

BORON OXIDES, BORIC ACID, AND BORATES

1. Introduction

Boron, the fifth element in the periodic table, does not occur naturally in its elemental form. Instead, boron is nearly always found bound to oxygen. With the exception of a few rare boron fluoride minerals, boron is found in nature as inorganic oxides in minerals and natural waters or in organic and biological systems as borate esters in which boron is bound to oxygen. There are more than 200 boron-containing minerals, known as borates, but relatively few of commercial significance (1). In fact, only the following minerals serve as sources for more than 90% of the borates used by industry: borax (tincal) and kernite, which are sodium borates; ulexite, a sodium–calcium borate; and colemanite, a calcium borate. These minerals are extracted in California and Turkey and, to a lesser extent, in South America, Russia, and Asia. These deposits currently supply the world's need for industrial borates (2). Most industrial borates are used directly as oxides, and a small proportion is used in the production of all other commercial boron compounds as well as elemental boron.

According to legend, borates were used by Egyptians in mummification and by the ancient Romans in glassmaking. The first historically verifiable use of borates was by Arabian gold- and silversmiths, who used borate minerals as refining and soldering agents in the eighth century A.D. Borates were used in ceramic glazes in China by the eleventh century A.D. (3,4). By the thirteenth century, borates were routinely transported from Tibet to Venice, Italy along ancient trade routes between East Asia and Europe (5).

The discovery and development of significant borate mineral deposits in the nineteenth century, first in Italy and then in North and South America, improved availability and resulted in greatly increased use, including as an ingredient in consumer products. Early in the twentieth century, larger and higher grade deposits were found in California—first in Death Valley and then in the Mojave Desert—increasing the rate of borate market growth. Other deposits were discovered in Turkey, making that country a major borate producer as well (5).

Refined borates are usually sold based on their B_2O_3 content and are defined by their water content, or degree of hydration. Borax pentahydrate (47.8% B_2O_3), borax decahydrate (36.5% B_2O_3), and boric acid (56.3% B_2O_3) are the three most widely sold refined borate products. The United States and Turkey together supply more than 80% of the worldwide demand of these refined borates.

Borates offer unique properties and cost-effective functionality in a wide variety of products and industrial processes. Most are used in the manufacture of energy-saving insulation fiberglass, textile fiberglass, specialized glasses, ceramic glazes, porcelain enamels, fire retardants, wood preservatives, fertilizers, industrial fluids, metallurgical processes, and cleaning and personal-care products, ranging from laundry additives to eye drops. Borates are essential for imparting strength, durability, heat, and impact resistance to glass and glass fibers. Thousands of everyday items, including flat screen televisions and computer displays, barbecue charcoal, brake fluid, and kitchenware all contain borates.

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In addition, borates play an important role in the manufacture of building materials as well as in solar and wind energy systems (6).

Boron is an essential element for all plants. Substantial evidence also supports the biological importance of boron, albeit in trace amounts, for animals. Because boron is naturally present in plants, people in a wide range of cultures consume ~1–2 mg of boron per day as part of a healthy diet (7). Because boron is important for the proper functioning of plants, it is a common worldwide agricultural practice to add boron fertilizers to deficient soils to improve crop quality and yields and increase food production.

At high concentrations, boron also can inhibit certain biological processes leading to biostatic effects, particularly for insects, bacteria, and decay fungi. This is the basis for borates' use in preservative applications. These include protection of wood, wood composites, wood-plastic composites, and other cellulosic materials against biodeterioration caused by fungal decay and insect attack.

Many specialized boron compounds are prepared from industrial borates. These include metal borates, such as zinc borates, boron phosphate (BPO_4), boron halides (BF_3 , BCl_3 , and BBr_3), fluoroborates, boron carbide (B_4C), boron nitride (BN), and alloys such as ferroboron. Compounds of boron that do not contain boron-oxygen bonds are used commercially in much smaller volumes than boron oxides. Boron hydrides comprise a unique and diverse class of compounds. Among these, only sodium borohydride (NaBH_4) finds relatively large industrial-scale use as a reducing agent used in the manufacture of pharmaceuticals, in water treatment, as a bleaching agent to whiten paper and clays, and in the storage and generation of hydrogen. Diborane (B_2H_6) is used in smaller amounts in synthetic reagents and as a semiconductor dopant for electronic materials and solar cells. Other boron hydrides, such as ammonia borane, H_3NBH_3 , show promise as hydrogen storage materials and a versatile reducing agent (8).

2. Nomenclature

Systems of nomenclature encountered in the literature for borate compounds are confusing and often ambiguous. In most cases, chemical formulas for these compounds can be written in various ways and different names are often applied to the same compound. Detailed structural data are now available for most of the commonly encountered crystalline borate compounds, but many names in frequent use date from earlier times and do not convey the more precise information now available about these compounds; they may even perpetuate misinformation.

The following methods are commonly used to present chemical formulas for borates: (1) the resolved oxide formula, (2) the semiempirical formula, and (3) the structural formula. The resolved oxide formula presents compositions in terms of molar ratios of hypothetical oxide components, metal oxides, boron oxide, and water in the form $a\text{M}_x\text{O}\cdot b\text{B}_2\text{O}_3\cdot c\text{H}_2\text{O}$. For example, the resolved oxide formula for what is generally called "borax decahydrate" is written as $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 10\text{H}_2\text{O}$. The semiempirical formula provides the molar ratio of elements in the compound but factors out noncation hydrogen and requisite oxygen as hypothetical water content. Thus, the semiempirical formula for borax

decahydrate is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (a true empirical formula would be $\text{Na}_2\text{B}_4\text{O}_{17}\text{H}_{20}$). The structural formula provides information about the elemental composition of the compound as well as the actual arrangement of chemical groups based on the known structure data, usually derived from x-ray crystallography. The structural formula for borax decahydrate is $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, revealing that this compound is the sodium salt of the tetraborate anion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and actually only contains 8 moles of water rather than 10 moles, where the extra waters appearing in the oxide and semiempirical formulas really are present as B–OH groups in the tetraborate anion. This latent B–OH water can be called hydroxy hydration. All of these formula methods are useful but unfortunately lead to different and sometimes conflicting names, depending on which formula is used to derive the name.

The names applied to borate compounds usually are based on the boron-to-cation ratio and the number of water molecules appearing in the semiempirical or resolved oxide formula. Thus, borate compounds often are categorized as triborates, tetraborates, pentaborates, etc. This system can be useful because the boron-to-cation ratio generally correlates with important properties of borate compounds and also may provide clues about their structures. Thus, borax decahydrate in the previous example, with semiempirical and oxide formulas of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, is usually given the chemical name “sodium tetraborate decahydrate” or, in adherence to International Union of Pure and Applied Chemistry (IUPAC) conventions, “disodium tetraborate decahydrate.” This system provides partial agreement with the structural formula for this compound, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, which contains the tetraborate anion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ but is actually an octahydrate. In another example, the borate mineral colemanite, with semiempirical and oxide formulas $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ and $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is often called calcium triborate pentahydrate because it has a B/Ca mole ratio of 3 and 5 moles of water appear in the formulas. This again is in partial agreement with a structural formula of $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$ because this compound contains the triborate structural unit but only 1 mole of water. In this case, the structural unit is actually a polytriborate chain, so a more precise name based on the known structure of this compound is calcium polytriborate monohydrate.

A complication in the previous naming system occurs when the semiempirical formula contains an odd number of boron atoms. This situation requires doubling the formula to obtain a whole number of B_2O_3 units to construct the oxide formula. This also results in a doubling of the water molecules associated with the oxide formula. For example, the compound with a semiempirical formula of $\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ has an oxide formula of $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$. This compound is generally referred to as a sodium pentaborate hydrate but is sometimes called a pentahydrate and sometimes a decahydrate, depending on which of these formulas is used to derive the name. In some cases, the numbers in the semiempirical formula are doubled to be $\text{Na}_2\text{B}_{10}\text{O}_{16} \cdot 10\text{H}_2\text{O}$, apparently out of desire to make the hydration values agree. The structural formula for this compound is $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$, revealing that it contains the pentaborate anion but really is a trihydrate. Another example is found with metaborates, which is the name applied to borates with $\text{B}_2\text{O}_3/\text{M}_x\text{O} = 1$ (the term monoborate is rarely used). There are two common hydrates of sodium metaborate with

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semiempirical formulas $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. These are often represented by the oxide formulas $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, respectively, and are generally referred to as articles of commerce as “sodium metaborate tetrahydrate” and “sodium metaborate octahydrate.” The actual structural formulas for these compounds are $\text{NaB}(\text{OH})_4$ and $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, indicating that more precise names for these compounds would be sodium metaborate and sodium metaborate dihydrate.

The Chemical Abstract Service (CAS) has adopted a classification system based on a series of hypothetical boric acids. For example, the compound with a semiempirical formula of $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ has been called dizinc hexaborate heptahydrate. The resolved oxide formula for this substance is $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, providing a basis for the IUPAC proposed name, zinc (2:3) borate heptahydrate, where 2:3 refers to the $\text{ZnO}:\text{B}_2\text{O}_3$ ratio. This latter system has gained some acceptance, but this compound is also referred to commercially as zinc hexaborate, which is not in agreement with the established conventions. X-ray crystallography shows that the actual structural formula for this compound is $\text{ZnB}_3\text{O}_3(\text{OH})_5 \cdot \text{H}_2\text{O}$, and this knowledge allows for a more precise description with the name zinc triborate monohydrate (9). This is listed by the CAS as “boric acid, $\text{H}_7\text{B}_3\text{O}_8$, zinc salt” [12429-73-1]. Because many authors continue to use older formulations, a second listing was devised by the CAS for the same compound (ie, boric acid, $\text{H}_4\text{B}_6\text{O}_{11}$, zinc salt [1:2] heptahydrate [12280-01-2]).

Several different nomenclature systems currently are being used for borate compounds in the scientific, commercial, and regulatory literature. To avoid confusion, it is recommended that written names for borate compounds are used in conjunction with chemical formulas. An understanding of how different equivalent formula types interconvert is also important to identify different names that might refer to the same compound.

The oxides and oxoacids of boron, as well as a variety of hydrated and anhydrous metal borates, are discussed herein. A listing of commonly encountered borate compounds is given in Table 1.

3. Borate Occurrence and Supply

3.1. Borate Minerals. Boron is present in measureable amounts everywhere on earth, including in rocks, soils, and natural waters. However, only a few geographic regions contain commercially viable borate deposits. The principal borate minerals of industrial importance are listed in Table 2. A more complete listing is available in the literature (1,10). Crystal structures of many borate compounds have been compiled (6).

3.2. Mineral Resources. The largest known borate deposits are located in southern California and northwestern Anatolia, Turkey. The Death Valley region of California historically has been a significant source of both colemanite and ulexite, but mining operations are not currently conducted in this area. Sodium borates are now produced in California from a large deposit located near the town of Boron, in the northwestern Mojave Desert, and as a coproduct from brines pumped from shallow depths at Searles Lake, west of Death Valley.

Table 1. Selected Borate Compounds

Compound	CAS Registry Number	Semiempirical formula	Oxide formula	Structural formula
diboron trioxide (boric oxide)	[1303-86-2]	B ₂ O ₃	B ₂ O ₃	industrial product is amorphous
orthoboric acid ^a	[10043-35-3]	H ₃ BO ₃	B ₂ O ₃ ·3H ₂ O	B(OH) ₃
metaboric acid	[13460-50-9]	HBO ₂	B ₂ O ₃ ·H ₂ O	B ₃ O ₃ (OH) ₃
anhydrous sodium tetraborate (anhydrous borax)	[1330-43-4]	Na ₂ B ₄ O ₇	Na ₂ O·2B ₂ O ₃	industrial product is amorphous
sodium tetraborate decahydrate (borax decahydrate)	[1303-96-4]	Na ₂ B ₄ O ₇ ·10H ₂ O	Na ₂ O·2B ₂ O ₃ ·10H ₂ O	Na ₂ B ₄ O ₅ (OH) ₄ ·8H ₂ O
sodium tetraborate pentahydrate (borax pentahydrate) ^b	[12045-88-4]	Na ₂ B ₄ O ₇ ·5H ₂ O	Na ₂ O·2B ₂ O ₃ ·5H ₂ O	Na ₂ B ₄ O ₅ (OH) ₄ ·3H ₂ O ^b
sodium tetraborate tetrahydrate (kernite)	[12045-87-3]	Na ₂ B ₄ O ₇ ·4H ₂ O	Na ₂ O·2B ₂ O ₃ ·4H ₂ O	Na ₂ B ₄ O ₅ (OH) ₄ ·2H ₂ O
disodium octaborate tetrahydrate	[12280-03-4]	Na ₂ B ₄ O ₇ ·4H ₂ O	Na ₂ O·4B ₂ O ₃ ·4H ₂ O	amorphous
sodium metaborate ^c	[16800-11-6]	NaBO ₂ ·2H ₂ O	Na ₂ O·B ₂ O ₃ ·4H ₂ O	NaB(OH) ₄
sodium metaborate hydrate ^d	[10555-76-7]	NaBO ₂ ·4H ₂ O	Na ₂ O·B ₂ O ₃ ·8H ₂ O	NaB(OH) ₄ ·2H ₂ O
sodium pentaborate pentahydrate	[12046-75-2]	NaB ₅ O ₈ ·5H ₂ O	Na ₂ O·5B ₂ O ₃ ·10H ₂ O	NaB ₅ O ₆ (OH) ₄ ·3H ₂ O
sodium perborate tetrahydrate (PBS-4)	[10486-00-7]	NaBO ₃ ·4H ₂ O	Na ₂ O·B ₂ O ₃ ·8H ₂ O	Na ₂ B ₂ O ₄ (OH) ₄ ·6H ₂ O
potassium pentaborate tetrahydrate	[12229-13-9]	KB ₅ O ₈ ·4H ₂ O	K ₂ O·5B ₂ O ₃ ·4H ₂ O	KB ₅ O ₆ (OH) ₄ ·2H ₂ O
potassium tetraborate tetrahydrate	[12045-78-2]	K ₂ B ₄ O ₇ ·4H ₂ O	K ₂ O·2B ₂ O ₃ ·4H ₂ O	K ₂ B ₄ O ₅ (OH) ₄ ·2H ₂ O
ammonium tetraborate tetrahydrate	[12228-87-4]	NH ₄ B ₄ O ₇ ·4H ₂ O	(NH ₄) ₂ O·2B ₂ O ₃ ·4H ₂ O	(NH ₄) ₂ B ₄ O ₅ (OH) ₄ ·2H ₂ O
ammonium pentaborate tetrahydrate	[12229-12-8]	NH ₄ B ₅ O ₈ ·4H ₂ O	(NH ₄) ₂ O·5B ₂ O ₃ ·8H ₂ O	NH ₄ B ₅ O ₆ (OH) ₄ ·2H ₂ O
barium metaborate hydrate	[13701-59-2]	BaB ₂ O ₄ ·xH ₂ O	BaO·B ₂ O ₃ ·xH ₂ O	Ba[B(OH) ₄] ₂ ·xH ₂ O
calcium polytriborate hydrate (colemanite)	[12291-65-5]	Ca ₂ B ₆ O ₁₁ ·5H ₂ O	2CaO·3B ₂ O ₃ ·5H ₂ O	CaB ₃ O ₄ (OH) ₃ ·H ₂ O
calcium magnesium hexaborate hydrate (hydroboracite)	[12046-12-7]	CaMgB ₆ O ₁₁ ·8H ₂ O	CaO·MgO·3B ₂ O ₃ ·8H ₂ O	CaMgB ₆ O ₈ (OH) ₆ ·3H ₂ O
sodium calcium pentaborate octahydrate (ulexite)	[1319-33-1]	NaCaB ₅ O ₉ ·8H ₂ O	Na ₂ O·2CaO·5B ₂ O ₃ ·16H ₂ O	NaCaB ₅ O ₆ (OH) ₆ ·5H ₂ O
sodium calcium pentaborate pentahydrate (proberite)	[12229-14-0]	NaCaB ₅ O ₉ ·5H ₂ O	Na ₂ O·CaO·5B ₂ O ₃ ·10H ₂ O	CaNaB ₅ O ₇ (OH) ₄ ·3H ₂ O
zinc triborate monohydrate	[12280-01-2]	Zn ₂ B ₆ O ₁₁ ·7H ₂ O	2ZnO·3B ₂ O ₃ ·7H ₂ O	ZnB ₃ O ₃ (OH) ₅ ·H ₂ O
zinc polytriborate ^e	[138265-88-0]	Zn ₂ B ₆ O ₁₁ ·3H ₂ O	2ZnO·3B ₂ O ₃ ·3H ₂ O	ZnB ₃ O ₄ (OH) ₃

^aCommonly referred to as boric acid.

^bCrystallographically Na₂B₄O₅(OH)₄·2.67H₂O.

^cKnown as an article of commerce as sodium metaborate tetrahydrate.

^dKnown as an article of commerce as sodium metaborate octahydrate.

^eKnown as an article of commerce as 2ZnO·3B₂O₃·3.5H₂O.

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Table 2. Commercially Important Borate Minerals

Mineral	CAS Registry Number	Semiempirical formula	Wt % B ₂ O ₃	Location
borax (tincal)	[1303-46-4]	Na ₂ B ₄ O ₇ ·10H ₂ O	36.5	United States, Turkey, Argentina
kernite	[12045-87-3]	Na ₂ B ₄ O ₇ ·4H ₂ O	51.0	United States
ulexite	[1319-33-1]	NaCaB ₅ O ₉ ·8H ₂ O	43.0	Turkey, South America
colemanite	[12291-65-5]	Ca ₂ B ₆ O ₁₁ ·5H ₂ O	50.8	Turkey
inderite	[12260-26-3]	Mg ₂ B ₆ O ₁₁ ·15H ₂ O	37.3	Kazakhstan
szaibelyite (ascharite) ^d	[12447-04-0]	Mg ₂ B ₂ O ₅ ·H ₂ O	41.4	China
suanite	[36564-04-2]	Mg ₂ B ₂ O ₅	46.3	China
hydroboracite	[12046-12-7]	CaMgB ₆ O ₁₁ ·6H ₂ O	50.5	Argentina
datolite	[1318-40-7]	Ca ₂ B ₂ Si ₂ O ₉ ·H ₂ O	21.8	Russia

^dThis material has two CAS Registry Numbers.

Reports have been made concerning the minerals of the Searles Lake, Boron-Kramer, and Death Valley mining districts of the United States (2,11).

In Turkey, the following are the main borate-producing districts: Kirka, which produces sodium borate; the Emet basin, which contains two large colemanite deposits; and the Bigadic basin, which produces both ulexite and colemanite from several deposits. Deposits in the United States and Turkey supply more than 80% of the worldwide demand for borates.

Portions of four South American countries—northern Argentina, northern Chile, southern Bolivia, and southern Peru—contain ulexite deposits. Northern Argentina is also home to the Tincalayu sodium borate deposit and several ulexite-colemanite deposits. Eastern China, where several relatively small magnesium borate deposits are located, as well as far eastern Russia, where a large borosilicate deposit is located, supply local markets and represent most of the remainder of the world's borate production.

The sodium borate minerals borax (tincal) and kernite are extracted from large open pit mines in Boron in California, Kirka in Turkey, and Tincalayu in northern Argentina. These three deposits, in addition to the brines from Searles Lake, California, furnish most of the sodium borates used throughout the world.

The calcium borate mineral colemanite is mined from several deposits in the Emet and Bigadic basins of western Turkey as well as small deposits in northern Argentina. This calcium borate is primarily used in the manufacture of products with low sodium requirements and to make boric acid.

The sodium-calcium borate mineral ulexite is the common marsh or playa (salar) borate. It is produced commercially from several playas in South America and from the Provinces of Quinghi and Xizang (Tibet) in western China. Ancient playa deposits, from 5 to 20 million years old, are the source of Turkish ulexite, ulexite found in Death Valley, and some ores in Argentina. Much of this material is ground and used as a mineral product in agriculture or to manufacture boric acid.

The less easily refined magnesium borates of China are found in the Liaodong peninsula adjacent to North Korea. These are mined by underground methods and are refined in local plants to produce sodium borates and boric acid

primarily for domestic use. A unique borosilicate deposit at Dalnegorsk, near the Pacific coast of Russia, is mined to produce boric acid.

Other borate deposits, some of which were once mined commercially, are reported in many other areas (Table 2). These include the Inder region of Kazakhstan, the Stassfurt district of eastern Germany, northern Iran, and Serbia. Numerous existing deposits in the western United States, western Turkey, and South America are not currently in production because of various economic reasons (11). A prospective borate-lithium deposit in northern Serbia is under development and is expected to be in production by 2015 or 2016.

Ore deposits that are defined as sodium borate mineral are typically tincal (native borax), kernite, or ulexite. Nonsodium borate deposits are colemanite, hydroboracite, and others. Borosilicate minerals typically are classified as metamorphic borates. Although currently only a minor source of industrial borate products, this latter category dominates the world's known borate deposits.

3.3. Ore Reserves. The identified global borate mineral resource base is estimated to contain more than 1 billion metric tons of B_2O_3 (11) and is concentrated in Turkey, the United States, South America, Russia, and China. Turkey and the United States represent roughly 73% of the known borate resources; however, not all known deposits are currently economically feasible. Remaining borate resources are located in South American (10%), Russian and Kazakhstan (6%), China (6%), and other locations (5%). New reserves are being explored in Eastern Europe. The main producers in Turkey and the United States have sufficient reserves to remain competitive over the long term. Two primary reserve bases exist (12). The Turkish national producer Eti Maden (Istanbul, Turkey) maintains the largest ore reserve base in Turkey with Rio Tinto's borate business, U.S. Borax Inc. (Los Angeles, Calif.) and Searles Valley Minerals (SVM, Trona, Calif.) having the second largest reserves.

3.4. Overall Industry. Global borate sales in 2009 were estimated at 1.4 million B_2O_3 tons, down from 1.7 million tons as a result of the global recession. However, the overall demand trend points to growth in both refined sodium borates and nonsodium borates and is expected to grow to more than 2.0 million B_2O_3 tons by 2013 or 2014. Demand for refined borates accounts for more than 85% of the total demand followed by mineral borates at 14% and specialty borates at around 1%.

