9. GROUP 13 ELEMENTS (IIIA)

SYNOPSIS:

GENERAL CHARACTERSTICS

- Boron, Aluminium, Gallium, Indium and belong to III_A group of the Periodic table.
- The general outer electronic configuration of III_A group elements is ns^2np^1
- B and Al show similar properties due to similar outer electronic configuration. They show differences in some of the properties due to the difference in the number of electrons present in their penultimate shells.

Electronic Configurations :

Element	Symbol	At No	E.C.
Boron	B	5	$[He]2s^2 2p^1$
Aluminum	Al	13	$[Ne]3s^2 3p^1$
Gallium	Ga	31	$[Ar]3d^{10} 4s^2 4p^1$
Indium	In	49	$[Kr]4d^{10} 5s^2 5p^1$
Thallium	Tl	81	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$

OCCURANCE :

- B does not occur in free state in nature.
- B occurs in the form of salts of boric acid
- Al is most abundant metal and third most abundant element (First O_2 , second Si) by weight. Al forms nearly 7.28% of the earth's crust.
- Al occurs in combined state as oxide, fluoride and silicates.
- Ga, In, and Tl occur in trace quantities along with sulphides of Zinc and Lead

Element	Abundance (%)
Boron	3×10^{-4}
Aluminum	8.13
Gallium	1.3×10^{-3}
Indium	1×10^{-5}
Thallium	$10^{-4} - 10^{-5}$

VARIATION OF PROPERTIES

- Boron is a non metal.

S.NO	Name of the Mineral	Formula
1	Borax	$Na_2B_4O_7.10H_2O$
	Kernite (or) Razorite	$Na_2B_4O_7.4H_2O$
	Boric acid	H_3BO_3
2	Colemanite	$Ca_2B_6O_{11}.5H_2O$
	Corundum	Al_2O_3
	Diaspore	$Al_2O_3.H_2O$
	Bauxite	$Al_2O_3.2H_2O$
	Gibbsite	$Al_2O_3.3H_2O$
	Cryolite	Na_3AlF_6 (or) $3NaF.AlF_3$
	Felspar	$KAlSi_3O_8$
3	Ga, In, Tl occur as sulphides .Ga is found the ores of Zn, Al, and Ge In and Tl occurs along with Zns (Zinc blende) and galena PbS	

- *Al* , Ga, In, and are metals.
- Atomic radius increases suddenly from B to *Al* .
  This is due to the greater screening effect of electrons present in the penultimate shell.
- The atomic radii of Al and Ga are same.
  This is because of the poor shielding effect of d-electrons in Gallium
- Density increases from Boron to Thallium
- The m.p.'s and b.p's of III_A group elements do not show any regular trend.
  This is due to the difference in their crystal structures.
- Melting points order $B > Al > Tl > In > Ga$
- Boiling points order $B > Al > In > Ga > Tl$
- Melting point of Gallium is very low because it contains Ga_2 molecules.
- Boron has high m.p because it exists as a giant covalent polymer both in liquid and solid
- Gallium exits as a liquid between 29.8°C and 2000°C. So Gallium is used in high temperature thermometry.
- The order of $B > Tl > In > Ga > Al$.
- The most electropositive element in III_A group is Al.
- The compounds of Al and Ga (Ex: $AlCl_3$ and $GaCl_3$) are covalent only in the anhydrous state and Ionic in aqueous solution because their hydration energies, compensate the ionaization energies.
- Boran forms an oxide and a nitride when burnt in air. But Al does not undergo any change and remains in tact because it forms an oxide layer
- At high temperature Al gives its nitrides.
- The common oxidation state of these elements is +3
- Boron shows -3 and +3 oxidation states.
- Ga, In and *Tl* exhibits +3 and +1 oxidation states

- Due to inert pair effect +1 oxidation state of Tl is more stable than its +3 oxidation state.

