BORON OXIDES, BORIC ACID, AND BORATES

1. Introduction

Boron, the fifth element in the periodic table, does not occur in nature in its elemental form. Rather, boron combines with oxygen as a salt or ester of boric acid. There are more than 200 minerals that contain boric oxide but relatively few that are of commercial significance. In fact, three minerals represent almost 90% of the borates used by industry: borax, a sodium borate; ulexite, a sodium–calcium borate; and colemanite, a calcium borate. These minerals are extracted in California and Turkey, and to a lesser extent in Argentina, Bolivia, Chile, Peru, and China. China and Russia also have some commercial production from magnesium borates and calcium borosilicates. These deposits furnish nearly all of the world's borate supply at this time (1).

According to legend, borates were used by Egyptians in mummification and by the ancient Romans in glassmaking. But the first historically verifiable use of borates was by Arabian gold- and silversmiths who used the minerals as refining and soldering agents in the eighth century A.D. The earliest confirmed use of borates in ceramic glazes was in China in the tenth century A.D. Three hundred years later, regular imports of borates from Tibet to Venice began along trade routes taken by Macro Polo's caravans.

The discovery of significant deposits of borates in both North and South America in the mid-nineteenth century and their subsequent development helped to lower the price and greatly increase global usage, particularly as a key ingredient in soaps and detergents. Early in the twentieth century, larger and higher grade deposits found first in Death Valley and then in the Mojave Desert also helped speed the rate of borate consumption. Another world-class deposit was discovered in Turkey in the late 1960s, making that country a major world producer.

Refined borates are usually sold on the basis of their B_2O_3 content and defined by their water or hydration content; borax pentahydrate or "5 mol," borax decahydrate or "10 mol," and boric acid are the three most commonly sold borate products. United States–based Borax, and Etibank, the Turkish national mineral producer, supply approximately 90% of the borates and refined borate products worldwide.

There is a large global market for borates because of their unique chemical properties and relative cost-effectiveness. Today, borates are used in a wide variety of products and processes; the major markets are for insulation fiberglass, textile fiberglass, detergents and bleaches, enamels and frits, and agricultural products. Borates are essential for imparting strength as well as heat- and impact-resistance to glass and glass fibers. The element boron is also an essential micronutrient for plants. Thousands of everyday items, including contact lens solutions, barbecue charcoal, brake fluid, and kitchenware—all contain borates.

Other developments include the increased usage of ulexite and colemanite in the manufacture of some insulation products, and expanding applications for borates as pest control products, fertilizers, herbicides, wood preservatives, and flame retardants.

Boron, in trace amounts, is an essential micronutrient for plants. Although it has not yet been proved that humans need boron to live, there is almost universal agreement that boron is nutritionally important to maintain optimal human health. Studies indicate that people in a wide variety of cultures consume ~1–3 mg of boron per day through a combination of foods and drinking water in their local diets.

Nevertheless, boron has come under some scrutiny in the latest revisions of drinking-water standards, and there has been some legislation proposed in Europe to limit the amount of borate in detergent formulations as a result.

Table 1. **Oxides and Borates Referred to in Text**

Compound	CAS Registry Number	Molecular Formula
ammonium pentaborate tetrahydrate	[12229-12-8]	$NH_4B_5O_8 \cdot 4H_2O$
barium metaborate hydrate	[13701-59-2]	$BaO \cdot B_2O_3 \cdot xH_2O$
boron dioxide	[13840-88-5]	BO_2
boron monoxide	[12505-77-0]	BO
boron oxide (6:1)	[11056-99-8]	B_6O
boron oxide (7:1)	[12447-73-3]	B_7O
boron oxide (13:2)	[56940-67-1]	$B_{13}O_2$
boron phosphate	[13308-51-5]	BPO_4
boron suboxide	[54723-68-1]	$B_{12}O_2$
boron oxide (12:2)	[54723-68-1]	$B_{12}O_2$
diammonium tetraborate tetrahydrate	[12228-87-4]	$(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$
diboron dioxide	[13766-28-4]	B_2O_2
boron oxide (2:2)	[13766-28-4]	B_2O_2
diboron trioxide	[1303-86-2]	B_2O_3
boron oxide (2:3)	[1303-86-2]	B_2O_3
dicalcium hexaborate pentahydrate	[12291-65-5]	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$
dipotassium tetraborate tetrahydrate	[12045-78-2]	$K_2O \cdot 2B_2O_3 \cdot 4H_2O$
disodium octaborate tetrahydrate	[12280-03-4]	$Na_2O \cdot 4B_2O_3 \cdot 4H_2O$
disodium tetraborate	[1330-43-4]	$Na_2O \cdot 2B_2O_3$
disodium tetraborate decahydrate (borax)	[1303-96-4]	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$
disodium tetraborate pentahydrate	[12045-88-4]	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$
disodium tetraborate tetrahydrate	[12045-87-3]	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$
dizinc hexaborate heptahydrate	[12280-01-2]	$Zn_2B_6O_{11} \cdot 7H_2O$
metaboric acid	[13460-50-9]	HBO_2
orthoboric acid	[10043-35-3]	$B(OH)_3$
potassium pentaborate tetrahydrate	[12229-13-9]	$KB_5O_8 \cdot 4H_2O$
sodium calcium pentaborate octahydrate	[1319-33-1]	$NaCaB_5O_9 \cdot 8H_2O$
sodium calcium pentaborate pentahydrate	[12229-14-0]	$NaCaB_5O_9 \cdot 5H_2O$
sodium metaborate dihydrate	[16800-11-6]	$NaBO_2 \cdot 2H_2O$
sodium metaborate tetrahydrate	[10555-76-7]	$NaBO_2 \cdot 4H_2O$
sodium pentaborate pentahydrate	[12046-75-2]	$NaB_5O_8 \cdot 5H_2O$
sodium perborate tetrahydrate	[10486-00-7]	$NaBO_3 \cdot 4H_2O$
sodium perborate trihydrate	[28962-65-4]	$NaBO_3 \cdot 3H_2O$
sodium perborate monohydrate	[10332-33-9]	$NaBO_3 \cdot H_2O$
zinc salt (1:2), hydrate	[12447-61-9]	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$
zinc diborate dihydrate	[27043-84-1]	$ZnO \cdot B_2O_3 \cdot 2H_2O$
zinc triborate monohydrate	[12429-73-1]	$Zn(B_3O_3(OH)_5) \cdot H_2O$

