

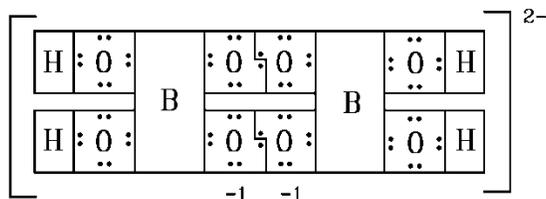
## Chapter 13

### THE GROUP 13 ELEMENTS

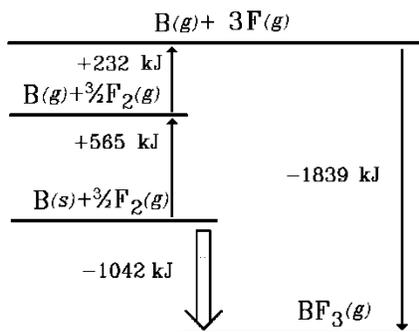
#### Exercises

- 13.1 (a)  $3 \text{K}(l) + \text{AlCl}_3(s) \rightarrow \text{Al}(s) + 3 \text{KCl}(s)$   
 (b)  $\text{B}_2\text{O}_3(s) + 2 \text{NH}_3(g) \rightarrow 2 \text{BN}(s) + 3 \text{H}_2\text{O}(g)$   
 (c)  $2 \text{Al}(s) + 2 \text{OH}^-(aq) + 6 \text{H}_2\text{O}(l) \rightarrow 2 [\text{Al}(\text{OH})_4]^{-}(aq) + 3 \text{H}_2(g)$   
 (d)  $2 \text{B}_4\text{H}_{10}(g) + 11 \text{O}_2(g) \rightarrow 4 \text{B}_2\text{O}_3(s) + 10 \text{H}_2\text{O}(g)$

- 13.3 The bridging oxygen atoms have an oxidation number of  $-1$ :



- 13.5  $\text{B}_2\text{H}_7^-$  corresponds to the generic formula  $[\text{B}_n\text{H}_{n+5}]^-$ . Thus it is the simplest *arachno*-cluster.
- 13.7 See the energy cycle diagram. The major factors in the very large enthalpy of formation are the weak fluorine-fluorine bond, the weakest of the halogen bonds; and the exceedingly strong boron-fluorine bond (the latter can be explained as either a result of partial ionic character of the very polar B–F bond or some degree of  $\pi$ -orbital formation involving a full  $2p$  orbital of the fluorine and an empty  $2p$  orbital of the boron).



- 13.9 In the hexahydrate ion, the  $\text{Al}^{3+}$  is surrounded by the partially negative oxygen atoms of the six water molecules, with the partially positive hydrogens of the water molecules pointing away from the ion. In effect, then, the charge is delocalized over the whole hydrated ion rather than being concentrated in the small  $\text{Al}^{3+}$  “core.”
- 13.11 The hydrated aluminum ion acts as a Bronsted-Lowry acid in the following way:  
$$[\text{Al}(\text{OH}_2)_6]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + [\text{Al}(\text{OH}_2)_5(\text{OH})]^{2+}(\text{aq})$$
- 13.13 The potential environmental hazards are “red mud”—the basic residue from the bauxite purification; hydrogen fluoride gas from hydrolysis of cryolite; the carbon oxides that are produced at the anode; and fluorocarbon compounds produced by reaction of fluorine with the carbon anode.
- 13.15 Aluminum fluoride is a typical ionic compound with a high melting point. Both aluminum bromide and aluminum iodide are covalently bonded dimers,  $\text{Al}_2\text{Br}_6$  and  $\text{Al}_2\text{I}_6$ . Aluminum chloride is a borderline case: in the solid, it has an ionic structure that can alternatively be considered as network covalent, while in the liquid phase, it consists of covalently bonded dimers,  $\text{Al}_2\text{Cl}_6$ .
- 13.17 A spinel has the formula  $\text{AB}_2\text{X}_4$ , where A is a dipositive metal ion, B is a tripositive metal ion, and X is a dinegative ion. The negative ion forms a cubic close-packed arrangement, and in the normal spinel, the A cations occupy tetrahedral sites and the B cations octahedral sites. In the reverse spinel, the A cations occupy octahedral sites while half of the B cations occupy the tetrahedral sites, the other half octahedral sites.
- 13.19 Gallium(III) fluoride must consist of an ionic lattice of gallium(3+) and chloride(1-) ions while gallium(III) chloride must contain discrete  $\text{GaCl}_3$  molecules.
- 13.21 Aluminum ion forms the highly insoluble aluminum hydroxide in neutral conditions. However, in acid conditions, such as lakes acidified by acid

rain, the soluble  $\text{Al}(\text{OH}_2)_6^{3+}$  is produced. The aluminum ion is very toxic to fish.

