

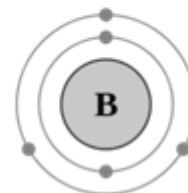
Group 13

Boron is the chemical element with atomic number 5 and the chemical symbol **B**. Boron is a trivalent metalloid element which occurs abundantly in the evaporite ores borax and ulexite.

5: Boron

2,3

Several allotropes of boron exist: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on Mohs' scale), and a poor conductor at room temperature.



Elemental boron is used as a dopant in the semiconductor industry, while boron compounds play important roles as light structural materials, insecticides and preservatives, and reagents for chemical synthesis.

Boron – Preparation, properties

Preparation & properties of

(a) Diborane

(b) Boric Acid

(c) Boron

Aluminium – (1) Ores

(2) Extractive metallurgy: - Electrolytic reduction

(3) Alumina, $AlCl_3$, Alums

(4) Qualitative analysis – Al^{+3}

General group properties + *Ga, In, TL*

(A) BORON:- B . At. wt. = 10.82 At. no. = 5 group -13(III (B)), $1s^2 2s^2 2p^1$, valency - 3 .

Boron used as flux. First prepared by Davy by electrolysis of boric acid. Also by heating flux B_2O_3 with k.

Boron → Metalloid

Two stable isotopes → 10 & 11 Mass No.

Allotropic forms → Crystalline & Amorphous.

Occurance → Does not occur in free state(.001% in crust)

Borax – $Na_2B_4O_7 \cdot 10H_2O$, $Na_2 B_4O_5 OH_4 \cdot 8H_2O$

Colemanite – $Ca_2B_6O_{11} \cdot 5H_2O \rightarrow Ca_2 B_3O_4 \cdot OH_3 \cdot 2H_2O$

Kernite - $Na_2B_4O_7 \cdot 4H_2O$

Borocite

Pandaramite

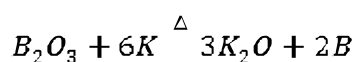
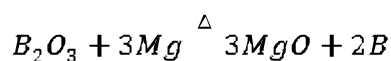
Ulexite

$Na_2 B_4O_5 \cdot OH_4$

Preparation of Boron

Preparation of amorphous Boron

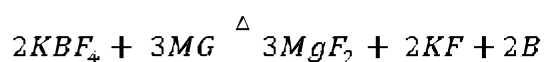
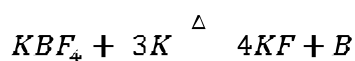
From Boron trioxide:



Boron is collected as a brown residue .It is 93.8% pure.

Purification: Contaminated with silicon & silica. Treated with hot *HF* when silicon & silica are removed and boron (98.3%) pure.

From potassium borofluoride: By heating the intimate mixture in a covered crucible(1000⁰c or above)



Preparation Of Crystalline Boron

- By cooling molten amorphous boron (m.p 2300⁰c)
- By subjecting a mixture of BCl_3 or BBr_3 vapour and H_2 to electric spark → yields crystalline Boron
- $2BCl_3 + 3H_2 \xrightarrow{\text{electric, spark}} 2B + 6HCl$
- By the thermal decomposition of BCl_3 or BBr_3 with electrically heated W filament at 1200⁰c
- B_2O_3 cannot be reduced by carbon even at white hot.
- Crystalline Boron can also be prepared by dissolving amorphous boron in molten *Al* at high temp. (2300⁰c). On cooling the resulting solution, deposits of crystals

of boron, which is boiled with NaOH solution is used to remove any *Al* present in it.

PROPERTIES OF BORON

Physical Properties

- ([Two isotopic forms $\rightarrow B_5^{10}$ & B_5^{11} in 20% & 80% *ratio*])
 - (i) Hard steel grey or a brown solid
 - (ii) Density = 1.73 (Amorphous) 2.34 (Crystalline) (Hard like diamond)
 - (iii) M.P = 2300°C
 - (iv) Metallic lusture.
 - (v) Nonconductor of heat & electricity.
 - (vi) 3 allotropic forms

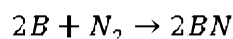
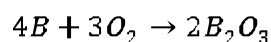
Chemical Properties

Crystalline Boron

Very hard and chemically inert. Not attacked when heated strongly in oxygen or air. Not attacked by hot & concentrated HCl , HNO_3 , H_2SO_4 or HF . Oxidised to borate when fused with sodium peroxide or a mixture of sodium carbonate and KNO_3 . Small size = 80pm

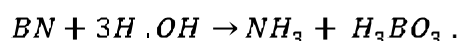
Amorphous

More reactive than crystalline Boron. At ordinary temperature not attacked but at 700°C it burns in air with a reddish flame producing B_2O_3 & BN .

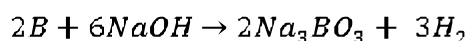
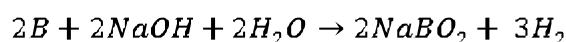


Action on N_2 : - When heated, BN , a slippery graphite like structure is formed, Inorganic graphite; $2B + N_2 \rightarrow 2BN$.

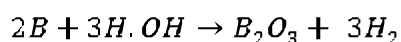
With steam BN decomposes to give NH_3 & H_3BO_3



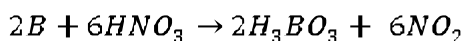
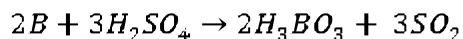
Action on alkalis : - Produces alkali metaborates borates and evolves H_2



Action on water:- Unaffected by water at ordinary temperature, but oxidized to B_2O_3 by superheated steam.

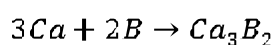
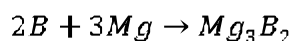


Oxidized by concentrated HNO_3 or H_2SO_4 but is unaffected by HCl

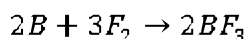


HNO_3 & H_2SO_4 are oxidizing acids

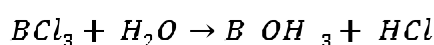
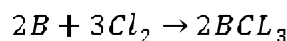
Action on metals:- In electric furnaces at high temperature metallic borides are formed which have higher electrical conductivity than the corresponding metals.



Action of Halogen :- Boron ignites in fluorine spontaneously producing BF_3



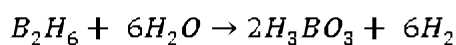
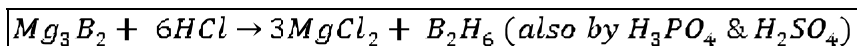
At elevated temperature.



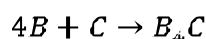
i.e. why Boron halides have acidic property.

Relative Acid strength $BBr_3 > BCl_3 > BF_3$

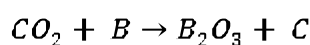
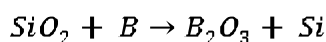
Action on Hydrogen:- Boron does not combine with hydrogen directly, but diborane B_2H_6 and borobutane B_4H_{10} are produced when Mg_3B_2 is treated with dil. HCl at $50^\circ C$. These hydrides of boron on hydrolysis give H_2 and H_3BO_3 .



Action on carbon:- In electric furnace at high temperature boron combines with carbon forming boron carbide. B_4C is next to diamond in hardness.



Reducing Property:- At high temperature Silica or CO_2 are reduced by boron



Distinction between Crystalline and amorphous Boron :

<u>Crystalline Boron</u>	<u>Amorphous Boron</u>
Crystalline Boron is a steel grey or black colored crystalline solid having a metallic lusture.	Amorphous Boron is brown powder.
Crystalline Boron is inert in nature.	Amorphous Boron is comparatively more active.
Crystalline Boron is not attacked by air or oxygen even at high temperature.	Amorphous Boron is attacked by air or oxygen at 700°C .
Specific Gravity of Crystalline Boron is 2.34	Specific Gravity of Amorphous Boron is 1.73
Crystalline Boron is not attacked by any oxidizing acid.	Amorphous Boron is attacked by concentrated HNO_3 , H_2SO_4

Use of Boron:

Abrasive & grinding material
In metallurgy for removing O_2 from molten metals
Ferro boron (20% B, 80% Fe) → Steel making
In medicine as boric acid and borax
In nuclear industry as metal borides; used as protective shields as B-10 absorb neutrons

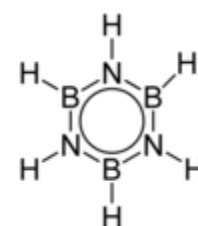
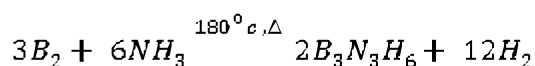
Boron does not form B^{+3} ion: -Boron only forms covalent compounds. The tendency of boron to form covalent bonds can be experienced as the basis of polarization power. According to Fajan's rule covalent bond is formed when the shape of the cation is very small and its charge is very high. The trivalent B^{+3} ion is very small and so it would exert large polarizing effect on the neighbouring atoms. This would result in the transference of electrons from other atoms to Boron ion which leads to the formation of covalent bonding by electron sharing. This explains why B^{+3} ion does not exist.

