

THE BORON FAMILY

Preface

This booklet is designed not only to reinforce the students formal knowledge about "**The Boron family**". The main objective behind putting up prudently organised strategic edition of this booklet is to develop their urge to excel & ability for original thinking, to offer them the unique joy that only solving of truly challenging problem can bring, to acquiring them with chemical ingenuity & idea which is new to them.

We have meticulously culled out the latest & the most relevant mechanism aspects of reaction & the latest challenging problems.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develop better understanding of the chapter and to have better grasping level in the class.

Total number of Questions in **The Boron Family** are :

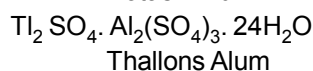
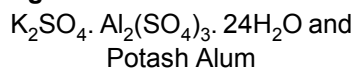
In Chapter Examples0

Solved Examples0

Total no. of questions**0**

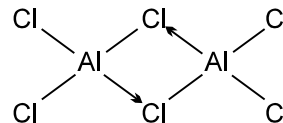
(xi) Like Alkali metals Tl (I) forms double salts with aluminium salts.

Eg.



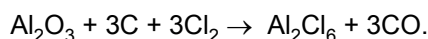
(xii) Thallium the last member of this group is known as Duckbill platypur as it shows similarities with many other elements.

(m) Al_2Cl_6 (Aluminium chloride) :- Exist as a dimer.

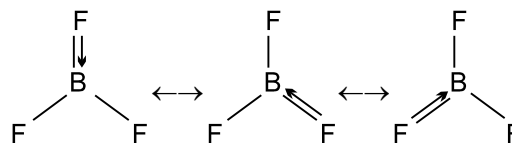


Above $700^\circ C$ Al_2Cl_6 converts to $AlCl_3$.

(n) Al_2O_3 on heating with coke & Cl_2 forms Al_2Cl_6 and this reaction is called as **Reductive Chlorination**.



(o) BF_3 do not form dimer while other forms because, the energy released by the formation of an additional bond to another boron atom is not sufficient to compensate for the loss in energy to the system in overcoming the B-F $p\pi-p\pi$ bonding in the monomer itself.



(p) Al, Ga, In & Tl do not show back bonding because of increase in the size of the element. Actually they make use of vacant p-orbitals to complete their octet by forming dimers.

4. CHEMICAL PROPERTIES ::

4.1 Formation of Halides :

(a) Halides formed have formula MX_3 & MX .

(b) Halides of B are MX_3 Halides
ie BF_3 , BCl_3 , BBr_3 , BI_3 .

(c) MX_3 halides of Ga & In are more stable while MX halides of Tl is more stable.

(d) Ga & In Halides are more ionic than Al one.

(e) $BCl_3 \rightarrow TlCl$ the rate of hydrolysis decreases because size increases so less is the ionic character more is the hydrolysis

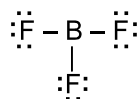
BCl_3
↓ Ionic character (Increases) so
hydrolysis decreases
Tl

(f) $TlCl \xrightarrow{H_2O}$ No reaction.

$TlCl$ will dissolve in H_2O but will not undergo hydrolysis.

(g) $AlCl_3$ to $TlCl$ Charge density decreases. So polarising power decreases & ionic character increases.

(h) On $BF_3 \rightarrow$ 9 lone pairs are available



(i) Acidic order $BF_3 < BCl_3 < BBr_3 < BI_3$.

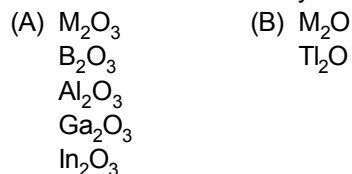
(j) In BF_3 , B has vacant 2p orbital and 2p orbital of F has lone pairs of e^- . The vacant 2p orbital of B overlaps 2p orbitals of F containing lone pairs e^- . This results in formation of a weak bond which is called as back bonding.

(k) Due to back bonding, the availability of vacant 2p orbital on boron of BF_3 decreases. so it acts as a weak Lewis acid.

