

CHAPTER

The p-block elements

Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells – p-block elements

- Gen. electronic configuration of outer shell is ns^2np^{1-6}

The inner core of e-config. may differ which greatly influences their physical & to some extent chemical properties.

- The block of elements in the periodic table consisting of the main groups :
- Group 13 (B to Tl)
- Group 14 (C to Pb)
- Group 15 (N to Bi)
- Group 16 (O to Po)
- Group 17 (F to At)
- Group 18 (He to Rn)

(1) Members at the top and on the right of the *p*-block are nonmetals (C, N, P, O, F, S, Cl, Br, I, At).

(2) Those on the left and at the bottom are metals (Al, Ga, In, Tl, Sn, Pb, Sb, Bi, Po).

(3) Between the two, from the top left to bottom right, lie an ill-defined group of metalloid elements (B, Si, Ge, As, Te)

GROUP 13 : The boron group

- Outer Electronic Configuration:- ns^2np^1
- group members: boron (B), aluminum (Al), gallium (Ga), indium (In) & thallium (Tl) . All, except boron, are metals.
- Boron show diagonal relationship with Silicon; both are semiconductors metalloids & forms covalent compounds.
- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom .
- diborane B_2H_6 , is simplest boron hydride

- Structure: three-center two-electron: the H atoms are simultaneously bonded to two B atoms the B-H bridging bond lengths are greater than B-H terminal.
- - Boron oxide is acidic (it reacts readily with water to form boric acid)
- aluminium compounds:aluminium oxide is amphoteric
- aluminum halides, e.g., AlCl_3 is dimer, an important catalyst in organic chemistry have anincomplete octet, acts as Lewic acid by accepting lone pairs from Lewic bases, forming adduct
- aluminum hydride, e.g., LiAlH_4 , a reducing agent
- Atomic Properties - Electronic Configurations

Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's Crust (in ppm)
Boron	B	5	$[\text{He}]2s^2 2p^1$	8
Aluminium	Al	13	$[\text{Ne}]3s^2 3p^1$	81,300
Galium	Ga	31	$[\text{Ar}]3d^{10}4s^2 4p^1$	15
Indium	In	49	$[\text{Kr}] 4d^{10}5s^2 5p^1$	1
Thallium	Tl	81	$[\text{Xe}] 5d^{10}6s^2 6p^1$	0.3

. Atomic and ionic radii

- The atomic and ionic radii of group 13 elements are compared to corresponding elements of group 2. From left to right in the period, the magnitude of nuclear charge increases but the electrons are added to, the same shell. These electrons do not screen each other, therefore, the electrons experience greater nuclear charge.
- In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.
- On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143 pm) is slightly more than that of Ga (135 pm).

Ionization energies

The first ionization energies of group 13 elements are less than the corresponding members of the alkaline earths.

The sharp decrease in I.E. from B to Al is due to increase in size. In case of Ga, there are ten d-electrons in its inner electronic configuration.

The very high value of 3rd I. E. of thallium indicates that +3 O.N. state is not stable, rather +1 is more stable for thallium .

Electropositive (or metallic) character

the elements of group 13 are less electropositive as compared to elements of group 2. On moving down the group the electropositive (metallic) character increases because ionization energy decreases. For e.g., Boron is a non-metal while the other elements are typical metals.

Oxidation states

The common oxidation states of group 13 elements are +3 and +1 .The stability of the + 1 oxidation state increases in the sequence Al < Ga < In < Tl, Due to Inert pair effect.

Element	B	Al	Ga	In	Tl
Oxidation state	+3	+3	+3, +1	+3, +1	+3, +1

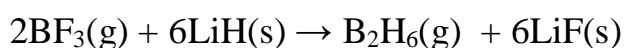
Chemical reactivity of Gr.13 Elements

All elements in their compounds exhibit the oxidation state of + 3 and +1.

