9. GROUP 13 ELEMENTS (IIIA)

SYNOPSIS:

GENERAL CHARACTERISTICS
- Boron, Aluminium, Gallium, Indium and belong to III<sub>a</sub> group of the Periodic table.
- The general outer electronic configuration of III<sub>a</sub> 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:

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>At No</th>
<th>E.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>B</td>
<td>5</td>
<td>[He]2s(^2)2p(^1)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>13</td>
<td>[Ne]3s(^2)3p(^1)</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga</td>
<td>31</td>
<td>[Ar]3d(^{10})4s(^2)4p(^1)</td>
</tr>
<tr>
<td>Indium</td>
<td>In</td>
<td>49</td>
<td>[Kr]4d(^{10})5s(^2)5p(^1)</td>
</tr>
<tr>
<td>Thallium</td>
<td>Tl</td>
<td>81</td>
<td>[Xe]4f(^{14})5d(^{10})6s(^2)6p(^1)</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>( 3 \times 10^{-4} )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>8.13</td>
</tr>
<tr>
<td>Gallium</td>
<td>( 1.3 \times 10^{-3} )</td>
</tr>
<tr>
<td>Indium</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>Thallium</td>
<td>( 10^{-4} - 10^{-5} )</td>
</tr>
</tbody>
</table>

VARIATION OF PROPERTIES
- Boron is a non metal.
Group 13 Elements (IIIA)

- $\text{AI}$, Ga, In, and are metals.
- Atomic radius increases suddenly from B to $\text{AI}$.
  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 $B > \text{AI} > Tl > In > Ga$
- Boiling points order $B > \text{AI} > In > Ga > Tl$
- Melting point of Gallium is very low because it contains $\text{Ga}_2$ 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 $B > Tl > In > Ga > \text{AI}$.
- The most electropositive element in III$_A$ group is Al.
- The compounds of Al and Ga (Ex: $\text{AlCl}_3$ and $\text{GaCl}_3$) are covalent only in the anhydrous state and Ionic in aqueous solution because their hydration energies, compensate the ionization 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.

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Name of the Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Borax</td>
<td>$\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Kenite (or) Razonite</td>
<td>$\text{Na}_2\text{B}_4\text{O}_7\cdot 4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Boric acid</td>
<td>$\text{H}_3\text{B}_2\text{O}_3$</td>
</tr>
<tr>
<td>2</td>
<td>Colemanite</td>
<td>$\text{Ca}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Corduamous</td>
<td>$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td></td>
<td>Diaspore</td>
<td>$\text{Al}_2\text{O}_3\cdot \text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Bauxite</td>
<td>$\text{Al}_2\text{O}_3\cdot 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Gibbsite</td>
<td>$\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Cryolite</td>
<td>$\text{Na}_2\text{AlF}_6$ (or) $3\text{Na}_2\text{AlF}_5$</td>
</tr>
<tr>
<td></td>
<td>Felspar</td>
<td>$\text{KAlSi}_3\text{O}_8$</td>
</tr>
<tr>
<td>3</td>
<td>Ga, In, Tl occurs as sulphides Ga is found the ores of Zn, Al, and Ge In and Tl occurs along with Zn (Zinc blende) and galena PbS</td>
<td></td>
</tr>
</tbody>
</table>

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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-metallic.
- It always forms covalent compounds.
- Boron shows 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 $\text{B(OH)}_3$ or $\text{H}_3\text{BO}_3$.
- Maximum covalency of boron is 4.
- Boron forms stable covalent hydrides which are known as bornanes.
- Boron never appears as a cation.
- Among halides of boron only $\text{BF}_3$ 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.
  \[ B_2O_3 + 3\text{Mg} \xrightarrow{\text{bright hot}} 2\text{B} + 3\text{MgO} \]
- $B_2O_3$ is obtained from borax.
- Borax is treated with hot conc. HCl gives $H_3\text{BO}_3$. Boric acid ($H_3\text{BO}_3$) on fusion loses water and forms $B_2O_3$.
  \[ \text{Na}_2B_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \xrightarrow{\text{250-275°C}} 2\text{NaCl} + 4\text{H}_3\text{BO}_3 \]
  (Orthoboric acid)
  \[ 4\text{H}_3\text{BO}_3 \xrightarrow{455\text{°C}} \text{H}_2\text{B}_4\text{O}_7 \text{ (tetraboric acid)} \xrightarrow{\text{red heat}} \text{B}_2\text{O}_3 \]
  \[ \text{H}_3\text{BO}_3 \xrightarrow{375\text{°C}} \text{HBO}_2 \text{ (metaboric acid)} \xrightarrow{\text{red heat}} \text{B}_2\text{O}_3 \]
- Pyrolysis of $\text{B}_2\text{I}_6$ (or) thermal decomposition of boranes also gives crystalline Boron.

