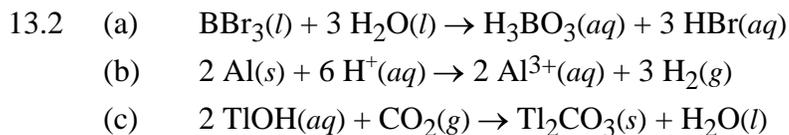


Chapter 13

THE GROUP 13 ELEMENTS

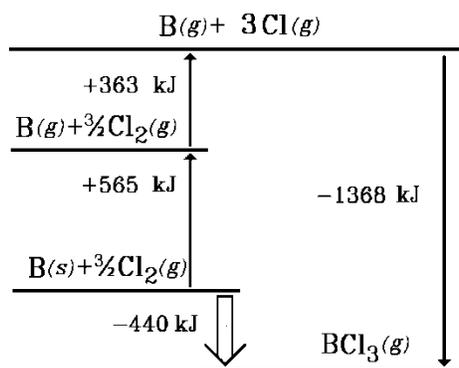
Exercises



13.4 B_{12}C_3 because boron commonly forms stable structures containing the B_{12} icosahedra. In this case, the carbon atoms link neighboring B_{12} units.

13.6 $\text{B}_{12}\text{H}_{12}^{2-}$ follows the generic formula $[\text{B}_n\text{H}_n]^{2-}$, thus it is a *closo*-cluster.

13.8 See the energy cycle in the diagram. The chlorine-chlorine bond is stronger than the fluorine-fluorine bond; hence a greater energy input is needed. The boron-chlorine bond, however, is weaker than the boron-fluorine bond; hence less energy is released during bond formation (one can argue either that there would be a lesser ionic contribution because the electronegativities are not as different as in the B–F bond, or that there would not be a significant $2p$ - $3p$ orbital overlap and so there would be no π -bond formation).

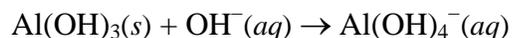
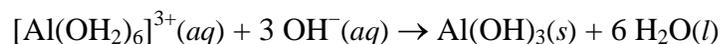
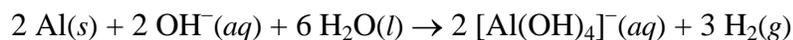
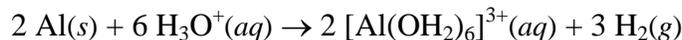
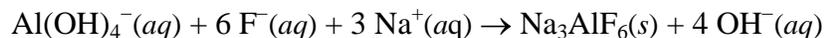
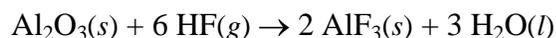
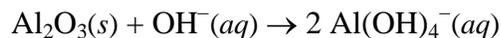
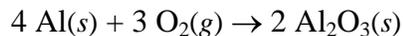
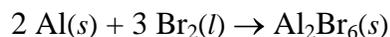
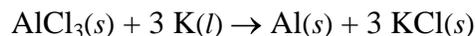
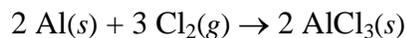


13.10 The surface layer of aluminum reacts to give aluminum oxide. The oxide ions fit into the lattice sites formerly occupied by the aluminum atoms, because they are about the same size. The aluminum ions are so small that

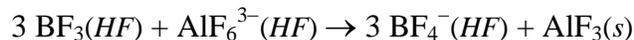
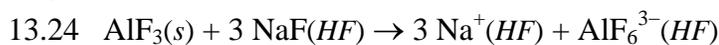
they fit into interstices in the lattice. The aluminum oxide layer, because it has not disturbed the aluminum crystal structure, forms an impervious layer preventing attack of the metal beneath.

