

6.2: Trends for the Group 13 Compounds

Boron is a non-metal with metalloidal tendencies. The higher ionization energies for boron than for its other Group homologs are far more than would be compensated by lattice energies, and thus, the B^{3+} ion plays no part in the chemistry of boron, and its chemistry is dominated by the formation of covalent compounds. In contrast, the elements aluminum through thallium each has a low electronegativity and the chemistry of their compounds reflects this characteristic. Each of the Group 13 metals forms both covalent compounds and ionic coordination complexes.

All of the Group 13 (IIIA) elements have a valence shell electron configuration of ns^2np^1 . As a consequence all of the Group 13 elements form compounds in which they adopt a +3 oxidation state. While the lighter elements do form compounds with lower oxidation state, they are not the norm; however, the +1 oxidation state is more prevalent for the heavier elements in particular thallium. The rationale for this is described as the *inert pair effect*. The inert pair effect is usually explained by the energy of the ns orbital is lower making it harder to ionize and stabilizing a ns^2np^0 valence shell. However, as may be seen from Table 6.2.1 the sum of the second and third ionization enthalpies is lower for indium (4501 kJ/mol), than for gallium (4916 kJ/mol), but with thallium intermediate (4820 kJ/mol). The true source of the inert pair effect is that the lower bond strengths observed for the heavier elements (due to more diffuse orbitals and therefore less efficient overlap) cannot compensate for the energy needed to promote the ns^2 electrons. For example, the bond energies for gallium, indium, and thallium in MCl_3 are 242, 206, and 153 kJ/mol, respectively. It has also been suggested that relativistic effects make a contribution to the inert pair effect.

Table 6.2.1: Summary of first three ionization enthalpies for the Group 13 metals.

Ionization enthalpy (kJ/mol)	Al	Ga	In	Tl
1	576.4	578.3	558.1	589.0
2	1814.1	1969.3	1811.2	1958.7
3	2741.4	2950.0	2689.3	2868.8

In summary, it may be stated that while the chemistry of gallium, indium and thallium is very similar, that of aluminum is slightly different, while boron's chemistry is very different from the rest of the Group.

A second effect is noticed in the transition from aluminum, to gallium, to indium. Based upon their position in the Group it would be expected that the ionic radius and associated lattice parameters should follow the trend:



However, as may be seen from Table 6.2.2 the values for gallium are either the same as, or smaller, than that of aluminum. In a similar manner, the covalent radius and covalent bond lengths as determined by X-ray crystallography for a range of compounds (Table 6.2.3).

Table 6.2.2: Lattice parameter (a) for zinc blende forms of the Group 13 phosphides and arsenides. Data from *Semiconductors: Group IV Elements and III-V Compounds*, Ed. O. Madelung, Springer-Verlag, Berlin (1991).

Element	Phosphide lattice parameter (Å)	Arsenide lattice parameter (Å)
Al	5.4635	5.6600
Ga	5.4505	5.6532
In	5.8687	6.0583

Table 6.2.3: Comparative crystallographically determined bond lengths.

Element	M-C (Å)	M-N (Å)	M-O (Å)	M-Cl (Å)
Al	1.96 – 2.02	2.03 – 2.19	1.74 – 1.93	2.09 – 2.11
Ga	1.97 – 2.01	1.95 – 2.12	1.89 – 1.94	2.12 – 2.23
In	2.14 – 2.17	2.23 – 2.31	2.19 – 2.20	2.39 – 2.47

Gallium is significantly smaller than expected from its position within the Group 13 elements (Table 6.2.4). The rationale for this may be attributed to an analogous effect as seen in the *lanthanide contraction* observed for the lanthanides and the 3rd row of transition elements. In multi-electron atoms, the decrease in radius brought about by an increase in nuclear charge is partially offset by increasing electrostatic repulsion among electrons. In particular, a “shielding effect” results when electrons are added in outer shells, electrons already present shield the outer electrons from nuclear charge, making them experience a lower effective charge on the nucleus. The shielding effect exerted by the inner electrons decreases in the order $s > p > d > f$. As a sub-shell is filled in a period the atomic radius decreases. This effect is particularly pronounced in the case of lanthanides, as the $4f$ sub-shell is not very effective at shielding the outer shell ($n = 5$ and $n = 6$) electrons. However, a similar, but smaller effect should be observed with the post-transition metal elements, i.e., gallium. This is indeed observed (Table 6.2.4).

Table 6.2.4: Comparison of the covalent and ionic radii of Group 13 elements.

Element	Covalent radius (Å)	Ionic radius (Å)
Aluminum	1.21	0.53
Gallium	1.22	0.62
Indium	1.42	0.80
Iron (low spin)	1.32	0.55
Iron (high spin)	1.52	0.64

The anomalous size of gallium has two positive effects.

1. The similarity in size of aluminum and gallium means that their Group 15 derivatives have near identical lattice parameters (Table 6.2.3). This allows for both epitaxial growth of one material on the other, and also the formation of ternary mixtures (i.e., $\text{Al}_x\text{Ga}_{1-x}\text{As}$) with matched lattice parameters. The ability to grow heterojunction structures of Group 13-15 compounds (III-V) is the basis for the fabrication of a wide range of important optoelectronic devices, including: LEDs and laser diodes.
2. The similarity in size of gallium(III) to iron(III) (Table 6.2.4) means that gallium can substitute iron in a range of coordination compounds without alteration of the structure. Because of a similar size and charge as Fe^{3+} , Ga^{3+} is widely used as a non-redox-active Fe^{3+} substitute for studying metal complexation in proteins and bacterial populations.

Bibliography

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