CHAPTER 2

c0002 The Chemistry of Boron in Water

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s0010 2.1 BORON AND ITS CHEMICAL PROPERTIES

p0010 Boron (B) is the fifth element in the periodic table with an atomic mass of 10.81. It is the most electronegative element of Group III, and boron's chemical properties closely resemble those of the nonmetals, particularly silicon.

Pure elemental boron was first isolated simultaneously and independently in 1808 by H. Davy in England, who observed that an electric current sent through a solution of borates produced a brown precipitate on one of the electrodes, and by J. Gay-Lussac and L. Thenard in France, who obtained boron by reducing boric acid with iron at high temperatures.¹

p0020 Elemental boron exists as a solid at room temperature, either as black monoclinic crystals or as a yellow or brown amorphous powder when impure. Amorphous boron can be obtained by the reduction of boron oxide with sodium or potassium fluoroborate with potassium¹:

$$B_2O_3 + 6Na = 2B + 3Na_2O$$

$$KBF_4 + 3K = 4KF_4 + B$$

p0025 Crystalline boron was first prepared when hydrogen and boron bromide vapors at a rather less-than atmospheric pressure were passed over a tantalum filament heated to 1000–1300 °C.² At this temperature, the bromide is reduced, and the boron thus becomes deposited on the filament as black hexagonal flakes and needles:

$$2BBR_3 + 3H_2 = 6HBr + 2B$$

p0030 Two crystalline modifications of boron, namely, α -rhombohedral boron (Figure 2.1) and β -rhombohedral boron (Figure 2.2) exist at atmospheric pressure. The latter is believed to be thermodynamically stable at high temperatures, whereas α -boron is sometimes called the low-temperature form.³

p0035 The chemical nature of boron is influenced primarily by its small size (covalent radius of boron of 0.8–1.01 Å) and high ionization energy (344.2 kJ/mol). The high affinity for oxygen is another dominant characteristic of boron, which forms the basis of the extensive chemistry of borates and related oxocomplexes. 2