- 13.12 Aluminum is an amphoteric metal, that is, it is a weak—"borderline"—metal.
- 13.14 The smelting process is highly energy intensive, so being near cheap electric power (such as from hydroelectric sources) is more important than being near the mining or consuming locations.
- 13.16 Alum, $K^+[Al(OH_2)_6]^{3+}(SO_4^{2-})_2 \cdot 6H_2O$, is an air-stable, inexpensive, highly water-soluble aluminum salt. Other aluminum salts are hygroscopic or insoluble.
- 13.18 Thallium(I) has a low charge density and thus behaves as a typical ionic species (like an alkali metal ion). Thallium(III) is a smaller, high charge ion; thus its high charge density favors covalent behavior.
- 13.20 Boron and silicon both form solid acid oxides, B_2O_3 and SiO_2 ; they both form weak acids, boric acid and silicic acid; they both form polymeric anions; and they both form a range of flammable, gaseous hydrides.
- 13.22 Boron:
- $$BF_3(g) + NH_3(g) \rightarrow F_3B:NH_3(s)$$
- $$2 BF_3(g) + 6 NaH(s) \rightarrow B_2H_6(g) + 6 NaF(g)$$
- $$B_2H_6(g) + 2 NaH(s) \rightarrow 2 NaBH_4(s)$$
- $$B_2H_6(g) + 3 O_2(g) \rightarrow B_2O_3(s) + 3 H_2O(l)$$
- $$B_2H_6(g) + 6 H_2O(l) \rightarrow 2 H_3BO_3(aq) + 3 H_2(g)$$
- $$BCl_3(l) + 3 H_2O(l) \rightarrow H_3BO_3(aq) + 3 HCl(aq)$$
- $$B_2O_3(s) + 3 Mg(l) \rightarrow 2 B(s) + 3 MgO(s)$$
- $$2 BCl_3(l) + 3 H_2(g) \rightarrow 2 B(s) + 6 HCl(g)$$
- $$2 B_2O_3(s) + 7 C(s) \rightarrow B_4C(s) + 6 CO(g)$$
- $$B_4C(s) + 2 TiO_2(s) + 3 C(s) \rightarrow 2 TiB_2(s) + 4 CO(g)$$

Aluminum:

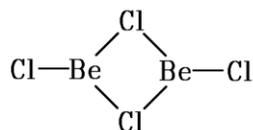


Beyond the Basics



The first reaction is a Lewis acid-base process with the aluminum fluoride as the acid and the fluoride ion as the base. The second reaction can be interpreted in hard-soft acid-base concepts, the hard-base fluoride ion preferring the hard-acid boron trifluoride.

- 13.26 The dimer will be analogous to that of B_2H_6 but with only one terminal atom on each end:



$$13.28 \quad \text{Mol of } 2+ \text{ ions} = (2.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1})(1.0 \times 10^6 \text{ L}) = 2.0 \times 10^3 \text{ mol}$$

$$\text{Molar mass, zeolite} = 2192 \text{ g}\cdot\text{mol}^{-1}$$

$$\text{Thus mass} = (2.0 \times 10^3 \text{ mol})(2192 \text{ g}\cdot\text{mol}^{-1}) = 4.3 \times 10^6 \text{ g}$$

But each zeolite unit can remove 6 dipositive ions (replacing the 12 sodium ions)

$$\text{The mass needed} = (4.3 \times 10^6 \text{ g})/6 = 7.3 \times 10^5 \text{ g} = 730 \text{ kg}$$

13.30 We can calculate the pH of the $\text{Al}^{3+} \rightarrow \text{Al}(\text{OH})_3$ line from the K_{sp} .

$$K_{sp}(\text{Al}(\text{OH})_3) = [\text{Al}^{3+}][\text{OH}^-]_3 = 1 \times 10^{-33}$$

Because $[\text{Al}^{3+}] = 1.0 \text{ mol}\cdot\text{L}^{-1}$ under standard conditions, $[\text{OH}^-] = 1 \times 10^{-11}$, $\text{pOH} = 11.0$, $\text{pH} = 3.0$ (note that there are considerable variations in K_{sp} values for aluminum hydroxide).

