

➤ The Carbon Family
➤ Atomic Properties of Carbon Family and Physical Properties of Carbon Family
➤ Chemical Properties
• Anomalous Behavior of Carbon
• Allotropes of Carbon
➤ Diamond, Graphite
➤ Fullerene, Coal Uses of Coal
• Compounds of Carbon
➤ Important Compounds of Carbon
➤ Carbon Monoxide
➤ Carbon Dioxide
➤ Halides of Carbon
➤ Carbides
• Silicon and Its Compounds
➤ Properties of Silicon
➤ Compounds of Silicon
➤ Silicates
➤ Classification of Silicates
➤ Organosilicon Compounds and the Silicones

BORON FAMILY

Boron is a representative non-metal, while aluminum is a metal with numerous chemical resemblances to boron. Additionally, gallium, indium, and thallium are primarily characterized by their metallic properties.

Group IIIA or 13

5 B B o r o n 10.81 ± 0.001
13 Al a l u m i n i u m 26.982 ± 0.001
31 Ga g a l l i u m 69.723 ± 0.001
49 In i n d i u m 114.82 ± 0.01
81 Tl t h a l l i u m 204.38 ± 0.01
113 Nh n i h o n i u m 286

Physical Properties of Boron Family

- Boron exhibits non-metallic properties.
- It is a hard, black solid with multiple allotropic forms.
- Its exceptionally high melting point is a result of its strong crystalline lattice.
- In contrast, the other members are soft metals with low melting points and excellent electrical conductivity.

Gallium, for instance, has a low melting point (303 K), allowing it to remain in a liquid state even during warm weather. Furthermore, its high boiling point (2676 K) makes it a valuable substance for high-temperature measurements.

Ionization Energy

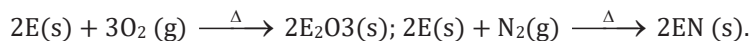
Initially, there is a decrease in ionization energy from boron (B) to aluminum (Al), but this trend reverses when progressing from aluminum to gallium (Ga). This change can be ascribed to the influence of the filling of the first-row transition elements. The intervening d electrons in these elements do not effectively shield the nuclear charge, resulting in the valence electrons in gallium being more securely held, leading to an increase in ionization energy. This same rationale can also explain irregular trends in various other physical properties, such as electropositive character.

In the 13th group elements, the sequence of ionization energy is as follows: B > Tl > Ga > Al > In.

Chemical Properties of Boron Family

Reactivity towards air

- In its crystalline state, boron exhibits low reactivity.
- Aluminum, on the other hand, develops a thin protective oxide layer on its surface, preventing further corrosion.
- Amorphous boron and aluminum metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature, they form nitrides.



- The characteristics of these oxides exhibit variations within the group. Boron trioxide displays acidity and reacts with basic (metallic) oxides to produce metal borates. Aluminum and gallium oxides are amphoteric, while the oxides of indium and thallium demonstrate basic properties.

Reaction with	Boron Family		
O ₂	$4E + 3O_2 \xrightarrow{\Delta} 2E_2O_3$		
	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3 Tl_2O_3	– – – – –	acidic amphoteric amphoteric basic basic
N ₂	$2E + N_2 \xrightarrow{\Delta} 2EN$ $EN + H_2O \xrightarrow{\Delta} E(OH)_3 + NH_3$ $\therefore E = B \text{ or } Al$		
X ₂ (Halogen)	$2E + 3X_2 \longrightarrow 2EX_3; (X=F, Cl, Br, I)$		
	BX_3 AlF_3 GaF_3 InF_3 TlI_3	– – – –	covalent (BI_3 cannot be formed directly) Ionic Ionic Ionic exist as $Tl^+I_3^-$ & TlI also form
H ₂ O	B – does not react with water <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">A</div> <div style="margin-right: 10px;">{</div> <div style="margin-right: 10px;"> $\xrightarrow[+H_2]{25^\circ C}$ $\xrightarrow[+H_2]{>480^\circ C}$ </div> <div> $Al(OH)_3$ Al_2O_3 </div> </div> <div style="margin-top: 10px;"> Ga In </div> <div style="margin-left: 40px;"> Not attacked by cold & hot water unless oxygen is present. </div> Tl – oxidises in moist air & decomposes steam at red heat.		