Hydrides

- None of the group 13 elements reacts directly with hydrogen. However, a no. of hydrides of these elements have been prepared by indirect methods. The boron hydrides are called boranes & classified in two series: (a) B_nH_{n+4} called nido-boranes (b) B_nH_{n+6} called arachno-boranes

- INDUSTRIAL PREPERATION :-



- Laboratory method:

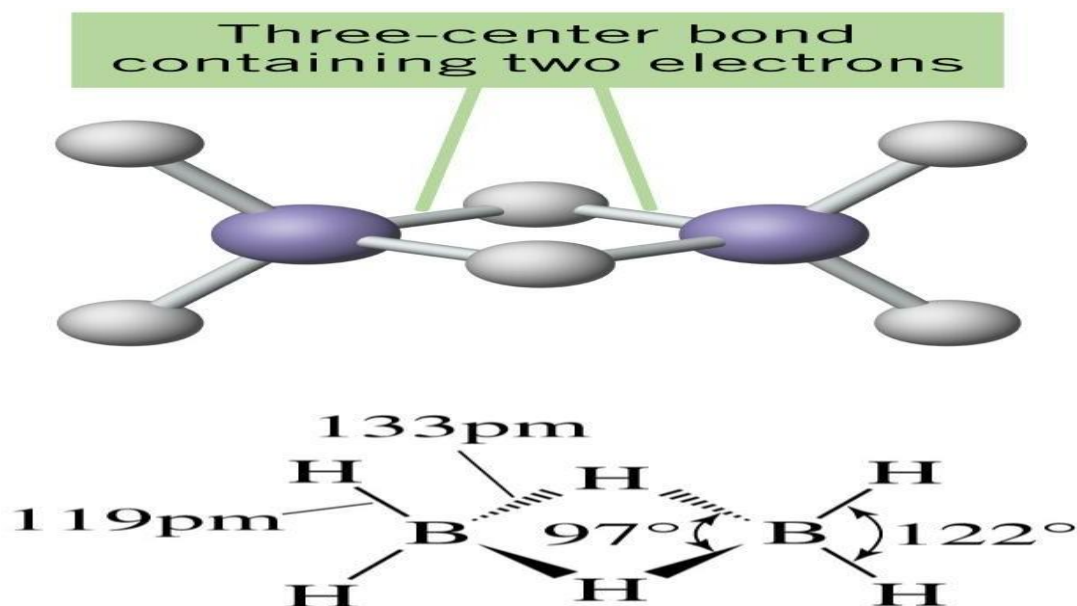
- By the reaction of iodine with sodium borohydride in a high boiling solvent.



- By reduction of BCl_3 with $LiAlH_4$

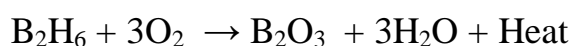


Structure of Diborane, B₂H₆



Some important characteristics of boranes:

- Lower boranes are colourless gases while higher boranes are volatile liquids or solids.
- They undergo spontaneous combustion in air due to strong affinity of boron for oxygen.

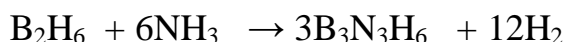


- Boranes react with alkali metal hydrides in diethyl ether to form borohydride complexes.



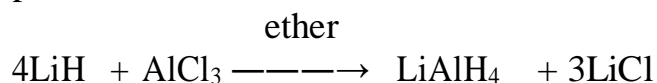
Metal borohydride

- (iv) Diborane reacts with ammonia to give borazine at 450 K.



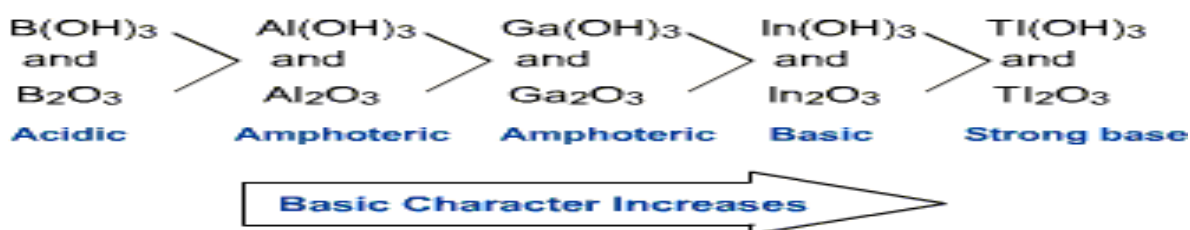
- Borazine has a cyclic structure similar to benzene and thus is called inorganic benzene
- The other elements of this group form only a few stable hydrides. The thermal stability decreases as we move down the group.