**PHYSICAL PROPERTIES:**
- Boron exists in two allotropic forms:
  a) Amorphous B
  b) Crystalline B.
- Amorphous B dissolves in molten Al at 1530°C 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 sublimates at ordinary pressure.

**CHEMICAL PROPERTIES:**
♦ **Action with air** (or) **O**₂: Amorphous B, on heating in air to about 700°C, form **B**₂**O**₃ and **B**N

\[ 4B + 3O_2 \rightarrow 2B_2O_3 \]

\[ 2B + N_2 \rightarrow 2BN \]

♦ **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

\[ 4B + 3O_2 \rightarrow 2B_2O_3 \]

\[ 2B + 3S \overset{1200°C}{\rightarrow} B_2S_3 \]

Hardest compound of Boron is Boron carbide (**B**₃**C**)

♦ **Reducing property**: B is a powerful reducing agent for **C**O₂ and **SiO**₂.

\[ 3SiO_2 + 4B \rightarrow 2B_2O_3 + 3Si \]

♦ With Conc. acids B gives boric acid

\[ B + 3HNO_3 \rightarrow H_3BO_3 + 3NO \]

\[ 2B + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3SO_2 \]

♦ When fused with alkalis, B liberates

\[ 2B + 6NaOH \rightarrow 2Na_2BO_3 + 3H_2 \uparrow \]

**USES**:

♦ B is a good neutron absorber. B and **B**₃**C** are used in the shielding of atomic piles and in the control rods used for controlling of chain reactions.

♦ High purity B is used as a semiconductor 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**₂**B**₂**O**₇.**10H**₂**O** or **Na**₂[**B**₂**O**₇ (**OH**)₄].**8H**₂**O**

Borax available in nature as tincal or kerinite or Razorite (**Na**₂**B**₂**O**₇.**4H**₂**O**). From these two minerals decahydrate is obtained by extractio

Structure of Metaborate ion (**H**₂**B**₂**O**₆⁻)

**PROPERTIES**:

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

\[ Na_2B_4O_7 + 2H_2O \rightarrow 2NaOH + H_2B_4O_7 \]

♦ Borax exists in three crystalline form

a) Prismatic borax (**Na**₂**B**₂**O**₇.**10H**₂**O**)
b) Octahedral borax \((\text{Na}_2\text{B}_4\text{O}_7.5\text{H}_2\text{O})\)

c) anhydrous sodium tetraborate \((\text{Na}_2\text{B}_4\text{O}_7)\)

**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 anhydrous sodium tetra borate. When it is fused, borax glass is obtained \(\text{B}_2\text{O}_3\), combined with metal oxides give coloured beads

\[
\text{Na}_2\text{B}_4\text{O}_7.10\text{H}_2\text{O} \xrightarrow{\text{fused}} \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaBO}_2 + 5\text{B}_2\text{O}_3
\]

\[
\text{B}_2\text{O}_3 + \text{CoO} \rightarrow \text{Co(BO}_2)_2\ \text{(Cobalt metaborate).}
\]

(Blue bead)

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Basic radical</th>
<th>Metal metaborate formed</th>
<th>Colour of the bead</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu (^{2+})</td>
<td>Cu(BO(_2))(_2)</td>
<td>Green</td>
</tr>
<tr>
<td>2</td>
<td>Fe (^{2+})</td>
<td>Fe(BO(_2))(_2)</td>
<td>Yellowish brown</td>
</tr>
<tr>
<td>3</td>
<td>Cr (^{3+})</td>
<td>Cr(BO(_2))(_2)</td>
<td>Yellow</td>
</tr>
<tr>
<td>4</td>
<td>Mn (^{2+})</td>
<td>Mn(BO(_2))(_2)</td>
<td>Violet</td>
</tr>
<tr>
<td>5</td>
<td>Ni (^{2+})</td>
<td>Ni(BO(_2))(_2)</td>
<td>Violet</td>
</tr>
</tbody>
</table>

**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:** \(\text{B}_2\text{O}_3\) in water gives boric acids

- Ortho boric acid \(\text{H}_3\text{BO}_3\) or \(\text{B}_2\text{O}_3.3\text{H}_2\text{O}\)
- Meta boric acid \(\text{HBO}_3\) or \(\text{B}_2\text{O}_3.\text{H}_2\text{O}\)
- Tetra boric acid \(\text{H}_4\text{B}_2\text{O}_7\) or \(2\text{B}_2\text{O}_3.\text{H}_2\text{O}\)
- Pyro boric acid \(\text{H}_6\text{B}_2\text{O}_7\) or \(2\text{B}_2\text{O}_3.3\text{H}_2\text{O}\)