3.5. Borate Producers by Country/Region. United States. The United States is a major producer of refined borate products. There are currently two borate producers in the United States, both with operations in California. The larger of these is Rio Tinto's borate business, U.S. Borax Inc., which operates its largest mining and manufacturing facility in the Mojave Desert of Southern California. This company also has mining and refining facilities in Argentina and a refining plant in France. The company operates shipping terminals in the United States, the Netherlands, France, and Spain and has major stock points and warehouses in Europe and Asia. Borax is owned by the major mining company, Rio Tinto plc.

Rio Tinto's borate business, U.S. Borax Inc., operates the largest open-pit mine in California, which is located about 125 km northeast of Los Angeles.

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This operation produces approximately 1 million tons of refined borates annually, which is enough to satisfy nearly half the world's demand. Processing plants at the mine site produce borax pentahydrate, borax decahydrate, and boric acid from tincal (borax) and kernite ores. Fusing plants at the mine site also produce anhydrous borax and boric oxide. The company also operates major shipping terminals at Wilmington, the Port of Los Angeles, Calif. and at Rotterdam, the Netherlands, as well as specialized borate-manufacturing plants at the Port of Los Angeles, Calif., and Coudekerque, France. The company is also developing a lithium-borate deposit in Serbia called Jadar.

Searles Valley Minerals, Inc. (SVM) is the second largest U.S. borate producer. This company is a subsidiary of the Indian chemical company Nirma Limited (Ahmedabad, India). The feed for the Searles Lake operations come from two salt horizons saturated with brines extracted by solution mining. The brines contain bicarbonate, borate, chloride, carbonate, potassium, and sulfate, which are separated by continuous and selective crystallization of different salts. This operation produces borax pentahydrate, borax decahydrate, boric acid, and anhydrous borax.

Turkey. The Turkish state-owned company Eti Maden (Ankara, Turkey) controls all borate resources in Turkey and is a major supplier of refined borates, including borax pentahydrate and boric acid, and is the largest supplier of calcium borate mineral concentrates. Eti Maden operates mines in several locations, including Kirka, Kestelek, Bigadic, and Emet. Most borates produced in Turkey, including refined sodium borate, boric acid, and colemanite and ulexite mineral concentrates, are exported. Eti Maden also operates borate manufacturing and shipping facilities in the Port of Bandirma, Turkey.

South America. Several borate producers operate in the Andes mountain regions of South America, including Argentina, Chile, Bolivia, and Peru (13,14). Because they operate at high elevations in mountainous terrain, most producers mine ore only during the nonwinter months.

Argentina hosts numerous borate producers. Under its Borax Argentina division, Rio Tinto conducts mining and refining operations in the Salta Province of northern Argentina, mining tincal (borax) from Tincalayu, hydroboracite from Sijes, as well as ulexite from Salar Diablillos and Cauchari. Most product mined by Borax Argentina supplies South American markets. Many smaller mining companies also operate in Argentina, mostly producing ulexite, colemanite, and hydroboracite mineral concentrates of varying qualities. These include Agenor, Quiborax, SQM, Minera Santa Rita, and Ulex S.A.

Borate producers operating in Chile include Quiborax Boroquimica and Sociedad Boroquimica y Minera de Chile (SQM), which mine ulexite reserves from salars in the north of the country. Some Chilean borate production is consumed locally for applications such as agriculture and a substantial amount is exported.

Several relatively small borate producers operate in Bolivia, mainly processing ulexite reserves. These reserves are located in the Bolivian Altiplano around Salar de Uyuni. The largest producer in this country is Cia Minera Tierra near the Chilean border.

The main borate production in Peru originates from Cia Minera Ubinas and Quimica Oquendo, which markets products under the Inkabor

name. Both are wholly owned by the Collorabia group in Italy. Like their South American competitors, they mine ulexite during nonwinter months. The ore is used to produce both a crude washed ulexite product as well as boric acid.

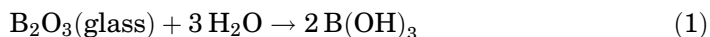
Russia. Although there are numerous borate deposits in the Dalnegorsk district, only one is a significant source of industrial borates. JSC Bor (Dalnegorsk, Russia) mines the borosilicate mineral datolite at Dalnegorsk, producing datolite concentrate and refined borates, primarily boric acid. This company also produces some specialized borate product, including synthetic calcium borate. Bor is the only Russian borate producer and exports mainly to Asian countries.

China. Like the South American countries, China also has many small producers. Most production originates from the Liaoning province in the Liaodong peninsula. The ores in this area of the world are mainly magnesium borates such as szaibelyite. However, ulexite, pinnoite, hydroboracite, and borax are also mined in Qinghai (13–15).

India. Suppliers in India have no domestic borate reserves and are dependent on imported ore and refined feedstocks supplied by other producers. Borax Moraji is one such manufacturer of borate products in India. Product produced in India is almost exclusively sold within India.

4. Boron Oxides

4.1. Boric Oxide. Boric oxide, B_2O_3 (formula wt 69.62) is the only boron oxide manufactured and sold in industrial volumes. It is also known as diboron trioxide, boric anhydride, or anhydrous boric acid. It is almost always encountered in the vitreous state. This colorless, glassy solid has a Mohs hardness of 4 and is usually prepared by dehydration of boric acid at elevated temperatures. It is mildly hygroscopic at room temperature, and the commercially available material typically contains ca 1 wt % moisture in the form of a surface layer of boric acid. The reaction with water (eq. 1) is exothermic, $\Delta H^\circ = -75.94$ kJ/mol B_2O_3 (16) and is expressed as follows:



Boric oxide is an excellent Lewis acid. It coordinates even weak bases to form four-coordinate borate species. A reaction with sulfuric acid produces $H[B(HSO_4)_4]$ (17). At high temperatures ($>1000^\circ\text{C}$) molten boric oxide dissolves most metal oxides and thus is corrosive to metals in the presence of oxygen. This property also provides a basis for the use of boric oxide as a flux in many metallurgical processes.

Molten boric oxide reacts readily with water vapor above 1000°C to form metaboric acid in the vapor state (eq. 2), which is expressed as follows:



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Table 3. Physical Properties of Vitreous Boric Oxide

Property	Value	Reference
vapor pressure, 1331–1808 K	$\log P = 5.849 - (16960/T)$	22
heat of vaporization, ΔH_{vap} , kJ/mol		
1500 K	390.4	23
298 K	431.4	23
boiling point, extrapolated	2316°C	16
viscosity, $\log \eta$, mPa·s(= cP)		
350°C	10.60	
700°C	4.96	
1000°C	4.00	
density, g/mL		
0°C	1.8766	
18–25°C	1.844	
18–25°C ^e	1.81	
500°C ^b	1.648	24
1000°C ^b	1.528	24
index of refraction, 14.4°C	1.463	
heat capacity (specific), J/(kg·K)		
298 K	62.969	16
500 K	87.027	16
700 K	132.63	16
1000 K	131.38	16
heat of formation, ^c ΔH_f , kJ, 298.15 K	-1252.2 ± 1.7	16

^aWell annealed.

^bQuenched.

^cFor $2 \text{ B(s)} + 3/2 \text{ O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{glass})$.

An enthalpy value of $\Delta H_{298} = -199.2 \pm 8.4$ kJ/mol has been calculated for this reaction, which has considerable economic importance to glass manufacturers because B_2O_3 losses during glass processing are greatly increased by the presence of water. For this reason, anhydrous borates or boric oxide are often preferred over hydrated compounds, such as borax or boric acid, for glass manufacture. The presence of MgO reduces the volatilization of B_2O_3 from molten glass batches (18).

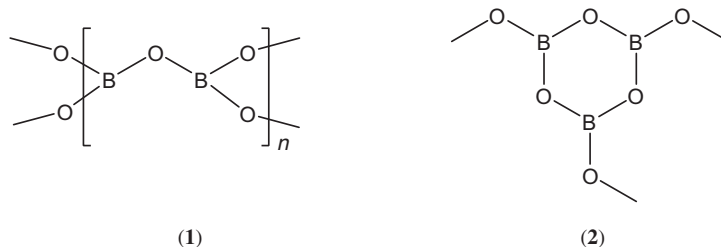
The physical properties of vitreous boric oxide, listed in Table 3, are somewhat dependent on moisture content and thermal history. Much of the older physical data has been revised after the development of more reliable techniques for sample preparation (19–24).

Many physical properties are sensitive to moisture present as metaboric acid, not as free water. Water can be reduced to 0.17% by heating in air at 1000°C and a level of 10 ppm has been achieved by prolonged heating in a vacuum, 0.13 kPa (1 mm Hg) in a carbon crucible. The removal of residual water causes the density to decrease and the softening point to increase. At 0.28 wt % of water, the density of boric oxide is 1.853 and the softening point is 240–275°C; nearly anhydrous B_2O_3 , with 20 ppm water, has a density of 1.829 g/mL and a softening point of 300–325°C (25). Thermal expansion, viscosity, and refractive index are all affected by moisture content. Boric oxide becomes pourable after heating to about 500°C. The viscosity of boric oxide with temperature is given in Table 4.

Table 4. Viscosity of Boric Oxide as a Function of Temperature

Temperature, °C	Viscosity, Pa·s	Temperature, °C	Viscosity, Pa·s
260	6.1×10^{10}	700	8.5×10
300	4.4×10^8	800	2.6×10
400	1.6×10^5	900	1.2×10
500	3.9×10^3	1000	7.4
600	4.8×10^2	1100	4.3

The structure of vitreous and molten boric oxide has been a subject of much debate (26). Only trigonal boron atoms exist in the solid glass in branched networks (1) wherein a substantial fraction of the boron is thought to exist in planar boroxol rings (2), with the three exocyclic oxygen atoms forming bridges to neighboring boroxol rings or other network BO_3 groups (27–29). This network breaks down as the glass melts, and spectroscopic features attributed to the boroxol group (eg, the strong Raman line at 808 cm^{-1}) decrease as the liquid is heated to 800°C . It has been proposed (21) that, higher than 800°C , the liquid consists of discrete but are strongly associated with small molecules, which are possibly the same monomeric units observed in the vapor state (30).



Two crystalline forms of boric oxide have been described with structures of both determined by single crystal x-ray diffraction studies (31). Phase relationships between the liquid and crystalline forms of B_2O_3 also have been developed (32). The more common hexagonal crystalline phase, B_2O_3 -I or α -form ($d = 2.46\text{ g/mL}$, $\text{mp} = 455\text{--}475^\circ\text{C}$), is more stable than the vitreous phase. The effect of residual water in crystalline B_2O_3 , as in the vitreous phase, is to lower the melting, softening, and freezing points (33). For the transformation, $\text{B}_2\text{O}_3\text{-I} \rightarrow \text{B}_2\text{O}_3$ (glass), $\Delta H^\circ = +18.24\text{ kJ/mol}$ (16). However, vitreous B_2O_3 does not readily crystallize in the absence of seed crystals or increased pressure. Crystallization of B_2O_3 can be induced by prolonged heating of melt containing $<18\%$ water below 235°C or in the presence of 5 wt % water and an addition of crystalline seed at 250°C . Crystals do not form at any temperature from a melt containing $<1\%$ water. Crystalline B_2O_3 also can be made by prolonged heating of boric acid seeded with boron phosphate at $220\text{--}260^\circ\text{C}$ (34). A second dense monoclinic crystalline phase, B_2O_3 -II or β -form ($d = 2.95\text{ g/mL}$, $\text{mp} = 510^\circ\text{C}$) can be obtained at 400°C and $>2.23\text{ GPa}$ ($>22,000\text{ atm}$). The crystal lattice of B_2O_3 -II consists of a highly compact network of tetrahedra in which the four apical oxygen atoms are shared by either two or three boron atoms. The acidic character associated with

trigonal boron groups is thus masked in B_2O_3 -II. Although this material is thermodynamically unstable under ordinary conditions, it reacts slowly with Lewis bases, such as water and fluoride ion.

As an industrial article of commerce, boric oxide is always found in the vitreous form. Crystalline boric oxide is not manufactured on an industrial scale. High purity grade (ca. 99%) vitreous boric oxide is manufactured by fusing boric acid in a gas-fired furnace to produce a molten material that is then solidified into a continuous ribbon using chill rolls. The amorphous solid product is then crushed, screened, and packaged as granular products in moisture-resistant containers. Commercial boric oxide may contain 1–3% water, which exists in the form of a thin layer of boric acid on the surface of the boric oxide particles. Smaller particle size grades of boric oxide tend to have a higher equivalent water content because of higher surface areas.

Boric oxide reacts with water to form boric acid, with halogens to form boron trihalides, with halogen salts to form glasses, and with P_2O_5 to form boron triphosphate. In the molten state, it is also a strong Lewis acid solvent for dissolving metal oxides, has low surface tension, and readily wets metal surfaces. Molten boric oxide can be used as a solvent for metal reductions such as $2CuO + C \rightarrow CO_2 + 2Cu$ for growing crystals of garnet, refractory oxides, and in the preparation of lead titanate, barium titanate, and calcium zirconates from the corresponding oxides.

The use of boric oxide relates to its behavior as a flux, acid catalyst, and chemical intermediate. The fluxing action of B_2O_3 is important in preparing many types of glass, ceramic glazes, and porcelain enamels. Boric oxide is used as a catalyst in many organic reactions. It also serves as an intermediate in the production of boron halides, esters, carbides, nitrides, and metal borides.

4.2. Other Boron Oxides and Suboxides. High temperature vapor phases of BO , B_2O_3 , and BO_2 have been the subject of several spectroscopic and mass spectrometric studies aimed at developing theories of bonding and electronic structure and determining thermochemical data (35). Values for the principal thermodynamic functions have been calculated and compiled for these gases (36). Vibrational emission spectra indicate that the B_2O_2 molecule has a linear $O=B-B=O$ structure. Values of 782 and 502 kJ/mol were calculated for the respective $B=O$ and $B-B$ bond energies (37).

Two noncrystalline solid forms of BO have been prepared (35). Several polymeric $(BO)_n$ or $(B_2O_2)_n$ structures have been proposed for these materials, which apparently contain $B-B$ bonds. The low temperature form is a white, water-soluble powder produced at 220°C by vacuum-dehydration of tetrahydroxydiborane(4), $(HO)_2B-B(OH)_2$ [13675-18-8], that can be prepared from tetrakis(dimethylamino)diborane(4) [1630-79-1] (38). This product is irreversibly converted to an insoluble, light-brown modification on heating above 500°C. The latter material also was prepared by reducing B_2O_3 by elemental boron at 1330°C or by carbon or boron carbides at 1250°C (eqs. 3 and 4 (39)). Both polymorphs are strong reducing agents that decompose slowly in water to yield hydrogen gas and boric acid. Equations 3 and 4 are expressed as follows:





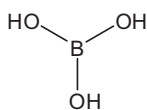
Several hard, refractory suboxides have been prepared either as by-products of elemental boron production (35) or through the reaction of boron and boric acid at high temperatures and pressures (40). The various oxides represented as B_6O , B_7O , B_{12}O_2 , and B_{13}O_2 all may be the same material in varying degrees of purity. A representative crystalline substance was determined to be rhombohedral boron suboxide, B_{12}O_2 , usually mixed with traces of boron or B_2O_3 (40). A study was done of the mechanical properties of this material, which exhibits hardness comparable with that of boron carbide (41). At temperatures above 1000°C , B_{12}O_2 gradually decomposes to $\text{B}(\text{s})$ and $\text{B}_2\text{O}_2(\text{g})$.

A large group of boron-containing solids are extremely hard refractory materials. In addition to the well-known, nonoxide boron compounds, cubic boron nitride and boron carbide, several boron oxides, such as B_{12}O_2 , are extremely hard and have unique crystal structures and interesting physical and chemical properties related to their strongly covalent and electron-deficiency character. Because of their unique combination of hardness, strength, durability, and lightness, boron-rich materials are uniquely suited to a variety of important technological applications.

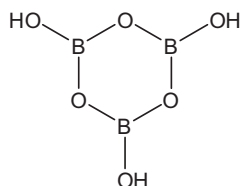
5. Boric Acid

Boric acid has an immense variety of applications in a wide range of industrial products and processes as well as in consumer products. The chemistry of boric acid is presented here and its uses are discussed in the section titled "Industrial Borate Uses."

5.1. Forms of Boric Acid. The name boric acid is usually associated with orthoboric acid, $\text{B}(\text{OH})_3$ (3), which is the only industrially important form of boric acid. It is found in nature as the mineral sassolite and is also the predominant form of boron in natural waters and an important form in biological systems.



(3)



(4)

The formula for orthoboric acid is sometimes written as H_3BO_3 . However, this expression is misleading because it suggests that it is a Brønsted acid. Instead, $\text{B}(\text{OH})_3$ is a Lewis acid, as discussed subsequently. Three crystalline modifications of metaboric acid also exist. All these forms of boric acid can be regarded as hydrates of boric oxide, formulated as $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ for orthoboric acid and as $\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ for metaboric acid (31).

Table 5. Vapor Pressure of Water Over Boric Acid as a Function of Temperature

Temperature, °C	Vapor pressure of H ₂ O over B(OH) ₃	
	HBO ₂ -III, kPa	HBO ₂ -II, kPa
25	0.048	0.16
100	8.4	16
130	39.9	62.5
150	102	143

Orthoboric acid, B(OH)₃ (formula wt 61.83), crystallizes from aqueous solutions as white, waxy, triclinic plates (sp gr^{14,4}, 1.5172). Its normal melting point is 170.9°C; however, when heated, it loses water to form metaboric acid, HBO₂ (formula wt, 43.82), which may exist in one of three crystal modifications. The orthorhombic-III or α -form ($d = 1.784$ g/mL, mp = 176°C) forms first around 130°C and gradually changes to the monoclinic-II or β -form ($d = 2.045$ g/mL, mp = 200.9°C). Water-vapor pressures associated with these decompositions are given in Table 5.

At temperatures above 150°C, dehydration continues, yielding viscous liquid phases beyond the metaboric acid composition (40). The most stable form of metaboric acid, cubic HBO₂-I or the γ -form ($d = 2.49$ g/mL, mp = 236°C), crystallizes slowly when mixtures of boric acid and HBO₂-III are melted in an evacuated, sealed ampule and held at 180°C for several weeks (42).

The relationships between condensed phases in the B₂O₃-H₂O system are shown in Figure 1 (43). No evidence has been found for stable phases other than those shown. Boric oxide melts and glasses containing less than 50 mol% water have mechanical and spectroscopic properties consistent with mixtures of HBO₂ and vitreous B₂O₃.

Vapor phases in the B₂O₃-H₂O system include water vapor and B(OH)₃ (g) at temperatures below 160°C. Boric acid is volatile in steam, and appreciable losses occur when aqueous solutions of boric acid are concentrated by boiling (44). At high temperatures (600–1000°C), HBO₂(g) is the principal boron species formed by equilibration of water vapor and molten (31). At still higher temperatures, a trimer—(HBO₂)₃, also known as metaboric acid-III (**4**)—is formed.

The crystal structure of orthoboric acid consists of planar sheets made up of hydrogen-bonded, triangular molecules. The stacking pattern of the molecular layers is disordered at room temperature, indicative of relatively weak van der Waals forces between the planes. This accounts for its slippery feel and the ease with which the crystals are cleaved into thin flakes (2). The structures of all three forms of metaboric acid are also known (45,46). The basic structural unit of HBO₂-III is the trimeric ring (**4**) and consists of only trigonal planar units. Metaborate-I has only tetrahedral boron structural units and HBO₂-II contains both trigonal and tetrahedral boron atoms in a ratio of 2:1. The HBO₂-III trimer may persist to some extent in the vapor phase, but infrared spectral data indicate that the monomeric species O=B—OH predominates in gaseous metaboric acid (47).

5.2. Properties. The standard heats of the formation of crystalline orthoboric acid and the three forms of metaboric acid are $\Delta H_f^\circ = -1094.3$ kJ/mol for

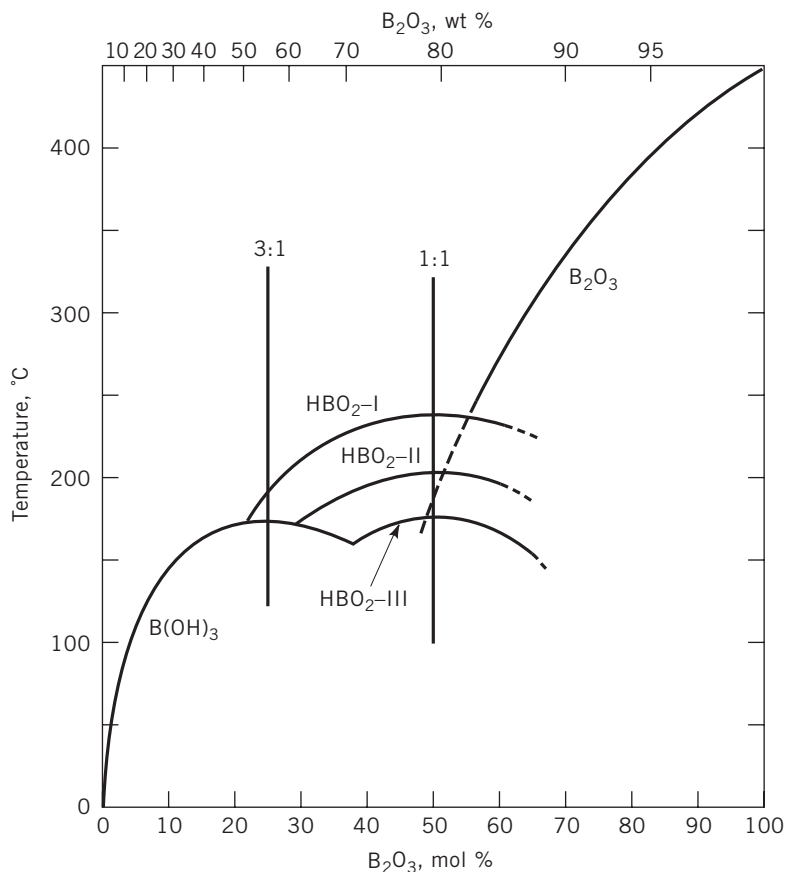


Fig. 1. Solubility diagram for the system $\text{H}_2\text{O}-\text{B}_2\text{O}_3$ (43). Courtesy of the *American Journal of Science*.