Small size = 80pm . $IE_1 = 800 \text{ KJ/mol}$, $IE_2 = 2427 \text{ KJ/mol}$ $IE_3 = 3658 \text{ KJ/mol}$.

Melting Point Of Boron is very high: The structure of Boron consists of a number of boron atoms. Each boron atom is strongly bonded with other boron atoms by strong covalent bond. Thus, all the boron atoms are joined together by strong sigma bonds forming a giant molecule. Due to the extremely high strength of covalent bonds holding numerous boron atoms together, boron is hard and a large amount of heat energy is required to break so many covalent bonds of the giant molecule of boron. This explains the high melting point of boron.

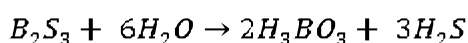
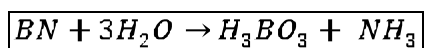
BN is called inorganic graphite:- Formerly Borazole, now Borazine

It is isoelectric with C_6H_6 . Colorless liquid with b.p= $55^{\circ}C$. It smells like that of C_6H_6 & forms a planar hexagonal ring by alternative arrangement of B & N atoms.



Pure borazole is light sensitive and explodes unless stored in a dark place.

The common form of BN consists of a layer lattice similar to that of graphite. Its structure consists of a number of 2-D sheets like parallel layers of B & N atoms. These B & N atoms are arranged in a network of flat regular hexagons. These layers are stacked one over the other such that the B atoms of one layer is directly over the B -atom of the other. The $B-N$ atoms in the same layer are joined by sp^2 hybrid orbitals. The distance between successive layers is 333pm whereas in graphite it is 335 pm. The bond distance ($B-N$) in each layer is 145 pm which is very close to 143 pm of graphite. Also the C_6 hexagon in graphite and $(BN)_3$ hexagon in BN is formed by the same no. of electrons. So BN is called inorganic graphite.



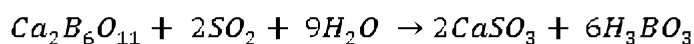
BORIC or ORTHOBORIC or BORACIC acid (H_3BO_3)

Preparation of boric acid

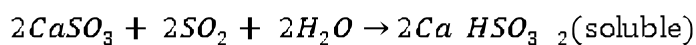
From mineral colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$):- On a large scale from native calcium borate (Colemanite). ($CO_2 \rightarrow$ milkiness)

Stream of $SO_2 \rightarrow$ boiling water, colemanite

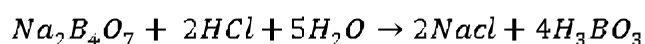
Finely suspended $\rightarrow CaSO_3$ and boric acid



Excess SO_2 , $CaSO_3 \rightarrow$ soluble calcium bisulphate. The mixture is then cooled when boric acid crystallizes out from the solution separated by filtration.

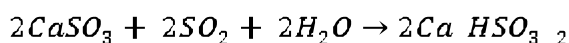
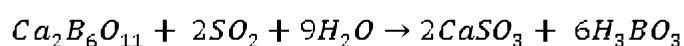


Boric acid from Borax ($Na_2B_4O_7 \cdot 10H_2O$):- Concentrated HCl or H_2SO_4 is added to a hot and saturated solution of borax, boric acid is produced. The product is cooled, when pearly white silky crystals of boric acid separate out. These are washed and purified by recrystallization from hot water.

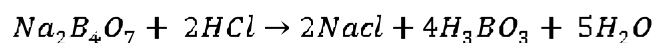


Preparation of Boron from (i) Colemanite (ii) Borax (iii) Boric acid

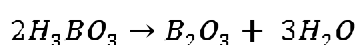
From Colemanite:



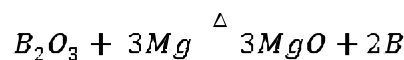
From Borax:-



Next H_3BO_3 is heated strongly when glass like transparent B_2O_3 is obtained.



The B_2O_3 is then reduced by Mg at high temperature to produce Boron



Properties Of Boric Acid

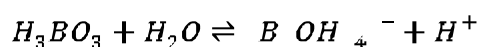
Physical Properties:-

- Soft, silky, pearly, white crystalline solid having a soft soapy touch.
- Less soluble in cold water but its solubility increases with the rise in temperature.
- Specific gravity = 1.46.
- Volatile in steam.

Chemical Properties:- Acidic Property : -

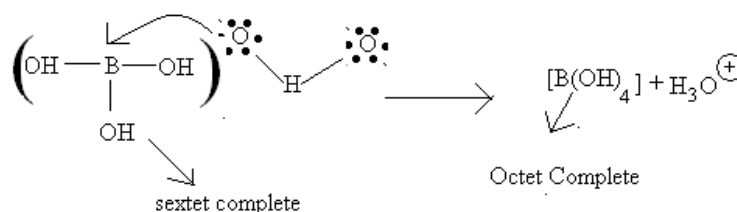
- Boric acid is a very weak acid, even weaker than carbonic acid. In spite of the presence of three H_2 atoms in its molecule; it is monobasic. Aqueous solution of H_3BO_3 turns blue litmus red but cannot change the color of methyl orange. Hence it cannot be

titrated against alkalis directly. In fact, H_3BO_3 cannot act as a Bronsted acid i.e. a proton donor but as a Lewis acid by accepting a lone pair. In aqueous Solution H_3BO_3 exists as :



The octet of H_3BO_3 is not complete. So in order to complete its

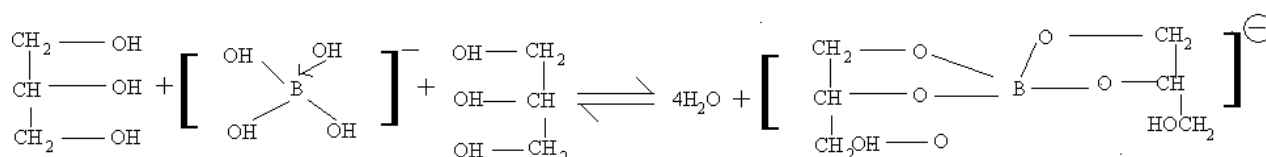
octet, B -atom
accepts a lone
pair of
electrons



In presence of certain polyhydroxy

compound it forms a stable complex, for which it behaves as a strong monobasic acid and hence can be titrated against $NaOH$.

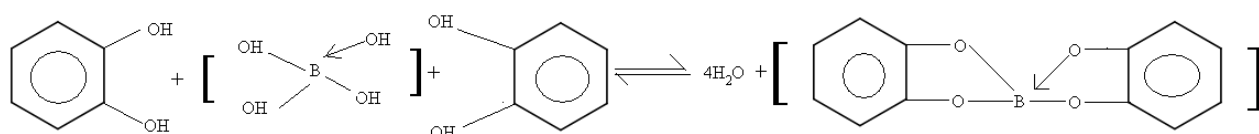
Glycerol: - With glycerol basic acid produces the following stable chelate complex compound for which equilibrium shifts towards right, releasing one $[H^+]$ and this proton neutralizes OH^- .