Possible health benefits and the safe health limits of boron in the human system are still undergoing intensive investigation.

The oxides and oxyacids of boron as well as a variety of hydrated and anhydrous metal borates are discussed herein. An alphabetical list of compounds referred to in the text is given in Table 1.

The confusing and often ambiguous systems of nomenclature encountered in the literature of inorganic borates have been described (2). The accumulation of detailed structural data for many of the crystalline compounds has led to derivation of more complex names and formulas in an effort to convey more precise information; *Chemical Abstracts* has adopted a classification system based on a series of the usually hypothetical boric acids. For example, the compound having empirical formula $Zn_2B_6O_{11}\cdot 7H_2O$ has been called dizinc hexaborate heptahydrate. Applying the resolved oxide system proposed by the IUPAC, the substance becomes $2ZnO\cdot 3B_2O_3\cdot 7H_2O$, known as zinc (2:3) borate heptahydrate. This latter system has gained wide acceptance and is followed herein. However, knowledge of the crystal structure allows a more precise structural formulation, $Zn(B_3O_3(OH)_5)\cdot H_2O$, ie, zinc triborate monohydrate, which is listed in *Chemical Abstracts* as boric acid, $H_7B_3O_8$, zinc salt [12429-73-1] (2). Because many authors continue to use the older formulations, a second listing has been devised by *Chemical Abstracts* for the same compound, ie, boric acid, $H_4B_6O_{11}$, zinc salt (1:2) heptahydrate [12280-01-2].

The principal borate minerals are listed in Table 2. A much more complete listing is available in the literature (4,5). Crystal structures of known borate compounds have been compiled (6).

Reports have been made concerning the minerals of the Searles Lake (7), the Boron-Kramer, and the Death Valley (7) areas in the United States.

The single largest tonnage use of borates worldwide is in insulation fiberglass, a soda lime borosilicate glass used as thermal and acoustic insulation and filtration media. Borates are essential components that impart a unique combination of melt and product properties (9). They contribute to insulating values of fiberglass by increasing the infrared absorption of the glass. The second

Table 2. **Commercial Borate Minerals**

Mineral	CAS Registry Number	Empirical Formula	B_2O_3 Content, wt %	Location
borax (tincal)	[1303-46-4]	$Na_2B_4O_7\cdot 10H_2O$	36.5	USA, Turkey, Argentina
kernite	[12045-87-3]	$Na_2B_4O_7\cdot 4H_2O$	51.0	USA
Ulexite (cottonball)	[1319-33-1]	$NaCaB_5O_9\cdot 8H_2O$	43.0	Turkey, South America
Colemanite	[12291-65-5]	$Ca_2B_6O_{11}5H_2O$	50.8	Turkey
Inderite	[12260-26-3]	$Mg_2B_6O_{11}\cdot 15H_2O$	37.3	Kazakhstan
Szaibelyite (ascharite)[a]	[12447-04-0]	$Mg_2B_2O_5\cdot H_2O$	41.4	China
Suanite	[36564-04-2]	$Mg_2B_2O_5$	46.3	China
Datolite		$Ca_2B_2Si_2O_9\cdot H_2O$	21.8	Russia

[a] This material has two CAS Registry Numbers.

largest application is in textile or continuous filament fiberglass, a calcium alumino borosilicate glass, used for electrical insulation and for reinforcement of plastics (10). The absence of alkali makes it difficult to melt and fiberize, which is overcome by the addition of boric oxide. Borates are also finding an increasing use in ceramic glaze. Since about 1990, there has been movement away from lead-containing glaze for tiles and tableware, and toward borosilicate glazes (11).

