GROUP 13 ELEMENTS Section - 2

Ionisation Energy

The first ionisation energies (IE_1) of group 13 elements are lower than the corresponding elements of group 2 (alkaline earth metals). This is due to the fact that group 13 elements have ns^2, np^1 configuration in their valence shell and the electron thus has to be removed from the *p*-orbital. This is much easier than removing an s-electron of group 2 elements which being nearer the nucleus is more strongly attracted.

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

Oxidation States

Due to ns^2, np^1 configuration of the valence shell, group 13 elements are expected to be trivalent but there is increasing tendency to form univalent compounds on descending the group. B and Al show an O.S. of +3 while Ga, In, Tl show O.S. of both +1 and +3. This is due to the Inert Pair Effect.

Metallic Character/Reducing Power

The order is : B < Al > Ga > In > Tl

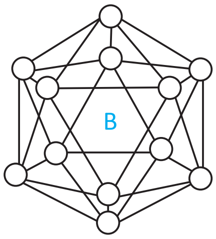
The increase in metallic character from B to Al is the usual trend on descending a group associated with increasing size. However Ga, In, Tl donot continue the trend. Ga, In and Tl follow immediately after a row of ten transition elements and thus have ten d electrons which are less efficient at shielding the nuclear charge than s,p electrons. Thus outer electrons being more firmly held by the nucleus are more difficult to remove than would be expected. This leads to contraction in size as well as decreases in metallic character than would be expected. The phenonmenon is know as *d*-block Contraction. Similarly Tl follows immediately after 14-*f*-block elements and the size and and metallic character are affected even more. This contraction due to the *f*-block elements is called Lanthanide Contraction. Note that the size increases down the group as usual but is less than that expected.

Acidic Character

On moving down the group acidic character decreases and basic character increases because ionization energy increases. Thus we find that $B(OH)_3$, and B_2O_3 are acidic ; $Al(OH)_3$ and Al_2O_3 are amphoteric; $Ga(OH)_3$ and Ga_2O_3 are amphoteric; and In $(OH)_3$, TlOH are basic.

Boron & its Compounds :

Physical Properties and Occurence :



Boron occurs in two allotropic forms :

(a) Crystalline - It is black, chemically inert and very hard.

(b) Amorphous - It is brown, chemically active, a non - conductor and difficiult to fuse.

All allotropic forms contain icosahedral units with atoms at all 12 corners. The important minerals of boron are :

Borax (Tincal)	$Na_2B_4O_7 . 10H_2O$	Boric aicd	H_3BO_3
Kernite (Rasorite)	$Na_2B_4O_7 . 4H_2O$	Boronatro calcite	$CaB_4O_7 . NaBO_2 . 8H_2O$
Colemanite	$Ca_2B_6O_{11} . 5H_2O$	Boracite	$2Mg_3B_8O_{15} . MgCl_2$
Panderite	$Ca_2B_6O_{11}.3H_2O$		

Extraction of Boron : It includes 2 steps :

1. Preparation of Boric anhydride (B_2O_3) :

[Method I]

$$\underset{\text{(powdered Borax)}}{Na_2B_4O_7} + \underset{\text{(conc.)}}{2HCl} \longrightarrow 2NaCl + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{(sparingly soluble orthoboric acid)}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O$$

[Method II]

$$\underset{\left(\substack{\text{powdered}\\ \text{colemanite}}\right)}{Ca_2B_6O_{11}} + \underset{\text{fused}}{2Na_2CO_3} \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

The fused mass is extracted with hot water. $CaCO_3$ remains insoluble and filtrate containing borax and sodium metaborate is put to crystallisation when borax crystals are obtained. The remaining solution is treated with carbon dioxide.

$$4NaBO_2 + CO_2 \longrightarrow \underset{\text{borax}}{Na_2B_4O_7} + Na_2CO_3$$

Then Method I is followed.

[Method III]

Suspension of colemanite mineral in water is formed and SO_2 gas is passed to obtain crystals of boric acid on cooling.

$$Ca_2B_6O_{11} + 4SO_2 + 4H_2O \longrightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11}$$

$$H_4B_6O_{11} + 7H_2O \longrightarrow 6H_3BO_3$$

$$\overline{\underline{Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3}}$$

$$\text{Then, } \underset{\text{crystals}}{2H_3BO_3} \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

2. Reduction of B_2O_3 :

[Method I]

$$\underbrace{B_2O_3 + 3M}_{\text{fused}} \xrightarrow[\text{crucible}]{\text{heated in}} 2B + 3MO \ (M = Na, K \text{ or } Mg)$$

The fused mass is stirred with iron rod so as to oxidise unreacted metal M. The mass is then boiled with dil.HCl to obtain insoluble amorphous boron powder which is 95% pure.