For the aluminate ion:

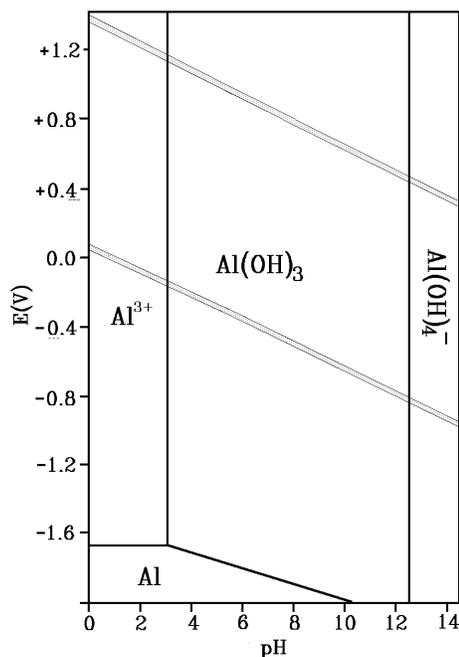
$$K = [\text{Al}(\text{OH})_4^-]/[\text{OH}^-] = 40$$

Thus $[\text{OH}^-] = 1/40$, $\text{pOH} = 1.6$ and $\text{pH} = 12.4$

Neither of these reactions involves change in oxidation state; thus they parallel the vertical axis.

Conversely, the reduction of the aluminum ion is potential, not pH dependent, and provides a horizontal line at $E = -1.68 \text{ V}$.

The appendix shows the reduction of the aluminate ion to be at -2.31 V , which is below the base of the plot, so a diagonal line continues to lower potential (see the figure).



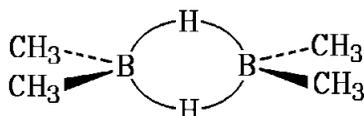
The only species in aqueous solution are the aluminum ion, aluminum hydroxide, and the aluminate ion. Note that aluminum metal is way below the water limits, and this shows why aluminum metal cannot be produced from aqueous solution.

In near-neutral waters, aluminum will be present as insoluble aluminum hydroxide. As the water pH decreases, increasing proportions of the aluminum will be solubilized as the toxic aluminum ion.



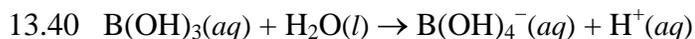
The aluminum ion is a hard acid, so it will prefer to pair with the hard oxide ion rather than with the soft sulfide ion.

13.34

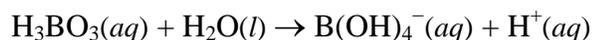


13.36 As sulfur is S^{2-} , the oxidation state of thallium would appear to be +2. Because thallium exhibits only oxidation states of +1 and +3, the compound is most likely $(\text{Tl}^{3+})(\text{Tl}^+)(\text{Se}^{2-})_2$.

13.38 Because gallium exhibits only oxidation states of +1 and +3, the compound is probably $[\text{Ga}^+][\text{GaCl}_4]^-$, the gallium in the anion being in the +3 oxidation state.

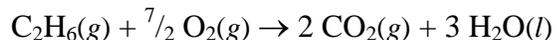
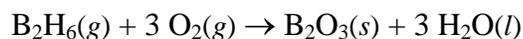


This can also be written as:



13.42 Energy per gram diborane = $(2165 \text{ kJ}\cdot\text{mol}^{-1})/(16.8 \text{ g}\cdot\text{mol}^{-1}) = 129 \text{ kJ}\cdot\text{g}^{-1}$

Energy per gram ethane = $(1560 \text{ kJ}\cdot\text{mol}^{-1})/(30.0 \text{ g}\cdot\text{mol}^{-1}) = 52.0 \text{ kJ}\cdot\text{g}^{-1}$



$$\Delta S \text{ for diborane combustion} = [(+54) + 3(+70) - (+232) - 3(+205)]$$

$$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$= -583 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

ΔS for ethane combustion

$$= [2(+214) + 3(+70) - (+230) - \frac{7}{2}(+205)] \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$= -310 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

The difference in values is a result of the boron oxide being a solid while the carbon oxide is a gas (much higher entropy). The practical disadvantages are the cost of the diborane, the difficulty in handling such a flammable fuel, and the clogging of the engine by the solid boron oxide product.

13.44