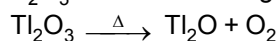
(l) From BF_3 to BI_3 . the tendency to undergo back bonding decreases so there will be greater availability of vacant 2p orbital on Boron and hence the Lewis acid character increases.

4.2 Formation of oxides

(a) Oxides formed are mainly of two types



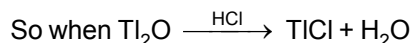
(b) Tl_2O_3 at $100^\circ C$ forms Tl_2O because Tl_2O_3 is strong oxidising so decompose into Tl_2O , while B_2O_3 & others will not go change on $100^\circ C$.



(c) Al_2O_3 is amphoteric oxide as it is dissolved in H_2O and neutralising same is with Ga.

(d) Al_2O_3 has high melting point & does not fuse easily.

(e) Oxides and Hydroxides gradually change from acidic to basic character through amphoteric (Gallium oxide and Gallic hydroxides). On moving down the group.



This reaction confirms that Tl_2O is basic.

- (f) Al_2O_3 has very high melting point & it can stand very high temp & so it is used in the form of Refractory lining for furnaces.
- (g) B_2O_3 is a weak acid due to when
 $\text{B}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{B}-\text{O}-\text{H}$
 $\text{B} \leftarrow \text{O} \leftarrow \text{H}$, B is in +ve oxidation state and it is electronegative and an element which has both above conditions, withdraw e^- from O & O will withdraw e^- from H and so the strength of bond between O & H become weak & so in aqueous medium B_2O_3 releases H^+ ion form $\text{B}-\text{O}-\text{H}$ and so behaves as a weak Acid.

4.3 Formation of Hydrates :

- (a) Boron Hydrides are called Boranes and has general formula as B_nH_{n+4} & B_nH_{n+6} (dihydroboranes).

Eg. B_2H_6 diborane while $\text{B}_4\text{H}_{10} \rightarrow$ dihydroxy tetra borane.

B_5H_9 Pentaborane while B_5H_{11} dihydroxy pentaborane.

- (b) Q. 1/2 mole of diborane on hydrolysis released moles of H_2 .

Ans. 3 moles.

$\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$ but in Q. i.e. 1/2 mole instead of 1 mole.

Note : As much hydrogen will be in hydrates it will give that much amount of H_2 on hydrolysis.

- (c) B_2H_6 to TIH the stability decreases because size of TI ion be large and in the lattice of TI ion there will be maximum repulsion. So least stable. (Ac. to Fajan's Rule.)

- (d) The Hydrates of IIIrd group combined with also act as strong reducing agents.

Eg. LiAlH_4 or NaBH_4 .
 $\text{LiAlH}_4 \rightarrow \text{Li}^+ + \text{AlH}_4^-$

4.4 Formation of Oxy Acids :

- (a) The only element which forms oxyacid is Boron (B).

$\text{B} \rightarrow \text{H}_3\text{BO}_3$.
 (Boric Acid)

- (i) Boric acid is used as an antiseptic to wash wounds.
- (ii) H_3BO_3 is also used as preservative
- (iii) Boric lotion (very dilute solution of H_3BO_3) \rightarrow used to wash eyes.

- (b) $\text{H}_3\text{BO}_3 \xrightarrow{100^\circ\text{C}} \text{HBO}_2 \xrightarrow{160^\circ\text{C}} \text{H}_2\text{B}_4\text{O}_7$
 Boric acid Meta Boric acid Tetra Boric Acid

4.5 Action of Air :

- (a) Pure boron is almost inert at ordinary temp.
- (b) Al reacts readily in air and also decompose water at ordinary temp.
- (c) Ga & In are not affected by air even when heated.
- (d) Tl farnish in air due to formation of Tl_2O .

5. FAMILY MEMBERS OF "BORON FAMILY" ::

5.1 Boron :

5.1.1 Compounds of Boron :

- (a) Borax i.e. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$: or Tincal :

- (i) It is also named as sodium tetra borate decahydrate.