[Method II] : Modern Method

A fused mixture containing boric anhydride, magnesium oxide and magnesium fluoride at 1100°C is electrolysed in a carbon crucible (anode). Iron rod is used as cathode.

Cathode :

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

$$Mg + B_2O_3 \longrightarrow \underset{\text{amorphous}}{B} + MgO$$

Anode :

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

[Method III]

To obtain *crystalline boron* in small amounts, B_2O_3 is reduced with aluminium powder.

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

Aluminium is removed by heating the fused mass with NaOH solution.

Chemical Properties of Boron :

1. Boron is unaffected by water under ordinary conditions but :

$$\underset{\text{(red hot)}}{2B} + \underset{\text{(Steam)}}{3H_2O} \longrightarrow B_2O_3 + 3H_2 \uparrow$$

2. Amorphous boron burns in air at 700°C with a reddish flame forming oxide and nitride.

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

3. Boron is unaffected by reducing acids. With oxidising acids it gives boric acid.

$$B + \underset{\text{O.A.}}{3HNO_3} \longrightarrow H_3BO_3 + 3NO_2 \uparrow$$

4. Boron dissolves in fused alkalies liberating hydrogen.

$$2B + \underset{\text{fused}}{6NaOH} \longrightarrow 2Na_3BO_3 + H_2 \uparrow$$

5. Boron often forms non-stoichiometric compounds with metals (not of Group 1)

$$2B + 3Mg \longrightarrow Mg_3B_2$$

6. Action of non-metals :

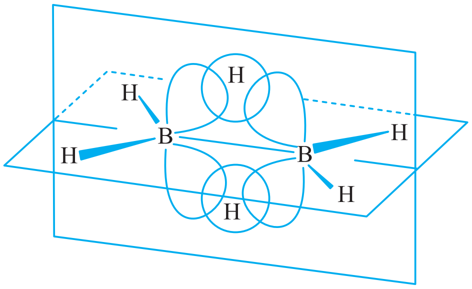
$$4B + C \xrightarrow[\text{electric furnance}]{\Delta} B_4C \ ; \quad 2B + 3Cl_2 \xrightarrow{\Delta} 2BCl_3$$

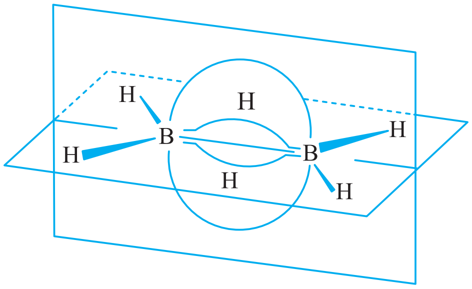
Uses : Boron carbide rods are used to control nuclear reactions. Boron has a very high cross-section to capture the neutrons. Also B absorbs neutrons to make boron having an even number of neutrons.

$$_5B^{10} + {}_0n^1 \longrightarrow {}_5B^{11}$$

[a] Diborane B_2H_6 :

Structure and Physical Properties :





The bridge hydrogens form abnormal 3 centre 2 electron ‘banana-shaped’ bonds with two B atoms. An sp^3 hybrid orbital from each boron atom overlaps with the 1s orbital of the hydrogen to give a delocalised molecular orbital covering all three nuclei.

Diborane is a colourless and highly reactive gas with a disagreeable odour. It is used as a reducing agent in organic reactions and as a catalyst in polymerisation reactions.

Preparation :

(i) $$4BCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiCl + 3AlCl_3$$

$$\xrightarrow{+H_2,\text{ silent electric discharge}} B_2H_6 + HCl$$

(ii) $$8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$$

Chemical Properties :

1. It is instantly hydrolysed by water or aqueous alkali.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2$$

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

2. It catches fire spontaneously in air and explodes with dioxygen.

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

Thus in the laboratory, it is handled in a vacuum frame.