Acids	$\text{B} \begin{cases} \xrightarrow[\text{(Hot \& Conc.)}]{+\text{H}_2\text{SO}_4} \text{H}_3\text{BO}_3 + \text{SO}_2 \\ \xrightarrow[\text{(Hot \& Conc.)}]{+\text{HNO}_3} \text{H}_3\text{BO}_3 + \text{NO}_2 \end{cases}$ <p>(Boron reacts with only oxidising acids)</p> $\text{Al} \begin{cases} \xrightarrow{+\text{HCl}} \text{AlCl}_3 + \text{H}_2 \\ \xrightarrow[\text{(Conc.)}]{+\text{HNO}_3} \text{Do not react because it forms passive oxide layer.} \end{cases}$ <p>Ga, In, Tl can also react with dilute mineral acids.</p>
NaOH	$2\text{B} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaBO}_2 + 3\text{H}_2$ $2\text{B} + 6\text{NaOH} \xrightarrow{\text{fused}} 2\text{Na}_3\text{BO}_3 + 3\text{H}_2$ $\text{Al} \begin{cases} \xrightarrow[\text{NaOH}]{\text{NaOH} + \text{H}_2\text{O}} \text{NaAlO}_2 \cdot 2\text{H}_2\text{O} + \text{H}_2 \\ \text{or} \\ \text{Na}^+[\text{Al}(\text{OH})_4]^- \\ \xrightarrow{\text{NaOH}} \text{Na}_3\text{AlO}_3 + \text{H}_2 \end{cases}$ <p>(Al & Ga readily dissolves in alkalis').</p> <p>In & Tl do not react with alkali.</p>
Metal	$3\text{Mg} + 2\text{B} \rightarrow \text{Mg}_3\text{B}_2$ $3\text{Ca} + 2\text{B} \rightarrow \text{Ca}_3\text{B}_2$
Reducing Property	$\text{B} \begin{cases} \xrightarrow[\Delta]{\text{SiO}_2} \text{B}_2\text{O}_3 + \text{Si} \\ \xrightarrow[\Delta]{\text{CO}_2} \text{B}_2\text{O}_3 + \text{C} \end{cases}$ $\text{Al} \begin{cases} \xrightarrow[\Delta]{\text{MnO}_2} \text{Al}_2\text{O}_3 + \text{Mn} \\ \xrightarrow[\Delta]{\text{Cr}_2\text{O}_3} \text{Al}_2\text{O}_3 + \text{Cr} \end{cases}$

Hydrides

Hydrogen does not directly react with these elements. Unlike boron, which does not produce simple monomeric species like BH_3 , it is known to form numerous polymeric compounds. These compounds fall into two categories with the general formulas B_nH_{n+4} and B_nH_{n+6} , with the latter being less stable. The covalent nature of boron hydrides classifies them as boranes, drawing an analogy with alkanes. Aluminium, on the other hand, produces only one high molecular weight polymeric hydride, denoted as $(\text{AlH}_3)_x$, commonly referred to as Alane. Alane's structure features aluminum atoms octahedrally

surrounded by six hydrogen atoms, forming a network of AlH_2Al bridges. Gallium also forms hydrides, specifically GaH_3 , named Gal Lane, but these are characterized by instability and volatility, resembling a volatile oil.

Indium hydride manifests as a polymeric solid. In contrast, thallium hydrides exhibit extreme instability.

Halides

Members of this group exhibit reactivity with halogens, resulting in the formation of trihalides (MX_3), with the exception of TlI_3 , which is inherently unstable. However, thallium (I) iodide proves to be a stable exception. The small boron ion, characterized by a high charge density, imparts a covalent character to its halides.

The fluorides of Al, Ga, In, and Tl display an ionic nature and possess elevated melting points. Conversely, the remaining halides are predominantly covalent in their anhydrous forms. Anhydrous AlCl_3 , for instance, exhibits covalent properties, but upon exposure to water, it undergoes hydrolysis to yield the Al^{3+} ion. This transformation from a covalent compound to an aqueous solution of ions primarily stems from the high hydration enthalpy of aluminum.

BCl_3 , upon hydrolysis, does not yield the B^{3+} ion due to the substantial ionization energy of B^{3+} . Boron halides utilize the vacant p-orbital to form tetrahedral complexes of the type BX_3L , where L represents a neutral or anionic donor. Conversely, the corresponding halides of aluminum adopt an alternate approach, forming dimers. Consequently, aluminum chlorides, bromides, and indium iodide exist as dimers both in the vapor state and in non-polar solvents. The halogens within these structures are arranged tetrahedrally, with bridged structures being characteristic of electron-deficient compounds. Gallium and indium also give rise to dihalides, with gallium dihalides more accurately represented as $\text{Ga}^+ [\text{GaCl}_4]^-$, illustrating gallium's +1 and +3 oxidation states. In the gaseous state, elements of group 13 form monohalides (MX), which are inherently unstable and exhibit a covalent nature. This covalent character diminishes down the group, culminating in thallium halides displaying an ionic nature.