ANOMALOUS PROPERTIES OF BORON

- Boron is non mental.
- It always forms covalent compounds
- Boron show diagonal relationship with Si.
- Boron does not displace hydrogen from acids
- Oxide of boron B_2O_3 is acidic oxide
- Hydroxide of boron is acidic $\left(B(OH)_3 \text{ or } H_3BO_3\right)$
- Maximum covalency of boron is 4
- Boron form stable covalent hydrides which are known as bornanes.
- Boron never appears as a cation
- Among halides of boron only BF_3 undergoes complete hydrolysis.

Boron

Preparation :

- In the laboratory, it is prepared by reducing B_2O_3 with metallic magnesium.
- 95-98% pure boron is obtained on reducing B_2O_3 with Mg or Na metal at high temperature. It is known as "Moissan Boron". This is amorphous Boron.

  $B_2O_3 + 3Mg \xrightarrow[\text{bright red hot}]{\Delta} 2B + 3MgO$
- B_2O_3 is obtained from borax
- Borax is treating with hot conc. HCl gives H_3BO_3 Boric acid (H_3BO_3) on fusion loses water and forms B_2O_3.
- $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$

  (Orthoboric acid)
- $4H_3BO_3 \xrightarrow[-H_2O]{435k} \underset{\text{tetraboric acid}}{H_2B_4O_7} \xrightarrow[-H_2O]{\text{red heat}} B_2O_3$
- $H_3BO_3 \xrightarrow[-H_2O]{375k} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow[-H_2O]{\text{red heat}} B_2O_3$
- Pyrolysis of BI_3 (or) thermal decomposition of boranes also gives crystalline Boron.

PHYSICAL PROPERTIES :

- Boron exists in two allotropic form
  a) Amorphous B b) Crystalline B.
- Amorphous B dissolves in molten Al at 1530^0C which on cooling gives yellow colored crystalline solid. Al is eliminated by dissolving in HCl. This results in very hard crystalline B.
- B is a non conductor of electricity
- B sublimes at ordinary pressure

CHEMICAL PROPERTIES :

- Action with air (or) O_2 : Amorphous B, on heating in air to about 700^0C, form B_2O_3 and BN

  $4B + 3O_2 \longrightarrow 2B_2O_3$

  $2B + N_2 \longrightarrow 2BN$

- With non metals : On heating amorphous B will react with N_2, O_2, S, F_2, Cl_2 *and* Br_2 directly forming binary compounds

  $4B + 3O_2 \longrightarrow 2B_2O_3$

  $2B + 3S \xrightarrow{1200^0C} \underset{Boron\ tri-sulphide}{B_2S_3}$

  Hardest compound of Boran is Boran carbide (B_4C)

- Reducing property : B is a powerful reducing agent for CO_2 *and* SiO_2.

  $3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$

- With Conc. acids B gives boric acid

  $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO$

  $2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$

- When fused with alkalies, B liberates

  $2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2 \uparrow$

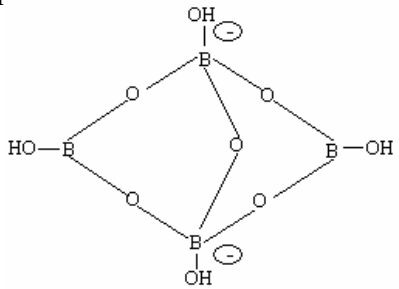
USES :

- B is a good neutron absorber. B and BC_3 are used in the shielding of atomic piles and in the control rods used for controling of chain reactions.
- High purity B is used as a semi conductor in the place of Ge and Si
- Boron is essential minor element for the healthy growth of plants

BORAX : The most common meta borate is borax. $Na_2B_4O_7.10H_2O$ *or* $Na_2\left[B_4O_5(OH)_4\right].8H_2O$

Borax available in nature as tincal or kerinite or Razorite $(Na_2B_4O_7.4H_2O)$. From these two minarals decahydrate is obtained by extracting