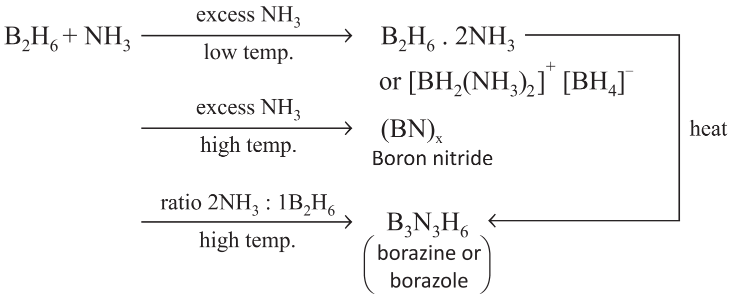
3. $$B_2H_6 \xrightarrow{\text{red heat}} 2B + 3H_2$$

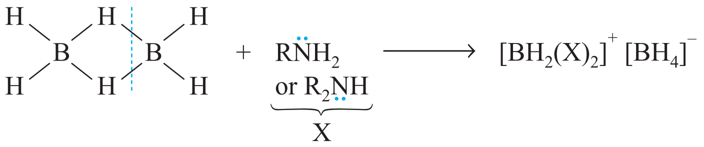
4. Other reactions :

$$B_2H_6 + 2LiH \xrightarrow{\text{ether}} 2LiBH_4 \quad ; \quad B_2H_6 + 3Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

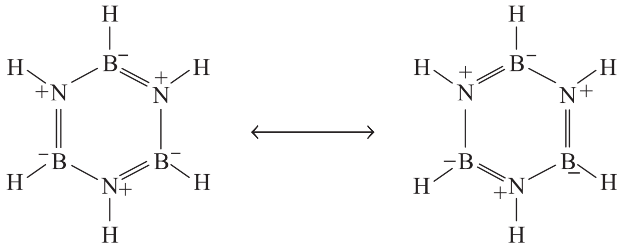
$$B_2H_6 + \underset{\text{dry}}{HCl} \xrightarrow[\text{AlCl}_3]{\text{anhyd.}} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + H_2$$

5. Reaction with ammonia and amines :

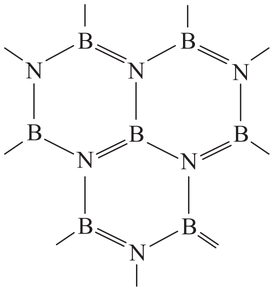




Borazole is called ‘ inorganic benzene’ due to its similar structure and aromatic character.



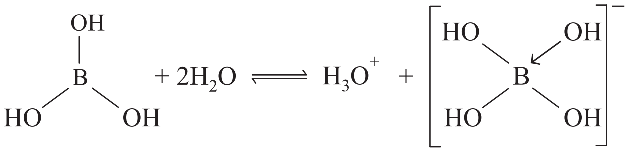
Boron nitride (BN) is a white slippery solid called ‘inorganic graphite’ which has a layer structure similar to graphite.



[b] Orthoboric Acid H_3BO_3 :

Sturcture and Physical Properties :

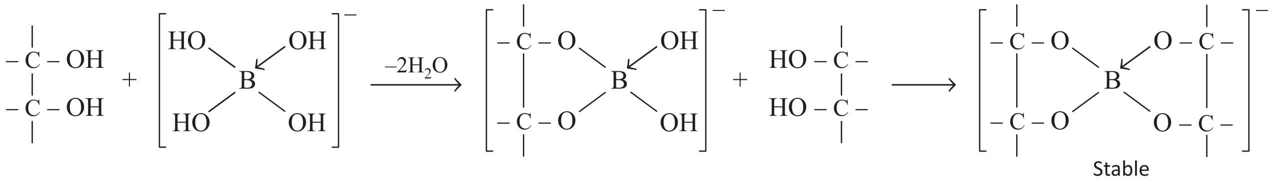
Orthoboric acid is a weak monobasic acid, sparingly soluble in water. It is a Lewis acid and better written as $B(OH)_3$.



Plane Triangle

Teretrahedral Metaborate Ion

Thus $B(OH)_3$ alone is not titrated with NaOH as a sharp end point is not obtained. However if a cis-diol is added then $B(OH)_3$ behaves as a strong monobasic acid and can now be titrated with NaOH using phenolpthalein as indicator Cis-diols form stable complexes with $[B(OH)_4]^-$ thus effectively removing them and carrying the reaction forward.



Chemical Properties :

1. Effect of heat :

$$\underset{\substack{\text{orthoboric}\\ \text{acid}}}{H_3BO_3} \xrightarrow{100°C} \underset{\substack{\text{Metaboric}\\ \text{acid}}}{HBO_2} \xrightarrow{160°C} H_2B_4O_7 \xrightarrow{\text{red heat}} \underset{\substack{\text{boron}\\ \text{sesquioxide}}}{B_2O_3}$$

Thus, B_2O_3 is also called boric anhydride as it is the anhydride of boric acid.