$\text{B}(\text{OH})_3$; -804.04 kJ/mol for $\text{HBO}_2\text{-I}$; -794.25 kJ/mol for $\text{HBO}_2\text{-II}$; and -788.77 kJ/mol for $\text{HBO}_2\text{-III}$ (36). Values for the principal thermodynamic functions of $\text{B}(\text{OH})_3$ are given in Table 6 (16).

The solubility of boric acid in water (Table 7) increases rapidly with temperature. The heat of solution is somewhat concentration dependent. For solutions with molalities in the range 0.03–0.9 mol, the molar heats of solution fit

Table 6. Thermodynamic Properties of Crystalline Boric Acid, $\text{B}(\text{OH})_3$ ^a

Temperature, K	$C_p^\circ, \text{J}/(\text{kg}\cdot\text{K})$	$S^\circ, \text{J}/\text{Kb}$	$H^\circ - H^\circ_{298}, \text{J}/\text{mol}$
0	0	0	-13,393
100	35.92	28.98	-11,636
200	58.74	61.13	-6866
298	81.34	88.74	0
400	100.21	115.39	9284

^aRef. 31.

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Table 7. **Aqueous Solubility of Boric Acid**

Temperature, °C	B(OH) ₃ , wt %	Temperature, °C	B(OH) ₃ , wt %
-0.76 ^a	2.47	60	12.97
0	2.52	70	15.75
10	3.49	80	19.10
20	4.72	90	23.27
30	6.23	100	27.53
40	8.08	103.3 ^b	29.27
50	10.27		

^aMelting point.

^bBoiling point.

the empirical relation given by the following equation (48):

$$\Delta H = [22062 - 222 m + 979 e^{-1230m}] \text{kJ/mol} \quad (5)$$

The presence of inorganic salts may enhance or depress the aqueous solubility of boric acid: it is increased by potassium chloride as well as by potassium or sodium sulfate but is decreased by lithium and sodium chlorides. Basic anions and other nucleophiles, notably borates and fluoride, greatly increase boric acid solubility by forming polyanions (31).

Boric acid is soluble in many organic solvents (Table 8), particularly polar and/or protic solvents. Some of these solvents (eg, pyridine, dioxane, and diols)

Table 8. **Solubility of Boric Acid, Borax Decahydrate, and Borax Pentahydrate in Organic Solvents**

Solvent	Temperature, °C	Solubility, wt %		
		B(OH) ₃	Na ₂ B ₄ O ₇ ·5H ₂ O	Na ₂ B ₄ O ₇ ·10H ₂ O
glycerol, 86.5%	20	21.1	47.1	
glycerol, 98.5%	20	19.9	52.6	
glycerol	25	17.5		
ethylene glycol	25	18.5	41.6	31.2
propylene glycol	25	15.1		21.9
diethylene glycol	25	13.6	18.6	10.0
mannitol, 10%	25	6.62		
methanol	25	173.9 ^a	19.9	16.9
ethanol	25	94.4 ^a		
<i>n</i> -propanol	25	59.4 ^a		
<i>n</i> -butanol	25	42.8 ^a		
2-methylbutanol	25	35.3 ^a		
isoamyl alcohol	25	2.39		
acetone	25	0.6	0.60	
methyl ethyl ketone	20	0.7		
ethyl acetate	25	1.5	0.14	
diethyl ether	20	0.008		
dioxane	25	~14.6 ^a		
pyridine	25	~70 ^a		
aniline	20	0.15		
acetic acid, 100%	30	6.3		

^aSolubility values are in g/L.

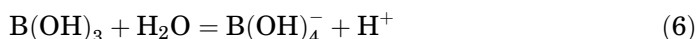
Table 9. Observed and Calculated pH Values for Boric Acid^a

Concentration, M	pH observed	pH calculated
0.0603	5.23	5.23
0.0904	5.14	5.14
0.1205	5.01	5.08
0.211	4.71	4.96
0.422	4.22	4.80
0.512	4.06	4.76
0.753	3.69	4.54

^aRef. 51.

are known to form boric acid complexes. Boric acid is practically insoluble in most hydrocarbons and nonpolar aprotic solvents.

Dilute aqueous solutions of boric acid contain predominantly monomeric, undissociated molecules. The acidic properties of boric acid result from its Lewis acid character and propensity to accept electron donor bases, rather than a tendency to donate a proton. For the following reaction, an equilibrium constant of 5.80×10^{-10} at 25°C is reported (49):



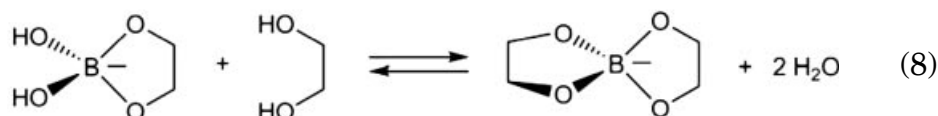
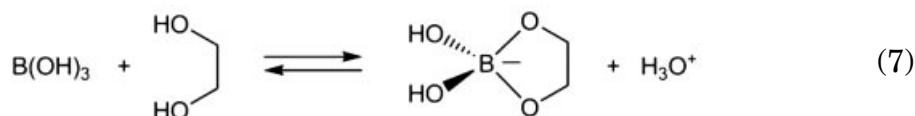
However, calculated pH values based on this constant deviate considerably from those measured as the boric acid concentration is increased, as shown in Table 9. The increased acidity has been attributed to secondary equilibria involving condensation reactions between B(OH)_3 and B(OH)_4^- , tetrahydroxyborate [15390-83-7], to produce polyborates. A trimeric species, $\text{B}_3\text{O}_3(\text{OH})_4^-$ [17927-69-4], seems to make an important contribution to these secondary equilibria (50,51).

The apparent acid strength of boric acid is increased both by strong electrolytes that modify the structure and activity of the solvent water and by reagents that form complexes with B(OH)_3 and/or polyborate anions. More than one mechanism may be operative when salts of metal ions are involved. In the presence of excess calcium chloride, the strength of boric acid becomes comparable with that of carboxylic acids, and such solutions may be titrated using a strong base to a sharp phenolphthalein end point.

Boric acid undergoes condensation reactions with alcohols to form borate esters of the type B(OR)_3 , known as orthoborate esters, and $\text{B}_3\text{O}_3(\text{OR})_3$, known as metaborate esters, as well as more complex esters. Normally, titrations of boric acid are carried out after the addition of glycerol, mannitol, or sorbitol, which form stable complexes with boric acid in a manner typical of 1,2- and 1,3-diols and polyhydroxy compounds that have appropriate configurations to form cyclic borate ester species. Equilibria of the type shown in equations 7 and 8 have been exploited in other applications besides analytical determinations of boric acid (52). For example, starch and dextrin adhesives used in corrugated boxes employ borates as a cross-linking agent (see the subsection ADHESIVES). Also, ion-exchange resins containing polyols have been developed that are highly specific for removing borates from solution (53,54), and several

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aliphatic and aromatic diols and amino-diols have been developed as extractants for borates and boric acid (55–58). In addition, the reactions given by equations 7 and 8 underlie much of the biological activity of boron. Because diols are abundantly present in biological systems and boric acid is the primary boron species present under most environmental and physiological conditions, it is not surprising that the important interactions of boron with biological systems would involve ester formation reactions of this kind (see the section “Environmental, Health, and Safety”).



In this context, it is useful to note that equations 7 and 8 are reversible, exist in rapid dynamic equilibrium, and display a strong dependence on pH.

Boric acid and fluoride ion react to form a series of fluoborates where OH^- is displaced by F^- . The stepwise formation of fluorotrihydroxyborate, BF(OH)_3^- [32554-53-3], difluorodihydroxyborate, [32554-52-2], and trifluorotrihydroxyborate, $\text{BF}_3(\text{OH})^-$ [18953-00-9] ions proceeds rapidly in acidic solutions, but tetrafluoroborate, BF_4^- [14874-70-5], forms more slowly (59). Other fluorosubstituted polyborates, including $\text{B}_3\text{O}_3\text{F}_6^{3-}$ [59753-06-9], also have been identified (50).

A wide variety of borate salts and complexes can be prepared by reactions of boric acid with inorganic bases, amines, metal cations, and oxoanions (31,60). Fusion of boric acid with metal oxides yields crystalline anhydrous metal borates or metal borate glasses.

6. Solutions of Boric Acid and Borates

6.1. Polyborates and pH Behavior. Although boric acid is essentially monomeric in dilute aqueous solutions, polymeric species may form at concentrations above ~ 0.1 mol. The conjugate base of boric acid in aqueous systems is the tetrahydroxyborate anion, B(OH)_4^- [15390-83-7]. This is also the principal anion in solutions of metal borates known as metaborates, such as sodium metaborate, $\text{NaB(OH)}_4 \cdot x\text{H}_2\text{O}$. A distinguishing feature of metaborate compounds is the 1:1 metal oxide:boron oxide mole ratio in their resolved oxide formulas. For example, the formula for sodium metaborate can be written as $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (61).

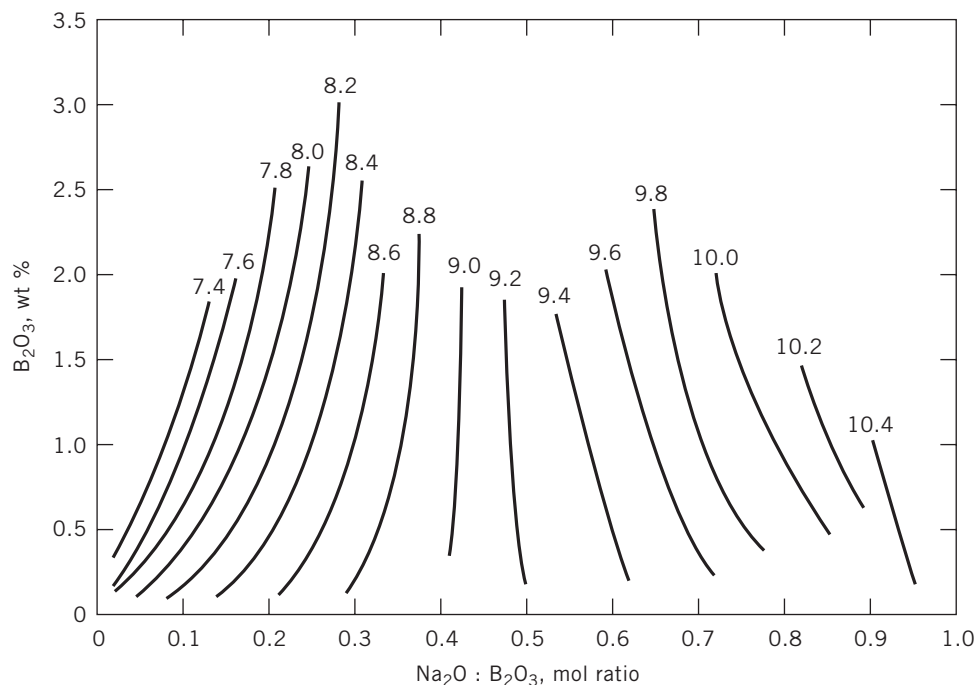


Fig. 2. Values of pH in the system at 25°C (62).

Mixtures of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ form classical buffer systems in which the solution pH is governed primarily by the acid:conjugate base ratio (ie, $[\text{H}^+] = K_a[\text{B}(\text{OH})_3]/[\text{B}(\text{OH})_4^-]$). This relationship is nearly correct for solutions of sodium and potassium tetraborates (eg, borax) in which the ratio $[\text{B}(\text{OH})_3] : [\text{B}(\text{OH})_4^-] = 1$, and in this case, the pH of their solutions remains close to 9 over a wide range of concentrations. However, for solutions with pH values much greater or less than 9, dilution has a marked effect on pH, as shown in Figure 2 (62).

This anomalous pH behavior results from the presence of polyborates, which dissociate into $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ as the solutions are diluted. Below a pH value of about 9, the solution pH increases after dilution, and the inverse is true above pH 9. This outcome is probably a result of the combined effects of a shift in the equilibrium concentration of polymeric and monomeric species and their relative acidities. At a $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ mole ratio equal to 0.41 at pH 8.91, or a $\text{K}_2\text{O}:\text{B}_2\text{O}_3$ mole ratio equal to 0.405 at pH 9, the pH is independent of concentration. These ratios and the pH values associated with them are the isohydric points of these borate solutions.

The presence of metal salts, particularly those containing alkaline earth cations, and/or halides, produces some shifts in polyborate equilibria. This finding may result from direct interaction with the boron-oxygen species or from changes in the activity of solvent water (63).

6.2. Solubility Trends. The formation of polyborates greatly enhances the mutual solubilities of boric acid and alkali borates. Solubility isotherms in

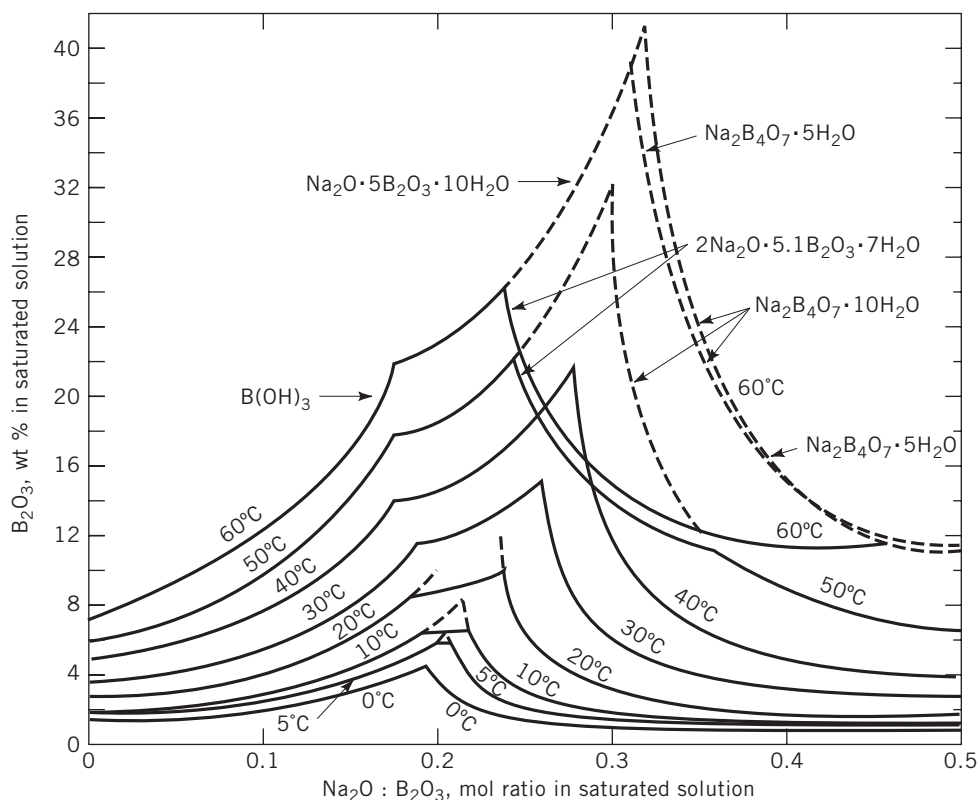


Fig. 3. Solubility isotherms for the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at $0-60^\circ\text{C}$. The compound $2\text{Na}_2\text{O}\cdot 5.1\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ (Suhr's borate or synthetic ezcurrite) usually does not appear because it crystallizes slowly in the absence of seed.

the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system are shown in Figure 3. When borax decahydrate, $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$, is added to a saturated boric acid solution, or when boric acid is added to a saturated borax solution, the B_2O_3 weight percent of the solution greatly increases. Condensation reactions decrease the concentrations of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ in equilibrium with the solid phases, thus permitting more borax or boric acid to dissolve.

Sodium borate solutions near the $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ maximum solubility ratio ($\text{B}/\text{Na} = 4$), can be spray dried to form an amorphous product with the approximate composition $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$, which is commonly referred to as disodium octaborate tetrahydrate (64). This material dissolves rapidly in water without a decrease in temperature to form supersaturated solutions. Such solutions have found many applications, including as a micronutrient fertilizer concentrate and as a treatment for wood and other cellulosic materials to impart decay and fire-resistant properties (see subsections "Agriculture" "Biocides" and "Fire Retardants").

6.3. The Polyborate Species. Rigorous pH and colligative property studies resulted in the calculation of a series of equilibrium constants

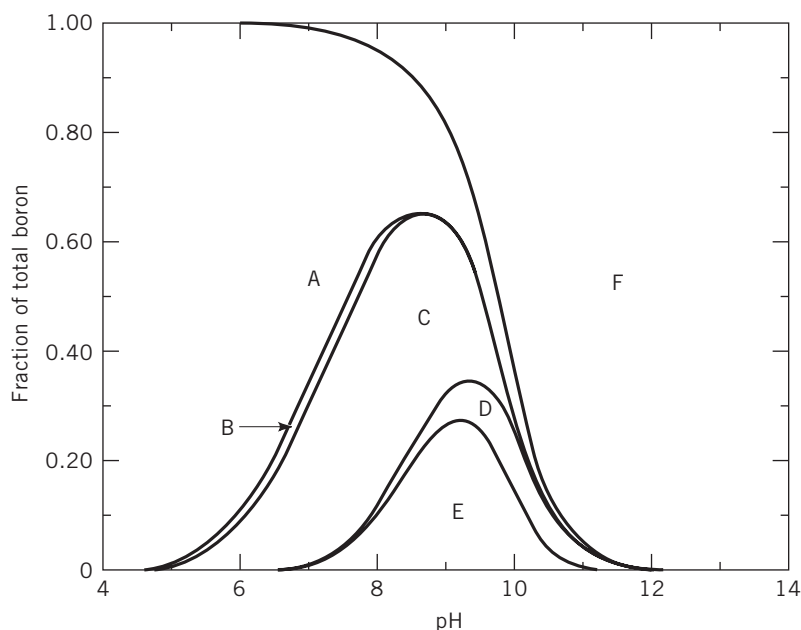
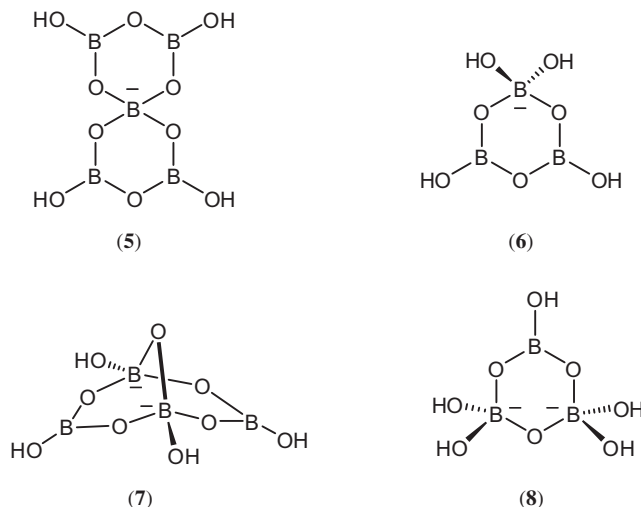


Fig. 4. Distribution of boron in (a), $B(OH)_3$; (b), $B_5O_6(OH)_4^-$; (c), $B_3O_3(OH)_4^-$; (d), $B_3O_3(OH)_5^{2-}$; (e), $B_4O_5(OH)_4^{2-}$; (f), $B(OH)_4^-$ where the total B_2O_3 concentration is 13.93 g/L. At a given pH, the fraction of the total boron in a given ion is represented by the portion of a vertical line falling within the corresponding range (65).

involving the species $B(OH)_3$, $B(OH)_4^-$, and the polyanions $B_3O_3(OH)_5^{2-}$ [12344-78-4], $B_3O_3(OH)_4^-$ [12344-77-3], $B_5O_6(OH)_4^-$ [12343-58-7], and $B_4O_5B(OH)_4^{2-}$ [12344-83-1] (65). The relative populations of these species as functions of pH are shown in Figure 4. It is clear that polyborate species containing three, four, and five boron atoms are present in significant concentrations at intermediate pH values. The ratio between the total anionic charge and the number of boron atoms per ion increases with increasing pH.

The polyanions occurring in solution all have known structural analogues in crystalline metal and nonmetal borates. Investigations by Raman (66) on ^{11}B nuclear magnetic resonance (NMR) spectroscopy (67) of borate solutions have confirmed the presence of the pentaborate monoanion, $B_5O_6B(OH)_4^-$ (5); triborate monoanion, $B_3O_3(OH)_4^-$ (6); and tetraborate dianion, $B_4O_5(OH)_4^{2-}$ (7), and the presence of the triborate $B_3O_3(OH)_5^{2-}$ (8) can be inferred. Solution structures of these anions are assigned based on similarities between the solution spectra and those of solid borates for which definitive structural data are available (50). Related polyborate structures have been postulated to be present in alkali metal borate glasses as well (see the section "Borates in Glass"). Rapid equilibrium exists among $B(OH)_3$, $B(OH)_4^-$, and the various polyborate species in aqueous solutions, with population distributions dependent on pH, concentration, and temperature.



The polyborate anions occurring in aqueous solution are formed by formal condensation of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ species according to the reaction $2\text{B}-\text{OH} \rightarrow \text{B}-\text{O}-\text{B} + \text{H}_2\text{O}$. These same anions, found in solid-state mineral and crystalline synthetic borates, provide the basis for numerous additional borate structures formed by continued condensation of these fundamental building blocks (FBBs). These additional structures are constructed from BO_3 and BO_4 groups that share oxygen atoms, with variable numbers of residual terminal $\text{B}-\text{OH}$ groups, forming generally anionic finite chains, rings, and cages as well as infinite chains, sheets, and networks. The relative rigidity of the $\text{B}-\text{O}-\text{B}$ angle results in an abundance of six-membered B_3O_3 rings, as shown in 5–8. In many cases, extended borate chains, sheets, and networks are constructed from conjoined six-membered rings. The hierarchy of FBBs occurring in borate minerals has been reviewed, and many analogies exist with synthetic borate structures (11).

Solid-state borates containing $\text{B}-\text{OH}$ groups are considered “hydrated” even if interstitial water molecules are not present in their structures because these borates eliminate water upon heating through the condensation of $\text{B}-\text{OH}$ groups. As noted in the “Nomenclature” section, all $\text{B}-\text{OH}$ groups present as borate compounds are factored out as water in both the semiempirical and resolved oxide formulas of these compounds. Analytically, hydroxy hydration often can be distinguished from interstitial water by the higher temperatures usually required for $\text{B}-\text{OH}$ condensation compared with the release of interstitial water.

