Physical properties of boron family are:-

ELECTRONIC CONFIGURATION

The elements of group 13 belong to p-block of the periodic table and these elements contain three electrons in the valence shell, therefore, their valence shell electronic configuration is ns^2np^1.

Element	At. No.	Electronic Configuration.	Valence Shell Configuration.
B	5	$[He]\ 2s^2,\ 2p^1$	$2s^22p^1$
Al	13	$[Ne]\ 3s^2,\ 3p^1$	$3s^23p^1$
Ga	31	$[Ar]^3\ 3d^{10},\ 4s^24p^1$	$4s^24p^1$
In	49	$[Kr]\ 4d^{10},\ 5s^25p^1$	$5s^25p^1$
Tl	81	$[Xe]\ 4f^{14},\ 5d^{10},\ 6s^2p^1$	$6s^26p^1$

ATOMIC RADII AND IONIC RADII

•   Atoms and their ions of group 13 elements have smaller size than those of alkaline earth metals of group-2, due to greater nuclear charge of former group than latter group.

•   Atomic radii increase on going down in the group with an abnormally at gallium and the unexpected decrease in the atomic size of Ga is due to the presence of electrons in d- orbitals which do not screen the nucleus effectively.

•   The ionic radii regularly increases from B^{3+} to Tl^{3+}

DENSITY

It increases regularly on moving down the group from B to Tl

MELTING AND BOILING POINTS

•   M.P. and b. p. of group 13 elements are much higher than those of group 2 elements

Element	B	Al	Ga	In	Tl
M.p. (K)	2453	933	303	430	576
B.p. (K)	3923	2740	2676	2353	1730

•   The m.p. decreases from B to Ga and then increases, due to structural changes in the elements

•   Boron has a very high m. p. because of its three dimensional (B_{12}- icosahedral) structure in which B atoms are held together by strong covalent bonds.

•   Low m. p. of Ga is due to the fact that it consists of only Ga_2 molecules, and Ga remains liquid upto 2273K therefore it is used in high temperature thermometry.

IONISATION ENERGY

•   The first I.E. values of group 13 elements are lower than the corresponding values of the alkaline earth metals, due to the fact that removal of electron is easy in former case (p-electron) than latter (s-electron).

This results in the increase of nuclear charge. Consequently the valence electrons are more tightly held leading to high I.E. Similarly we can explain the irregularity in case of Tl on the basis of ineffective shielding of intervening electrons

•   On moving down the group IE, decreases from B to Al but the next element Ga has slightly higher IE, than Al, it again decreases in In and increases in the last element Tl as follows :

Element	B	Al	Ga	In	Tl
IE, (kJ mol^{-1})	800	577	578	558	590

•   The irregularity observed in case of Gallium is due to the ineffective shielding of nuclear charge because of intervening d electrons, which cause the increase in nuclear charge leading to high I.E.

INERT PAIR EFFECT

- It is the reluctance of the s-electrons of the valence shell to take part in bonding and occurs due to ineffective shielding of the ns^2 electrons by the intervening d and f electrons.

- It increases down a group and thus the lower elements of group show lower oxidation states.

OXIDATION STATES

- B and Al show an oxidation state of +3 only while Ga, In and Tl show oxidation states of both +1 and +3.

- As we move down in the group 13, due to inert pair effect, the tendency to achieve +3 oxidation state goes on decreasing and the tendency to acquire +1 oxidation state goes on increasing.

- Stability of +1 oxidation state follows the order Ga < In < Tl

- Tl^+ compounds are more stable than Tl^{3+} compounds.

ELECTROPOSITIVE (METALLIC) CHARACTER

- These elements are less electropositive than the elements of the group 1 and 2 due to their smaller size and higher ionisation energies.

- On moving down the group, the electropositive character first increases from B to Al and then decreases from Ga to Tl, due to the presence of d and f orbitals in latter elements.