2. $H_3BO_3 + 3CH_3OH \xrightarrow{\Delta} \underset{\substack{\text{methyl}\\ \text{borate}}}{B(OCH_3)_3} + 3H_2O$

H_2O is removed by conc. H_2SO_4 and the mixture burns with green flame. This is used as a test for boron compounds.

3. Boric acid dissolves in HF(aq) to give fluoroboric acid HBF_4 which is a strong acid. In dry HF borates give BF_3 which burns with a green colour.

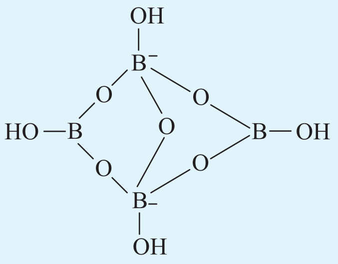
Uses :

Boric acid is used in glass industry and as an antiseptic and eyewash under the name 'Boric Lotion'.

[c] Borax :

Sturcture :

Borax ($Na_2B_4O_7 \,.\, 10H_2O$) is better written as $Na_2[B_4O_5(OH)_4] \,.\, 8H_2O$ having 8 water molecules and the ion $[B_4O_5(OH)_4]^{2-}$ associated with Na^+.



There are two tetrahedral and two triangular units in $[B_4O_5(OH)_4]^{2-}$

Chemical Properties :

1. When borax dissolves in water equal amounts of weak acid and its salt are formed. Thus it is used as a buffer.

$$[B_4O_5(OH)_4]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 + 2[B(OH)_4]^-$$

2. Borax reacts with 2 moles of acid because only $[B(OH)_4]^-$ formed will react with H^+.

$$2[B(OH)_4]^- + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$

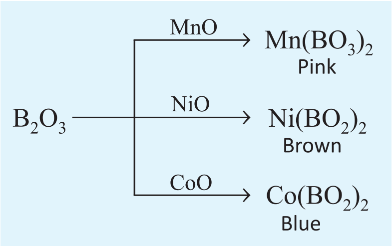
or $\quad Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$

The indicator used is methyl orange as it is unaffected by the boric acid formed.

3. Borax Bead Test :

Metaborates [$M(BO_2)$] of many transition elements have characteristic colours and this provides a means of identifying the metal through this test.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + \underset{\text{(glassy bead)}}{B_2O_3}$$



Uses :

(i) It is used as a flame retardant for wood and fabric.
(ii) It is used as a flux in brazing and silver soldering.
(iii) Used in glass industry.
(iv) Used in Borax Bead Test in analytical chemistry.

Aluminium :

1. Aluminium metal is moderately soft but much stronger and lighter when alloyed with metals. Some alloys of Aluminium are :

Alloys	Composition	Uses
Magnalium	Al - 95%, Mg - 5%	In construction of airships, balances.
Duralumin	Al - 95%, Cu - 4%, Mg - 0.5%, Mn - 0.5%	In areoplanes and automobile parts.
Aluminium bronze	Cu - 90%, Al - 9.5%, Sn - 0.5%	For making utensils, cheap artificial jewellery.
Alnico	Steel - 77%, Al - 20%, Ni - 2%, Co - 1%	For making permanent magnet.

2. Thermodynamically Al should react with water and air but in fact it is stable in both. The reason is that a very thin oxide film of Al_2O_3 forms on the surface and protects it. Due to this resistance to corrosion and high thermal conductivity it is used in making domestic utensils.

3. Reduction of some metal oxides like Mn_3O_4 and Cr_2O_3 require temperature high enough for carbon to be used as a reducing agent. Thus Al, a highly electropositive metal which liberates a large amount of energy on oxidation to Al_2O_3 is used as the reducing agent. This is known as thermite process. The thermite reaction is :

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s) + \text{energy} \qquad \Delta H^\circ = -1670\text{kJ}$$

4. Al is amphoteric and dissolves in both acids and bases.

$$2Al + 6HCl \longrightarrow 2Al^{3+} + 6Cl^- + 3H_2$$

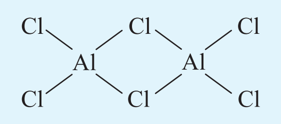
$$2Al + 2NaOH + 6H_2O \longrightarrow 2Na[Al(OH)_4] \text{ or } \underset{\text{Sodium aluminate}}{2NaAlO_2 \cdot 2H_2O} + 3H_2$$

However, conc. HNO_3 renders it passive due to the formation of a protective oxide layer.

