3.3: The Anomalous Chemistry of Lithium

While lithium shows many properties that are clearly consistent with its position in Group 1, it also has key differences to the other alkali metals. In fact, in many ways it is more similar to its diagonal neighbor magnesium (Mg) than the other Group 1 metals - a phenomenon known as **the diagonal effect**.

Charge/radius

The ionic radius for the +1 cation of lithium is very small in comparison with its next highest homolog, sodium (Table 3.3.3.14). This results in a correspondingly high value for the charge density (z/r). As may be seen from Table 3.3.1 the charge density for lithium is significantly higher than that of its Group 1 relations.

Table 3.3.1: Comparison of charge densities for lithium, sodium, potassium, and magnesium.

Element	z	r (Å)	z/r ($Å^{-1}$)
Li	+1	0.68	1.47
Na	+1	0.97	1.03
K	+1	1.33	0.75
Mg	+2	0.66	3.03

As a result of the high charge density, the Li^+ ion is a highly polarizing ion. One of the main consequences of this is that lithium tends to form polar covalent bonds rather than ionic interactions. For example, alkyl lithium compounds (RLi) contain covalent Li-C bonds in a similar manner to the Mg-C bonds in Grignards (RMgX, where X = Cl, Br)

Lattice energy

Lithium compounds have high lattice energies as compared to the other Group 1 metals (Table 3.3.2). As a consequence lithium compounds would be less soluble than the highly soluble sodium compounds. In some cases (Li_2O, Li_3N) they react with water.

Table 3.3.2: Comparison of lattice energies for compounds of lithium, sodium, potassium, and magnesium.

Compound	Lattice energy (kJ/mol)
LiF	-1046
NaF	-923
KF	-821
MgF_2	-2957

Coordination number

The small size of lithium results in a lower coordination number (4) for compounds and complexes than observed for the other Group 1 metals. However, lithium and magnesium complexes and organometallic compounds both have most commonly four-coordinate metal centers (in the absence of large steric constraints).

Chemical reactivity

A review of some of the reactions of lithium, magnesium and the other Group 1 metals shows the anomalous behavior of lithium and its similarity to magnesium. Both lithium and magnesium reacts with carbon or nitrogen to form the corresponding carbide and nitride. Whereas sodium and the other Group 1 metals show no reaction under ambient conditions. The combustion of either lithium or magnesium in air results in the formation of the oxides, Li_2O and MgO, respectively. In contrast, sodium forms the peroxide, Na_2O_2.

It is not only in the reactivity of the elements that this relationship between lithium and its diagonal neighbor exists. Many of the compounds of lithium have a similar reactivity to those of magnesium rather than sodium. For example, the carbonates of lithium

and magnesium decompose under thermolysis to yield the oxides, (3.14) and (3.15), in contrast, sodium carbonate (Na_2CO_3) is stable to thermolysis.

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \tag{3.3.1}$$

$$MgCO_3 \rightarrow MgO + CO_2 \tag{3.3.2}$$