REDUCING CHARACTER

It decreases down the group from Al to Tl because of the increase in electrode potential values for M^{3+}/M. Therefore it follows the order.

Al > Ga > In > Tl

| Element B	Al	Ga	In	Tl
E° (V) at 298 K for M^{3+}/M	−1.66	−0.56	−0.34	+1.26

COMPLEX FORMATION

Due to their smaller size and greater charge, these elements have greater tendency to form complexes than the s-block elements.

NATURE OF COMPOUNDS

- The tendency of formation of ionic compounds increases from B to Tl.

- Boron forms only covalent compounds where as Al can form both covalent (e.g., anhydrous $AlCl_3$) and ionic compounds (e.g., hydrated $AlCl_3$) because when anhydrous $AlCl_3$ is hydrated, the hydration energy released is sufficient to overcome the ionisation energy of Al.

- Gallium forms mainly ionic compounds although anhydrous $GaCl_3$ is covalent.

HYRIDES

- Elements of group 13 do not combine directly with H_2 to form hydrides, therefore, their hydrides have been prepared by indirect methods for example.

$BF_3 + 3LiBH_4 \xrightarrow{\text{dry ether}} 2B_2H_6 + 3LiF$
diborane
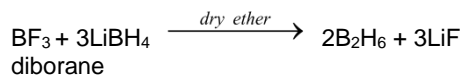
- Boron forms a number of hydrides which are called boranes with general formula B_nH_{n+4} (e.g., B_2H_6) and B_nH_{n+6} (e.g., B_4H_{10})

- Boranes catch fire in the presence of oxygen with the evolution of heat energy

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$; $\Delta H = -2008$ kg/mol
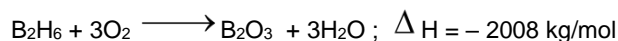
- Boranes are hydrolysed by water as follows :

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

- Boranes are quite stable but the stability of hydrides of Al, Ga, In, and Tl decreases on moving down the group because the strength of the M–H bond decreases with increasing size of the element.

- Structure of diborane : The simplest boron hydride, i.e. BH_3 does not exist as such but exists as a dimer, B_2H_6, having following structure
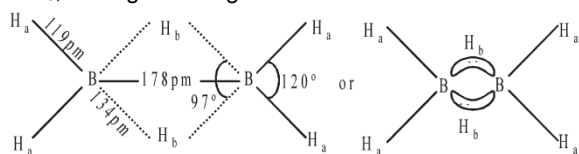

- In above structure B atoms are in sp^3 hybrid state. There are six B-H bonds out of which four B-H_a bonds are normal covalent bonds (two centre electron - pair bonds i.e, 2c–2e) present in the same plane while rest two B-H_b bonds behave as bridges containing three centre two electron pairs bonds i.e., 3c–2e (known as banana bonds) and present above and below the plane of the molecules which do not have sufficient number of electrons to form normal covalent bonds are called electron - deficient molecules. Ex. B_2H_6.

- Aluminium forms a polymeric hydride of general formula $(AlH_3)_x$ which decomposes into its elements on heating.

- B, Al and Ga form complex anionic hyd

PREPARATION OF HALIDES

- All the elements of boron family (except thallium which forms thallous monohalides) form trihalides of type MX_3 where X= F, Cl, Br and I.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$
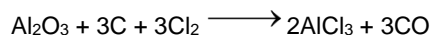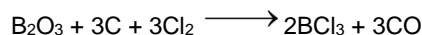
- All the boron trihalides, BX_3 and aluminium trihalides AlX_3 (except AlF_3 which is ionic) are covalent compounds whereas former exist as only monomers and latter as dimers, because boron atom is too small to coordinate with four large halide ions and in case of much smaller F^- ion , the energy released during the formation of the bridge structure is not sufficient for the cleavage of the typical $p\pi$ -$p\pi$ bond in BF_3.
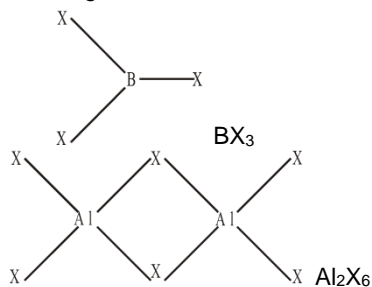
- BF_3 is a colourless gas, BCl_3 and BBr_3 are colourless fuming liquids whereas BI_3 is a white fusible solid at room temperature.