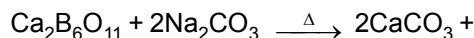
- (ii) Common Indian name is Suhaga.

- (iii) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is known as Jeweller's Boron. - also named as sod.tetra borate penta hydrate.

- (iv) $\text{Na}_2\text{B}_4\text{O}_7$ is known as Boron glass

- (b) Preparation :

Form colemanite :



Both these $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaBO}_2$ are fused together.

Both $\text{Na}_2\text{B}_4\text{O}_7$ and NaBO_2 are solid & soluble in water and so both these are separated by crystallisation. {which involves heating of solution & then slow cooling}

When crystallisation is done, less soluble, one is first obtained and so $\text{Na}_2\text{B}_4\text{O}_7$ will first obtained and so $\text{Na}_2\text{B}_4\text{O}_7$ will first appear as crystals & then NaBO_2 .

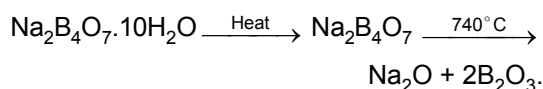
Note:

- (i) If crystallisation is done below 60°C then ordinary Borane is formed. (Decahydrated).
- (ii) Above 60°C jeweller's Borane will be obtained. i.e. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$.
- (iii) Anhydrous Borane will never be precipitated from the aqueous solution.

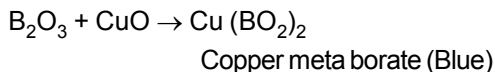
- (c) **Chemical Properties :**

Action of Heat on Borane :

- (i) Borane swells up on heating.
- (ii) On heating borax loses water and swells into a white mass which on further heating melts to forms transparent glassy solid called Borax glass and Borax bead.



(iii) The borax bead is due to the formation of B_2O_3 which when fused with metal salts form corresponding metaborate.



(iv) Colour of meta borates

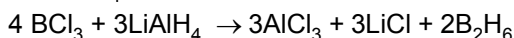
Cu	Fe	Co	Ni	Cr
Blue	Green	Blue	Brown	Green

5.1.2 DIBORANE (B_2H_6) :

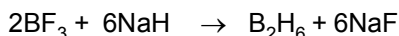
It exists in gaseous state & is highly inflammable in air and poisonous.

(a) **Method of preparation :**

(i) By $LiAlH_4$:

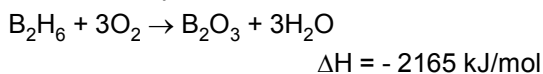


(ii) Industrially it is obtained by reduction of boron trifluoride with sodium hydride.



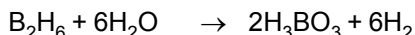
5.1.3 Properties :

(a) **Action of Air :** Reaction is highly exothermic and due to high evolution of energy it can be employed as industrial fuel not domestic because it is poisonous

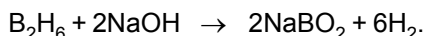


(b) **Stability :** It is stable only at low temperature when heated between 100°C to 250°C , it changes to a number of higher hydrides.

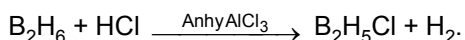
(c) **Hydrolysis :**



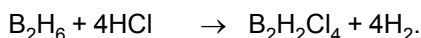
(d) **Reaction with alkali :** Form meta borates



(e) **Reaction with hydrogen halides :**

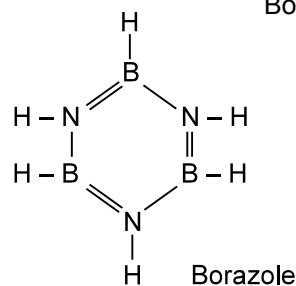
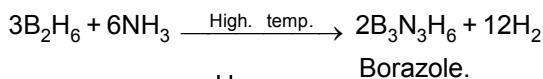


(f) **Chlorination :**



This formation of $B_2H_2Cl_4$ show that the 2H left in $B_2H_2Cl_4$ are responsible for dimer formation (Bridge H). Diborane has only four replacable H and with their replacement, the dimeric structure continuous to be as such. Remaining 2Hydrogen when they get deplaced, the dimeric structure breaks indicating that these two hydrogens are acting as bridging hydrogens.