### Beyond the Basics

13.23 The metallic radius is a measure of the atomic size when packed in a metal crystal lattice. It will not be much smaller than the van der Waals (nonbonding) radius. The covalent radius will be smaller because there is orbital overlap with the atom to which it is covalently bonded. The ionic radius is by far the smallest because all the valence electrons have been lost and the measure is simply of the core of the ion.

13.25  $\text{Cl}_3\text{Al}[\text{O}(\text{C}_2\text{H}_5)_2]$ , where a lone pair on the oxygen of the ether occupies the fourth bonding site around the aluminum ion.

13.27 As we might expect from the diagonal relationship (Chapter 9), the beryllium ion will resemble the aluminum ion. Hence:



13.29 Let number of ions of magnesium =  $x$ , then:

$$1 \times (\text{K}^+) + x \times (\text{Mg}^{2+}) + 1 \times (\text{Al}^{3+}) + 3 \times (\text{Si}^{4+}) + 10 \times (\text{O}^{2-}) + 2 \times (\text{OH}^-) = 0$$

$$1(+1) + x(+2) + 1(+3) + 3(+4) + 10(-2) + 2(-1) = 0$$

$$x = +3.$$

13.31 Setting up the disproportionation reaction:



$$\Delta H = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$= [1(-525) + 2(0)] - [1(+38)] = -563 \text{ kJ}\cdot\text{mol}^{-1}$$

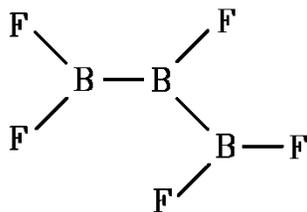
Because there are equal moles (in the same phase) on each side of the equation, the free energy for the disproportionation should be equally high. Thus disproportionation should occur.



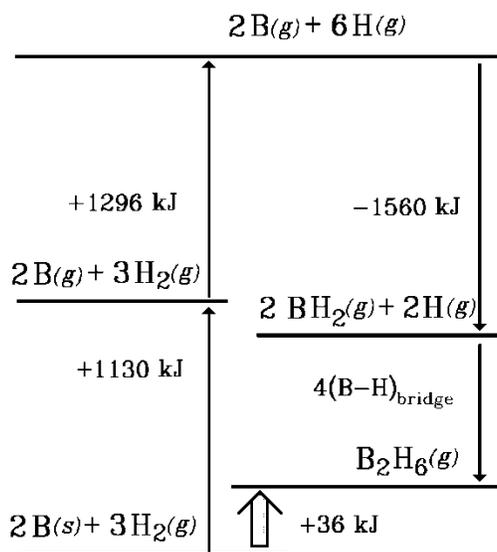
Addition of acid (hydronium ion) will shift the equilibrium to the left.

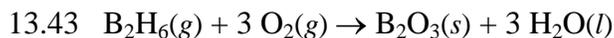
13.37 Aluminum, lacking any “inner”  $d$  electrons, behaves more like a Group 3 element than a Group 13 element. Thus its hydride is more likely to resemble that of scandium. The hydride of gallium follows from that of boron in being a small-molecule covalent dimer. [in fact, the scandium hydrides are ionic, thus aluminum being network covalent would fit well above it]

13.39



13.41 We can calculate the B–H bridging bond energy by means of an energy diagram. The bond formation can be divided into two steps: the formation of four B–H terminal bonds and the formation of four B–H bridging bonds (see below). When we do this, a value of  $208 \text{ kJ}\cdot\text{mol}^{-1}$  per mole of B–H bridging bonds is obtained almost exactly half the value of the  $389 \text{ kJ}\cdot\text{mol}^{-1}$  of a normal B–H bond. This fits well with the concept of a single bonding pair shared by the two bonds.





$$\Delta H_{\text{comb}}(\text{C}_2\text{H}_6) = \Delta H_{\text{f}}(\text{B}_2\text{O}_3) + 3 \times \Delta H_{\text{f}}(\text{H}_2\text{O}) - \Delta H_{\text{f}}(\text{B}_2\text{H}_6)$$

$$[-2165] = \Delta H_{\text{f}}(\text{B}_2\text{O}_3) + 3(-286) - (+36) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{\text{f}}(\text{B}_2\text{O}_3) = -1271 \text{ kJ}\cdot\text{mol}^{-1}$$

- 13.45 For sodium chloride packing, the radius ratio  $r_+/r_-$  must be between 0.414 and 0.732.

From the icosahedral structure of  $\text{B}_{12}$  (Figure 13.1), the radius of the boron cluster would seem to be about the sum of two atoms, 176 pm. If we assume the zirconium(IV) ion, this would give a radius ratio of about 0.41, essentially what could be expected to form an NaCl lattice. Using the atomic radius of zirconium would give a ratio of sizes of close to unity: not what one would expect for an NaCl packing pattern. The structure must be  $[\text{Zr}^{4+}][\text{B}_{12}^{4-}]$ .