- The covalent character of trihalides decreases on moving from Ga to Tl.

- Hybridisation of Boron in BCl_3 is sp^2

NATURE OF TRIHALIES

- Trihalides of group 13 elements behave as lewis acids due to having a strong tendency to accept a pair of electrons.

- The relative strength of lewis acids of boron trihalides increases in the order :
$BF_3 < BCl_3 < BBr_3 < BI_3$.

- The halides of group 13 elements behave as lewis acids and the acidic character decreases as follows:
$BX_3 > AlX_3 > GaX_3 > InX_3$ (where X=Cl, Br or I)

- BF_3 and anhydrous $AlCl_3$ are used as a catalyst in Friedel Crafts reactions.

- $TlCl_3$ decomposes to $TlCl$ and Cl_2 above 40ºC and hence acts as an oxidising agent, whereas $TlBr_3$ converts into $Tl[TlBr_4]$ at room temperature.

$$TlCl_3 \xrightarrow[>40°C]{\Delta} TlCl + Cl_2 ; \quad 2TlBr_3 \longrightarrow Tl[TlBr_4] + Br_2$$
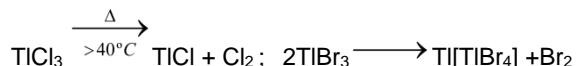
While TlI$_3$ is an ionic compound containing Tl(I) and I_3^- ions.

OCCURRENCE AND IMPORTANT MINERALS OF BORON

It does not occur in the free state in nature. It forms electron deficient compounds.
Its important minerals are :

- Borax (or Tincal), $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4]8H_2O$
- Kernite, $Na_2B_4O_7.2H_2O$ or $Na_2[B_4O_5(OH)_4]$
- Orthoboric-acid H_3BO_3
- Colemanite, $Ca_2B_6O_{11}.5H_2O$ or $Ca_2[B_3O_4(OH)_3]_2$ $2H_2O$
- Boracite, $2Mg_3B_8O_{15}. MgCl_2$

ISOLATION

Elemental boron in the form of dark brown powder is obtained by following methods :

- By reduction of boric oxide with highly electropositive metals like K, Mg, Al, Na etc. in the absence of air

$B_2O_3 + 6K \xrightarrow{Heat} 2B + 3K_2O$
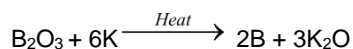
- By the reaction of boron halides with hydrogen at high temperature.

$2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$
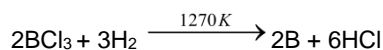
- By thermal decomposition of boron triiodide over red hot tungsten filament.

$2BI_3 \xrightarrow{W\ heat} 2B + 3I_2$
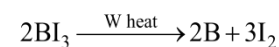
- By thermal decomposition of boron hydrides $B_2H_6 \xrightarrow{\Delta} 2B + 3H_2$

PREPARATION
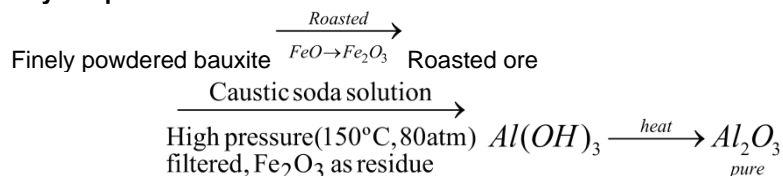By the reaction of boron and halogens at high temperature.

$2B + 3X_2 \xrightarrow{heat} 2BX_3$
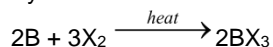
PROPERTIES

- BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid and BI_3 is a solid at room temperature.