[a] Aluminium Oxide Al_2O_3 (Alumina)

Alumina is a white crystalline powder, insoluble in water. It is stable, quite unreactive and amphoteric in nature. The α-form of Al_2O_3 is called *corundum* and found as a mineral in nature.

[b] Aluminium Chloride $AlCl_3$:



$AlCl_3$ exists as a dimer, thus attaining an octet of electrons. It is largely covalent when anhydrous or in a non-polar solvent such as benzene. However, when dissolved in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[Al.(H_2O)_6]^{3+}$ and $3Cl^-$ ions. At low temperature, $AlCl_3$ exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes.

Crystalline $AlCl_3$ exists as $AlCl_3.6H_2O$. This on heating cannot give anhydrous salt just like $MgCl_2.6H_2O$ (diagnol relationship). Instead it undergoes hydrolysis on heating :

$$2AlCl_3\ .\ 6H_2O \xrightarrow{\Delta} 2Al(OH)_3 + 6HCl + 6H_2O$$

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

The anhydrous compound is prepared by action of dry chlorine gas on aluminium or alumina :

$$Al + Cl_2 \longrightarrow AlCl_3$$

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

IN-CHAPTER EXERCISE - A

1. *Give reason for the following :*

- **(a)** *Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.*
- **(b)** *Red phosphorus is less volatile than white form.*
- **(c)** *Diborane is called an electron-deficient compound.*
- **(d)** *Anhydrous $AlCl_3$ fumes in moisture.*
- **(e)** *A mixture of NaOH and Al pieces is used to open the drain.*

2. *Identify the unknown compounds in the following reactions :*

(a) $Na_2B_4O_7 + conc.H_2SO_4 \longrightarrow A \xrightarrow[2.\ Ignite]{1.\ C_2H_5OH} B$

B is identified by the characteristic colour of the flame. Identify A and B.

(b)
$$\begin{tikzcd} BCl_3 + LiAlH_4 \arrow[r] & A \arrow[r, "excess\ NH_3"] \arrow[l, bend left, "+C"] & B \end{tikzcd}$$

(c) $BCl_3 + NH_4Cl \xrightarrow{140°C} A \xrightarrow{Na[BH_4]} B \xrightarrow{+3HCl} C$

(d) $H_3BO_3 + HF\ (non\ aqueous) \longrightarrow A \xrightarrow{LiH} B \xrightarrow{excess\ LiH} C$

3. *AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes stable. On addition of BF_3 ; AlF_3 is precipitated. Write the balance chemical equations.*

4. *RCN, RNO_2 and RCHO can be reduced by B_2H_6. What are the products due to reduction ?*

Choose the correct alternative. Only One Choice is Correct. However, questions marked with '*' may have More than One Correct options.

5. H_3BO_3 is :

(A) Weak monobasic Lewis acid **(B)** Weak monobasic Bronsted acid

(C) Strong monobasic Lewis acid **(D)** Weak tribasic Bronsted acid

6. Alumina may be converted into anhydrous aluminium chloride by :

(A) heating it with conc. HCl

(B) heating in a current of dry chlorine

(C) heating it with rock salt

(D) mixing it with carbon and heating the mixture in a current of dry chlorine

***7.** Colemanite on reaction with sodium carbonate gives :

(A) CaO **(B)** $CaCO_3$ **(C)** $NaBO_2$ **(D)** B_2O_3

***8.** Which of the following compounds have dimers with three center two electron bonds ?

(A) BH_3 **(B)** $Al(CH_3)_3$ **(C)** BCl_3 **(D)** $AlCl_3$

9. Statement : 1 Boron always forms covalent bonds.

Statement : 2 The small size of B^{3+} favours formation of covalent bond.

(A) Statement-1 is True, Statement-2 is True and Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True and Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

GROUP 14 ELEMENTS Section - 3

Oxidation States :

C and Si show oxidation state of +4 while Ge, Sn, Pb show oxidation states of both +2 and +4 due to the Inert Pair Effect.

Metallic Character :

It decreases down the group. Thus, C and Si are non-metals, Ge is a metalloid and Sn and Pb are metals .

Catenation :

Due to smaller size and higher electron negativity of carbon atom it has the property of linking to other carbon atoms forming long chains. However as we move down, the tendency for catenation decreases in the order :

$$C >> Si > Ge \approx Sn >> Pb.$$