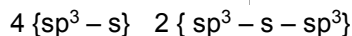
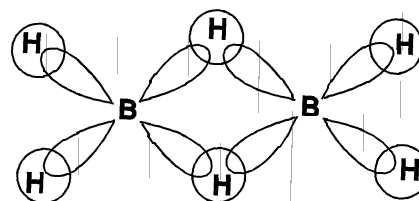
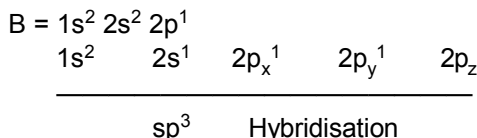
(g) **Action of Ammonia :**



(i) Borazole has been called as inorganic benzene because it is very close to benzene in structure and properties.

(ii) When compared with Benzene Borazole is less stable & more reactive due to pality of N & H in compound.

5.1.4 Structure of Diborane :



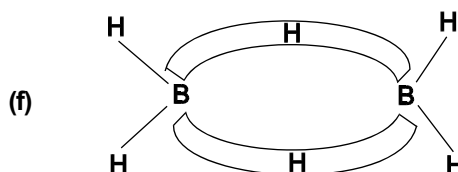
(a) 4 Terminal H-are bonded by σ bond & remaining 2H are bridging hydrogens and of these are broken then dimer become monomer.

(b) Boron undergoes sp^3 hybridisation 3 of its sp^3 hybridised orbitals contain one e^- each & fourth sp^3 hybrid orbital is vacant

(c) 3 of these sp^3 hybrid orbitals get overlapped by s orbitals of 3 hydrogen atoms.

(d) One of the sp^3 hybrid orbitals which have been overlapped by s orbital of hydrogen gets overlapped by vacant sp^3 hybrid orbital. of 2nd Boron atom. and its vice versa.

(e) By this two types of overlapping take place $4(sp^3 - s)$ overlap bonds & $2(sp^3 - s - sp^3)$ overlap bonds.

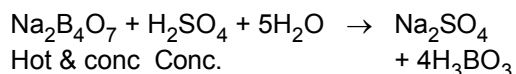


H is held in this bond by forces of attraction from B & This bond is called 3 centred two electron bonds. also called Banana bonds. Due to repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are bent away from each other on the middle giving the shape of banana.

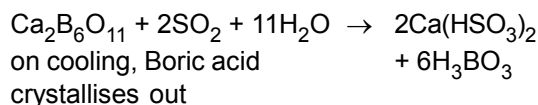
5.1.5 H₃BO₃ (Orthoboric Acid, Boric acid or Boracic acid)

Preparation :

(1) From borax :

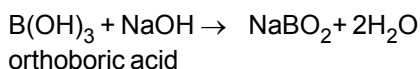


(2) From colemanite :

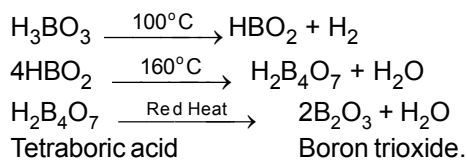


Properties :

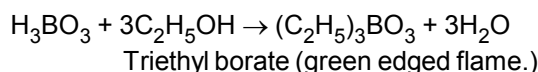
- (1) It forms soft pearly - white needle like crystals.
- (2) It is steam volatile.
- (3) **Acidic nature** - It is a very weak acid and ionises mainly as a monobasic acid. It is not a proton donor but behaves as a Lewis-acid i.e. it can accept a lone pair of electrons from OH⁻ ions. It reacts with strong alkalis forming salts known as metaborates.



(4) **Action of heat** →



(5) **Reaction with ethanol** -



Uses :

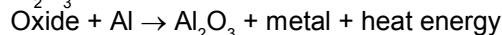
- (1) As a antiseptic, as eye wash (eye-lotion) and as food preservatives.
- (2) In leather - industry
- (3) In the preparation of glass and enamels.