It can be noted that structural characteristics of borates generally correlate with the ambient solution conditions under which they form, with higher temperatures and concentrations and longer reaction times usually correlating with lower degrees of hydration and higher degrees of condensation. A progression toward more highly condensed borate structures leads from finite anions to infinite anionic chains, then to sheets, and finally, to network structures (11). Borates based on finite anions and finite chains, sheets, and networks are termed neso-, ino-, phyllo-, and tectoborates, respectively. However, upon dissolution in aqueous media, these more complex solid-state borate structures hydrolyze and

revert back to either $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ at low concentrations or to the fundamental polyborate species found in aqueous solutions (5–8) at higher concentrations, with population distributions dependent on pH, concentration, and temperature.

7. Sodium Borates

7.1. Borax Decahydrate. The substance commonly referred to as borax decahydrate has the structural formula $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$ (formula wt 381.37, monoclinic, sp gr, 1.71) and the corresponding oxide formula $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ (68,69). The formula for this compound also is often presented as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and these latter formulas provide the basis for the name borax “decahydrate.” This substance occurs in nature as the mineral tincal, which is also known as native borax. Borax decahydrate has a specific heat of 1.611 kJ/(kg K) at 25–50°C and a heat of formation of –6.2643 MJ/mol (70). Its crystal habit, nucleation, and growth rate are sensitive to inorganic and surface active organic modifiers (71).

The solubility-temperature curves for the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system are given in Figure 5 and Table 10. The solubility curves of the penta- and deca-hydrates intersect at 60.6–60.8°C, indicating that the decahydrate, when added to a saturated solution above this temperature, dissolves with crystallization of the pentahydrate and that the reverse occurs below this temperature. This transition temperature may be lowered by the presence of inorganic salts (eg, 49.3°C in solutions saturated with sodium sulfate and 39.6°C with sodium chloride). The heats of solution for borax have been determined (72).

The pH of aqueous borax solutions increases slightly with an increasing concentration, as shown in Table 11, and drops slightly with increasing temperature. The vapor pressures of saturated borax solutions at various temperatures are given in Table 12 (72–76), and values for the specific heats of solution as a function of weight percent borax decahydrate are given in Table 13 (72).

If borax decahydrate has been previously warmed to 50°C, it dehydrates reversibly to the pentahydrate. The equilibrium vapor pressure for this transition at various temperatures is 15°C, 0.933 kPa (7.0 mm Hg); 19.8°C, 1.33 kPa (10.0 mm Hg); 25°C, 1.87 kPa (14.0 mm Hg); and 59°C, 17.7 kPa (133.0 mm Hg) (75,76). If the decahydrate has not been warmed above 50°C, then it develops a vapor pressure of only 0.213 kPa (1.6 mm Hg) at 20°C. In this case, when placed over the drying agent P_2O_5 , it does not form crystalline borax pentahydrate but instead gradually decomposes to form an amorphous product with an approximate composition of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 2.4\text{H}_2\text{O}$.

The heat of dehydration per mole of water vapor liberated for conversion of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is 54.149 kJ, and for conversion $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ is 54,074 kJ (75). Borax decahydrate stored over a saturated sucrose–sodium chloride solution maintains exactly 10 moles of water and thus can be used as an analytical standard. Commercial borax tends to lose water if stored at higher temperatures or in dry air.

Single-crystal x-ray diffraction studies show that borax decahydrate contains the tetraborate anion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ (7), with the sodium cations

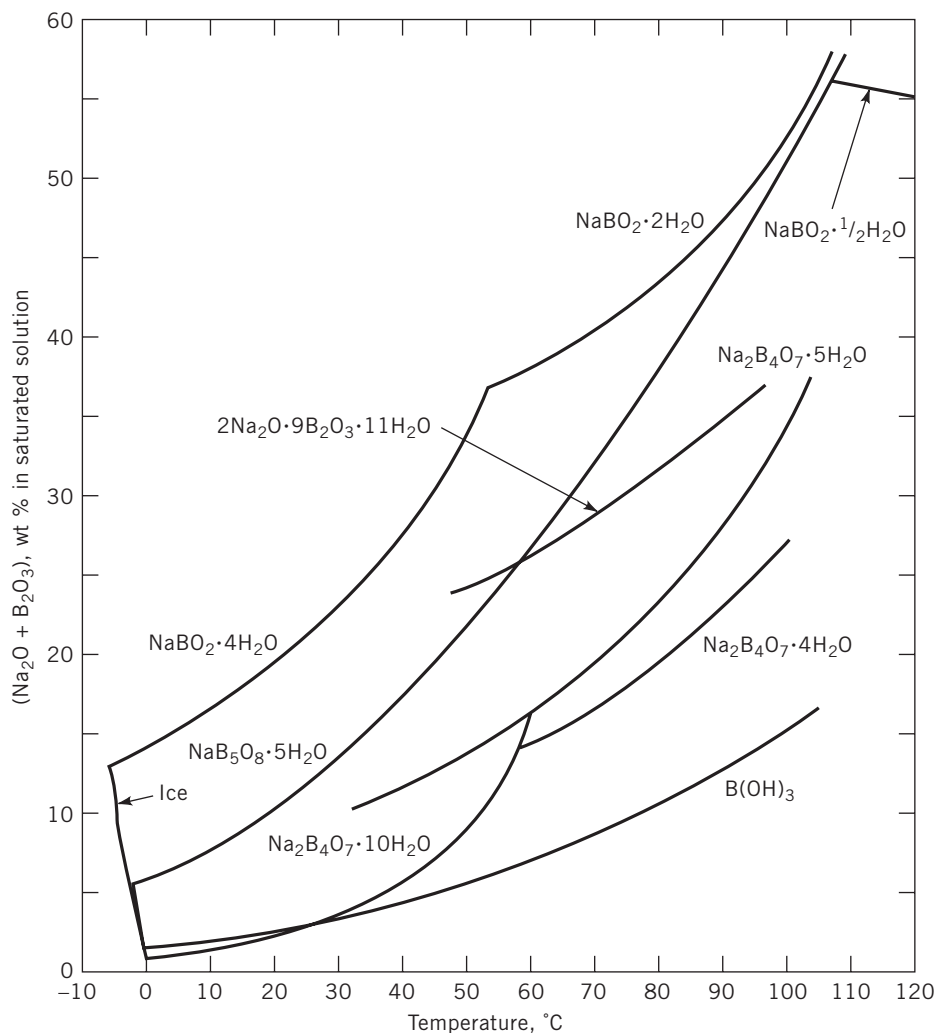


Fig. 5. Solubility-temperature curves for boric acid, borax, sodium pentaborate, and sodium metaborate (73). Courtesy of The American Chemical Society.

occupying two unique crystallographic sites and eight surrounding water molecules. The additional two moles of water making up the “decahydrate” composition exist as hydroxyl groups associated with the tetraborate anion. The structural formula is best represented as $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$ (68,69). The same tetraborate anion exists in borax pentahydrate, explaining the ready interconversion between the penta- and decahydrates (77). Slow dehydration of borax decahydrate results in the loss of 8 moles of water between 50°C and 150°C .

Rapid heating of either borax decahydrate or pentahydrate causes the crystals to begin to melt before substantial dehydration has occurred, resulting in puffing. At about 140°C , puffing occurs from rapid vaporization of water to form particles with as much as 90% void volume and low bulk densities (78). Puffed borax has been manufactured and sold as a commercial product.

Table 10. Aqueous Solubilities of Alkali Metal and Ammonium Borates at Various Temperatures

Compound	CAS Registry Number	Solubility, wt % anhydrous components, at °C											
		0	10	20	25	30	40	50	60	70	80	90	100
LiB ₅ O ₈ ·5H ₂ O ^a	[37190-10-6]							20.88	24.34	27.98	31.79	36.2	41.2
Li ₂ B ₄ O ₇ ·4H ₂ O	[39291-91-3]	2.2-2.5	2.55	2.81	2.90	3.01	3.26	3.50	3.76	4.08	4.35	4.75	5.17
LiBO ₂ ·8H ₂ O ^b	[41851-38-1]	0.88	1.42	2.51	3.34	4.63	9.40						
LiBO ₂ ·2H ₂ O	[15293-74-0]						7.40	7.84	8.43	9.43	10.58	11.8	13.4
NaB ₅ O ₈ ·5H ₂ O	[12046-75-2]	5.77	7.90	10.55	12.20	13.72	17.50	21.72	26.88	32.25	38.1	44.3	51.0
Na ₂ B ₄ O ₇ ·10H ₂ O	[1303-96-4]	1.18	1.76	2.58	3.13	3.85	6.00	9.55	15.90				
Na ₂ B ₄ O ₇ ·4.67H ₂ O ^d	[12045-88-4]								16.40	19.49	23.38	28.37	34.63
Na ₂ B ₄ O ₇ ·4H ₂ O ^e	[12045-87-3]								14.82	17.12	19.88	23.31	28.22
NaBO ₂ ·4H ₂ O ^f	[10555-76-7]	14.5	17.0	20.0	21.7	23.6	27.9	34.1					
NaBO ₂ ·2H ₂ O	[16800-11-6]								14.82	17.12	19.88	23.31	28.22
KB ₅ O ₈ ·4H ₂ O	[12229-13-9]	1.56	2.11	2.82	3.28	3.80	5.12	6.88	9.05	11.7	14.7	18.3	22.3
K ₂ B ₄ O ₇ ·4H ₂ O	[12045-78-2]		9.02	12.1	13.6	15.6	19.4	24.0	28.4	33.3	38.2	43.2	48.4
K ₂ B ₁₀ O ₁₇ ·5H ₂ O ^g	[27516-44-5]		42.3	43.0	43.3	44.0	45.0	46.1	47.2	48.2	49.3	50.3	
RbB ₅ O ₈ ·4H ₂ O	[37190-12-8]	1.58	2.0	2.67	3.10	3.58	4.82	6.52	8.69	11.4	14.3	18.1	23.75 ^h
CsB ₅ O ₈ ·4H ₂ O ⁱ	[12229-10-6]	1.6	1.85	2.5	2.97	3.52	4.8	6.4	8.31	10.5	13.8	18.0	23.45 ^j
(NH ₄) ₂ B ₄ O ₇ ·4H ₂ O	[10135-84-9]	3.75	5.26	7.63	9.00	10.8	15.8	21.2	27.2	34.4	43.1	52.7	
(NH ₄)B ₅ O ₈ ·4H ₂ O	[12229-12-8]	4.00	5.38	7.07	8.03	9.10	11.4	14.4	18.2	22.4	26.4	30.3	

^aIncongruent solubility below 37.5 or 40.5°C.

^bTransition point to tetrahydrate, 36.9 or 40°C.

^cAt 101.2°C.

^dCommonly known as the pentahydrate (74), transition point to decahydrate, 60.7°C, 16.6% Na₂B₄O₇.

^eTransition point to decahydrate, 58.2°C, 14.55% Na₂B₄O₇.

^fTransition point to tetrahydrate, 53.6°C, 36.9% Na₂B₂O₄.

^gKnown as Auger's potassium borate (72).

^hAt 102°C.

ⁱCesium tetraborate pentahydrate, Cs₂B₄O₇·5H₂O [12228-83-0], and cesium diborate heptahydrate, Cs₂B₂O₄·7H₂O [66634-85-3], also exist. The former has incongruent solubility; the latter has a solubility of 36.8 wt % anhydrous salt at 18°C.

^jAt 101.65°C.

26 BORON OXIDES, BORIC ACID, AND BORATES

Table 11. pH Values of Aqueous Borate Solutions

Compound	Concentration, wt %						
	0.1	0.5	1.0	2.0	4.0	10.0	15.0
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}^a$	9.2	9.2	9.2	9.2	9.3		
$\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$			8.5	8.5	8.1	7.6	7.3
$\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$			8.5	8.4	8.1	7.6	7.3
$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	10.5	10.8	11.0	11.2	11.4	11.8	11.9
$\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$	10.6	10.9	11.1	11.3	11.5	11.8	12.0
$\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	9.2	9.1	9.1	9.2	9.3		
$\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$		8.4	8.4	8.3	7.9	7.6	
$\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$	8.5	8.4	8.3	8.2	7.8	7.3	

^aSaturated solution, 4.71 wt %.

Table 12. Vapor Pressures of Saturated Aqueous Borax Solutions versus Temperature

Temperature, °C	Pressure, kPa
57.94	17.25
57.99	17.33
58.23	17.51
58.56	17.74
58.82	17.94
58.91	18.05
59.42	18.42

7.2. Borax Pentahydrate. Borax pentahydrate typically is denoted by the semiempirical formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ or by an resolved oxide formula of $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (formula wt 291.30, trigonal, sp gr 1.880 [measured], 1.894 [crystallographic], specific heat 1.32 kJ/kg K (13), and heat of formation -4.7844 MJ/mol (70)). Single crystal x-ray diffraction studies show that borax pentahydrate has a structural formula of $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2.67\text{H}_2\text{O}$ (formula wt 285.35). Like borax decahydrate, this compound contains the tetraborate anion (7) and two sodium cations but has a different number of interstitial water molecules. These water molecules occupy three unique crystallographic sites where

Table 13. Specific Heat Values for Aqueous Borax Solutions

Borax decahydrate, wt %	Specific heat, kJ/(kg K)
1.9	4.13
4.7	4.08
7.2	4.04
9.5	3.99
19.0	3.84
22.8	3.78
26.6	3.71
30.4	3.65
38.0	3.52
45.6	3.57
55.1	3.68

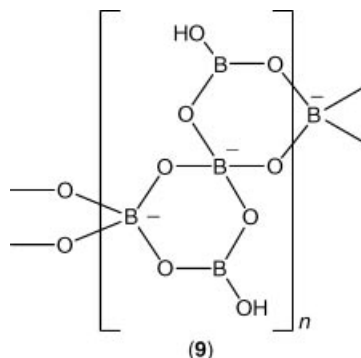
one site is not fully occupied. The name borax “pentahydrate” is based on rounding up the composition found crystallographically— $\text{Na}_2\text{B}_4\text{O}_5 \cdot 4.67\text{H}_2\text{O}$, to $\text{Na}_2\text{B}_4\text{O}_5 \cdot 5\text{H}_2\text{O}$ (74). Crystals of this compound may contain slightly different amounts of water depending on ambient humidity conditions. Borax pentahydrate is found in nature as the fine-grained mineral tincalconite, which forms by dehydration of tincal (native borax).

Solubility data in water are given in Figure 5 and Table 10, the solution pH values are shown in Table 11, and the solubility in organic solvents is shown in Table 8. The heats of solution in water have been determined (13,73). In contact with its aqueous solution, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is metastable with respect to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ (kernite) at temperatures above 58.2°C and is metastable with respect to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ below $60.6\text{--}60.8^\circ\text{C}$. Kernite can be slowly crystallized from a nearly saturate solution heated close to the boiling point for several days.

Borax pentahydrate is converted reversibly to an amorphous dihydrate at 88°C and 0.26 kPa (2 mmHg) or by boiling with xylene (73,76). The heat of dehydration for conversion of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ to $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ has been calculated at 53.697 kJ per mole of water (75). Thermogravimetric analyses show that 2.75 mol of water are lost after heating to 140°C . Like borax decahydrate, rapid heating of borax pentahydrate also yields a product that has a low bulk density of about 0.042 g/mL (79).

7.3. Kernite. Kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, is an important industrial mineral that is used in the large-scale manufacture of boric acid. It has the structural formula $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (formula wt 273.28, monoclinic, sp gr, 1.908, specific heat ca 1.2 kJ/kgK (62), and heat of formation -4.4890 MJ/mol (70)). Kernite is best known as a mineral but also can be prepared synthetically. Its crystals have two cleavage planes and when broken form long splinters.

The corresponding oxide formula for kernite is $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, making it seem to be a lower hydrate of borax. However, kernite is structurally different from borax penta- and decahydrate. The structure of kernite consists of parallel infinite chains of polymeric anions, $[\text{B}_4\text{O}_6(\text{OH})_2]_n^{2n-}$ (9), comprising six-membered rings that share tetrahedral boron centers (80,81). Two sodium cations and three water molecules are associated with each repeating unit to give the structural formula $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. The polymeric nature of the borate anion in kernite is consistent with its slow rates of dissolution and crystallization.



The water solubility of kernite is given in Figure 5 and Table 10. Kernite is the stable phase in contact with its solution from 58.2°C up to about 95°C (73). Its rate of crystallization is, however, much slower than that of the borax pentahydrate. Large kernite crystals can be grown slowly by seeding saturated borax solutions.

At relative humidities above 70%, kernite absorbs water irreversibly to form borax. Kernite loses water slowly when stored over P₂O₅ under vacuum or upon heating at 100–120°C to form a crystalline dihydrate known as metakernite, which reverts to kernite at 60% relative humidity (75).

7.4. Anhydrous Borax. Sodium tetraborate, Na₂B₄O₇ or Na₂O·2B₂O₃ (formula wt 201.22, sp gr 2.367[glass], 2.27 [α -crystalline form], and heat of formation –3.2566 MJ/mol [glass], –3.2767 MJ/mol [α -crystalline form] (16)), exists in several crystalline forms as well as a glassy form (72). As an industrial article of commerce, anhydrous borax is always found in its glassy or vitreous form. Crystalline forms of anhydrous borax primarily are known as laboratory-scale samples prepared for research purposes. The most common α -crystalline form, which melts congruently at 742.5°C, is obtained by dehydrating borax hydrates and is the stable form above 600–700°C (72). Extensive heat capacity data has been reported (16,82–84). Anhydrous borax glass dissolves in water more slowly than the hydrated forms but with substantial heat release. Heats of solution have been measured, and a value of –213.8 kJ/kg has been reported (70). The solubility of finely divided crystalline disodium tetraborate at 25°C, expressed as weight percent, is 16.7% in methanol, 30% in ethylene glycol, and 40.6 g/L in formamide (62).

Crystalline anhydrous borax takes up some water from moist air even at 300°C. It becomes anhydrous near 700°C and melts at 742.5°C. The heat of hydration to borax has been calculated at –161 kJ/mol of (72,85). The heat of fusion is reported to be 81.2 kJ/mol (16). A single-crystal, x-ray diffraction study indicates that the borate anion in anhydrous borax is polymeric and is formed via oxygen bridging of triborate and pentaborate groups (86). The chemistry of anhydrous borax has been reviewed (2,72).

As an article of commerce, anhydrous borax is always found as a vitreous material that is sold as granular or powder products. These products generally contain about 1% of water resulting from the absorption of moisture from the atmosphere. This water primarily takes the form of a thin layer of borax decahydrate on the surface of the particles.

7.5. Disodium Octaborate Tetrahydrate. The composition of a commercially available synthetic sodium borate known as disodium octaborate tetrahydrate corresponds closely with Na₂B₈O₁₃·4H₂O or Na₂O·4B₂O₃·4H₂O and contains 66.3 wt % B₂O₃ (64). This composition is amorphous and is prepared by spray drying a solution of this composition. It is a white powder that dissolves rapidly in water without the temperature decrease that occurs when hydrated or hydroxy-hydrated crystalline borates dissolve. It readily forms supersaturated solutions when hot concentrated solutions are cooled to room temperature. Solutions of disodium octaborate are slightly alkaline with the pH decreasing as the concentration increases, as shown in Table 11. The solubility of this composition compared with that of borax is shown in Table 14.

Table 14. Solubilities of Aqueous Borate Solutions.

Temperature, °C	Solubility, disodium octaborate tetrahydrate, wt %	B ₂ O ₃ concentration in saturated solution, wt %	
		Disodium octaborate tetrahydrate	Borax
0	2.4	1.6	0.7
10	4.5	3.0	1.1
20	9.5	6.3	1.7
30	21.9	14.5	2.6
40	27.8	18.4	4.1
50	32.0	21.2	6.5
60	35.0	23.2	11.1
75	39.3	26.0	14.7
94	45.3	30.0	21.0

7.6. Sodium Pentaborate. The common form of sodium pentaborate hydrate has the structural formula $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (formula wt 295.12 (87)). This corresponds to the oxide formula $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$. The formula is also written as $\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$. Consequently, this compound sometimes is referred to as “sodium pentaborate pentahydrate.” The compound exhibits monoclinic crystals with sp gr, 1.713. It exists in nature as the mineral sborgite [12272-01-4]. Heat capacity, entropy, and other thermal measurements have been made for this compound in the 15–345 K temperature range (88).

Sodium pentaborate can be easily crystallized from a solution that has a $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ mol ratio of 0.2. Its water solubility (Fig. 5 and Table 10) substantially exceeds that of borax and boric acid. Its pH decreases with the solution concentration (Table 11). It is stable in contact with its own solution between 2°C and 59.5°C. When a saturated pentaborate solution is agitated for some time at temperatures near boiling, the compound $2\text{Na}_2\text{O} \cdot 9\text{B}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$, also known as Taylor’s borate (sp gr, 1.903), crystallizes slowly if seed is present. Pentaborate pentahydrate, which is metastable to Taylor’s borate at higher temperatures, readily forms supersaturated solutions and crystallizes as the kinetic product. In the absence of seed crystals, however, the stable phase above 106°C shifts to pentaborates of lower hydration (72). Crystalline sodium pentaborate pentahydrate is stable in the atmosphere. When heated under vacuum, it is stable up to 75°C; however, above this temperature, it loses 4 mol of water (72).

