## IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

The tri-chlorides, bromides, and iodides of these elements are covalent compounds and undergo hydrolysis when placed in water. In an aqueous environment, species such as tetrahedral $[M(OH)4]^-$ and octahedral $[M(H_2O)6]^{3+}$ exist, with the exception of boron. This deviation is due to the absence of d orbitals, limiting boron's maximum covalence to 4. In contrast, elements like aluminum and others possess d orbitals, allowing for the potential of covalence’s exceeding 4.

### Occurrence

| Element | Abundance | Source |
|---|---|---|
| B (Boron) | 9 ppm (Rare element) | ➢ Borax: $Na_2[B_4O_5(OH)_4].8H_2O$<br>➢ Colemanite: $Ca_2B_6O_{11}.5H_2O$<br>➢ Kernite: $Na_2[B_4O_5(OH)_4].2H_2O$<br>➢ Boric acid: $H_3BO_3$ |
| Al (Aluminum) | 83000 ppm (Most abundant metal, 3rd most Abundant element) | ➢ Bauxite: $Al_2O_3.H_2O–Al_2O_3.3H_2O$<br>➢ Aluminosilicate rocks (feldspars, mica)<br>➢ Cryolite: $Na_3AlF_6$ |
| Ga (Gallium) | 19 ppm | ➢ Ores of Al, Zn, Ge |
| In (Indium) | 0.24 ppm | ➢ ZnS & PbS ores |
| Tl (Thallium) | 0.5 ppm | ➢ ZnS & PbS ores |

### Allotropy

| Elements | Allotropes |
|---|---|
| B | 5 crystalline forms: β-rhombohedral |
| | 2 amorphous forms |
| Al | No allotrope |
| Ga | No allotrope |
| In | No allotrope |
| Tl | α-Thallium |
| | β-Thallium |

### Atomic & Physical Properties

Boron is characterized as a non-metal. It presents itself as a solid with exceptional hardness and a black color. Boron exhibits multiple allotropic forms. Its remarkably high melting point is attributed to its strong crystalline lattice. In contrast, the remaining members of the group are soft metals with low melting points and high electrical conductivity. Gallium, for instance, has a low melting point (303 K) to the extent that it can be in a liquid state during the summer. Its high boiling point (2676 K) renders it useful for measuring elevated temperatures. Aluminum displays excellent heat and electricity conductivity and possesses malleable and ductile properties. As we move down the group from boron to thallium, the density of these elements increases.

## Boron family

1. Borax is represented chemically as $Na_2B_4O_7 \cdot 10H_2O$ or alternatively as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$.
2. Colemanite has the chemical formula $Ca_2B_6O_{11} \cdot 5H_2O$.
3. Boric acid is denoted by the chemical formula $H_3BO_3$.

| Property | | B | Al | Ga | In | Tl |
|---|---|---|---|---|---|---|
| Character | | Metalloid | Metallic | Metallic | Metallic | Metallic |
| Atomic Number | | 5 | 13 | 31 | 49 | 81 |
| Atomic Mass/g $mol^{-1}$ | | 10.81 | 26.98 | 69.72 | 114.82 | 204.38 |
| Electronic configuration<br>General electronic configuration = $(ns^2\,np^1)$ | | [He] $2s^2$ $2p^1$ | [Ne] $3s^2\,3p^1$ | [Ar] $3d^{10}$ $4s^24p^1$ | [Kr] $4d^{10}$ $5s^2\,5p^1$ | [Xe] $4f^{14}$ $5d^{10}$ $6s^26p^1$ |
| Covalent Radius / pm<br>(B < Ga < Al < In < Tl) | | 85 | 143 | 135 | 167 | 170 |
| | | In Ga, poor shielding of 10 d-electrons | | | | |
| Ionic Radius $X^-$ / pm<br>(B < Al < Ga < In < Tl) | | 27 | 53.5 | 62 | 80 | 88.5 |
| Ionization enthalpy<br>(kJ $mol^{-1}$)<br>(B > Al < Ga > In < Tl) | $\Delta_iH_1$ I | 801 | 577 | 579 | 558 | 589 |
| | $\Delta_iH_2$ II | 2427 | 1816 | 1979 | 1820 | 1971 |
| | $\Delta_iH_3$ III | 3659 | 2744 | 2962 | 2704 | 2877 |
| | | Poor shielding of d-orbital and f-orbital in Ga & Tl respectively | | | | |
| Electronegativity<br>(B > Al < Ga < In < Tl) | | 2.0 | 1.5 | 1.6 | 1.7 | 1.8 |
| | | Marginal increase after Al | | | | |
| Melting point / K | | 2453 | 933 | 303 | 430 | 576 |
| Boiling point / K<br>(B > Al > Ga > In > Tl) | | 3923 | 2740 | 2676 | 2353 | 1730 |
| Density/[g $cm^{-3}$ ( at 293 K)<br>(B < Al < Ga < In < Tl) | | 2.35 | 2.70 | 5.90 | 7.31 | 11.85 |
| Oxidation State | | +3 | +3 | +3, +1 | +3, +1 | +3, +1 |
| | | +1 oxidation state arises due to inert pair effect. | | | | |
| | | Stability of Oxidation state: +1: Ga < In < Tl<br>+3: Al > Ga > In > Tl | | | | |

## Diagonal Relationship Between Boron and Silicon

1. Neither of these elements is naturally found in a free state; instead, they are encountered as oxo compounds, such as borates and silicates.
2. Both elements share similar physical properties, existing in both amorphous and crystalline forms.
3. The stability of both B–O and Si–O bonds is comparable.
4. Both elements have the capacity to form hydrides from their magnesium salts. This is evident in reactions such as:

$$Mg_3B_2 + 6\ HCl \rightarrow 3\ MgCl_2 + B_2H_6$$
$$Mg_2Si + 4\ HCl \rightarrow 2\ MgCl_2 + SiH_4$$

5. Boron (III) oxide and silicon dioxide exhibit solid states with macromolecular structures, dissolving exclusively in alkaline solutions. This phenomenon is exemplified by reactions like:

$$B_2O_3 + 2\ NaOH \rightarrow 2\ NaBO_2 + H_2O$$
$$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O$$

6. The acids of both elements can generate volatile esters when heated with alcohol in the presence of concentrated $H_2SO_4$. This is demonstrated through reactions such as:

$$B(OH)_3 + 3\ ROH \rightarrow B(OR)_3 + 3H_2O$$
$$Si(OH)_4 + 4\ ROH \rightarrow Si(OR)_4 + 4\ H_2O$$