Accepts electrons & forms complexes with
[CIS-DIOLS]

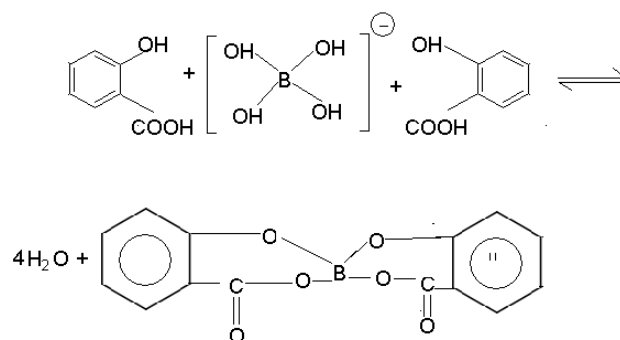
Boric Acid Glycerol
Chelate Complex

Catechol:-

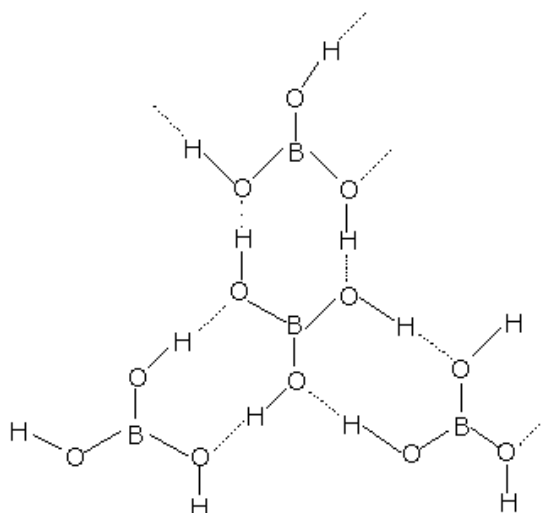


Boric Acid Catechol Chelate Complex

Salicylic acid:-



Structure OF Boric Acid: - Boric acid has layer type structure in which planar BO_3 units are linked to one another through H – atoms. The H – atoms constitute covalent with one unit and hydrogen bond with the other unit.

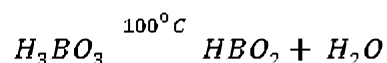


Dotted Lines representing H – bonds

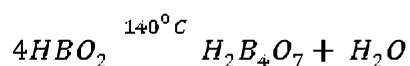
- ❖ Orthoboric acid is monobasic.
- ❖ Boron & water do not react.
- ❖ Basic ions forming colored salts show borax bead test

Action of heat:- On heating, orthoboric acid loses water in three successive steps :

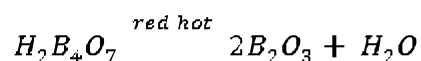
- At 100°C , it loses water forming metaboric acid.



- At 140°C , it loses more water forming pyroboric acid.

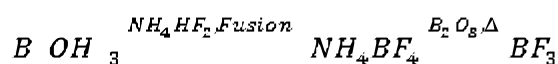


- At red hot condition it loses all water producing glassy mass of boron trioxide.



Uses:-

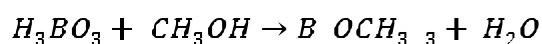
- Medicine:** antiseptic, eye lotion, ointment
- Manufacture of borax, glass and glazes in enamel industries.
- Preservation of food



Ammonium borofluoride

Test of Boric Acid & Borates:-

- A little boric acid is mixed with methyl alcohol in a test tube. The test tube is then heated gently and the vapor coming out of it is ignited. The issuing vapors burn with green edged flame.
Boric acid reacts with methyl alcohol to produce methyl borate, a volatile ester, which on ignition burns with a green edged flame.



(Inorganic volatile ester)

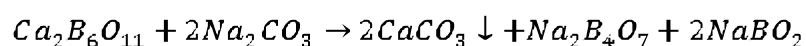
- For borates, paste of borate and concentrated H_2SO_4 is taken in a test tube and a little methyl alcohol is added to it. The mixture is then gently heated and the vapors coming out of it is ignited which is burnt with green edged flame.

Borax: -

Sodium pyroborate or sodium tetraborate (sohaga) decahydrate

Preparation of Borax: -

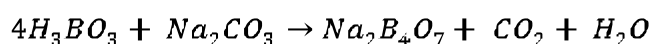
From Colemanite:- Colemanite is treated with boiling Na_2CO_3 when insoluble calcium carbonate is precipitated and a mixture of borax and sodium metaborate remains in the solution. Insoluble $CaCO_3$ removed by filtration. The concentrated mixture of borax and sodium metaborate is allowed to cool, when crystals of borax separate out.



For further yield, CO_2 is passed through the mother liquor when sodium metaborate is converted to borax.



From Boric Acid:- When a solution of boric acid is boiled with sodium carbonate, borax is produced. The solution is concentrated by evaporation and cooled, when crystals of borax separate out



From Tincal:- Tincal is 55% borax.

Finely powdered tincal is treated with boiling water and filtered. The filtrate is made concentrated. The concentrated solution is then cooled when almost pure borax separates out as crystals.

Properties of Borax

Physical Property:

At ordinary temperature borax forms transparent crystals having 10 molecules of water of crystallization.

At $65^\circ C \uparrow$, it forms pentahydrate $\rightarrow Na_2B_4O_7 \cdot 5H_2O \rightarrow$ Jeweller's borax. Harder than ordinary, borax and does not efflorescence in air.

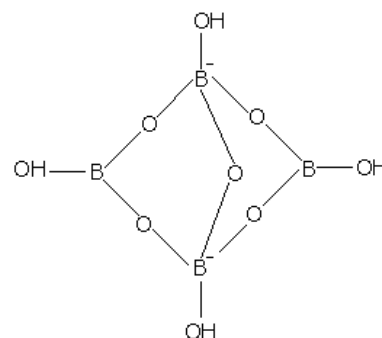
$$\rho = 1.72$$

Fairly soluble in water, which increases with rise of temperature.

Crystalline borax contains tetra nuclear units of $B_4O_5(OH)_4^{2-}$.

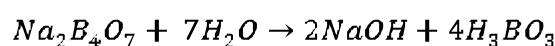
Hence its corrected formula is $Na_2 B_4O_5(OH)_4 \cdot 8H_2O$

.Structure of $B_4O_5(OH)_4^{2-}$ ions is



Chemical Property:-

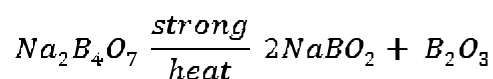
Aqueous solution of borax is alkaline:-Borax undergoes hydrolysis yielding a mixture of sodium hydroxide and boric acid. As $NaOH$ is a strong alkali and H_3BO_3 is a weak acid, the final solution exhibits alkaline properties.



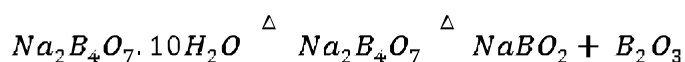
The aqueous solution of borax gives a violet red color with phenolphthalein due to hydrolysis of borax. The hydrolysis of borax can be prevented if glycerol is added to the solution. So, when phenolphthalein is added to an aqueous solution of borax, a pink color develops but when glycerol is added to it, the pink color is discharged. Glycerol forms a chelate complex with H_3BO_3 producing one proton (H^+) and this proton neutralizes $NaOH$. Thus the solution becomes neutral again i.e. colorless.

Action Of Heat:-

Borax swells up on heating due to evaporation of water of crystallization from its molecule. On strong heating the mass melts and ultimately forms a transparent glass like mass, which is composed of sodium metaborate and boron trioxide.



Borax Bead Test This test is used for identification of basic radicals. A heated loop is dipped in powdered borax. Small quantity of borax adheres to the loop of the platinum wire. The loop with borax is heated again, when borax swells up, loses water and then fuses to give a colorless glassy bead on the loop. Glassy bead → Sodium metaborate & boric anhydride

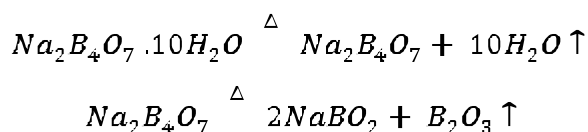


Then the hot bead is touched with a little of colored metallic salt to be identified. The bead along with the adhered salt is heated first in oxidizing and then in the reducing flame.

As boric anhydride is non-volatile, it displaces the more volatile acidic part of the salt and combines with the basic radical to form metaborate.

Metallic Radicals	The colour of the bead	
	In oxidizing flame	In reducing flame
Copper	Transparent green(hot),transparent blue(cold)	Opaque red(CBR)
Iron	Reddish yellow when hot, yellow when cold.	Bottle green
Cobalt	Deep Blue	Deep Blue
Manganese	Amethyst(purple)	colorless
Chromium Nickel	Green Brown	Green Brown

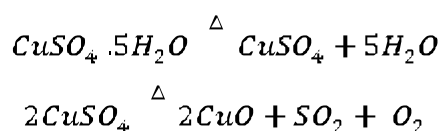
Chemical reactions in borax bead test: - Being heated in the loop borax melts to form a glass like transparent bead which is composed of $NaBO_2$ and boron trioxide.