7.7. Sodium Metaborates. Two common hydrated sodium metaborates have structural formulas of $\text{NaB}(\text{OH})_4$ and $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (89,90). These correspond with the oxide formulas $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, respectively. Consequently, these compounds are commonly referred to as articles of commerce as “sodium metaborate tetrahydrate” and “sodium metaborate octahydrate.” Adding to the confusion, formulas for these compounds also are frequently written as $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ and are referred to as the “dihydrate” and “tetrahydrate,” respectively. The higher hydrate $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (formula wt 137.86, triclinic; sp gr 1.743) is easily formed by cooling a solution containing borax and an amount of sodium hydroxide just in excess of the theoretical value. It is the stable phase in contact with its saturated solution between 11.5°C and 53.6°C. At temperatures above 53.6°C, the lower

hydrate, NaB(OH)_4 (formula wt 101.83, triclinic, sp gr, 1.909) becomes the stable phase. The lower hydrate of sodium metaborate can be prepared by heating a slurry of the higher hydrate above 54°C , by crystallizing from metaborate solutions at $54\text{--}80^\circ\text{C}$ or by dehydrating the higher hydrate under vacuum. Large crystals can be grown by heating the solid in its mother liquor for several days. The lower hydrate is the stable phase in contact with its saturated solution between 53.6°C and 105°C . At higher temperatures, an unusual sodium triborate is formed with the structural formula $\text{Na}_3\text{B}_3\text{O}_5(\text{OH})_2$ ($\text{NaBO}_2 \cdot 0.33\text{H}_2\text{O}$) (91). This compound has been described in the literature as sodium metaborate hemihydrate and is referred to by the formula $\text{NaBO}_2 \cdot 0.5\text{H}_2\text{O}$ (72). The water solubility of sodium metaborate is given in Figure 5 and in Table 10, and pH values as a function of concentration are given in Table 11.

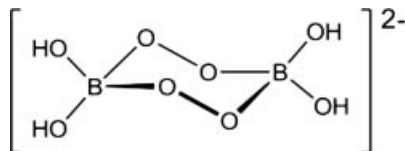
Heat capacity data for metaborate solutions have been reported (92). The solubility of $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O}$ in methanol at 40°C is 26.4 wt % (62). The solubility of NaB(OH)_4 in ethanol is 0.3 wt % at boiling, and in methanol is 17.8% at 22°C , is 19.5% at 40°C , and is 24.6% at 60°C (62).

The relative humidity over a saturated solution of $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O}$ at $14\text{--}24^\circ\text{C}$ is $90 \pm 1\%$, and the humidity of mixtures of the two hydrates is 42% at 22°C , is 43% at 24.8°C , is 45% at 27.0 , and is 39% at 91.3°C (93). Crystals of $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O}$ melt in the released water of crystallization at about 54°C . The thermogravimetric analysis shows that this compound loses ca 6% of its water at 130°C , 25% at 140°C , 38% at 280°C , and all of its water upon heating to 800°C (94).

The heat of dehydration of the lower hydrate, $\text{NaB(OH)}_4 = \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, has been calculated at 58.1 kJ/mol of H_2O (93). Its melting point is $90\text{--}95^\circ\text{C}$, compared with 54°C for the higher hydrate, $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O} = \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. The heat of hydration for conversion of the lower hydrate to higher hydrate has been calculated at 52.51 kJ per mole of water (93). Both sodium metaborates absorb CO_2 from the atmosphere, slowly forming borax and sodium carbonate.

Sodium metaborates are used as reagents in textile sizing and finishing and in adhesives and cleaning products. They also are used in photographic solutions. The lower hydrate, NaB(OH)_4 , known as an article of commerce as sodium metaborate tetrahydrate, is more thermally stable and less prone to caking than the higher hydrate, $\text{NaB(OH)}_4 \cdot 2\text{H}_2\text{O}$, which is known as sodium metaborate octahydrate according to its oxide formula.

7.8. Sodium Perborates. Peroxyborate compounds commonly are known as perborates, with formulas written as if the perborate anion were BO_3^- . However, x-ray crystal structures show that they contain the dimeric anion $(\text{HO})_2\text{B}(\text{O}_2)_2\text{B}(\text{OH})_2^{2-}$ (10) (95). Three sodium perborate hydrates are known. Only the so-called mono- and tetra-hydrates, referred to as PBS-1 and PBS-4, are used commercially as bleaching agents in consumer products and other oxidative processes.



(10)

The sodium perborate hydrate $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (PBS-4), or $\text{Na}_2[(\text{HO})_2\text{B}(\text{O}_2)_2 \cdot \text{B}(\text{OH})_2] \cdot 6\text{H}_2\text{O}$, is triclinic, with a heat of formation of -2112 kJ/mol (crystal) and -921 kJ/mol (1 M soln). It contains 10.4 wt % active oxygen and melts at 63°C by dissolving in its own water of hydration. Upon heating to 250°C , it decomposes rapidly and completely to oxygen and sodium metaborate. Its decomposition in water, which is important in its use as a bleach, is accelerated by catalysts or elevated temperature. Typical solutions at room temperature are unstable and lose active oxygen unless a stabilizer is present. The rate of decomposition increases with decreasing pH. The solubility in water is 2.5 wt % at 20°C and 3.6 wt % at 29°C (96). The solubility is enhanced by certain polyhydroxy compounds that form complexes with borates, such as tartaric acid, citric acid, mannitol, glycerol, and most significantly, alkali polyphosphates. Dilute solutions contain the monoperoxyborate anion, $(\text{HO})_3\text{BOOH}^-$. More concentrated solutions contain this anion plus $(\text{HO})_2\text{B}(\text{OOH})_2^-$, $(\text{HO})\text{B}(\text{OOH})_3^-$ and $\text{B}(\text{OOH})_4^-$, and polyperoxyborate anions (97,98). These species act as oxidizing agents similar to hydrogen peroxide but have been shown to be more selective. Sodium perborates can be used as convenient and versatile oxidizing agents for organic syntheses (99).

Commercial production of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ is achieved with the reaction of a sodium metaborate solution, prepared from sodium hydroxide and borax pentahydrate, with hydrogen peroxide followed by crystallization (100–103). The other hydrates can be formed by reversible dehydration of the tetrahydrate.

The sodium perborate hydrate, $\text{NaBO}_3 \cdot 3\text{H}_2\text{O}$, or $\text{Na}_2[(\text{HO})_2\text{B}(\text{O}_2)_2 \cdot \text{B}(\text{OH})_2] \cdot 4\text{H}_2\text{O}$, is triclinic and contains 11.8 wt % active oxygen (104). It is thought to have better thermal stability than $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ but has not been used commercially. This hydrate can be made by the dehydration of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ or by crystallization from a sodium metaborate and hydrogen peroxide solution in the presence of seed crystals. Between 18°C and 50°C , this hydrate is more stable but slower to crystallize than the higher hydrate. Below 15°C , $\text{NaBO}_3 \cdot 3\text{H}_2\text{O}$ spontaneously converts to $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$.

The sodium perborate $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ (PBS-1), or $\text{Na}_2[(\text{HO})_2\text{B}(\text{O}_2)_2\text{B}(\text{OH})_2]$ contains 16.0 wt % active oxygen. It is prepared commercially by dehydration of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$. This compound also contains the same peroxyborate anion (10) as the higher hydrates and is the sodium salt of this anion without interstitial water. Continued dehydration results in the decomposition of the peroxyborate anion.

8. Other Alkali Metal Borates

8.1. Lithium Borates. Lithium borate hydrates have commercial importance as specialty chemicals. Lithium tetraborate $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ or $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ($d = 1.88 \text{ g/mL}$) has a structural formula of $\text{Li}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$. It crystallizes with difficulty from a supersaturated solution of lithium hydroxide and boric acid, which on standing forms a gelatinous deposit that converts to hydrate crystals after boiling for several hours. This hydrate is stable up to 180°C and then begins to lose water, becoming anhydrous at about 320°C and fusing at 890°C .

Lithium metaborate $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$ or $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ (hexagonal, $d = 1.825$ g/mL) has the structural formula $\text{LiB}(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ (105). Upon heating to 70°C , the six interstitial waters are lost. Another two waters are lost by condensation of B—OH groups between 140°C and 280°C , leaving anhydrous lithium metaborate, LiBO_2 (106). This hydrate is the stable solid phase in contact with its solution below 36.9°C . Above this temperature, a lower hydroxy hydrate, $\text{LiBO}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, becomes the stable solid phase. This lower hydrate has a structure formula of $\text{LiB}(\text{OH})_4$ (orthorhombic, $d = 1.825$ g/mL). In solution above 150°C , a hemihydrate of composition $\text{LiBO}_2 \cdot 0.5\text{H}_2\text{O}$ forms and anhydrous lithium metaborate crystallizes above 225°C .

Single crystals of anhydrous lithium borates, grown from high temperature molten salts, find use in optoelectronic devices. The crystalline lithium triborate, LiB_3O_5 , is a nonlinear optical material that is used to convert laser light frequencies. The anhydrous lithium tetraborate, $\text{Li}_2\text{B}_4\text{O}_7$, is a piezoelectric and nonlinear optical material that has been used in mobile communication devices including phones and pagers.

8.2. Potassium Tetraborate. The potassium tetraborate hydrate $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, or $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, has the structural formula $\text{K}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (formula wt, 305.50, orthorhombic; sp gr, 1.919 (107)). This compound contains the same tetraborate anion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, as found in borax (7) but is much more soluble in water than borax. Solubility data are given in Table 10 and pH as a function of concentration is given in Table 11.

Phase relationships in the system $\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ have been described, and a portion of the phase diagram is given in Figure 6. The tetrahydrate, which can be dried at 65°C without loss of water of crystallization, begins to dehydrate between 85°C and 111°C depending on the partial pressure of water vapor in the atmosphere. This conversion is reversible and has a heat of dehydration of 86.6 kJ per mole of H_2O . Thermogravimetric curves indicate that 2 moles of water are lost between 112°C and 140°C , 1 mole is lost between 200°C and 230°C , and the last mole of water is lost between 250°C and 290°C (108).

8.3. Potassium Pentaborate. Potassium pentaborate hydrate typically is referred to by the semiempirical formula $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ or by the equivalent resolved oxide formula $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. Its structural formula is $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (109) (formula wt, 293.21, orthorhombic prisms; sp gr, 1.74, and heat capacity at 296.6 K). It contains the same $\text{B}_5\text{O}_6(\text{OH})_4^-$ anion (5) found in sodium pentaborate (87). Potassium pentaborate is much less soluble in water than sodium pentaborate (Table 10). Heat capacity measurements on the solid have been made over a wide temperature range (88). Potassium pentaborate is stable under normal storage conditions. Its heat of dehydration has been calculated at 110.8 kJ/mol between 106.5°C and 134°C (108). Its thermal stability is highly dependent on the partial pressure of atmospheric water. It is stable when heated under vacuum to 105°C and up to 170°C in an atmosphere saturated with water at 90°C .

Although potassium tetraborate and pentaborate described here are the most common commercial potassium borates, several other crystalline potassium borates exist, including a series of potassium metaborates, $\text{K}[\text{B}(\text{OH})_4] \cdot x\text{H}_2\text{O}$ and

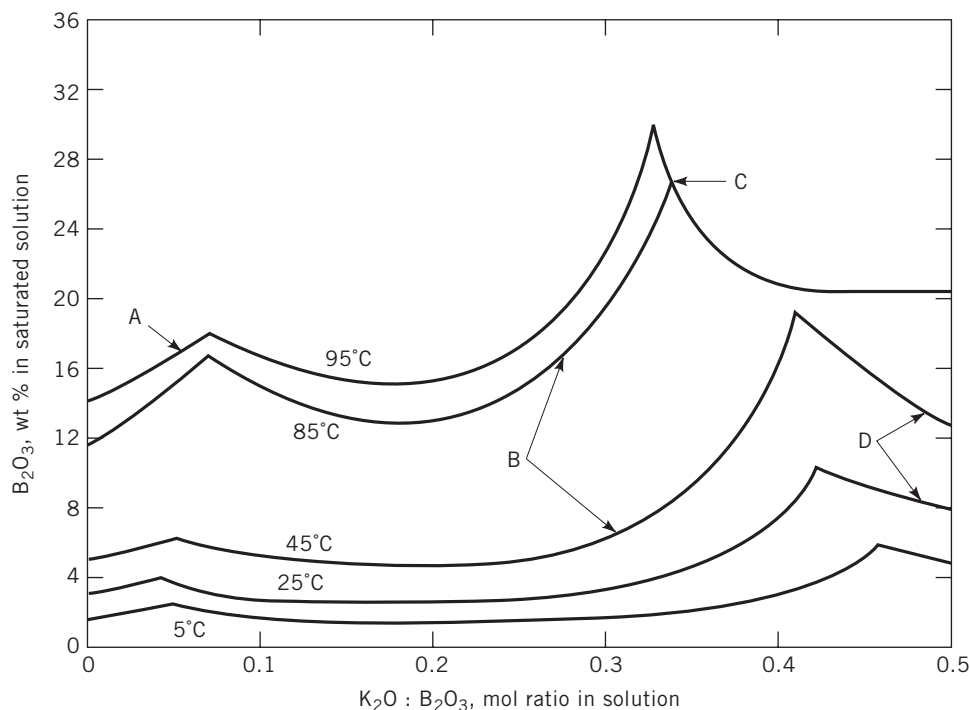


Fig. 6. Solubility isotherms for the $K_2O-B_2O_3-H_2O$ system at temperatures from $5^\circ C$ to $95^\circ C$ where A, B, C, and D represent the solid phases $B(OH)_3$, $K_2O \cdot 5B_2O_3 \cdot 8H_2O$, $2K_2O \cdot 5B_2O_3 \cdot 5H_2O$ (Auger's potassium borate) and $K_2O \cdot 2B_2O_3 \cdot 4H_2O$, respectively (113).

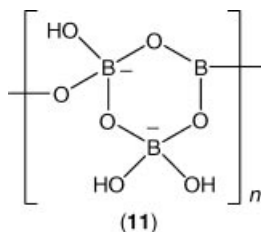
Auger's potassium borate, $2K_2O \cdot 5B_2O_3 \cdot 5H_2O$, which are featured in Figure 6 (72).

9. Calcium-Containing Borates

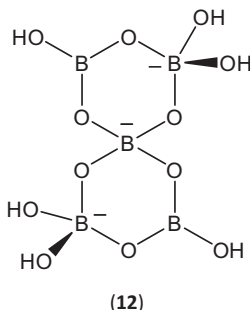
9.1. Colemanite. Colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$ or $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, is almost exclusively known as the mineral. It has the structural formula $CaB_3O_4(OH)_3 \cdot H_2O$ (formula wt, 205.55; monoclinic; sp gr, 2.42; and heat of formation, -3.469 kJ/mol (110)). Its solubility in water is about 0.10% at $25^\circ C$ and 0.38% at $100^\circ C$. Heats of solution have been determined in HCl (110). Colemanite is formed slowly when heating saturated solutions of inyoite, $CaB_3O_3(OH)_5 \cdot 4H_2O$, or other higher hydrates. Colemanite violently decrepitates at $480^\circ C$, losing all of its water and forming a low bulk density anhydrous powder (111).

The crystal structure of colemanite contains polytriborate chains (11). The structural relationships between colemanite and other minerals in the series $2CaO \cdot 3B_2O_3 \cdot nH_2O$, where $n = 1, 5, 7, 9,$ and 13 , as well as structural changes

accompanying the ferroelectric transition of colemanite, have been described (112).



9.2. Ulexite. Ulexite, $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ or $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$, is known as an article of commerce exclusively as mineral concentrates of varying levels of purity. It has a structural formula of $\text{CaNaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ (formula wt, 405.24; triclinic; sp gr, 1.95). The structure of ulexite (113) consists of isolated pentaborate trianions (12).



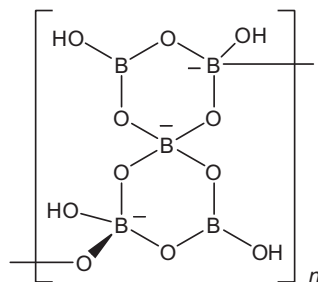
Sold in mineral and specialty shops as “TV rock,” some specimens of ulexite have fiber optic properties with a surprisingly good resolution of projected images. The fibers are aligned along the c -axis with an index of 1.529. Cladding results from a random orientation of crystals around the fiber direction, producing a core-to-cladding index difference ranging from 0 to a maximum of $\gamma - \alpha = 0.038$ (114).

Ulexite can be prepared by seeding a solution comprising 110 g of calcium metaborate, $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$, 40 g boric acid, 100 g of borax decahydrate, 450 g of CaCl_2 , and 2.5 L of water (115). Crystalline ulexite also is obtained within 24 hours by adding CaCl_2 to a solution that has a $\text{B}_2\text{O}_3:\text{Na}_2\text{O}$ mole ratio of 1:7 with a sufficient borate excess to maintain constant pH (116). Ulexite is slowly converted to probertite, $\text{NaCaB}_5\text{O}_7(\text{OH})_4 \cdot 3\text{H}_2\text{O}$, when seed is added to a moistened sample at 80–100°C. The solubility of ulexite in water at 25°C is ~0.5% as the anhydrous component NaCaB_5O_9 . Calcining at 200–500°C increases its solubility to 9–13 g/L.

When crystals of ulexite are heated slowly, dehydration begins at about 60°C and is complete by 500°C (117). Detailed dehydration studies show that the primary loss of the first 4 moles of water occurs in the 70–90°C temperature range. An additional 8 moles of water are lost between 100°C and 120°C, and

the remaining 4 moles are lost between 120°C and 400°C based on the oxide formula $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$ (118).

9.3. Probertite. Probertite, $\text{NaCaB}_5\text{O}_9\cdot 5\text{H}_2\text{O}$ or $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 10\text{H}_2\text{O}$, is known in both mineral and synthetic forms and has a structural formula of $\text{NaCaB}_5\text{O}_7(\text{OH})_4\cdot 3\text{H}_2\text{O}$ (formula wt 351.19; monoclinic; sp gr, 2.14 (119)). Probertite can be prepared by heating a mixture of two parts ulexite and one part borax to about 60°C (120) or by heating a solution of borax and calcium metaborate at 105°C for several days (75). By thermogravimetric analysis, 2 moles of water are lost at 100°C, 4 moles are lost between 100°C 180°C, and the last 4 moles are slowly lost up to 400°C. The structure of probertite contains polymeric chains of condensed pentaborate structural units (13).



(13)

Probertite is not an important commercial product but is relevant to the manufacture of sodium borates because its formation can lead to the scaling of process equipment owing to its lower solubility. As such, it provides an example of the structure–property relationships in borate chemistry.

10. Other Metal Borates

Borate compounds containing virtually every metal have been prepared. For most metals, a series of hydrated and anhydrous compounds may be obtained by varying the starting materials and/or reaction conditions. Some of these synthetic metal borates have significant commercial importance.

In general, hydrated borates of transition and posttransition metals are prepared by mixing aqueous solutions or suspensions of the metal oxides, sulfates, or halides and boric acid or alkali metal borates such as borax. The precipitates formed from basic solutions are often sparingly soluble amorphous solids with variable compositions. Crystalline products tend to form more readily from slightly acidic solutions. In some cases, the initially formed amorphous products will slowly crystallize upon standing in contact with mother liquor.

Anhydrous metal borates may be prepared by heating the hydrated compounds from 300°C to >1000°C or by the direct fusion of metal oxides with boric acid or B_2O_3 . Many binary and tertiary anhydrous systems containing vitreous phases form over certain ranges of composition and vitreous phases may convert to refractory crystalline phases upon heating beyond temperature thresholds (121–123).

10.1. Zinc Borates. Several crystalline hydrated and anhydrous zinc borates are known, a few of which find important commercial applications. Documented hydrated zinc borates include those with oxide formulas $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ (124–127), $\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\sim 1.12\text{H}_2\text{O}$ (128), $\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\sim 1.87\text{H}_2\text{O}$, $6\text{ZnO}\cdot 5\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ (129), $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ (130), $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ (126,131,132), $3\text{ZnO}\cdot 5\text{B}_2\text{O}_3\cdot 14\text{H}_2\text{O}$ (133), and $\text{ZnO}\cdot 5\text{B}_2\text{O}_3\cdot 4.5\text{H}_2\text{O}$ (129), which have $\text{B}_2\text{O}_3\text{:ZnO}$ mole ratios ranging from 0.25 to 5.0.

The use of zinc borates, particularly as fire-retardant additives, dates back at least to the 1940s (134). Early applications primarily involved $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$. However, the low dehydration onset temperature of this phase limited its usefulness. In the late 1960s, the zinc borate phase $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, with a dehydration onset of $>290^\circ\text{C}$, was discovered and commercialized (131,132). The higher thermal stability of this phase allows for use in a wide range of polymers and construction products.

Zinc borate $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ has the structural formula $\text{ZnB}_3\text{O}_3(\text{OH})_5\cdot\text{H}_2\text{O}$. It is a nesoborate containing the isolated $\text{B}_3\text{O}_4(\text{OH})_5^{2-}$ triborate anion (6) and interstitial water, which accounts for its low dehydration temperature (130). In contrast, $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ has a structural formula of $\text{ZnB}_3\text{O}_4(\text{OH})_3$. It is an ino-borate containing a polytriborate chain similar to those found in colemanite (11) interconnected by the coordination of borate oxygen atoms with Zn^{2+} cations (126). Because it contains no interstitial water, it has a high dehydration onset temperature. This has been the most widely used form of zinc borate since the 1970s. As an article of commerce, it is known as $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ or $4\text{ZnO}\cdot 6\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$, which are formulas that predate structure determination for this compound (126).

The compound $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ has a remarkably high dehydration onset temperature for a hydrated borate ($\sim 411^\circ\text{C}$). This compound was commercialized in the early 1990s as a fire-retardant synergist for polymers requiring high processing temperatures, such as polyamides. The structural formula $\text{Zn}_2(\text{BO}_3)\text{OH}$ initially proposed for this compound (126) was confirmed by a subsequent x-ray structure determination (127). Its structure consists of corrugated sheets of oxygen-sharing ZnO_3OH tetrahedra interconnected by oxygen-sharing BO_3 triangles into an infinite network.

The structure of the hydrothermally prepared zinc borate $\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\sim 1.12\text{H}_2\text{O}$ consists of $[\text{B}_{12}\text{O}_{24}]^{12-}$ units interconnected into an extended network by cationic Zn_3O_3 clusters (128), resulting in an open framework containing zinc-coordinated water molecules and a nonstoichiometric amount of additional interstitial water.

Zinc borates, particularly $\text{ZnB}_3\text{O}_3(\text{OH})_3$ or $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, which is known as an article of commerce as $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$, are used on an industrial scale as fire-retardant synergists for polymers, as preservatives for engineered wood products and wood-plastic composites, and as in-can preservatives, and as film fungicides in coatings. The zinc borate $\text{Zn}_2(\text{BO}_3)\text{OH}$, commercially referred to by its oxide formula $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$, is used as a fire retardant in polymers requiring high processing temperatures.