- These are covalent in nature and act as lewis acids. The decreasing order of acid strength is. $BI_3 > BBr_3 > BCl_3 > BF_3$
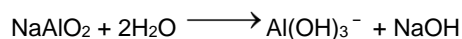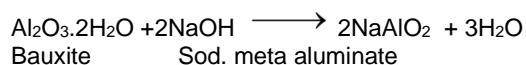
Aluminium metal is extracted from bauxite. It involves following steps.

1. **Purification of bauxite** : Bauxite usually contains silica as impurity. These impurities must be removed before electrolysis, since aluminium, once prepared, cannot be freed of other metals by refining it. The bauxite is first purified by any of the following processes depending upon the nature of impurities present in it.

Bayer's process :

Finely powdered bauxite $\xrightarrow[FeO \to Fe_2O_3]{Roasted}$ Roasted ore

$\xrightarrow[\substack{High\ pressure(150^oC, 80atm) \\ filtered, Fe_2O_3\ as\ residue}]{Caustic\ soda\ solution} Al(OH)_3 \xrightarrow[pure]{heat} Al_2O_3$

The reactions involved are given below.

$Al_2O_3.2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$
Bauxite   Sod. meta aluminate

$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3^- + NaOH$

$2Al(OH)_3 \xrightarrow{1473K} Al_2O_3 + 3H_2O$ Alumina

ANHYDROUS ALUMINIUM CHLORIDE, AlCl$_3$ (or Al$_2$Cl$_6$)

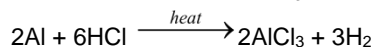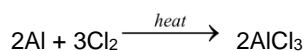**PREPARATION**
It can not be prepared by heating AlCl$_3$. 6H$_2$O because of its hydrolysing tendency by its own water as below.

2AlCl$_3$. 6H$_2$O $\xrightarrow{\Delta}$ 2Al(OH)$_3$ + 6HCl
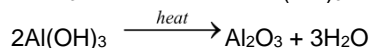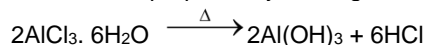
2Al(OH)$_3$ $\xrightarrow{heat}$ Al$_2$O$_3$ + 3H$_2$O
However, it can be prepared by following methods:
• By passing dry chlorine or HCl gas over heated Al.

2Al + 3Cl$_2$ $\xrightarrow{heat}$ 2AlCl$_3$

2Al + 6HCl $\xrightarrow{heat}$ 2AlCl$_3$ + 3H$_2$
• By heating a mixture of alumina and carbon in a current of dry chlorine.

Al$_2$O$_3$ + 3C + 3Cl$_2$ $\xrightarrow{heat}$ 2AlCl$_3$ + 3CO
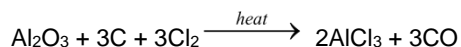
PROPERTIES
• It fumes in moist air due to hydrolysis

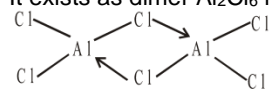AlCl$_3$ + 3H$_2$O $\longrightarrow$ Al(OH)$_3$ + 3HCl
The resulting solution is acidic due to the formation of HCl.
• It behaves as lewis acid.
• It is a covalent solid and dissolves in organic solvents like C$_6$H$_6$ etc.

STRUCTURE
It exists as dimer Al$_2$Cl$_6$ in which each Al atom is tetrahedrally surrounded by four Cl atoms as below.

USES
• As a catalyst in Friedel - Craft reactions
• As a mordant in dyeing

ALUMINIUM OXIDE OR ALUMINA, Al$_2$O$_3$

It is the most stable compound of aluminium and occurs in nature as colourless corundum and several coloured oxides, (when present in combination with different metal oxides) like ruby (red), topaz (yellow), sapphire (blue), amethyst (violet) and emerald (green), which are used as precious stones (gems).

THERMITE

A mixture of aluminium powder and ferric oxide in the ratio 1: 3.