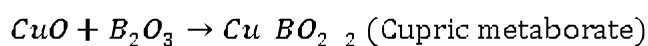
When Cu, Fe, Co, Cr salts are heated with the bead, the salts are decomposed first to give their respective oxides. These oxides react with B_2O_3 of the bead to form the respective metaborate compound having different colors.

Copper Salts:-

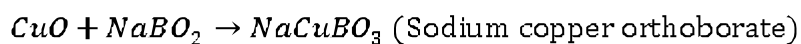
- In oxidizing flame: - Copper salts on being heated in oxidizing flame are converted to cupric acid.



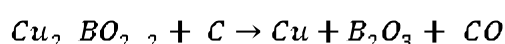
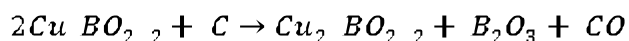
CuO thus produced combines with B_2O_3 of the bead to form copper metaborate, the color of which is transparent green when hot and transparent blue when cold. By observing the color, it is identified.



Some orthoborate is also produced.



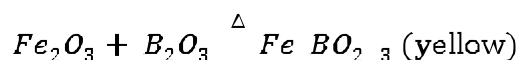
- In reducing flame:- The blue transparent bead containing cupric metaborate or being heated in reducing flame is reduced by the fine particles of carbon of the flame to produce cuprous metaborate. The colorless cuprous metaborate is further reduced to metallic copper which is red in color. Thus, the bead becomes opaque red in the reducing flame.



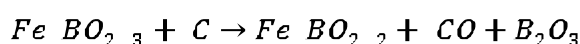
(Opaque red)

With Fe salts

- In oxidizing flame: - Fe salts on being strongly heated in the oxidizing flame are converted to ferric oxide. Fe_2O_3 combines with B_2O_3 to produce ferric metaborate, the color of which is reddish yellow when hot and yellow when cold.



- In reducing flame: - The yellow bead of ferric metaborate on being heated in a reducing flame is reduced to ferrous metaborate the color of which is bottle green.



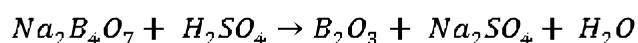
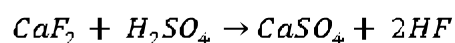
Uses of Borax:-

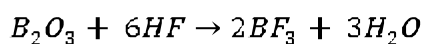
- Flux in welding & soldering.
- Glazes for earthenware, porcelain.
- In lab for making Pyrex glass, antiseptic soap.

Test for identification of Borax, Boric acid, Borates:-

- Flame test:-A platinum wire after moistening in concentrated H_2SO_4 is made to touch with a little borate, or boric acid & CaF_2 and then heated in the non luminous flame.

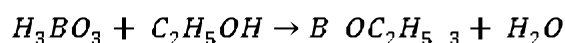
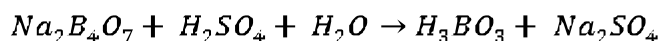
A green flame is produced.





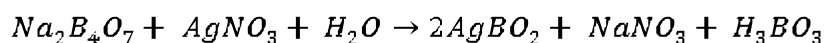
- In a porcelain basin a mixture of ethyl alcohol, borate salt or H_3BO_3 and concentrated H_2SO_4 are taken and ignited.

The mixture is found to burn with green edged flame.

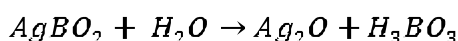


Cobalt Nitrate test:- A small amount of borate or boric acid or borax is taken in the cavity of a charcoal block and heated in the oxidizing flame. After sometime two drop of cobalt nitrate solution is added to the residue and heated again in the oxidizing flame. The color of the residue in the cavity of the charcoal turns blue.

Wet Test: - To a neutral solution of a borate salt $AgNO_3$ solution is added. A white precipitate of silver metaborate is obtained.



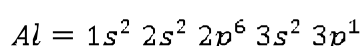
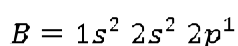
The precipitate is boiled with water. The white precipitate turns black due to formation of Ag_2O



Comparison of properties of B & Al:- Boron and Aluminum occupy group – IIIB in the periodic table. In spite of being members of the same group, they have very slight resemblance with each other. Boron is however diagonally related with Silicon in IV B.

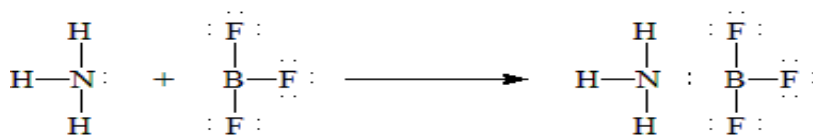
Points of Similarity:-

- Electric configuration :-

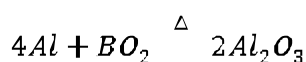
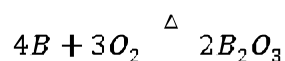


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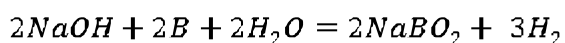
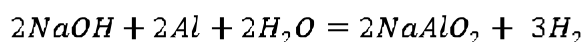
- Both the elements exhibit a covalency of 3 in their halides. These halides act as Lewis acid (acceptors) whenever donor molecules are present.



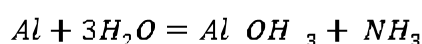
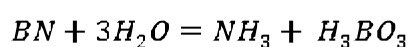
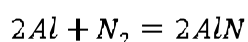
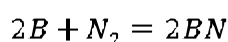
- Both B & Al combine with O_2 on being heated in air or O_2 .



- Reaction with strong alkalis: - Both the elements react with strong alkalis ($NaOH$, KOH) and evolve hydrogen.



- Boron and Aluminum react with Cl_2 producing the respective chlorides, which are covalent and are easily hydrolysed by water.
- Both combine with N_2 producing nitrides which undergo hydrolysis liberating NH_3



Points of Difference:-

Boron	Aluminium
Boron is a typical non – metal.	Aluminum is a metal.
Boron is a bad conductor of electricity.	Aluminum is a good conductor of electricity.
Boron exhibits allotropy.	Aluminum does not exhibit allotropy.
Boron forms compounds by covalency.	In gaseous state, though Al compounds are not covalent but ionize in aqueous solution.
Boron forms a number of stable hydrides.	Aluminum does not form any stable hydride.
B_2O_3 is an acidic oxide.	Al_2O_3 is an amphoteric oxide.
Boron has no action on dilute HCl	Dilute HCl liberates H_2 with Aluminium.
BCl_3 is a gas at ordinary temperature. It is converted to a colorless liquid when cooled.	$AlCl_3$ is a solid and sublimates on heating.

Comparison of Properties:-

Properties	Carbon	Boron
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Allotropy	Two allotropes – crystalline & amorphous.	Two allotropes – crystalline & amorphous.
Melting point	3000 ⁰ C	2300 ⁰ C
Combustion	CO ₂ is produced.	B ₂ O ₃ & BN are produced.
Action on acid	Graphite is oxidized by nitric → graphitic acid.	HNO ₃ or concentrated H ₂ SO ₄ . B → H ₃ BO ₃ .
Oxide	CO ₂ gas → neutral oxide.	B ₂ O ₃ → solid → boric acid in water.
Hallides	CF ₄ → Inert gas, CCl ₄ liquid, stable in water.	BF ₃ → gas, BCl ₃ → liquid, both, hydrolyzed.
Carbides	Carbides with metals	Borides with metals g ₃ B ₂ .
Borides	CaCO ₂ .	

Comprehensive:-

B → Ist Member of the elements of Group – 13 in periodic table. Only non metal in this group 1s² 2s² 2p¹ → 3 Electrons in valence shell

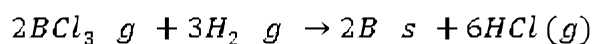
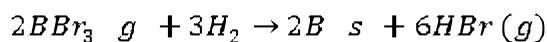
Boron differs in properties from those of other member because of:-

- Its small size.
- Low electro negativity.

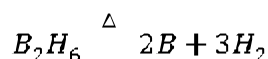
Compounds are electron deficient and behaves as Lewis acid

Preparation of Boron:-

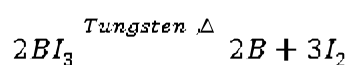
- By reduction of boron halides: - The reduction of the volatile boron halides is carried by dihydrogen at high temperature or by electric spark.



- By thermal decomposition of Boron hydrides :-



- By thermal decomposition of BI₃ (Van Arkel method) :-



Hydrides of Boron: -

Boron is expected to form BH_3 coz of its trivalent nature. But BH_3 has not been isolated. Boron combines with dihydrogen to form a number of hydrides as B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} etc. These hydrides are covalent in nature and are collectively called boranes.