Since about 1970 the industrial-scale manufacture of zinc borates typically has been carried out by reactions of zinc oxide with boric acid in water under appropriate concentration and temperature conditions. Zinc borates also are

produced commercially by reactions of sodium borates with zinc salts, but the zinc oxide-boric acid route has the advantage of producing only water as the reaction by-product.

10.2. Barium Metaborates. Both hydrated and anhydrous barium metaborates find commercial use. Three hydrates of barium metaborate, $\text{BaO}\cdot\text{B}_2\text{O}_3\cdot x\text{H}_2\text{O}$, are known. The tetrahydrate (135) and pentahydrate (136) both contain the $\text{B}(\text{OH})_4^-$ anion, and have structural formulas of $\text{Ba}[\text{B}(\text{OH})_4]_2\cdot x\text{H}_2\text{O}$, where $x = 0$ and 1. These compounds crystallize when solutions of barium chloride and sodium metaborate are combined at room temperature (137). The higher hydrate is favored when excess sodium metaborate is used. Saturated aqueous solutions contain 13.5 g/L of $\text{BaO}\cdot\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ equivalent at 25°C. Both forms dehydrate at temperatures above 140°C. Barium metaborate also is prepared from barium sulfide formed by the prior reduction of barium sulfate. The presence of sulfide impurities in the product prepared by this route may render it unsuitable for some applications (62). Crystals of a hydrate, $\text{BaO}\cdot\text{B}_2\text{O}_3\cdot 1.67\text{H}_2\text{O}$, form from a boiling solution that has a B:Ba mole ratio > 2 . Dehydration of this hydrate at 300°C yields $\text{BaO}\cdot\text{B}_2\text{O}_3$, containing boron atoms that are both triangularly and tetrahedrally coordinated (138). Barium metaborate is used as a corrosion inhibitor as well as fire retardant and biocide for paints, plastics, textiles, and paper products (139).

Crystalline anhydrous barium metaborate, $\beta\text{-BaB}_2\text{O}_4$, also has commercial importance as a nonlinear optical material. Useful attributes for this application include transparency over a wide range of frequencies and phase matching ranges, a large nonlinear coefficient, high damage threshold, and good optical homogeneity (140).

10.3. Miscellaneous Metal Borates. Other metal borates are used in numerous smaller volume applications. These include both hydrated and anhydrous borates. Hydrated borates of copper, manganese, cobalt, and other metals precipitate when borax and other borate salts are added to aqueous solutions of salts of these metals (118). Anhydrous metal borates, which may exist as crystalline or vitreous materials, are prepared by fusing various metal oxides with boric acid or boric oxide. These compounds, in hydrated or anhydrous forms, find many applications, including nonlinear optical materials, paint driers, scintillating agents, and catalysts.

11. Nonmetal Borates

The ammonium cation, NH_4^+ , is one of the simplest nonmetal cations. Being only slightly less acidic than boric acid itself, the ammonium cation does not form salts with borate anions more basic than the tetraborate, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and even this salt has only marginal stability. Therefore, the hypothetical ammonium metaborate, $\text{NH}_4^+[\text{B}(\text{OH})_4]^-$, does not exist as a stable compound because the cation and anion are too acidic and too basic, respectively, to coexist. Substituted ammonium cations form a wide range of borates, including some containing unusual borate anions (141,142).

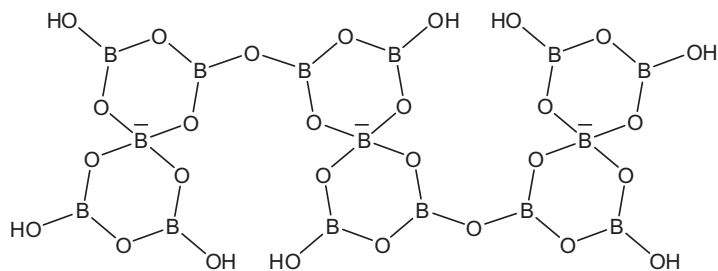
11.1. Ammonium Tetraborate. This compound has semiempirical and oxide formulas $(\text{NH}_4)_2\text{B}_4\text{O}_7\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ (formula wt,

263.37, monoclinic; sp gr, 1.58) and is often called ammonium tetraborate tetrahydrate. Its structural formula is $(\text{NH}_4)_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and thus has only two interstitial water molecules (143). It contains the same tetraborate anion as borax (7). It is readily soluble in water (Table 10) with the pH of its solutions being 8.8 and independent of concentration. This compound has been manufactured on a commercial scale and exhibits sufficient stability for shipment and storage. However, it is somewhat unstable and exhibits an appreciable vapor pressure of ammonia. Phase relationships for ammonium tetraborate have been outlined (143).

11.2. Ammonium Pentaborate. Often denoted by the semiempirical formula $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ or the oxide formula $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, this compound is generally called ammonium pentaborate tetrahydrate. It exists in two crystalline forms—an orthorhombic α -form and a monoclinic β -form. The structural formula of the more common and commercially available α -form is $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (formula wt, 272.14; sp gr, 1.567; heat capacity, at 301.2 K) and thus has only two interstitial water molecules (144). This compound contains the same pentaborate anion, $\text{B}_5\text{O}_6(\text{OH})_4^-$ (5), found in sodium and potassium pentaborate. It crystallizes as the kinetic product. A β -form is the thermodynamic product but is slow to crystallize. Its heat capacity has been measured over a broad temperature range (88). Solubility data are given in Table 10 and pH data in Table 11.

Unlike ammonium tetraborate, ammonium pentaborate is stable with respect to ammonia loss. This is related to the lower basicity of the pentaborate compared with the tetraborate anion. On heating from 100 to 230°C, ammonium pentaborate loses ~75% of its water content but less than 1% of its ammonia. At 200°C, under reduced pressure, the water content drops to 1.15 mol, but only 2% of the ammonia is lost (62). At still higher temperatures, all ammonia and water are expelled, leaving boric oxide (145).

11.3. Ammonioborite and Lardarellite. Prolonged reflux of an aqueous slurry of ammonium pentaborate results in quantitative conversion to $(\text{NH}_4)_3\text{B}_{15}\text{O}_{20}(\text{OH})_8 \sim 4\text{H}_2\text{O}$, which is the synthetic form of the uncommon mineral ammonioborite. This compound contains an unusual 15-boron anion, $\text{B}_{15}\text{O}_{20}(\text{OH})_8^{3-}$ (14), which is formally produced by the condensation of three pentaborate anions (146). Lardarellite is a related ammonium borate mineral and has the structural formula $\text{NH}_4\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is an ino-borate containing pentaborate chains formed by an infinite extension of 14 (147).

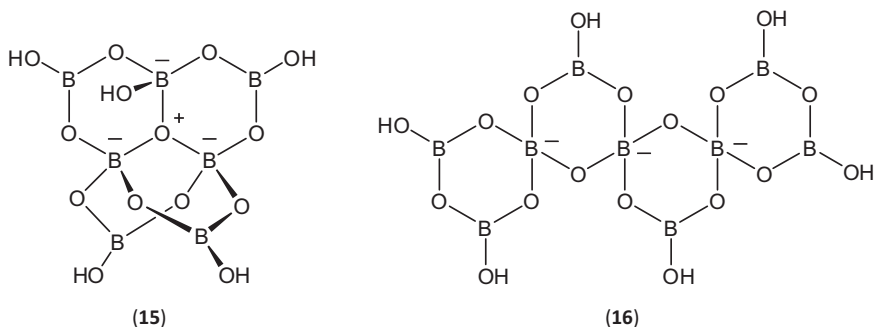


(14)

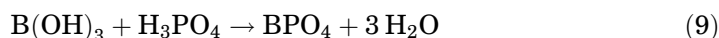
11.4. Other Nonmetal Borates. In addition to ammonia, other sufficiently strong nonmetal bases react with boric acid in aqueous or alcoholic solutions to form crystalline nonmetal borates (141–143,148). Several ammonium borates also have been characterized. Numerous examples now demonstrate the ability of nonmetal cations to stabilize unusual borate anions, leading to increased interest in this field in recent years.

Early examples of substituted ammonium borates include tetraalkylammonium borates (149,150). For example, the tetraethylammonium cation can be used to crystallize the compound $(\text{NEt}_4)_2[\text{BO}(\text{OH})_2]_2\cdot\text{B}(\text{OH})_3\cdot 5\text{H}_2\text{O}$, which contains a rare structurally characterized example of the Arrhenius conjugate base of boric acid, $\text{BO}(\text{OH})_2^-$ (149). This unusual anion also is found in the related urea inclusion compound $(\text{NMe}_4)_2[\text{BO}(\text{OH})_2]\cdot 2(\text{NH}_2)_2\text{CO}\cdot\text{H}_2\text{O}$ (150).

Other unusual borate species found only with nonmetal cations include the heptaborate, $\text{B}_7\text{O}_9(\text{OH})_5^{2-}$ (**15**) and nonaborate, $\text{B}_9\text{O}_{12}(\text{OH})_6^{3-}$ (**16**) anions (151,152). For example, imidazolium and guanidinium nonaborates, $(\text{C}_3\text{H}_5\text{N}_2)_3\text{B}_9\text{O}_{12}(\text{OH})_6$ and $[\text{C}(\text{NH}_2)_3]_3\text{B}_9\text{O}_{12}(\text{OH})_6$, form readily when boric acid is reacted with appropriate amounts of imidazole or guanidinium carbonate, respectively, in aqueous solution. The use of nonmetal cations has been shown to stabilize other unusual large polyborate anions, such as $\text{B}_{14}\text{O}_{20}(\text{OH})_6^{4-}$ (153). At higher temperatures, the use of nonmetal cations can result in the formation of unusual extended borate structures (154).



11.5. Boron Phosphate. Boron phosphate, BPO_4 , is a white, infusible solid that vaporizes slowly above 1450°C without apparent decomposition. It is normally prepared by dehydrating mixtures of boric acid and phosphoric acid at temperatures up to 1200°C (eq. 9). Complete dehydration requires temperatures above 1000°C . Equation 9 is expressed as follows:



The structure of boron phosphate prepared under normal atmospheric conditions consists of tetragonal bipyramids analogous to the high cristobalite form of silica. Both the boron and phosphorus atoms are tetrahedrally coordinated by oxygen. Similar silica-like structures are found in BaSO_4 and TaBO_4 . A quartz-like form of boron phosphate can be prepared by heating the common form to 500°C at 5.07 GPa (50,000 atm).

Tri-, tetra-, penta-, and hexa-hydrates of boron phosphate have been reported. All of these compounds decompose rapidly in water to give solutions of the parent acids. Anhydrous boron phosphate hydrolyzes in a similar fashion, although the reaction proceeds slowly for material that has been fused at high temperatures.

The main application of boron phosphate is as a heterogeneous acid catalyst for dehydration reactions (155). Although boron phosphate is derived from two of the three most common glass-forming oxides, it exhibits little tendency to form a glass itself. Boron phosphate is a primary phase over a large region of the phase diagram (156).

12. Analytical Methods

12.1. General Analytical Methods. A variety of methods have been developed for the analysis of borates as commercial products or in geologic and biologic specimens. The most common method for concentrated borate samples is colorimetric titration. Samples containing low concentrations typically are analyzed using inductively coupled plasma (ICP) spectroscopy after sample digestion. Digestion typically is done using strong acids, which convert any borate in the sample into boric acid.

12.2. Boric Acid. Colorimetric titration is used for routine quality control and for the analysis of relatively high concentrations of boric acid in samples. ICP typically is used to measure low concentrations of boric acid in samples. Boric acid is such a weak acid that it cannot be accurately determined by direct acid–base titration methods. However, it can be transformed into a relatively strong acid by adding polyols such as glycerol, mannitol, and sorbitol. The resulting ester complexes are much stronger acids and can be titrated accurately (157).

In practice, the boric acid sample is first dissolved in hot water and boiled to remove carbon dioxide, which interferes with the titration. Mannitol or sorbitol is then added, and the resulting solution is titrated with NaOH solution using phenolphthalein as the endpoint indicator. The B_2O_3 content is calculated from the volume and the normality of the NaOH titrant consumed.

12.3. Na, K, and NH_4 Borates. Alkali metal and ammonium borates are generally analyzed for B_2O_3 and M_2O or $(NH_4)_2O$ content by varying the colorimetric titration used for boric acid. This is done by dissolving the compound in water, titrating for M_2O or $(NH_4)_2O$ content with dilute HCl, and then determining B_2O_3 content by complexation with excess mannitol or sorbitol followed by titration with NaOH (158). The purity of the product is calculated by dividing the actual B_2O_3 content by the theoretical B_2O_3 content in the chemical formula as well as comparing the B_2O_3/M_2O mole ratio with the theoretical value. This titration can be done using commercial autotitrators. Commercial hydrated borates are often somewhat overdried, leading to apparent assays greater than 100%.

12.4. Crude (Mineral) Borates. The B_2O_3 content of calcium borates and other borates of low water solubility is determined by extraction into acid solution followed by mannitol or sorbitol complexation and titration with dilute base. The titrimetric determination of B_2O_3 content in crude borates, such as

tincal, kernite, colemanite, and ulexite, is prone to interference. Common interfering elements and compounds are iron, alumina, soluble silica, and manganese. To remove these substances, a procedure called the barium carbonate method was developed by the Pacific Coast Borax Company, which is now Rio Tinto's borate business, U.S. Borax Inc. (159). This procedure is based on the fact that barium borate, formed by the addition of barium carbonate to boric acid, is relatively soluble. It acts as a buffer solution to cause precipitation of the hydroxides of heavy metals. However, in modern practice, mineral samples generally are digested, diluted, and analyzed by ICP spectroscopy. Some mineral samples, particularly borosilicates, may require fusion prior to acid digestion.

12.5. Other Analytical Methods. Boron compounds become a characteristic green color when burned in a flame, providing a crude qualitative test for boron. Flame atomic absorption spectroscopy is used for borate analysis, but this method largely has been replaced by ICP methods. Borate reacts with curcumin [458-37-7], $C_{12}H_{20}O_6$, in the presence of a mineral acid to give a colored 1:2 boric acid: curcumin complex that is used in the colorimetric microanalysis of boron. Carminic acid [1260-17-9], $C_{22}H_{20}O_{13}$ (160), and azomethine-H (161) also form colored complexes that are useful for the detection of borates at relatively low concentrations. Methods for analysis of industrial borates have been reviewed (162).

13. Manufacturing, Production, and Processing

13.1. Manufacturing. Both sedimentary and metamorphic borate mineral deposits are mined for the large-scale production of industrial borates, although sedimentary deposits are by far the larger sources. Ore extraction is typically accomplished using conventional surface mining techniques from large open cast mines. Underground mining commonly was used for borate mining in the past and may be practiced today by some smaller producers. Solution mining from lake bed deposits also is employed. Sedimentary sodium, calcium, and sodium-calcium borate minerals, borax, kernite, colemanite, and ulexite, and the metamorphic mineral datolite are the principal ore types exploited around the world.

Before mining begins, geologists collect core samples and prepare three-dimensional models of the ore body. These models include information about ore body geometry, mineralogy, grade, and impurity types and concentrations. Information gleaned from these models are used to develop an optimal mine plan and to determine appropriate refining requirements.

Commercial borate ores fall into two types—sodium borates, which are relatively soluble in water, and calcium or sodium-calcium borate ores, which are sparingly soluble in water. Because of these intrinsic properties, sodium borate ores are often used to produce refined borate products, including various sodium borates and boric acid, whereas calcium and sodium-calcium borate ores are often used to supply beneficiated mineral borates.

In large-scale surface mining operations, overburden material is drilled, blasted, and stripped away using large shovels and trucks to expose the ore body. Once the ore is exposed, it is blasted to loosen it. Electric or hydraulic

shovels load the ore into large haul trucks. The trucks carry the ore to crushers for size reduction. Crushers reduce the particle size to prepare the ore for additional processing.

Some commercial applications of borates permit the use of unrefined borates. Borate ores, primarily colemanite and ulexite, may be used in these limited cases but still require upgrading to provide suitable consistency and quality. Ore upgrading is done with crushing, blending, washing, and gravity or magnetic separation techniques. Gravity separation takes advantage of the differences in the specific gravity between the borate mineral and the surrounding clay matrix. Magnetic separation takes advantage of the weakly magnetic properties of clay impurities. Borate recovery from these separation processes is often relatively poor, but the cost of processing can be relatively low, depending on the quality of the ore feed.

Most commercial applications of borates require the use of refined borates, and borate ores typically do not have sufficient quality to be used directly in these industrial applications. Therefore, refining of borate ores is required to produce saleable industrial borate products. The refining process includes the following primary steps: leaching, concentrating, crystallizing, and drying.

For sodium borate ores, refining takes advantage of their highly soluble nature. In the first step of refining, crushed sodium borate ore is leached with hot water using agitation and steam. This process produces a hot, saturated salt solution containing sodium borates and a suspension of insoluble matter.

After concentration by removing insolubles, the concentrated borate solutions are cooled in crystallizers to produce slurries of high purity sodium borate or boric acid crystals. In the case of sodium tetraborate, the conditions used in the crystallizers determine the product form as either the pentahydrate or the decahydrate. In the industry, these hydrated sodium tetraborates are often called "5 Mol" and "10 Mol" borax, where "Mol" is short for the chemical quantifier mole, and refers to the amount of apparent water found in the oxide formula.

In boric acid production, the first step in purification is essentially the same; however, sulfuric or other mineral acid is used for acid leaching to extract soluble boric acid and sodium or calcium sulfate. This results in a hot, concentrated solution of boric acid along with sodium or calcium sulfate and other impurities. Impurities typically consist of insoluble clays or other minerals. Removal of these impurities, which is essentially a borate concentration step, is accomplished by passing the solution through a series of screens, settling tanks, and filters.

The boric acid slurry is dewatered in centrifuges or belt filters, producing a moist cake of borax or boric acid crystals. These crystals may be washed to concentrate the product by removing soluble and fine particulate impurities. The final processing step involves drying to drive off the remaining moisture. To avoid overdrying, the product temperature is kept below 50°C. Heated air is passed across the flow of borate crystals, removing free moisture and producing a dry, flowable granular product. Powdered boric acid is produced by milling the granular material.

Boric acid is produced on a large scale by Rio Tinto's borate business, U. S. Borax Inc. (Boron, Calif.), by treating crushed kernite ore, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, with sulfuric acid in an acid leaching process. Coarse gangue is removed with rake

classifiers, and fine gangue is removed in thickeners in a concentrating process. Boric acid is crystallized from strong liquor, nearly saturated in sodium sulfate in continuous crystallizers, and the crystals are washed in a multistage counter-current wash circuit, dewatered, washed again, and then dried.

Boric acid is produced from colemanite by Eti Maden in Turkey and by smaller producers in South America and elsewhere. When boric acid is made from colemanite, the ore is ground to a fine powder and stirred vigorously with diluted mother liquor and sulfuric acid at about 90°C. The by-product calcium sulfate [7778-18-9] is removed by settling and filtration, and the boric acid is crystallized through cooling the filtrate.

At Searles Lake (Trona, Calif.), boric acid is produced from sodium borate brines using a liquid-liquid extraction process originally developed by American Potash & Chemical Corp. (Oklahoma City, Ok.) in the 1960s. This process is operated by Searles Valley Minerals, a subsidiary of Nirma Chemical Works of India. Both potassium sulfate and sodium sulfate are produced as coproducts in this process. Boric acid produced by this process can be distinguished by a slight organic residue.

The principal impurities in technical-grade boric acid are by-product sulfates, <0.04%, and minor impurities present in the borate ores. A boric acid titration assay is not always an effective measure of purity because overdrying may result in partial conversion to metaboric acid and lead to $B(OH)_3$ assays greater than 100%. High purity boric acid is prepared by recrystallizing technical-grade material.

The potassium and ammonium borates are relatively low volume borate products compared with borax penta- and decahydrates, boric acid, and anhydrous borates, with annual production in the range of several hundred metric tons. Potassium tetraborate hydrate may be prepared from an aqueous solution of KOH and boric acid that has a $B_2O_3:K_2O$ ratio of approximately 2 or by separation from a KCl-borax solution (163). Potassium pentaborate is prepared analogously but using strong liquor that has a $B_2O_3:K_2O$ ratio close to 5.

Ammonium tetraborate hydrate is prepared by crystallization from an aqueous solution of boric acid and ammonia that has a $B_2O_3:(NH_4)_2O$ ratio of about 0.86. Ammonium pentaborate is similarly produced from an aqueous solution of boric acid and ammonia that has a $B_2O_3:(NH_4)_2O$ ratio of 5. Supersaturated solutions are easily formed, and the rate of crystallization is proportional to the extent of supersaturation (164). A process for the production of ammonium pentaborate by precipitation from aqueous ammonium chloride-borax has been described (145).

Finished borate products are stored in silos or warehouses to await packaging. Because borate products are white, contamination from rust and dirt is readily apparent. For this reason, storage is normally fully enclosed to eliminate contamination.

13.2. Shipment. Distribution and supply reliability are important aspects of the global borate sector because of the relatively few commercial sources of borates as well as the wide range and spread of industries that rely on them. This is as true today as it was centuries ago when borates were carried to Europe along the same ancient trade routes used by Marco Polo and in the late

1800s when the famous Borax 20 Mule Teams carried borates out of Death Valley to the nearest railhead in Mojave, a 10-day journey across rugged terrain.

Borates are moved today by almost every available form of transportation. Bulk intercontinental shipments are made in ocean-going vessels with capacities up to 40,000 tons. Barges, railcars, and trucks move borate products from sources or shipping ports to customers. Intermediate stock points are located around the world to provide working inventories and to guard against supply disruption. The major producers maintain worldwide logistics networks, sales representatives, agents, and distributors to interact with customers and to ensure reliable supplies and service.

14. Borates In Glass

14.1. Borate Melts and Glasses. Boric oxide is a key ingredient in glassmaking. Like silicon oxide and lead oxide, boric oxide (B_2O_3) is a natural glass network-forming oxide that forms strong covalent bonds. These glass-forming oxides are capable of existing in the vitreous state either alone or in combination with other oxides. When heated, alkali metal oxides, hydroxides, or carbonates fuse with boric acid or hydrated and anhydrous alkali metal borates to form clear liquid melts. If these liquids are high in boric oxide content (M_2O/B_2O_3 mole ratio = 0–2, where M is an alkali metal), then they become viscous upon cooling and form glasses.