Structure of Metaborate ion $\left(H_4B_4O_9^{2-}\right)$:



PROPERTIES :

- Borax is sparingly soluble in cold water. Its aqueous solution is alkaline in nature due to hydrolysis

  $Na_2B_4O_7 + 2H_2O \longrightarrow .2NaOH + H_2B_4O_7$

- Borax exists in three crystalline form

  a) Prismatic borax $(Na_2B_4O_7.10H_2O)$

b) Octahedral borax $\left(Na_2B_4O_7.5H_2O\right)$

c) anhydrous sodium tetraborate $\left(Na_2B_4O_7\right)$

BORAX BEAD TEST :

- This test is useful in the identification of basic radicals in qualitative analysis. On heating borax, swells into a white, opaque mass of anhydrons sodium tetra borate. When it is fused, borax glass is obtained B_2O_3. combined with metal oxides give coloured beads

$Na_2B_4O_7.10H_2O \longrightarrow Na_2B_4O_7 \xrightarrow{fused} 2NaBO_2 + B_2O_3$

$B_2O_3 + CoO \longrightarrow Co\left(BO_2\right)_2$ (Cobalt metaborate).

(Blue bead)

S.NO	Basic radical	Metal metaborate formed	Colour of the bead
1	Cu^{2+}	$Cu\left(BO_2\right)_2$	Green
2	Fe^{2+}	$Fe\left(BO_2\right)_2$	Yellowish brown
3	Cr^{3+}	$Cr\left(BO_2\right)_2$	Yellow
4	Mn^{2+}	$Mn\left(BO_2\right)_2$	Violet
5	Ni^{+2}	$Ni\left(BO_2\right)_2$	Violet

USES OF BORAX

- Borax bead test is used in the identification of basic radicals. This test uses borax
- Borax is used as a flux in soldering, in welding and in certain metallurgies
- In making optical glasses Pyrex glass.
- In leather industry for cleaning hides and skin
- As preservative borax is useful

BORIC ACIDS : B_2O_3 in water gives boricacids

Ortho boric acid H_3BO_3 or $B_2O_3.3H_2O$

Meta boric acid HBO_2 or $B_2O_3.H_2O$

Tetra boric acid $H_4B_2O_7$ or $2B_2O_3.H_2O$

Pyro boric acid $H_6B_4O_7$ or $2B_2O_3.3H_2O$

PREPARATION OF BORIC ACID :

- Ortho boric acid is prepared from Colemanite $\left(Ca_2B_6O_{11}\right)$. Finally powdered colemanite is suspended in hot water and SO_2 gas is passed to saturate it. The reaction is

$Ca_2B_6O_{11} + 9H_2O + 2SO_2 \rightarrow 2CaSO_3 + 6H_3BO_3$

- When hot solution of borax is mixed with H_2SO_4 gives boric acid

$N_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$

PROPERTIES

- It is a mono basic acid
- H_3BO_3 loses water on heating

$$H_3BO_3 \xrightarrow{at\,100^0C} HBO_2 + H_2O$$

$$4H_3BO_3 \xrightarrow{160^0C} H_2B_4O_7 + 5H_2O$$

$$2H_3BO_3 \xrightarrow{high\,temp} B_2O_3 + 3H_2O$$

BORON HYDRIDES :

- The ores of Boron are
- The hydrides of boron are called boranes.
- These are electron deficient molecules.
- They can be classified as boranes $\left(B_nH_{n+4}\right)$ and hydroboranes $\left(B_nH_{n+6}\right)$

$\left(B_nH_{n+4}\right)$ type $\left(B_n + H_{n+6}\right)$ type

B_2H_6 Diborane B_4H_{10} Tetra borane

B_5H_9 Penta borane -9 B_5H_{11} Penta borane -11.

B_6H_{10} Hexa borane -10 B_6H_{12} Hexa borane -12 .

$B_{10}H_{14}$ Deca borane-14 $B_{10}H_{16}$ Deca borane -16.