Occurrence:- Boron occurs sparsely probably due to disruption of its nucleus by bombardment with sub-atomic particles produces from natural radioactivity.

General Properties:- Except Boron which is a non-metal all the others are metals. Non-metallic character of Boron is due to:-

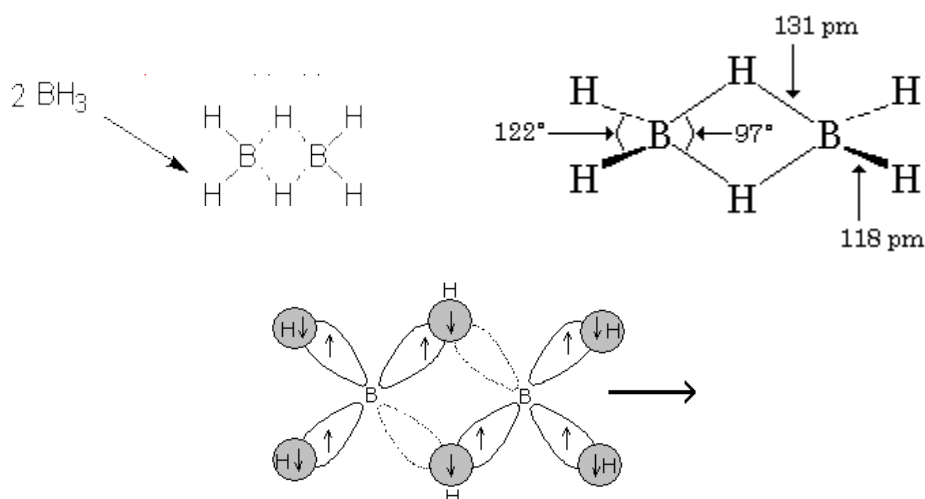
- Its small atomic size
- High ionization energy.

Because of similarity in electric configuration of their outermost shell, they closely resemble in their physical and chemical properties.

However, the penultimate shell (last but one) of these five elements differ in configuration. The penultimate shell of Boron has s^2 electrons, *Al* has s^2p^6 and for the other three it is $s^2p^6d^{10}$. Boron & *Al* differ from each other as well as from the other three members as they (*B* & *Al*) have noble gas kernel s^2p^6 & s^2 structure.

DIBORANE:-

The structure of diborane by electron diffraction is as follows:-



The four terminal hydrogen atoms and the two boron atoms lie in the same plane. These are two hydrogen atoms above and below the plane which form bridge between the boron atoms. These hydrogens are called bridging hydrogens. The terminal $B-H$ bonds are regular covalent bonds but the bridged $B-H$ bonds are different.

B_2H_6 is an electron deficient compound because it has 12 valence electrons instead of the 16 electrons required for the formulation of conventional covalent bonds.

The two bridge hydrogen atoms are in different environment than the four terminal hydrogen's and are present in a plane perpendicular to the rest of the molecule. Each bridge hydrogen is bonded to the 2 B atoms only by sharing of 2 electrons. Such covalent bond is called 3-center 2-electron (pair) bond. These 3-center bonds are also called **banana bonds**.

The structure of boranes was studied in details by William Lipscomb who was awarded Nobel Prize in 1976 in Chemistry.

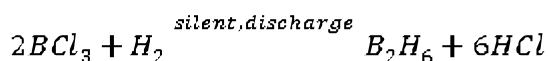
Boranes (BH_3):-

Boranes can exist only as complex compounds like BH_3Z with donors (Z) like CO , CH_3 , $3N$ and PF_3 . The boranes are classified into:-

- $B_nH_{n+4} \rightarrow$ Nidoborane.
- $B_nH_{n+6} \rightarrow$ Arachnoboranes.

Preparation of Diborane:- Boranes have great affinity for water and oxygen, hence they do not occur in nature. Moreover, boranes cannot be prepared directly from its elements as they have positive enthalpies and positive free energies of formation. Hence, boranes are always prepared indirectly.

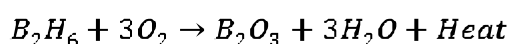
- By reaction of iodine with sodium boro hydride in a high boiling solvent (diglyme solution):- $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$.
- By reduction of BCl_3 with $LiAlH_4$:- $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$.
- By reduction of BF_3 with $NaBH_4$:- $3NaBH_4 + 4BF_3 \xrightarrow{\text{(diglyme)}} 3NaBF_4 + 2B_2H_6$.
- By passing silent electrical discharge through BCl_3 and H_2 :-



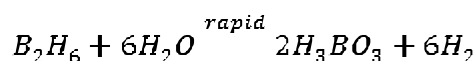
- $\text{Mg}_3\text{B}_2 + \text{H}_3\text{PO}_4 \rightarrow$ Mixture of Boranes (Mainly B_4H_{10}) $\xrightarrow{\Delta} \text{B}_2\text{H}_6$
- $2\text{NaBH}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2 + \text{B}_2\text{H}_6$
- $4 \text{Et}_2\text{O} \cdot \text{BF}_3 + 3\text{Li AlH}_4 \xrightarrow{\text{ether}} 2\text{B}_2\text{H}_6 + 3\text{Li AlF}_4 + 4\text{Et}_2\text{O}$
- $3\text{Li AlH}_4 + \text{NaBH}_4 \xrightarrow{\text{diglyme}} 2\text{B}_2\text{H}_6 + 3\text{Na BF}_4 + \text{Et}_2\text{O}$

Properties:-

- Diborane (melting point = 165.5°C , boiling point = 92.5°C) is colorless gas with a foul smell and is extremely toxic (Lower boranes are colorless gases while higher boranes are volatile liquids and solids).
- Action of Oxygen: - They burn or explode in air (although some are stable) with the evolution of much heat. Hence these are used as rocket fuels.



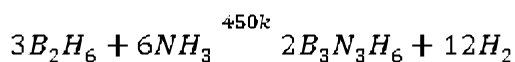
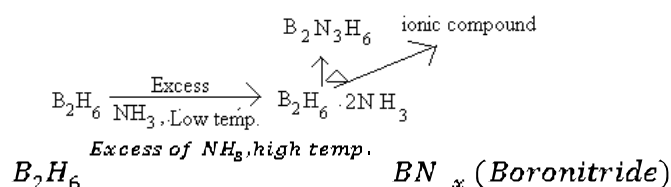
- Hydrolysis: - Boranes are hydrolyzed by water forming boric acid and H_2 . These are therefore used as reducing agents.



- Boranes react with alkali metal hydrides in diethyl ether to form borohydride complexes $\text{B}_2\text{H}_6 + 2\text{MH} \rightarrow 2\text{M}^+ \text{BH}_4^-$ [$\text{M} = \text{Li or Na}$]

Metal borohydride

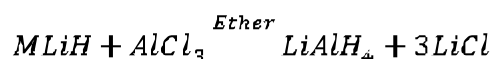
- Action on NH_3 : - Diborane reacts with NH_3 under different conditions to give different products.



Borazole or Borazine

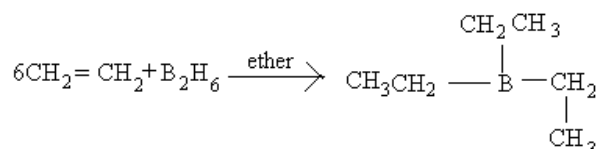
Borazole has been called as inorganic benzene because it is very close to benzene in structure and properties. In contrast of hydrides of boron, the other elements of this group form only a few stable hydrides. AlH_3 is formed by Al . It is a colorless polymeric

solid of the formula $AlH_3 \cdot x$ and contains $Al - H - Al$ bridges. In addition, a complex hydride of Al , $LiAlH_4$ is known. IT is a very powerful reducing agent.



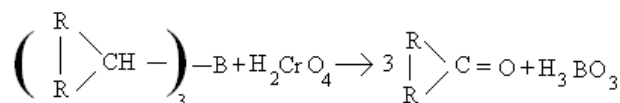
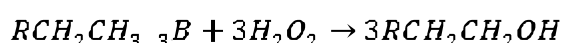
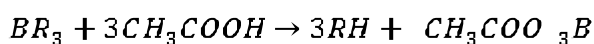
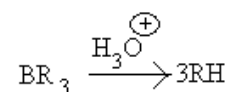
Gallium \rightarrow complex hydride, $Li[GaH_4]$

Reaction with Olefins:-Diborane readily adds at $0^\circ C$ to $25^\circ C$ to the olefinic or acetylenic compound to form trialkyl-boranes. The reaction is known as hydroboration.