Much interest in alkali metal borate glasses has centered on reports of the existence of maxima and minima in some physical properties of the glasses, including viscosity, density, and thermal expansion coefficients, that occur with increasing metal oxide content. This phenomenon has been called the boron oxide anomaly (165). Modern theory on borate glass structure, however, indicates that these property changes are not anomalous but result from well-defined structural changes in the glass at the molecular level. Called superstructural units, four different borate structural groups have been theorized to be present in alkali borate glasses below 34 mol % M_2O (166). These groups, shown in Figure 7, are analogous to those occurring in aqueous solution and crystalline borates (see 5–8). However, in glasses, these structural groups contain terminal unprotonated oxygen atoms with negative charges balanced by associated cations. Other distal oxygen atoms act as bridges to other boron atoms in the network. Terminal unprotonated oxygen atoms are rarely observed in hydrated borates. The argument that pure vitreous B_2O_3 consists of flat triangles in the form of boroxol rings connected by chains is strongly supported by spectroscopy, including boron NMR, nuclear quadrupole resonance, and Raman spectroscopy (167). Successive addition of alkali oxide to boron oxide to form an alkali borate glass continuously results in the transformation of triangles to tetrahedra. After the addition of up to 20 mol % M_2O , tetraborate groups are formed. Between 20 and 34 mol % M_2O , diborate groups form at the expense of tetraborate groups. Infrared (166) and Raman (29) data on borate glasses as well as the analogous crystalline anhydrous borates support this reasoning. Changes in the physical properties of the glass with M_2O content represent compromises

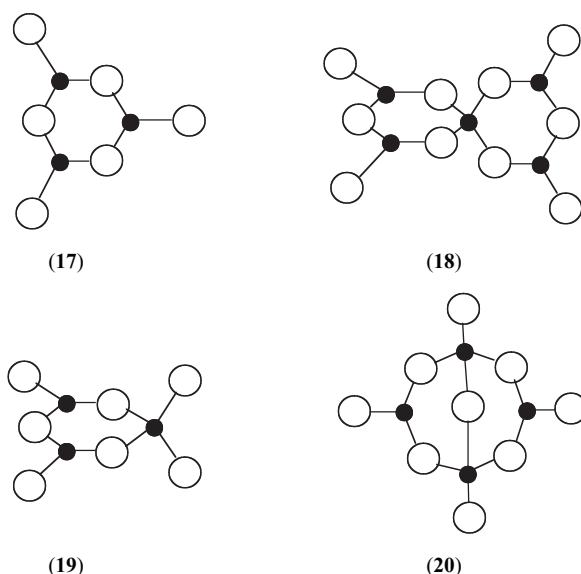


Fig. 7. The borate glass structural groups: boroxol (17), pentaborate (18), triborate (19), and diborate (20) \circ = oxygen, \bullet = boron (135).

between the effect of adding more metal ions to the system and the effect of making borate structural entities more rigid as well as reducing the degrees of freedom by converting trigonally coordinated boron atoms into tetrahedrally coordinated boron atoms and forming polyborate structural units.

Another widely studied phenomenon in alkali borate glasses is the mixed alkali effect, which is the nonlinear change in glass properties when a second kind of alkali metal oxide is added to a glass containing a single alkali metal. Models have been suggested to explain the mixed alkali effect (168,169).

Several reviews have appeared covering the various aspects of borate glasses. The structure, physical properties, thermochemistry, reactions, phase equilibria, and electrical properties of alkali borate melts and glasses have been presented (72). The application of x-ray diffraction, NMR, Raman scattering, infrared and electron spin resonance spectroscopy to structural analysis is available (26). Phase-equilibrium diagrams for numerous anhydrous borate systems are included in a compilation (123), and thermochemical data on the anhydrous alkali metal borates have been compiled (16).

15. Industrial Borate Uses

Borates have numerous industrial applications, and demand is driven by urbanization, energy efficiency and green energy trends, the need to increase the quantity and quality of the food supply, and other social trends related to increasing standards and standards of living. Many boron-containing products are found in the home, including building materials, housewares, and consumer

electronics. A complete listing of all industrial uses of borates is beyond the scope of this review. Some of these uses are discussed briefly to illustrate the diversity of practical applications of borates (170).

15.1. Glass. The manufacture of different types of glass represents the largest end use sector for borates followed by the closely related ceramics sector. Boric oxide is important to glass technology because it creates combinations of properties that are either technically impossible or prohibitively expensive to achieve using other additives.

In the glass sector, the manufacture of different types of fiberglass uses the largest amount of borates. Two main types of fiberglass include insulation fiberglass and textile fiberglass. The manufacture of glass for flat screen televisions as well as display panels for computers and mobile devices is also a major use of borates. Borates are consumed in the production of heat-resistant or low thermal expansion glass (often called Pyrex, a trademark of Corning Inc., Corning, N.Y.), sealing glass, glass ceramics, optical glass, nuclear waste storage glass, and in the manufacture of the heat insulating glass, Vycor (a trademark of Corning Inc.). Borates also are used to produce glass frits to produce ceramic glazes and porcelain enamels. Typical composition ranges in common commercial glasses are given in Table 15. Borates generally are not used in container or flat glass.

Insulation Fiberglass. Insulation fiberglass (IFG) or glass wool is a major insulating material used in residential and commercial construction and plays an important role in energy conservation. Comprising thin, intermingled fibers spun from molten glass, IFG traps and holds air to form an effective thermal barrier. IFG is also widely used for acoustical insulation and finds extensive use in automobiles and consumer appliances.

IFG is a soda lime borosilicate glass formulated to satisfy performance requirements of the finished product as well as manufacturing processing requirements (171). The borate content of borate in IFG is typically 4–7% B_2O_3 . It is typically added to the batch raw materials as borax pentahydrate, although beneficiated mineral borates such as ulexite are also used. Borates are incorporated into IFG formulations to improve the durability of the finished product and to aid in melting and inhibit devitrification during manufacture. It allows for the fiberization of a durable glass formulation at practical working

Table 15. **Typical Borate Content of Commercial Glasses**

Glass type	wt % B_2O_3
fiberglass	
textile (E-glass)	0–13
insulation	3–7
sealing glass	8–30
heat resistant (Pyrex) ^a	12–15
Vycor ^a	20 ^b
porcelain enamel (frit)	11–13

^aPyrex and Vycor are registered trademarks of Corning Inc. (Corning, N.Y.).

^bThis is the percent B_2O_3 in the phase separated glass prior to leaching to form Vycor.

temperatures. Borates also give resiliency to fiberglass, allowing it to recover after the prolonged compression required during transport. In addition, the borate component in IFG improves the R-value, or thermal insulating performance, of fiberglass.

Textile Fiberglass. Another major type of glass that frequently incorporates borates is textile fiberglass (TFG) or E-glass (172,173). This is a continuous strand fiberglass that has many applications. TFG is used in electronic circuit boards leading to a requirement for low sodium levels to limit its electrical conductivity. This material is a lime aluminosilicate glass that has low or no alkali metal content, which combines the properties of good tensile strength with durability. Borate is used as a flux to reduce the melting and fiberizing temperature through control of viscosity and liquidus temperature. Alkali metals increase electrical conductivity and reduce chemical resistance, so their use typically is limited to a maximum of 1.0–1.5 wt %.

Today, TFG is widely used as reinforcement for plastics and construction products, but the low sodium requirement still applies. Major applications of TFG include automotive composites, appliances, power tools, housewares, sporting goods, construction products, pipes, tanks, electronic circuit boards, and electrical connectors. Roofing and flooring tiles often are reinforced with TFG. Textile fiberglass also is used in reinforced gypsum wallboard and heating/air-conditioning filters. Finally, TFG is used to make blades in windmills used to generate wind energy.

Borates are added as either colemanite or boric acid. Some sodium borate, such as borax pentahydrate or ulexite, also may be added up to the maximum permitted alkali content to aid in melting and to reduce raw material costs.

Borosilicate Glass. Borosilicate glass is a general classification for glasses that have common characteristics of containing relatively high levels of B_2O_3 . Borates impart many distinct properties to borosilicate glass, including thermal shock resistance, chemical resistance, aqueous durability, and physical strength. For this reason, borosilicate glasses find a wide range of uses in kitchenware, such as coffee pots and oven-to-table cookware, lighting products, metal-to-glass sealing compositions, laboratory ware, optical lenses, glass tubing, and many other applications requiring durable and temperature-insensitive glass. Borosilicate glass also is used in solar-thermal water heating systems, especially in Asia. Boric acid, boric oxide, borax pentahydrate, and anhydrous borax all are used in the manufacture of borosilicate glass.

Film Transistor-Liquid Crystal Display Glass. Thin film transistor-liquid crystal display (LCD) glass is a variant of LCD glass and has mostly replaced the CRT for television and computer displays. Manufacturing technology for this type of glass has advanced rapidly with the demand for the production of large-screen television displays. The liquid crystal is sandwiched between two thin glass sheets (~0.7 mm). The glass is an alkaline earth aluminoborosilicate, where approximately 10% B_2O_3 typically is added as a flux to control melt viscosity and liquidus temperature. The glass formulation is free of alkali metals and borate is added either as boric acid or as boric oxide.

15.2. Ceramics. The manufacture of ceramics represents a major use of borates. The ceramics industry uses borates in the form of frit, which is a powdered glass ingredient for ceramic glazes and porcelain enamels. The ceramic frit

industry uses either boric acid or colemanite as raw material to make borosilicate frits. The manufacture of enamel frits typically use refined sodium borate as the raw material. Borate-based frits are used widely in the manufacture of floor and wall tiles.

Borates also are applied to the surface of ceramic roofing tiles before firing to improve appearance and performance, including freeze-thaw resistance. The addition of borates, including boric acid and zinc borate, to ceramic bodies has been shown to improve green strength and reduce firing times and temperatures (174,175).

15.3. Industrial Fluids. Borates are widely used in the manufacture of industrial fluids, including automotive antifreeze/coolants, brake fluids, lubricating oils, greases, metalworking, and hydraulic fluids. The benefits of borates in industrial fluids include lubrication enhancement, buffering capacity, corrosion inhibition, and thermal stability. In many cases, borates are used in industrial fluids in the form of borate esters, amine complexes, or alcoholamine-borate ester complexes.

15.4. Water Treatment. Borates are used to control corrosion in recirculating water systems, including steam boilers, central heating and cooling systems, and heat exchangers. In these systems, borates inhibit corrosion through nonoxidizing anodic passivation as well as by buffering aqueous media to alkaline pH regimes in which corrosion is electrochemically less favored. Borax pentahydrate, borax decahydrate, and sodium metaborate are frequently used in these applications.

15.5. Adhesives. Borates are used in several different types of commercial adhesives. Of these, the most common types are starch and dextrin adhesives. These adhesives are widely employed to glue together corrugated cardboard boxes and to manufacture a range of other paper-based products such as grocery bags, cartons, paper tubes, and wall coverings. Borates are used in starch and dextrin adhesives as a cross-linking agent to increase viscosity, provide tack, and yield better fluid properties. These qualities are essential for their use in corrugated paperboard machines and other high speed forming operations.

The chemistry of borate cross-linking of starch and dextrin is described by the general reaction shown in equation 8 (see the subsection "Properties"), involving the formation of C-O-B ester linkages between starch hydroxyl groups and boric acid. However, in this application, the equivalent of boric acid generally is supplied by other borates such as borax pentahydrate, borax decahydrate, or sodium metaborate. Because this reaction produces a proton, alkaline conditions will shift the equilibrium to the right. Thus, borate cross-linking is promoted by raising the pH. Because borax and sodium metaborate can be regarded as the equivalent to boric acid neutralized by a strong base, these reagents supply sufficient alkalinity to promote a high degree of cross-linking. As a result, sodium borates, such as borax, are generally used rather than boric acid in the manufacture of starch-based adhesives. Borates also act as cross-linking agents in other adhesives systems, such as those based on polyvinyl alcohols.

15.6. Oil Recovery. Borates have a variety of important uses in oil recovery. The same reaction involved in cross-linking in adhesives (eq. 8) is also exploited to produce fracturing fluids and proppant packs used in oil drilling

operations. For example, a solution of guar gum or another polyhydroxy compound might be cross-linked using borax to provide rheological fluids useful in oil drilling.

The addition of borates to various types of cements, including Portland cement, retards their setting rates. This effect is used for cements used in oil wells where delay in set time is critical.

15.7. Agriculture. Boron is an essential micronutrient for plants. It is critical to the fertilization, fruiting and seed production in plants as well as vital to improving crop quality and yields. For this reason, it is common agricultural practice to apply boron fertilizers to crops wherever soils are boron deficient. Boron fertilizers often are applied to peanuts, apples, grapes, olives, alfalfa, oil palm, corn, cotton, canola, sugar beets, and many other fruits and vegetables. Because of their important role in improving crop yields, boron fertilizers are important to worldwide food security (176).

15.8. Biocides. Engineered Wood Products. The specific type of zinc borate known as an article of commerce as $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ (see the subsection "Zinc Borates") is added during the manufacture of wood composite building materials to control damage caused by wood destroying organisms, such as white and brown rot decay fungi. These building materials include oriented strand board and other engineered wood products used in protected, above-ground applications for residential and commercial construction siding, sheathing, roofing, and millwork. Zinc borate also helps to protect wood composite materials from damage caused by wood-destroying insects, such as subterranean termites. A zinc borate preservative generally is used at levels of 0.75 wt % and higher to provide protection against decay fungi and subterranean termites. Zinc borate is sparingly soluble in water and is therefore leach resistant. Zinc borate also is used to control microbial growth on wood plastic composites used in outdoor settings (177).

Lumber. Borates are frequently used as preservatives for lumber used in protected, above-ground construction. Disodium octaborate tetrahydrate, being particularly soluble in water, is used as a diffusible wood preservative to protect wood against attack by termites (including Formosan subterranean), wood boring beetles, and carpenter ants (177).

Coatings. The zinc borate known as an article of commerce as $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ (see the subsection "Zinc Borates") functions as an in-can preservative and film fungicide (178). This form of zinc borate carries specific registrations for these biocidal uses in the United States. Additional uses of zinc borate in coatings include corrosion inhibitor, fire retardant, and tannin stain blocker.

Swimming Pools. Borates are used in combination with chlorine sanitizers, such as calcium hypochlorite, to control algal growth in swimming pools. Borates have some efficacy against algae on their own, and when used in combination with chlorine sanitizers, they are reported to be highly effective in controlling algae at reduced chlorine levels. Often borax and boric acid are used in combination to achieve appropriate pH levels for swimming pools.

Pest Control. Boric acid, borax pentahydrate, borax decahydrate, and disodium octaborate tetrahydrate are registered for use in the control of several insect pests, including cockroaches, termites, wood destroying beetles, and

carpenter ants. Boric acid is widely used in the control of cockroaches. Concentrated aqueous solutions of disodium octaborate tetrahydrate are applied by pest control operators for the remedial treatment of termite infestations in residential dwellings.

Fuel Additives. Borate esters are used as preservatives for diesel and aviation fuels. These fuels inevitably pick up moisture from the air through condensation. This moisture collects as water a layer at the bottom of storage and use tanks. Fungi and slime bacteria tend to grow at the water–fuel interface and eventually create suspended sediments that can clog fuel filters. The specialized glycol borates, which have appropriate partition coefficients to distribute between the aqueous and organic phases, prevent microbial growth and result in better fuel performance. Borate esters also are reported to reduce engine wear and improve fuel efficiency when added to gasoline.

15.9. Cleaning and Personal-Care Products. Borates have been used for more than 100 years to assist in cleaning and laundering processes as well as to enhance the performance of personal-care products. Primary functions of borates in these applications include buffering and pH control, emulsification of waxes and oils, water softening, viscosity control, foam stabilization, enzyme stabilization or inhibition, odor control, corrosion inhibition, and either mild abrasivity or lubricity depending on the borate used.

A wide variety of consumer cleaning and laundering products routinely contain borates. These including laundry detergents, dish washing liquids, and hard surface cleaners. In detergent formulations, borax functions as a builder, providing alkalinity and pH buffering to assist in stain removal, water softening by sequestration of calcium ions, and removal of oily soils through the lowering of interfacial tension. Borax assists in the suspension of soil particles, reducing the tendency for redeposition of soils onto fabrics. Borates also provide corrosion control for metal washing machine parts. This combination of effects makes borate a better performer than some more traditional detergent builders. Borax decahydrate traditionally is used in this application because of its more rapid dissolving rate compared with borax pentahydrate. In hard surface cleaners, borax decahydrate is also a milder abrasive than borax pentahydrate.

Borates inhibit the activity of a spectrum of enzymes, including proteolytic enzymes commonly used in cleaning products. Because these enzymes self-degrade when concentrated in cleaning products, a borate addition can be useful in stabilizing enzyme systems for reactivation on dilution during use. This property of borates is related to their ability to form complexes via reversible ester formation at the active site of enzymes. The inhibition of urease enzyme, in particular, provides a mechanism for the odor-controlling properties of borates.

In personal-care products, high purity grades of boric acid serves as a mild excipient in contact lens solutions and eyewashes, hand lotions, hair rinses, and protective balms and ointments. Sodium borates are used to buffer pH, emulsify waxes, and stabilize formulations. Boric acid also provides lubricity to cosmetics, and cross-linking with polyols provides viscosity control.

15.10. Fire Retardants. Borates, including boric acid, sodium borates, zinc borates, and ammonium borates, are generally good fire retardants and are particularly effective in reducing the flammability of cellulosic materials and certain plastics. Applications include treatment of wood products, cellulose

insulation, cotton batting, and other nonwoven cellulose. Zinc borate is also used as a fire-retardant synergist in various types of polymers (179).

Fire-Retardant Mechanism. The combustion of cellulosic materials, including wood, paper, and natural fiber-based products, can occur as follows: (1) flaming combustion, in which visible flames are present; and (2) smoldering or glowing combustion, in which flames are absent. Unlike halogen compounds, which primarily act as gas-phase fire retardants during flaming combustion, borates act as solid-phase fire retardants. They promote the formation of a vitreous char that protects the substrate and inhibits pyrolysis and release of combustible gases. The borate-promoted char layer ties up carbonaceous fuel and inhibits air oxidation of the substrate, reducing the occurrence of smoldering combustion. The release of water from boric acid, borax pentahydrate, or borax decahydrate also may play a secondary role in reducing combustion.

Sodium borates, including borax pentahydrate and decahydrate, are effective in reducing flaming combustion and flame spread in cellulosic materials but may be less effective in the suppression of smoldering combustion because sodium promotes glowing combustion in these materials. Because many standard fire tests include afterglow criteria for passage, excessive smoldering combustion may be unacceptable. For this reason, boric acid, or a mixture of boric acid and borax, is often used in fire-retardant treatments. A certain amount of sodium often can be tolerated, which is the reason that mixtures of boric acid and borax can be used. Such mixtures can be produced by blending borax and boric acid in the product being treated or in aqueous solution prior to treatment. Otherwise, borates such as disodium octaborate tetrahydrate or sodium pentaborate are used for convenience as these borates are equivalent to a borax-boric acid mixture at fixed ratios. An advantage of these borates is their higher water solubility. Ammonium borates are also used, particularly in neutral pH or slightly alkaline systems, but ammonia can be released at pH values above approximately 9.

Cellulose Insulation. Cellulose insulation is widely used in residential construction and retrofitting to improve energy efficiency. One disadvantage to cellulose is flammability. For this reason, cellulose insulation products are always treated with fire retardants during manufacture. Borates have been the standard fire retardant for cellulose insulation since the 1970s. Typical treatments include mixtures of borax and boric acid or boric acid and ammonium sulfate. All borate formulations are regarded as superior in this application because ammonium sulfate can off gas some ammonia and can contribute to the corrosion of metal construction fasteners under some circumstances.

Cotton Batting. Mattresses are required to pass specified fire- and smolder-resistance tests in most regions. Boric acid typically is used as a fire-retardant treatment for cotton and cotton-polyester batting for use in mattresses and futons. Boric acid typically is applied as a fine powder, often dispersed in an oil, to provide adherence to the cotton fibers or as an aqueous solution.

Lumber. The usual method for treating dimensional lumber and plywood is vacuum/pressure impregnation with aqueous solutions of fire retardants. Depending on the lumber-based article being treated and the fire performance required, borates can be effective fire retardants on their own. Borates used include disodium octaborate tetrahydrate, boric acid, and/or borax pentahydrate.

Borates also are used frequently in combination with other fire retardants, including ammonium phosphates, guanylurea phosphate, ammonium sulfate, bromide salts, and zinc chloride. Borates typically need to be used at levels ranging from 8% to 15% by weight of dry board to pass the recognized fire test standards, but trials need to be conducted under relevant test conditions to determine whether acceptable fire performance can be achieved with specific test articles.

Polymers. As a polymer additive, zinc borates serve as fire-retardant synergists, char promoters, antidrip agents, smoke and afterglow suppressants, and modifiers of electrical properties (180). Zinc borates are used extensively in polyvinyl chloride, polyamides (181), unsaturated polyesters, polyolefins, and rubber compounds. It is frequently used in combination with halogenated fire retardants but also finds use in halogen-free systems, generally with alumina trihydrate or magnesium hydroxide. In polyamides, zinc borate is used to improve the tracking index of electrical connectors intended for use at higher voltages. Zinc borate also has been used as an adhesion promoter in steel-belted tires.

Fabrics. Borates can be used as fire-retardant treatments for woven fabrics as well as nonwoven products made from cotton and other natural fibers and some synthetic materials, such as rayon. However, because borates are water soluble, they cannot be used for apparel or fabric requiring laundering or outdoor exposure. Examples of materials in which borate have been used effectively include draperies, rugs, ironing board covers, fabric heat deflectors for stoves and fireplaces, canvas fire blankets, and Christmas tree decorations.

15.11. Metallurgy. Borates have a wide range of metallurgical uses. They are used in smelting operations for the recovery of precious metals and non-ferrous base metals, wire drawing, manufacture of alloys, amorphous metals, rare earth magnets, boronizing, brazing, welding, and soldering fluxes, and jewelry making. They are also used to convert dusty stainless steel slags into hard aggregates.