Structure :

In H₃BO₃ (boron is sp² hybridised), the planar triangular ortho-boric acid units, are bonded through hydrogen bonds into two dimensional sheets.

5.1.6 Gold Schmidt's Alumino-Thermic process

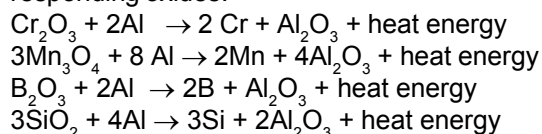
Aluminium has the power of displacing elements less electropositive than itself from their oxides as it has great affinity for oxygen at high temperatures. The reaction being so strongly exothermic that the metal set free is obtained in the molten condition and it is protected from oxidation by a layer of fluid slag consisting of Al₂O₃.



molten state

The reaction forms the basis of the aluminothermic process. It was discovered by Gold Schmidt. The process has two main applications :

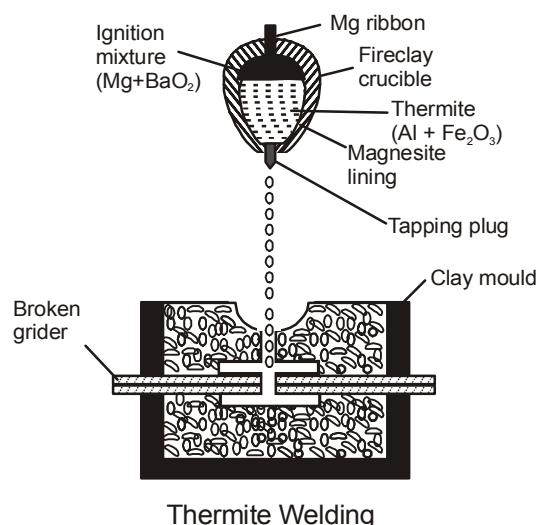
(i) **Extraction of metals and non-metals** : The metals like Cr, Mo, Mn and non-metals like boron, silicon, etc. can be extracted from their corresponding oxides.



(ii) **Thermite welding of metals** :

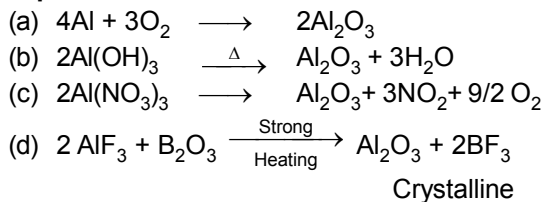
A mixture of aluminium powder and Fe₂O₃ in the ratio of 1:3 (known as thermite) is taken in a crucible lined with magnesite and having a plug hole. This is covered with a mixture of magnesium powder and barium peroxide with a magnesium ribbon inserted into it. The thermite is ignited with magnesium ribbon. Iron oxide is reduced to iron and temperature rises to about 2500°C. Molten iron thus produced is tapped into the parts to be welded. The heated surface of the broken iron melts and mingles with the molten iron, thus giving a perfect weld.

5.2 Compounds of Aluminium



5.2.1 Al₂O₃ (Alumina, Aluminium oxide or Corundum)

(i) Preparation :

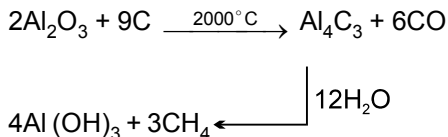


Two most stable crystalline forms :

- (a) α -Al₂O₃ (Rhombic Lattice) : It is dense, hard and resistant to chemical attack. It is used as an abrasive.
- (b) γ -Al₂O₃ (Cubic Lattice) : It is less dense, soft and has a high surface Area.