Triethyl borane

The alkyl boranes are not usually isolated but may be converted to hydrocarbons by treatment with aqueous acids or carbonylic acids, to alcohols by treatment with alkaline H_2O_2 and to ketones or carbonylic acids by oxidation with chromic acid.



The mild conditions required for the initial hydride addition and variety of products which can be produced using different reagents to break the $B - C$ bond make hydroboration reaction a simple and useful process.

Properties showing e-deficiency:-Diborane is electron deficient and hence it reacts with several molecules having l.p (s) of electrons (e.g. CO , ether, amines etc) to form complex(addition) compounds.

Use of Diboranes:-

- Catalyst in polymerization.
- Reducing agent in organization reactor.
- For welding torches.
- Preparing hydrocarbons, propellants, alcohols, ketones and acids.

$B_2H_6 \rightarrow$ Structure

The presence of two types of boron-hydrogen bonds is confirmed by the chemical evidence that only four of the hydrogen atoms of Diborane are replaceable by methyl groups. Any attempt to further substitute results in cleavage of the molecule into two fragments, each containing one boron atom. Tetramethyl Diborane does not pass any terminal H_2 atom. The B -atoms are sp^3 hybridized. Two sp^3 orbitals overlap with two $1-s$ orbitals of M_t and 1 sp^3 containing one electron combines with $1s$ orbital of H_b which is the electron pair then delocalized among two B -atoms & one H atom to give $3C - 2C$ bond. Due to close proximity of the bridged H -atoms, there is strong electrostatic repulsion between the positive charges on the two hydrogen nucleus to minimize these repulsive, the delocalized orbitals of bridges are bent away from each other in the middle giving the shape of banana, thus the $3C - 2C$ bonds are also known as banana bonds.

Anomalous behavior of Boron & resemblance with Silicon:- Because of extremely small size of its atom and high electro negativity, boron differs in its properties from other elements of the group. On the other hand, it resembles silicon to some extent due to diagonal relationship.

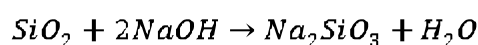
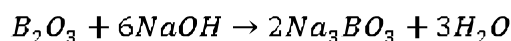
Anomalous properties of boron:-

Boron	Aluminium
Boron is non-metal	Aluminium is metal
bad conductor	good conductor
exists in two forms-crystalline and amorphous	It is a soft metal and does not exist in different forms
Only covalent compounds are present	Some ionic compounds are present
Melting point & boiling point of Boron is much greater than aluminium	Melting point & boiling point of aluminium is much lesser than boron
Hydrides and oxides of boron are acidic	Hydrides and oxides of aluminium are amphoteric
Trihalides of boron exist as monomers BX_3	Trihalides of aluminium exist as monomers Al_2X_6
Hydrides are quite stable	Hydrides are unstable

Diagonal resemblance with Si:-

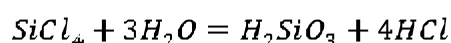
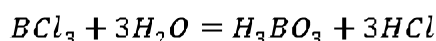
- B and Si exhibit the typical property of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.

- B_2O_3 and silica (SiO_2), both are acidic and dissolve in alkali solutions to form borates and silicates respectively.

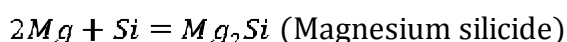
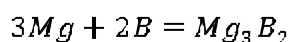


Borates and silicates have tetrahedral BO_4 and SiO_4 structural units respectively.

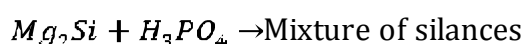
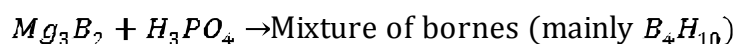
- The chlorides of both get hydrolyzed by water to boric acid and silicic acid respectively.



- The hydrides of boron and silicon are quite stable. A numerous volatile hydrides of these are also known which catch fire on exposure to air and are easily hydrolyzed.
- Boron forms binary compounds with several metals known as borides just as silicon forms metal silicides.



Some of these borides and silicides are known to react with H_3PO_4 and H_2SO_4 to yield boranes and silanes.

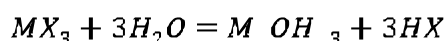


- Both elemental boron and silicon are semiconductors.

Points to remember:-

- Boron forms electron deficient compounds as it has only three electrons in the outermost shell which it can share with other atoms. Hence in the compounds, there are only six electrons present around B -atom i.e. incomplete octet.
- AlF_6^{3-} exists but BF_6^{3-} does not because boron does not have d-orbitals to extend its co-ordination to six.
- $B-X$ bond distance is shorter in BX_3 than the theoretically expected value due to $p\pi - p\pi$ back bonding of the fully filled p -orbital of halogen & empty p -orbital of boron.
- Gold has much higher first ionization energy than boron yet Au is a metal and B is a non-metal because Au in its crystal structure has a co-ordination number of 12 while boron has 6 or less than 6.

- Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3$ is electrovalent because in presence of H_2O Al_2Cl_6 dissociates into hydrated Al^{+3} and Cl^- ions due to high heat of hydration of these ions.
- Tl has a tendency to show +I oxidation state than +III cause of inert pair effect.
- Trihalides of group-13 elements fume in moist water because they are hydrolyzed by water forming hydrogen halides.



General Properties:-

- **Density:** - Density increases down the group due to increase in mass per unit volume. Al has exceptionally low density.
- **Atomic and Ionic radius:** - Atomic radius increases from Boron to Thallium, due to addition of new energy shells.

Element	<i>B</i>	<i>Al</i>	<i>Ga</i>	<i>In</i>	<i>Tl</i>
Atomic Radius(Å)	80	1-24	1-24	1-50	1-55

The abrupt increase in the atomic radius of Al is due to greater screening effect in Al , it has eight electrons in the penultimate shell than in B (which has two electrons).

Further there is not much increase at Gallium and Thallium and the observed atomic radius of Ga is slightly smaller than that of Al because on going from Al to Ga the electrons are filled into d-subshell. Since, these intervening electrons do not screen the nuclear charge effectively, therefore the electrons in Ga experience more force of attraction due to the increased nuclear charge than in Al , causing a decrease in its radius.

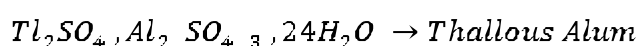
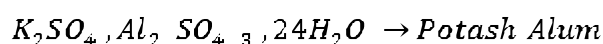
The atomic radii of members belonging to group-B are smaller than the corresponding group-2 elements. Because when we move from group-2 elements to group-B elements in the same period, the magnitude of the nuclear charge increases but the electron that gets added is in the same shell. Since, electrons in the same shell do not screen each other, therefore the electrons experience a strong nuclear pull and hence the size decreases. The ionic radii (M^{+3}) increases from B to Tl .

- **Melting & Boiling point:** - Melting and boiling point do not vary regularly due to structural changes in the elements. Boron has a very high melting point 2300°C as it exists as a giant covalent polymer in both solid and liquid states. The melting point decreases from *B* to *Ga* and then increases. Low melting point of *Ga* is due to the fact that it consists of only Ga_2 molecules, it remains liquid up to 2000°C and hence used in high temperature thermometry. The solid *Ga* is less dense than the liquid unusual crystal structure.
- **Ionization Energy:** - In spite of large nuclear charge and small size, the first ionization energies of these elements are less than the corresponding value of s-block elements. It is because in the elements of group-13 the first electron is to be removed from a p-orbital which is less penetrating and more shielded than s-electrons in case of group-2 elements which are more tightly held by the nucleus due to greater penetration of s-orbital. Therefore less energy is required to remove an electron from p-orbital than from s-orbital.
However the 2^{nd} & 3^{rd} ionization energy of these elements are quite high because the 2^{nd} & 3^{rd} electrons are removed from ns-orbital. Among the members of this group, the ionization energies decrease down the group due to increase in size, however, the I-E of *Ga* is higher than that of *Al*, because of the smaller size of *Ga* compared to *Al*.
- **Electropositive (metallic) character:-** The elements are less electropositive (metallic) than elements of group-1 & group-2 due to their relatively smaller size and higher ionization energies. Electropositive character increases from *B* to *Th* due to decrease in ionization energy. Boron is a non-metal (crystalline form is hard, inert, and poor conductor of electricity. *Al* and other elements are metallic and good conductor of electricity) and has more or less an equal electropositive character. This is indicated by their first ionization energies which differ only slightly from one another.
- **Oxidation States:-** The atoms of group-13 elements have three valence electrons i.e. two in s-sub shell and one in p-sub shell. So, accordingly to electronic configuration of ns^2np^1 , these should allow +1 and +3 oxidation states (with +3 being the more common one). But in practice only Boron shows +3 oxidation states while other elements show +1 as well as +3 oxidation states. The (+1)

oxidation state becomes more and more stable as we move down the group from B to TL. Thus TL (I) is more stable than TL (III).

