitride is a slippery white solid which melts under pressure at 3000 °C.

2. It is chemically inert to O₂, Cl₂, Br₂, I₂ etc.

3. It decomposed by water forming B₂O₃ and NH₃



4. BN reacts with F₂ forming BF₃ and N₂



5. BN reacts with HF forming NH₄BF₄



6. It is also decomposed on fusion with KOH or K₂CO₃



Structure:

The common form of BN consists of a layer lattice structure similar to graphite. In each layer, B and N form planar hexagons. Both B and N are sp² hybridized. The layers are stacked over each other such a pattern that B of one layer lies over N of another layer. In graphite, the hexagonal rings of alternate layers are directly top of one another.

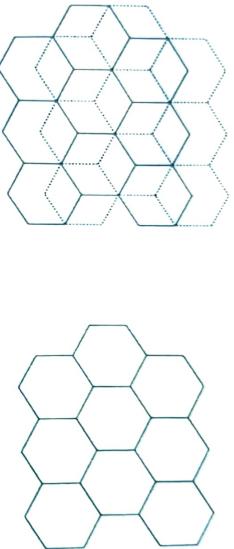
Distance between successive layers: In BN 333 pm, In graphite: 335 pm

Distance between atoms in each layer: In BN, B-N 145 pm; In graphite C-C: 142 pm

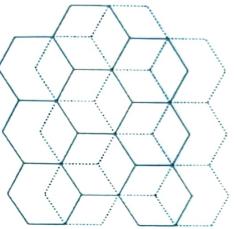
B+N atomic radii = 88+70 = 158 pm

The lower bond distance in BN indicates π -delocalization within the B-N hexagonal layers.

Due to structural similarities with graphite BN is sometimes called '*inorganic graphite*'. However, unlike graphite BN is colourless and insulator.



Graphite



Boron nitride

Hexagonal BN is converted to a cubic form comparable to diamond when heated at 1800 °C under 85000 atm. pressure, preferably in the presence of alkali or alkaline earth metal catalyst. The compound is termed as *borazon*. Borazon is extremely hard and used in cutting diamond.