Properties :

- (1) It is very stable and unreactive
- (2) Melting point \longrightarrow 2050°C
Boiling point \longrightarrow 2980°C
- (3) It is amphoteric oxide :
- $$\begin{aligned} \text{Al}_2\text{O}_3 + 6\text{HCl} &\longrightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O} \\ \text{Al}_2\text{O}_3 + 2\text{NaOH} &\longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O} \end{aligned}$$
- (4) Reaction with carbon :



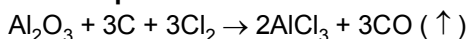
Uses :

- (i) It is used as a refractory material.
- (ii) In chromatography for separation of mixture.
- (iii) In preparation of Artificial gems.

5.2.2 Aluminium chloride :(AlCl₃)

(a) Preparation :

(i) Macaffc's process :

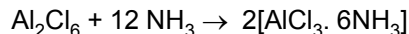


(b) Properties :

- (i) It sublimes below 200°C.
- (ii) Aluminium chloride is a white crystalline substance which fumes in moist air
- $$\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{HCl} (\uparrow)$$
- (iii) Its vapour density at below 350°C indicates that its formula is Al₂Cl₆.

The vapour density at 750° corresponds to AlCl₃ as its molecular formula.

- (iv) It is highly covalent therefore it is soluble in alcohol, ether and benzene.
- (v) Anhy. AlCl₃ forms addition compound with NH₃, PH₃, COCl₂.



(c) Alums :

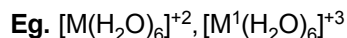
Alums are double sulphates with their general formula as M₂SO₄ · M₂¹(SO₄)₃ · 24H₂O where M = Mono valent radical like Na⁺, K⁺, NH₄⁺ & M¹ = Trivalent radicals like Al⁺³, Cr⁺³, Fe⁺³ etc.

(d) The different alums are :

- (i) Potash alum : K₂SO₄ · Al₂(SO₄)₃ · 24H₂O
- (ii) Chrome Alum : K₂SO₄ · Cr₂(SO₄)₃ · 24H₂O
- (iii) Ammonium Alum : (NH₄)₂SO₄ · Al₂(SO₄)₃ · 24H₂O
- (iv) Iron Alum : (NH₄)₂SO₄ · Fe₂(SO₄)₃ · 24H₂O

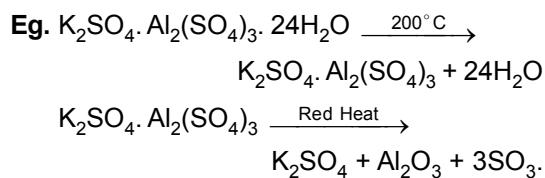
Note :

- (i) Li does not form alum because Lithium ion too have a Co-ordination number of six.
- (ii) In alums each metal ion is surrounded by six water molecules.
- (iii) In univalent cation which are large in size, the six water molecule are too far from the ion while in trivalent cations, being small in size.

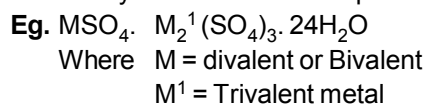


Important Points :

- (a) All Alums are isomorphous.
- (b) On heating it losses its water of crystallisation and swells up.



- (c) It is highly acidic in aq. solution due to the hydrolysis.
- (d) Pseudo alums : Double sulphates of divalent ions and trivalent ions with 24 water molecules in their crystals are known as pseudo alums.



- (e) Highly toxic element of Boron family is Tl.

5.2.3 Alloys of aluminium

Name of the alloy	Approximate Composition	User
1. Magnalium	95% Al, 5% Mg	In the construction of airships, balances and pistons of motor engines.
2. Duralumin	95% Al, 4% Cu, 0.5% Mg, 0.5% Mn	Aeroplanes and automobile parts as its strength of toughness is comparable to mild steels
3. Aluminium Bronze	90% Cu, 9.5% Al, 0.5% Sn	For making utensils, cheap artificial jewellery, photo frames, coins, golden paints.
4. Nickeloy	95% Al, 4% Cu, 1% Ni	Aircraft parts
5. Y-alloy	93% Al, 4% Cu, 2% Ni, 1% Mg	For making pistons and machinery parts.
6. Alnico	Steel 77%; Ni = 2%, Al = 20%, Co = 1%	For making permanent magnets.