The +1 oxidation state is exhibited when the s-electrons of the valence shell do not participate in bond formation. Such reluctance on the part of electron pair to participate in bond formation is called inert pair effect. The inert pair effect becomes more predominant down the group because the nuclear charge increases much more than the corresponding increase in distance of the electrons from the nucleus and outer electrons from the nucleus and also the attraction increases because of poor shielding by d-electron. Thus the effect of increase in nuclear charge is not neutralized by the increase in distance due to which the s-electrons of the valence shell become more penetrating i.e. are held more tightly, and hence show reluctance for participation in bonding. Gallium, Indium, Thallium show inert pair effect in their compounds. TL (I), salts resemble alkali metals because it has large size and low oxidation state. Points of resemblance are:-

- TlOH is soluble in water giving strong alkaline solution similar to *NaOH*.
- Like alkali metals, it forms double salts with *Al*

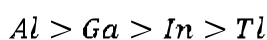


Gallium is divalent in few compounds e.g. $GaCl_2$. This is because this compound has structure of $Ga^+ GaCl_4^-$ which contains the univalent (Ga^+) as well as trivalent (Ga^{+3}) ion.

- **Tendency to form ionic compounds:-** The tendency of formation of ionic compounds increases from B to TL. Boron only forms covalent compounds. This is due to its extremely high ionization energy which is not compensated either by lattice energies of its ionic compounds or by the hydration energies of ions in aqueous solution. The small size and high charge of Al^{+3} ion give it a high charge density which is responsible for its tendency to show :-
 1. Covalency in its compounds in the gaseous state
 2. High hydration energy which stabilizes its compounds in solution.
 3. High lattice energy of its compounds in the solid state.

Thus, Al can form both covalent (e.g. anhydrous $AlCl_3$) and ionic compounds. Gallium forms mainly ionic compounds, although anhydrous $GaCl_2$ is covalent. Thallium compounds are only ionic. (B^{+3} ion \rightarrow Fajan's rule \rightarrow covalency).

- **Oxidation Potential (Reducing properties):** - The order of decreasing "reducing power" of group-13 elements is as follows:-



Since, we know that the measurement of reduction potential involves three different energy changes during the process i.e. $\Delta H_{sublimation}$, I.E and $\Delta H_{hydration}$, therefore the net resultant of these three factors gives us the resultant value of reduction potential. More negative is the value of reducing character.

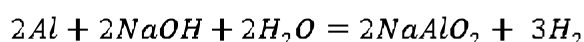
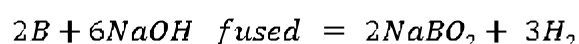
The standard oxidation potentials of these elements are quite high except for B which does not form positive ion in aqueous solution. This may be due to the large heat of hydration resulting from the high charge and small radii of trivalent ions, H^{+3} . Al is a strong reducing agent and in fact better than carbon because Al can reduce even those oxides which are not reduced by Carbon. This is due to low ionization energy of Al than carbon. (Alumino thermite process).

- **Complex Formation:** - On account of their small size and greater charge, these elements have a much greater tendency to form complexes than the s-block elements.

Chemical Properties:-

1. Action of air and water: - Pure boron is almost inert at ordinary temperature. It reacts with oxygen only when heated. It does not react with water. Al can react readily in air and also decomposes water at ordinary temperature to form a protective layer of its oxide which prevents it from further action, Al decomposes steam by liberating H_2 . Ga & In are unaffected by air even when heated. These are attacked neither by cold nor by hot water unless oxygen is present. In moist air a layer of $TLOH$ is formed.

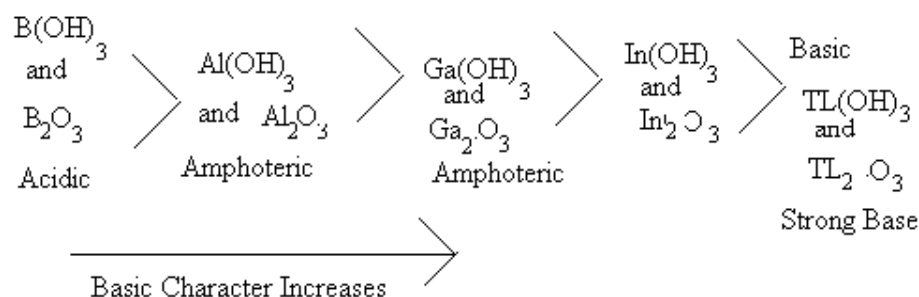
2. Action of acids: - Boron does not react with non-oxidizing acids; however it dissolves in concentrated HNO_3 & H_2SO_4 forming boric acid. Al, Ga, In, M^{+3} ion. However Gallium and Aluminum becomes passive on treatment with HNO_3 due to the formation of protective film of oxide. Thallium dissolves in acids forming it passive due to the formation of water insoluble thallium chloride.
3. Action of alkalis: - Boron dissolves only in fused alkalis. Aluminum and gallium dissolves in fused as well as in aqueous alkalis liberating H_2 .



In remains insoluble in caustic alkalis even on heating.

Oxides and Hydroxides: -

Almost all elements of group-13 form oxides and hydroxides of the



composition M_2O_3 & MOH_3 . The nature of these oxides/hydroxides changes from weakly acidic to amphoteric and amphoteric to basic in moving down the group from *B* to *Tl*.

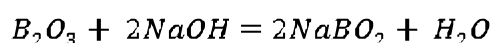
Reason:-As we go down the group, the atomic size of elements goes on increasing whereas ionization energy decreases. As a result, the strength of M-O bond goes on decreasing accounting for the increase in basic character down the group.

Preparation of *B* & *Al* oxides:-

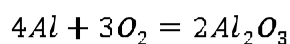
1. B_2O_3 is prepared by burning boron in presence of oxygen. $4B + 3O_2 \rightarrow 2B_2O_3$.

B_2O_3 is a good dehydrating agent and reacts with water to form orthoboric acid.

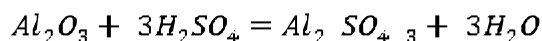
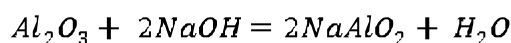
B_2O_3 being predominantly an acidic oxide dissolves in alkalis to give borates as



2. Al_2O_3 is also obtained by heating *Al* in presence of O_2



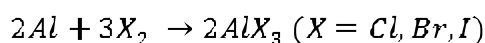
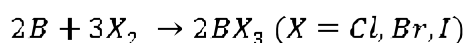
It is an amphoteric oxide soluble in acid as well as bases.



Crystalline alumina Al_2O_3 exists in many forms. Corundum is very hard and is used as an abrasive. It is prepared by heating amorphous alumina to about 2000K.

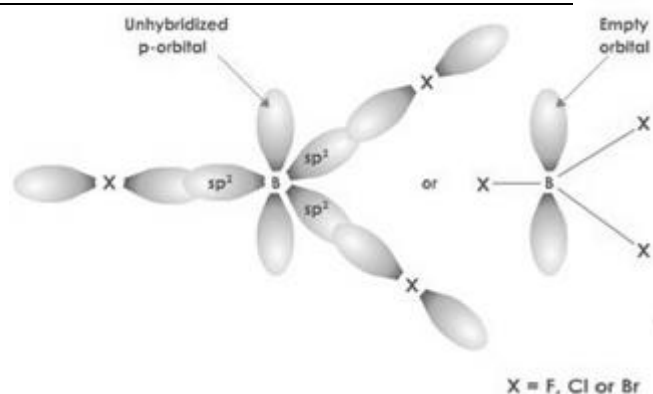
Hallides: -

Both Boron and Al combine with halogens to form trihalides, having the general formula MX_3 . These halides can be prepared by heating the elements directly with halogens.