PREPARATION OF B_2H_6 :

- Industrial method : BF_3 on reduction with LiH gives Diborane.

$$2BF_3 + 6LiH \xrightarrow{450K} B_2H_6 + 6LiF$$

- BCl_3 on reduction with $LiAlH_4$ gives B_2H_6 (Lab method)

$$4BCl_3 + 3LiAlH_4 \xrightarrow{dry\,ether} 2B_2H_6 + 3LiCl + 3AlCl_3$$

- A mixture of BCl_3 and H_2 at low pressure when subjected to silent electric discharge gives B_2H_6 (Lab method)

PROPERTIES OF B_2H_6 :

- It is stable in the absence of grease and moisture.
- It reacts with water forming boric acid and H_2

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2\uparrow$$

- It reacts with alkalies with evolution of H_2.

$$B_2H_6 + 2KOH + 2H_2O \rightarrow \underset{potassium\,metaborate}{2KBO_2} + 6H_2\uparrow$$

- It reacts with Cl_2 to give BCl_3 .

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl$$

$$B_2H_6 + Br_2 \rightarrow B_2H_5Br + HBr$$

- It burns in O_2 gas to give B_2O_3

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

- In presence of , diborane reacts with HCl to give chloro diborane

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

- It reacts with CO at 100°C and 20 atm pressure to give borane carbonyls.

  $$B_2H_6 + 2CO \rightarrow 2BH_3CO$$

- It reacts with sodium amalgam to give $B_2H_6Na_2$
- It reacts with ammonia at 120°C to form diammoniate of diborane .
  Which is on strong heating gives borazole and hydrogen

$$B_2H_6 + 2NH_3 \xrightarrow[\Delta]{120^0 C} B_2H_6.2NH_3$$

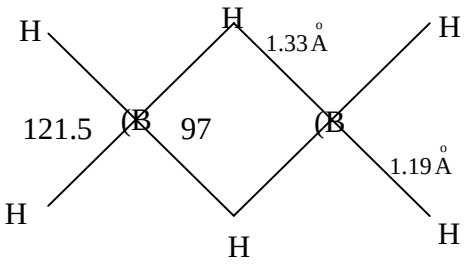
$$B_2H_6.2NH_3 \xrightarrow[\Delta]{200^0 C} \underset{\substack{borazole \\ or\ inorganic\ benzene}}{B_3N_3H_6}$$

At high temperature

$$n\ B_3N_3H_6 \xrightarrow{\Delta / at\ 200^0 C} 3(BN)_n + 3nH_2$$

STRUCTURE OF B_2H_6:

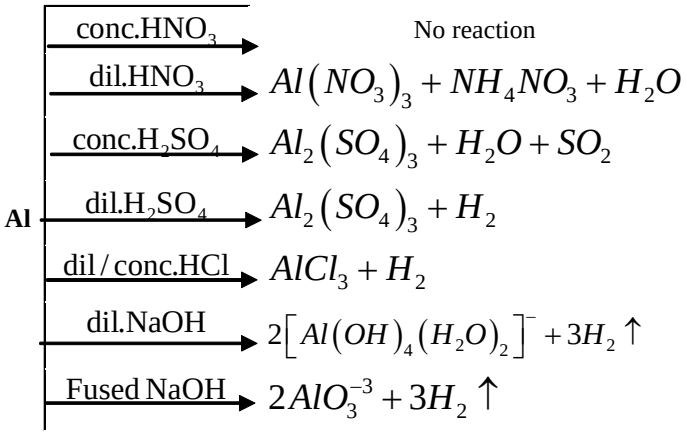
- The hybridisation of Boron in Diborane is sp^3 .
- In B_2H_6 two Boron atoms and four hydrogen atoms are in one plane.
- The four hydrogen atoms which lie in one plane are called terminal hydrogen atoms. The remaining two hydrogen atoms are called bridge hydrogen atoms.
  This is further confirmed by methylation of diborane to give $Me_4B_2H_2$
- One of the bridge hydrogen atom is above the plane of the molecule and the other bridge hydrogen atom is below the plane of the molecule
- The terminal H atoms involve in covalent bonds. Bridge H atoms are involved in three centred two electron bond.
- This is called Banana bond or Hydrogen bridge bond or Tau bond.
- The bridge hydrogen atoms involve three centre two electron bonds.
- Diborane molecule has 4 covalent bonds, 2 de-localised bonds.
- There is no direct bond between 2 Boron atoms.