Precious Metal Recovery. The gold- and silver-refining industries, as well as precious-metal assaying laboratories, routinely use anhydrous borax in primary flux formulations. When added to the impure metal in a furnace, the borate associates with metal oxide contaminants and brings them to the surface of the melt in the form of the slag that can be skimmed or poured off, leaving behind the purified precious metal.

Base Metal Refining. Borates are employed in the recovery of base metals and alloys (such as lead, zinc, copper, brass and bronze) from ores, scrap, or slag left over from primary smelting operations. Similar to precious metal recovery, borates are used as fluxes during melting to combine with non-metal oxides and bring them to the surface as a slag that can be decanted or skimmed off.

Tube and Wire Drawing. Industrial steel wire and tube drawing operations traditionally have made use of borates as buffers, corrosion inhibitors, and lubricant carriers. The forming of steel and stainless steel tubes is accomplished by shaping hot steel billets in the presence of anhydrous borax, which acts as a lubricant and corrosion inhibitor. In wire drawing, steel or stainless steel rod is drawn through a series of dies using a lubricant, typically a metal carboxylate, until the desired diameter is attained. The steel rod is first cleaned

of rust and scale by dipping it in an acid-cleaning tank. Excess acid is removed in a rinse tank and grease may be removed in a detergent tank. A final rinse typically is made in a tank containing a borax solution. The function of the borax is to neutralize any residual acid and to protect the steel from corrosion prior to the drawing operation. Residual borax on the steel also acts a lubricant carrier, helping the lubricant adhere to the metal.

Manufacture of Alloys. Boron is a useful alloying agent for many metals particularly to make high performance alloys of aluminum, copper, and steel. Boron is added at low levels, often in the form of commercially available master alloys, in the production of specialized high strength steel and aluminum alloys. Ultra high strength boron steel is used in lightweight automobile frames and parts as well as turbine blades and other demanding applications.

Boronizing. Boronizing is a thermochemical treatment that produces an extremely hard protective layer on the surface of metal articles. Boronizing relies on the formation of a thin continuous metal boride layer on metal surfaces. Because metal borides are among the hardest known substances, boronizing confers a high degree of resistance to wear and abrasion on metal parts. Boronizing also provides substantial resistance to environmental corrosion and chemical attack.

Many methods of boronizing have been developed, often involving the application of borax or other metal borates to metal surfaces along with the activation of substances in the form of a powder or paste followed by heating. Other methods, such as plasma spraying of borates and electrochemical treatment in a molten anhydrous borax bath, also are used. Boronized steel finds many applications in tools, dies, blades, and engine parts to increase service life and improve resistance to both wear and corrosion.

Amorphous Metals. Amorphous metals are metallic materials that, unlike typical metals, lack ordered crystalline structures. These materials usually are produced by rapidly cooling molten alloys of specific compositions. An important application of amorphous metals is to make ferroboration, containing 13–16% boron, which is used to make highly efficient electrical transformers for electrical power distribution.

Rare-earth Magnets. Rare earth-iron-boron alloy permanent magnets are widely used because of their excellent magnetic properties. These magnets, with an approximate composition of $\text{Nd}_2\text{Fe}_{14}\text{B}$, are used in a wide variety of applications including audio speakers, electric motors, generators and windmills, meters, and scientific instruments.

Electroplating. Boric acid has been used in electroplating since the nineteenth century. The addition of boric acid to electroplating baths, particularly in nickel, zinc, and chrome plating operations, helps to control pH and current densities and enhances the quality of the plated metal.

Brazing, Welding, and Soldering Fluxes. Welding rods, as well as many fluxes used for welding, brazing, and soldering, contain borates. The function of a flux in welding or brazing is to dissolve oxides on the metal surface, leaving it clean for joining. Borates used in this area include boric acid, anhydrous borax, and potassium borates.

Stainless Steel Slag Stabilization. Some steel slags, notably those from stainless steel production, form dusty powders upon cooling. The dusty nature

of these slags makes them hard to dispose of and difficult to use in practical applications. Dusty slags can be prevented by the addition of borates to the molten slag. Upon cooling, the resulting slag forms a hard aggregate rather than a fine dust and can be diverted from the waste stream for use as an aggregate in road construction. Anhydrous borax is most often used in this application (181).

15.12. Gypsum Wallboard. Gypsum board is widely used by the construction industry for internal walls and ceilings in residential and commercial buildings. The addition of boric acid improves product performance, user convenience, and production efficiency. Boric acid is added to the gypsum slurry during production to increase the strength of the board, reduce board weight, provide better adhesion of the paper backing to the board, reduce curing time, prevent wrinkle formation on the board surface, and create a hard gypsum edge that withstands nailing and handling during construction. Boric acid particularly enhances sag resistance under humid conditions for light-weight gypsum wallboard (182).

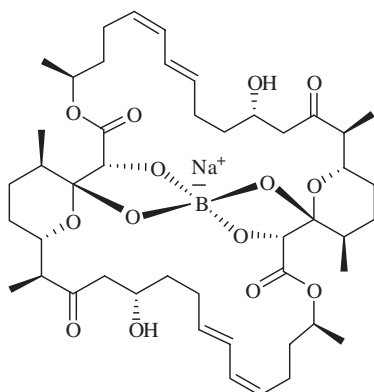
15.13. Nuclear. Because boron compounds are good absorbers of thermal neutrons, owing to the presence of the ^{10}B isotope ($\sim 20\%$ natural abundance), the nuclear industry has developed many applications for boron-containing materials. High purity boric acid is added to the cooling water used in high pressure water reactors and thermally stable boron materials, such as boron carbide, which may be isotopically enriched in ^{10}B , are used in nuclear control rods. Special quality nuclear-grade borate products are sold for this application.

15.14. Pulp and Paper. Borates are used in Kraft pulping in a process called partial autocausticizing. The Kraft process involves the digestion of wood furnish using aqueous sodium sulfide and sodium hydroxide to extract lignans and other organic components from cellulose fiber to render pulp for paper production. The remainder of the Kraft process involves recovery of the reagents used for digestion. Digestion and pulp separation results in an organic laden combustible solution, called black liquor, which is burned in a large furnace containing heat recovery coils known as a recovery boiler. The noncombustible inorganic components are drawn from the bottom of the furnace and cooled to produce a vitreous solid known as smelt. The smelt is added to water to produce a mixture of sodium carbonate and sodium sulfide in solution. Calcined lime is then added to react with sodium carbonate and to regenerate hydroxide, or causticity, which is returned to the digester to complete the cycle. The resulting calcium carbonate is separated and passed through a rotary calciner to regenerate calcined lime.

Borate autocausticizing provides a means of regenerating caustic soda without using lime. In practice, it is not usually practical to replace the lime circuit completely, and so, partial autocausticizing is often employed. In this process, a sufficient level of borate is used to replace 20–30% of the lime circuit demand. Borax reacts with sodium carbonate in the recovery boiler to produce highly alkaline borate species of approximate composition $\text{Na}_4\text{B}_2\text{O}_5$. This borate hydrolyzes in water to regenerate causticity. Partial autocausticizing is particularly useful for Kraft mills that have constrained lime circuit capacities (183).

16. Environmental, Health, and Safety

Boron is present everywhere in the environment and is found in measurable amounts in virtually all soils and natural waters. It is also an essential element for all plant life and part of a healthy human diet. Boron-containing natural products are now known to be common. Among the earliest of such compounds to be isolated were antibiotics produced by microorganisms, including aplasmomycin, (184,185), boromycin (186,187), and tartralon B (**21**, (188)). As in these examples, boron interacts with organic and biological substrates through the formation of B—O—C esters linkages, often involving condensation with diols moieties, which are abundant in biological systems.



(21)

More recently, boron has been found to play a crucial role in quorum sensing in marine bacteria in which a borate-sugar diester complex is involved in important cell-cell communication via an autoinducer molecule (189). Boron plays a vital role in the functioning of plants and evidence exists for similar roles of marine algae and diatoms, fungi, bacteria, and macrophytyes (190–194). Mounting evidence also points to the nutritional importance of boron in animals, as briefly described subsequently.

16.1. Human Exposure. The primary source of boron exposure for human populations is ingestion from food (195–198). This is largely because of the essential nature of boron as a micronutrient in plants (199), which has been established since the 1920s (200). Plant-derived foods such as fruits, vegetables, grains, and nuts contain significant amounts of boron. Foods containing the highest concentrations of boron include avocado, peanuts and peanut butter, prune juice, grape juice, chocolate powder, wine, pecans, granola, raisins, and bran cereals. (196).

In occupational settings, inhalation is generally considered the most significant route of exposure. Dermal exposure is not usually a concern because boric acid and borates are poorly absorbed through intact skin.

16.2. Environmental Exposure. Terrestrial systems receive boron from atmospheric deposition, burning of wood and coal, and rock weathering. Sea salt aerosols are the largest source of atmospheric boron flux

(1.44 Tg B/year) (201). Weathering of rocks is a much smaller source (0.19 Tg B/year), approximately equal to coal combustion (0.20 Tg B/year) and less than the burning of biomass (~0.33 Tg B/year). The global industrial use of boron is estimated at about 0.31 Tg B/year (202), with approximately half of this production being used in immobilized forms, such as glass. Of the estimated 2200 Tg B in surface soil, about 4.5 Tg B/year is taken in by plants globally, with most of this material being returned to the soil as organic matter (201). Soil concentrations normally range from 2 ppm to 100 ppm (203). Soil concentrations reflect the underlying rock, with typical boron concentrations increasing from igneous rock, sedimentary rock, arid saline soils, and marine shale. Typical soil concentrations are reported to be 10–33 ppm (194,204).

Freshwater concentrations of boron range from nondetectable to several mg B/L, with the highest occurrences usually associated with geothermal inputs, such as the Firehole River in Yellowstone (205). Seawater contains about 5 mg B/L. A survey of public water supplies in the United States found that the median boron concentration was 0.04 mg B/L with a maximum of 3.3 mg B/L and an average of 0.17 mg B/L (206). This survey reflected 134 surface water sources and 273 groundwater sources. The U.S. Environmental Protection Agency reported the results of a survey of groundwater sources used for drinking water and found that boron was detected (~0.005 mg B/L) in about 82% of all groundwater but exceeded 0.7 mg B/L in only about 4.3% of the samples and exceeded 1.4 mg B/L in 1.7% of the groundwater used as public water supplies (207). Boron is relatively mobile in the environment compared with other inorganic substances. Boric acid and borates are water soluble and have a relatively low tendency to bind to soil, as indicated by low Freundlich partitioning coefficients of about 1.6.

16.3. Essentiality in Plants. Boron was known to occur naturally in plants since the nineteenth century and was suspected to be essential (208). Its essential role in plants eventually was established by the pioneering work of Katherine Warington at the Rathamsted Experimental Station in England in the 1920s (200). It is now understood that plants require an adequate and continuous supply of boron for flowering, pollen tube growth, pollen germination, and fruiting. In general, plants require more boron for reproductive growth than for normal vegetative growth, making boron a critical element for optimal crop yields and food production.

Boron is required for the proper functioning of plant cell walls. One of its physiological roles is in the cross-linking of the complex polysaccharide rhamnogalacturonan II in primary cell walls (209). This borate cross-linking serves to strengthen the cell walls and to facilitate cell adhesion. Boron also seems to be necessary for various metabolic processes, such as nitrogen metabolism, nucleic acid metabolism, and membrane integrity and stability.

Boron uptake by plants was believed for a long time to be a passive, unregulated process. However, it is now known that plants actively transport and regulate boron. Specific plasma membrane-localized efflux transporter proteins, BORs, first identified in the roots of *Arabidopsis thaliana* (BOR1), are used by plants for the xylem loading of boron (210–212). Plants with impaired BOR activity have higher boron requirements for normal function (213). Although plants require boron, excessive concentrations are toxic. Thus, plants maintain boron within an optimum concentration range by regulating transport processes to

avoid both deficiency and toxicity. In addition to BOR exporter proteins for xylem loading, plants also use boric acid-selective membrane channels (NIPs) to regulate the response to boron availability (214). By altering the expression of these boron transporters, plants have some capacity to respond to environmental boron levels and to tolerant stresses produced by low and high boron levels (215).

Although plants have some capacity to regulate boron, required levels vary such that essential levels for one species may be toxic to another (194). The concentration–response curve for boron is likely to be U-shaped for many species, with adverse effects observed at high and low concentrations, whereas no adverse effects are observed at intermediate concentrations (216).

Numerous studies have now documented boron applications for 132 crops in more than 80 countries, demonstrating the widespread benefits of agricultural uses of boron (217–219). The importance of boron as a micronutrient is demonstrated through use in agriculture in which boron may be applied as a soil treatment or foliar spray. Agricultural application of boron depends on the plant and cultivar as well as the local soil. Recommended application rates may be as high as 4.5 kg B/ha (220) but typically are in the range of 1–2 kg B/ha (219).

16.4. Biological Importance in Animals (Vertebrate). Boron is critical for normal reproduction and embryonic development in several animal species, and mechanisms for this essentiality are beginning to be revealed (221). Like many essential elements, it is likely that boric acid exhibits a U-shaped dose–response curve in animals. A beneficial effect to fish at low concentrations was shown for carp and rohu (222). Work with rainbow trout and zebrafish has shown that embryo and larval development was adversely affected in waters deficient in boron (223–225). Fort and co-workers (226,227) reported abnormal development in frog embryos (*Xenopus laevis*) when larval stages were exposed to low boron conditions of 0.003 mg B/L or less. But boron may not be essential for all species. The growth of vitamin D₃-deficient chicks was stimulated by supplementation of boron (3 mg B/kg diet) in a low-B basal diet (228). Boron supplementation in pig diets (5 mg B/kg diet) decreased the inflammatory response to an intradermal injection of phytohemagglutinin in pigs, altered plasma lipid metabolites, and tended to increase the production of cytokines after stress (229–231). In rats, maternal exposure to a low-boron diet was associated with a reduction in embryo implantation sites (232). *In vitro* exposures of mouse embryos to low-B growth medium showed a reduced blastocyst formation and increased embryo degeneration (233).

16.5. Biological Importance in Humans. Extensive research points to the nutritional importance of boron in humans. Several authors have proposed a role for boron in the metabolism of vitamin D and estrogen (234–236). In addition, dietary boron deprivation studies in both rats and humans have consistently found an effect of boron intake on brain electrophysiology as well as in humans on performance of tasks measuring eye–hand coordination, attention, and short-term memory (237). Although, to date, insufficient data is available to confirm essentiality in humans, the U.S. Food and Nutrition Board in 2001 published a Tolerable upper intake level (UL) for boron of 20 mg/day and confirmed its nutritional importance for humans (238). The U.K. Expert Group on Vitamins and Minerals (239) and the European Food Safety Authority (240)

also regarded boron as nutritionally important and determined an acceptable daily intake for boron (0.16 mg/kg/day).

Epidemiological studies have shown a correlation of reduced risk of prostate cancer incidence and mortality with increased boron intake as well as local groundwater boron concentrations (241–243), suggesting that a higher boron intake has a beneficial effect in the prevention of prostate cancer. Recent studies are beginning to identify mechanisms for the role of boron in the inhibition of human prostate cancer cell proliferation (243–249). Potential mechanisms include inhibition by boric acid of stored Ca^{2+} release, regulating Ca^{2+} signaling, and inhibition of NAD^+ and NADP^+ in prostate cancer cells (247,248). In addition, another study (250) reported a significantly higher incidence of esophageal cancer in a low boron region compared with an area that had boron exposure.

16.6. Toxicology. Several detailed hazard assessments and reviews of the toxicology of borates have been published (198,238,240,251–261). Boron compounds have been tested on numerous species with the goal of improving their safe handling, use, and complying with regulations. These species include invertebrates; vertebrates, such as fish and frogs; and mammalian species, such as rats, mice, and dogs. These studies have been conducted to measure the effect of high levels of boron on animals as follows: *acute*, meaning a single high dose; and *chronic*, meaning repeated exposures over longer periods of time. For comparative purposes, dose levels of borates usually are expressed in terms of B equivalents based on the fraction of boron content on a molecular weight basis. Conversion factors are given in Table 16. These conversion factors are important as some studies express dose in terms of B, whereas other studies express dose in units of parent compound (eg, boric acid or sodium tetraborate decahydrate). The B equivalents used are a generic designation rather than a designation of elemental boron.

16.7. Animal Studies: Acute Toxicity. The literature contains historic data from animal studies. Boric acid and the sodium tetraborates have low acute toxicity in mammals, including rats, mice, and dogs. No substantial differences in acute toxicity were observed in rats, mice, and dogs in the limited studies available, although dogs exhibit an emetic effect in response to high doses of borates. The main symptoms of toxicity observed in all species tested were central nervous system depression, ataxia, and convulsions. Humans display different acute symptoms compared with most animals. The oral LD50 in dogs was

Table 16. Conversion Factors to Boron Equivalents

Boron compound	Formula	Conversion factor for equivalent dose of B
boric acid	$\text{B}(\text{OH})_3$	0.175
sodium tetraborate decahydrate (borax decahydrate)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.113
disodium octaborate tetrahydrate (DOT)	$\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$	0.21
zinc borate	$2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}^a$ or $\text{ZnB}_3\text{O}_4(\text{OH})_3$	0.149

^aKnown as an article of commerce as $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$.

determined to be >3980 mg boric acid/kg and >6150 mg sodium tetraborate decahydrate/kg (administered in a capsule). The dogs vomited shortly after treatment at all doses (158 mg boric acid/kg and 246 mg sodium tetraborate decahydrate/kg were the lowest doses tested). No other adverse symptoms were noted (262,263). The acute oral LD50 of zinc borate is greater than 10,000 mg/kg (limit of tested dosages) in albino rats.

Low acute inhalation toxicity was observed for those borates tested with a 4-h LC50 being >2 mg/L for boric acid, sodium tetraborate decahydrate, sodium tetraborate pentahydrate, and disodium octaborate tetrahydrate.

As anticipated, because of their minimal skin absorption, the acute dermal toxicity was low for those borates tested (eg, LD50s were >2000 mg/kg for boric acid, boric oxide, disodium octaborate tetrahydrate, sodium tetraborate decahydrate, and sodium tetraborate pentahydrate, and >10,000 mg/kg [limit of tested dosages] for zinc borate).

Boric acid and borate compounds generally do not cause irritation to intact skin and generally are considered nonirritating to eyes in normal industrial use. However, sodium tetraborates have been shown to be irritants in tests with animals and thus may be classified accordingly. No evidence has been found of skin sensitization in humans or animals as a result of boron exposure. Occasional mild irritation effects to nose and throat may occur from the inhalation of dusts at levels >10 mg/m³ (263,264).

16.8. Animal Studies: Chronic Toxicity. Boron compounds also have been tested to determine their long-term or chronic toxic effects. The results of these studies are highlighted in the following paragraphs (256). Numerous studies testing the effect of boron compounds on both bacteria and mammalian cells prove that they are not mutagenic (ie, they do not cause genetic mutation), nor are boron compounds considered carcinogenic, or cancer-causing.

The main treatment-related effects from long-term dosing studies in laboratory animals relate to reproductive and development effects. For instance, effects on the testes have been observed in both subchronic and chronic studies in three species (rats, mice, and dogs). The effects tend to be similar in all three species, although most data derive from rat studies. The reproductive effects in rats at lower doses and shorter time periods start with reversible inhibition of spermiation. In rats, a single dose of 175 mg B/kg body weight (bw) caused reversible disruption of tubular spermiation (265), although no such effects were observed after a single dose of 350 mg B/kg (2000 mg boric acid/kg) (266). Data in dogs are derived from two limited 2-year feeding studies. Unfortunately, the published study does not reflect the information detailed in the original study reports (263,267). In addition, the Weir and Fisher studies estimated the dietary intakes from standard intake figures (263). However, the original study reports contained the actual dietary intake allowing for a more accurate measurement of the boron intake. Amended figures have been reported elsewhere (267). The adjusted intake for groups of dogs fed either boric acid or sodium tetraborate decahydrate at doses up to 10.2 mg B/kg bw/day (62.4 mg boric acid/kg bw/day and 84.7 mg sodium tetraborate decahydrate/kg bw/day) in one study and up to 39.5 mg B/kg bw/day (233.1 mg boric acid/kg bw/day and 373.2 mg sodium tetraborate decahydrate/kg bw/day) in a second study. The no observable adverse effect level

(NOAEL) was 10.2 mg B/kg bw/day. Although this data should be considered inadequate for risk assessment, it does confirm the effects and NOAEL observed in other species.

Boric acid has been tested in developmental studies. Effects were observed at high doses in rats, mice, and rabbits. Most studies have been carried out in rats. In two separate studies conducted in the same laboratory, rats received numerous dose levels (approximately 3.3, 6.3, 9.6, 13.7, 25, 28, and 59 mg B/kg bw/day on gestation days 0–20 and 94 mg B/kg bw/day on gestation days 6–15) in feed. The NOAEL for developmental effects was 9.6 mg B/kg bw/day, respectively (268).

16.9. Humans. A large database is available of accidental or intentional poisoning incidents for humans. Many were the result of accidental use as an antiseptic for irrigating body cavities, treating wounds, or as a treatment for conditions such as epilepsy. Such medical uses are now obsolete. Historical accidental misuses also include the preparation of baby formula (1–14 g boric acid in the formula) and the topical use of pure boric acid powder for infants, which led to poisonings. This database is reviewed in several reports from poisoning centers as well as in a detailed review of cases described in the literature from the mid-1800s to the 1970s (269–273).

16.10. Occupational Studies. In general, occupational studies of exposure to borate dusts suggest that these substances can be perceived in the workplace as sensory irritants, primarily of the nose. However, the severity of response is low. Maximal responses to dust are likely to occur within tens of minutes of exposure and did not result in any residual effects over years of workplace exposure.

Three major studies of the reproductive health among boron-exposed groups have been reported. These were published by Whorton and colleagues based on studies at the large borate mine at Boron, Calif. (274); by Sayli based on studies of families living in boron-rich areas of Turkey (275); and by Robbins, Wei, and colleagues based on studies at Chinese sites, comparing workers in the borate industry with others living in the local community (naturally high in boron) and a distant community (276). An additional study was reported on Russian workers, but the reliability of this study has been questioned (277).

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