- AlH_3 is a colourless solid polymerized via Al - H - Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis base (B:) to give compounds of the type MH_3 (M = Al or Ga). They also form complex-tetrahydrido anions, $[\text{MH}_4]^-$. The most important tetrahydrido compound is $\text{Li}[\text{AlH}_4]$

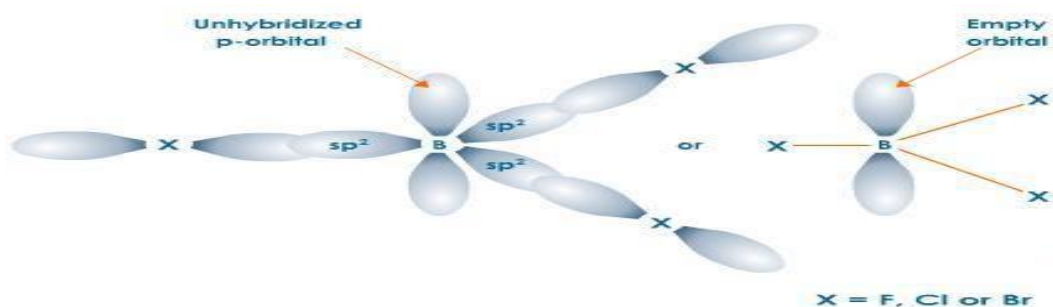


OXIDES & HYDROXIDES

- M_2O_3 & $\text{M}(\text{OH})_3$

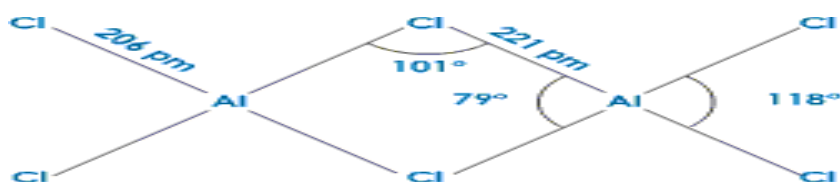


HALIDES: Structure of boron trihalides



Dimeric structure of aluminium chloride

- Boron halides do not form dimers because the size of boron is so small that it is unable to coordinate four large-sized halide ions.

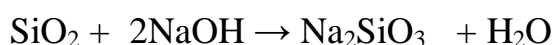
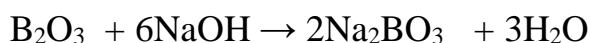


- Anomalous properties of boron

1. Boron is a non-metal & bad conductor of electricity whereas aluminium is a metal & good conductor. B is hard but Al is a soft metal.
2. Boron exists in two forms-crystalline and amorphous. But Al does not exist in different forms.

3. The melting and boiling point of boron are much higher than that of Al .
4. Boron forms only covalent compounds whereas Al forms even some ionic compounds.
5. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.
6. The trihalides of boron exist as monomers. On the other hand, aluminium halides exist as dimers .
7. The hydrides of boron are quite stable while those of aluminium are unstable

- Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.
- Boron oxide (B₂O₃) and silica (SiO₂) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.



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



- The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolyzed.
- Both elements are semiconductors.

Behavior in Aqueous Solutions

1 Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like [M(OH)₄]⁻, [M(H₂O)₂(OH)₄]⁻, [M(OH)₂]₆³⁺ for M = Al, Ga, In, exist in aqueous solution.

2. Al, Ga, In and Tl ions exist as octahedral aqua ions, [M(OH)₂]₆³⁺ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.

3. Aluminiumsulphate forms double salts - called alum, having the general formula



USES OF BORON & ALUMINIUM

- Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu, Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is also used in the aluminothermite process for production of chromium and manganese from their ores.