**PREPARATION OF BORIC ACID:**

- Ortho boric acid is prepared from Colemanite \((\text{Ca}_2\text{B}_2\text{O}_7)\). Finally powdered colemanite is suspended in hot water and \(\text{SO}_2\) gas is passed to saturate it. The reaction is

\[
\text{Ca}_2\text{B}_2\text{O}_7 + 9\text{H}_2\text{O} + 2\text{SO}_2 \rightarrow 2\text{CaSO}_3 + 6\text{H}_3\text{BO}_3
\]

- When hot solution of borax is mixed with \(\text{H}_2\text{SO}_4\) gives boric acid

\[
\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 4\text{H}_3\text{BO}_3
\]
PROPERTIES
♦ It is a mono basic acid
♦ $H_2BO_3$ loses water on heating

\[ H_2BO_3 \xrightarrow{\text{at 100°C}} HBO_2 + H_2O \]
\[ 4H_3BO_3 \xrightarrow{\text{160°C}} H_2B_2O_7 + 5H_2O \]
\[ 2H_3BO_3 \xrightarrow{\text{high temp}} B_2O_3 + 3H_2O \]

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 ($B_nH_{n+4}$) and hydroboranes ($B_nH_{n+6}$)

- $B_2H_6$ 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)

\[ 4BCl_3 + 3LiAlH_4 \xrightarrow{\text{dry ether}} 2B_2H_6 + 3LiCl + 3AlCl_3 \]

♦ 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 $H_2$

\[ B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2 \]

♦ It reacts with alkalies with evolution of $H_2$.

\[ B_2H_6 + 2KOH + 2H_2O \rightarrow 2KBO_2 \xrightarrow{\text{potassium metaborate}} + 6H_2 \]

♦ It reacts with $Cl_2$ to give $BCl_3$. 

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Group 13 Elements (IIIA)
\[ B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl \]

\[ B_2H_6 + Br_2 \rightarrow B_2H_5Br + HBr \]

- 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
  \[ B_2H_6 + 2NH_3 \xrightarrow{\Delta \text{120°C}} B_2H_6.2NH_3 \]

\[ B_2H_6.2NH_3 \xrightarrow{\Delta \text{200°C}} B_3N_3H_6 \]

At high temperature
\[ n \ B_3N_3H_6 \xrightarrow{\Delta \text{at 200°C}} 3(\text{BN})_n + 3nH_2 \]

**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:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>conc.HNO$_3$</td>
<td>No reaction</td>
</tr>
<tr>
<td>dil.HNO$_3$</td>
<td>$Al(NO_3)_3 + NH_4NO_3 + H_2O$</td>
</tr>
<tr>
<td>conc.H$_2$SO$_4$</td>
<td>$Al_2(SO_4)_3 + H_2O + SO_2$</td>
</tr>
<tr>
<td>dil.H$_2$SO$_4$</td>
<td>$Al_2(SO_4)_3 + H_2$</td>
</tr>
<tr>
<td>dil/ conc.HCl</td>
<td>$AlCl_3 + H_2$</td>
</tr>
<tr>
<td>dil.NaOH</td>
<td>$2[Al(OH)_4(H_2O)_2] + 3H_2$</td>
</tr>
<tr>
<td>Fused NaOH</td>
<td>$2AlO_3^{3-} + 3H_2$</td>
</tr>
</tbody>
</table>

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, chocolates etc.

ALLOYS OF ALUMINIUM:

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Alloy</th>
<th>Composition</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnalium</td>
<td>2-15% Mg, 85-98% Al</td>
<td>Balance beams, Lab articles etc.</td>
</tr>
<tr>
<td>2</td>
<td>Aluminum Bronze</td>
<td>10-12% Al, 90-88% Cu</td>
<td>Utensils, jewellery</td>
</tr>
<tr>
<td>3</td>
<td>Duralumin</td>
<td>95% Al, 4% Cu, 0.5% Mg, 0.5% Mn</td>
<td>In making air ships</td>
</tr>
<tr>
<td>4</td>
<td>$\gamma$-alloy</td>
<td>92.5% Al, 2.0% Ni, 4.0% Cu, 1.5% Mg</td>
<td>In making aeroplane Parts</td>
</tr>
</tbody>
</table>
ALUMS:
♦ Alums are double sulphates.
♦ The general formula of an alum is $X_2SO_4 \cdot Y_2(SO_4)_3 \cdot 24H_2O$
  
  $X$ is a mono valent ion like $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$
  
  $Y$ is a trivalent ion like $\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$

♦ Potash Alum - $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

♦ ChromeAlum - $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

♦ FerricAlum - $(NH_4)_2 SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$

♦ SodiumAlum - $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

♦ 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 $\{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3\}$ is boiled with dilute $H_2SO_4$ and a calculated amount of potassium sulphate and crystallized to get alum.

♦ Alum shale or pyrites shale $(Al_2O_3 \cdot xSiO_2 + FeS_2)$ 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.