ALUMINIUM :

- Bauxite is the important mineral
- Bauxite contains impurities such as Fe_2O_3 (red Bauxite) and SiO_2 (white Bauxite)

CHEMICAL PROPERTIES OF AL :



Aluminium metal is used in

- Making electrical cables.
- Making trays and picture frames
- In metallurgy as deoxidiser for removing blow holes.
- Making light and strong alloys. These alloys are used in making parts of air crafts.
- Painting Iron surface to prevent its rusting.
- Thermite welding.
- Al foils are used for wrapping cigarettes, chacolates etc.

ALLOYS OF ALUMINIUM :

S.NO	Alloy	Composition	Uses
1	Magnalium	2-15% Mg 85-98% Al	Balance beams, Lab articles etc.
2	Aluminum Bronze	10-12% Al 90-88% Cu	Utensils, jewellery
3	Duralumin	95% Al 4% Cu 0.5% Mg 0.5% Mn	In making air ships
4	γ – alloy	92.5% Al 2.0% Ni 4.0% Cu 1.5% Mg	In making aeroplane Parts

ALUMS:

- Alums are double sulphates .
- The general formula of an alum is

  $X_2SO_4.\ Y_2\left(SO_4\right)_3.\ 24H_2O$

  X is a mono valent ion like

  $Na^+, K^+, Rb^+, Cs^+, NH_4^+$

  Y is a trivalent ion like $Fe^{3+}, Al^{3+}, Cr^{3+}$
- Potash Alum - $K_2SO_4.\ Al_2\left(SO_4\right)_3.\ 24H_2O$

  ChromeAlum - $K_2SO_4.\ Cr_2\left(SO_4\right)_3.\ 24H_2O$

  FerricAlum - $\left(NH_4\right)_2 SO_4.\ Fe_2\left(SO_4\right)_3.\ 24H_2O$

  SodiumAlum - $Na_2SO_4.\ Al_2\left(SO_4\right)_3.\ 24H_2O$
- The co-ordination number of any cation in the alum is 6. Every cation in any alum is co-ordinated with six water molecules.
- Lithium cannot form the alums because the maximum covalency of Lithium ion is only 4.
- Aqueous solution of any alum is acidic due to the hydrolysis of cation.

PREPARATION OF POTASH ALUM

- By concentrating solution, containing equimolar quantities of potassium sulphate and Aluminium sulphate, to the point of crystallization alum separates out.
- Alunite $\left\{K_2SO_4.Al_2\left(SO_4\right)_3.4Al\left(OH\right)_3\right\}$ is boiled with dilute H_2SO_4 and a calculated amount of potassium sulphate and crystallized to get alum.
- Alum shale or pyrites shale $\left(Al_2O_3.xSiO_2 + FeS_2\right)$ is roasted in air and the mass is digested with dil H_2SO_4. Ferrous sulphate formed in the roasting process is removed by fractional crystallization.

PROPERTIES ALUM :

- It is an ionic compound and so does not exist in the molecular forms in solutions
- It is a crystalline substance, soluable in H_2O. The aqueous solution is acidic in nature due to hydrolysis
- It loses its water of crystallization on heating.

USES OF POTASH ALUM :

- Used in the purification of water
- As a mordant in dyeing industry.
- For tanning leather.
- As a styptic to arrest bleeding.