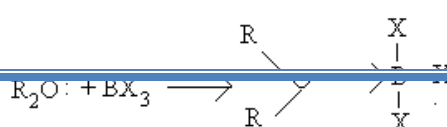
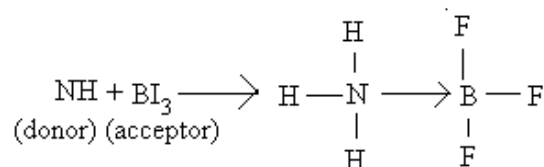
Boron Trihalides:

Due to small size and high electron negativity of boron, all boron halides are covalent in nature. This has been indicated by the fact that they are soluble in organic solvents and are bad conductor of electricity. The boron trihalides are covalent in nature and exists as monomeric molecules having planar triangular geometry. In these halides boron assumes sp^2 hybrid state and three $B-X$ bonds are formed by axial overlap of sp^2 hybrid orbital of boron and p -orbital of halogen.



Electron-deficiency of boron in boron halides:-

Since, there are only six electrons in the valence shell of boron atom in boron halides, therefore it has a great tendency to accept two more electrons to acquire stable octet. Thus, boron



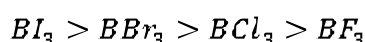
trihalides act as Lewis acids. They rapidly combine with electron donors such as NH_3 , F^- ion, amines, ether etc.

In general,

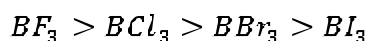
As a result of its strong Lewis acid character BI_3 is used as a catalyst in several industrial processes.

Relative Lewis acid character of boron trihalides:-

The relative Lewis acid character of boron trihalides has the following order:-

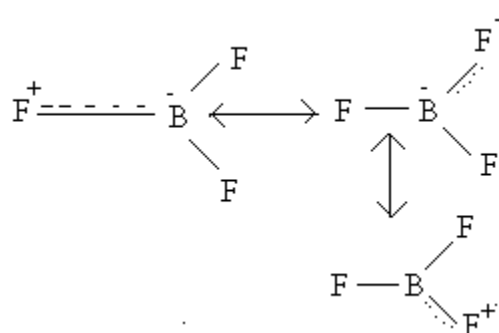


However, the above order is just the reverse of the normally expected order on the basis of relative electronegativities of the halogens. Fluorine being the most electronegative should create the greatest electron deficiency on boron and thus B in BF_3 should accept electron pair from a donor very rapidly than in other boron halides. So, the expected order of Lewis acid strength of BX_3 on the basis of electronegativity of the halogen should be:-



The anomalous behavior can be explained on the basis of the relative tendency of the halogen atom to back donate (halogen – boron back π -bonding). Its unutilized electrons to the vacant p -orbitals of boron atom.

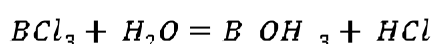
For example in BF_3 , each fluorine has completely filled unutilized $2p$ orbitals while boron has a vacant $2p$ -orbital. Now, since both of these orbitals belong to the same energy level ($2p$), they can overlap effectively as a result of which fluorine electrons are transferred into the vacant $2p$ orbital of boron resulting in the formation of additional $p\pi - p\pi$ bonding. This type of bond formation is known as dative or back bonding.



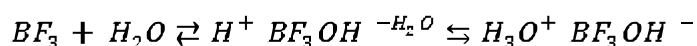
Thus, $B - F$ bond has some double bond character. Since, back bonding may take place between B and any of the three fluorine atoms, BF_3 is a resonance hybrid of three

structures, resonance is supported by the fact that all the three $B - F$ bonds are equal in length and that their lengths is smaller than the $B - F$ single bond length.

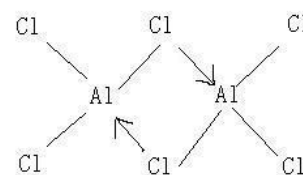
As a result of back donation of electrons from fluorine to boron, the electron deficiency is decreased. The tendency for the formation of back bonding ($p\pi - p\pi$) bond is maximum in BF_3 and decreases very rapidly from BF_3 to BI_3 . This is probably due to the fact that overlapping of the vacant $2p$ orbital of boron cannot take place easily with the p -orbital of higher energy levels ($3p$ in Cl , $4p$ in Br , $5p$ in I). Thus, $BI_3 > BBr_3 > BCl_3 > BF_3$ in Lewis acid character. Lewis acid character in group-B is $B > Al > Ga > In$. All boron halides, except boron trifluoride are hydrolyzed to boric acid.



On the other hand, boron trifluoride due to strong $B - F$ bond does not undergo hydrolysis with water but forms an addition product.



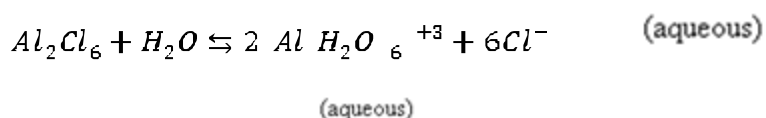
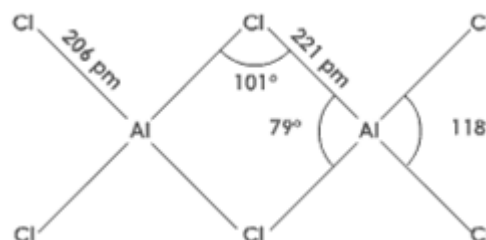
The reason for BF_3 not undergoing hydrolysis is that the high resonance energy of BF_3 is not compensated by the hydration energy. Due to great resistance of BF_3 to hydrolysis and its tendency to act as a Lewis acid, BF_3 is extensively used as a catalyst in organic reactions like Friedel crafts alkylation and acylation, esterification etc. Boron halides form



complex halides of the type, $BF_4^- H^+$, in which boron atom extends its co-ordination number to four by utilizing its empty p -orbital. It cannot extend its co-ordination number beyond four due to non-availability of d -orbitals. However, the other trihalides of this group forms complex halides of the type AlF_6^{3-} , $GaCl_6^{3-}$ and $InCl_6^{3-}$ etc, where the central atom achieves co-ordination number 6 by use of d -orbitals. The fluorides of Al , Ga , In , Tl are ionic and have high melting points. The high m.p's can be explained on the basis that their cations are sufficiently large and have vacant d -orbital for attaining a co-ordination number of six towards the relatively small fluorine atom. Other halides of Al , Ga , In , Tl are largely covalent when anhydrous. It is important to note that these halides do not show back bonding because of the increase in the size of the element. Actually, they make use of vacant p -orbitals by other method i.e. metal atoms complete their octet by forming dimers. Thus, $AlCl_3$, $AlBr_3$, InI_3 exist as dimers both in the vapor state and in non-polar solvents.

In these bridged structure the halogen atoms are arranged tetrahedrally around the central atom. The bridged ($3-C$ bond) structure (typical of electron deficient compounds) for Al_2Cl_6 is considered by the following facts:-

- Vapor density of $AlCl_3$ measured at $400^\circ C$ corresponds to Al_2Cl_6 at higher temperature. Al_2Cl_6 dissociates to trigonal planar $AlCl_3$ module.
- Bond distance between $Al-Cl$ bond forming bridge is greater (2.21\AA) than the distance between $Al-Cl$ bond in the end. (2.06\AA).
- The dimeric structure disappears when the halides are dissolved in water. This is due to high heat of hydration which splits the dimeric structure into $Al(H_2O)_6^{3+}$ and $6Cl^-$ ions, as a result the solution becomes a good conductor of electricity [$AlCl_3$ hydrated is ionic in nature]. The dimeric structure may also be split by reaction with donor molecules e.g. R_3N . This is due to formation of complexes of the type R_3NAlCl_3 .



Al_2Cl_6 has no lp of electrons and hence it does not behave as a Lewis acid. Aluminium halides and aluminium alkyls make up electron deficiency by bridging with halide or alkyl groups i.e. they exist as dimer while the corresponding boron halides exist as monomers.

Exp:- Boron halides do not form dimers because the size of boron is so small that it is unable to accommodate or co-ordinate dimers of four large sized ions viz Cl^- , Br^- , I^- . However, this property cannot be applied on BF_3 because the F^- ion being smaller should easily be accommodated by boron which is evident from the stability of BF_4^- ion. The non-existence of the dimer of BF_3 is because the energy that is released by the formation of additional boron to another boron atom is not sufficient to compensate for the loss in energy to the system in overcoming $B-F$ $p\pi-p\pi$ bonding in monomer itself.