A number of boron-containing products are prepared directly from boric acid. These include synthetic inorganic borate salts: zinc borates, barium metaborate, boron phosphate, fluoroborates, boron trihalides, boron carbide; and, metal alloys such as ferroborn. There is a growing interest in use of boron in refractory boron compounds such as boron nitrides and boron carbide.

Inorganic boron compounds—namely, boric acid, sodium borates, zinc borates, and ammonium borates — are generally good fire retardants and are particularly effective in reducing flammability for both plastic and cellulosic materials (12). On heating cellulosic materials, formation of borate esters are believed to block the pyrolytic decomposition to volatile flammable products. In both cellulose and plastics, borates also function as a flux, forming glassy vitreous char that protects against further pyrolysis.

Boron is an essential micronutrient for plants and is added to boron-deficient soils to increase crop vitality and fruit yield. The element has also been shown to be of nutritional importance in humans and has been classified as “probably essential in animals” (13). In biological systems, it is generally thought that the Lewis acid properties and crosslinking ester formation is important in boron’s role. At high cencentrations, this interaction can also inhibit metabolism and leads to the biostatic effects utilized in the preservative applications of borates. These include biodeterioration control, particularly the protection of wood and cellulosic products against termites, other insects, and fungi.

Compounds of boron that do not contain oxygen directly bonded to boron are of lesser commercial volume; these include boron halides and boron hydrides (13) (see BORON HALIDES). The only commercially important boron halides are boron trichloride, BCl_3, and to a smaller extent boron tribromide, BBr_3. The boron halides are strong Lewis acids due to the B−X bond being strongly polarized and of high π-bonding character. These boron halides react with Lewis bases having reactive O, S, N, or P moieties. The boron halides are primarily used as Friedel−Craft polymerization catalysts and in chemical vapor deposition (CVD) processes for the production of elemental boron fibers for high strength reinforcement applications. Boron hydrides are represented by a unique and diverse class of compounds, but have few commercial applications because of their high cost. Only sodium borohydride, $NaBH_4$, has significant commercial use as a powerful reducing agent used primarily as a bleaching agent to whiten paper and clays. Diborane, B_2H_6, is used in very small amounts as a semiconductor dopant in the electronics industry (see BORON HYDRIDES HETEROBORANES, AND THEIR METALLA DERIVATIVES (14).

The application of crystallographic data to borate geology has been described (15).

2. Occurrence

The known world-class borate deposits are located in southern California and northwestern Anatolia, Turkey. In California, sodium borates are produced from a large deposit located in Boron in the northwestern Mojave Desert, and as a coproduct from brines pumped from shallow depths at Searles Lake west of Death Valley. Minor amounts of colemanite are extracted from a deep underground mine on the edge of Death Valley National Park.

In Turkey, there are three main producing districts: Kirka, which produces borax; the Emet basin, which contains two large colemanite deposits; and the Bigadic basin, which produces both ulexite and colemanite from several deposits.

Portions of four South American countries—northern Argentina, northern Chile, southern Bolivia, and southern Peru—contain numerous ulexite deposits. Northern Argentina also hosts the Tincalayu borax deposit and several ulexite–colemanite deposits. These deposits supply the South American market and export a minor amount to Pacific Rim countries. Eastern China, where a number of relatively small magnesium borate deposits are located, and far eastern Russia, which mines a large borosilicate deposit, supply their local markets and represent most of the remainder of the world's borate production.

Borax, and to a lesser extent kernite, are mined from huge open pits at Boron in California, Kirka in Turkey, and Tincalayu in northern Argentina. These three deposits, plus the brines from Searles Lake, California, furnish most of the sodium borates used by industry. Sodium borates are easily soluble in water, making them preferable for many end uses. All four of these facilities also produce boric acid at nearby refineries.

Colemanite is mined from several deposits in the Emet and Bigadic basins of western Turkey, one Death Valley deposit, and small deposits in northern Argentina. This calcium borate is used in end products that have a low sodium requirement, and in making boric acid.

Ulexite is the common marsh or playa (salar) borate. It is produced commercially from numerous playas in South America and the Provinces of Quinghi and Xizang (Tibet) in western China. Ancient playa deposits 5–20 million years old—are the source of Turkish ulexite, ulexite found in Death Valley, and some of the ore produced in Argentina. Much of this material is ground and used as a crude 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 refined in small, local plants to produce sodium borates and boric acid for domestic use. A unique borosilicate deposit near Dalnegorsk in far-eastern Russia is mined to produce boric aicd. Borates from this souce were once shipped by rail to western Russia and eastern Europe when they operated under the Former Soviet Union but now are shipped through local ports to markets in the Far East.

Other borate deposits, some of which were once mined commercially, are reported in a number of other areas as well (Table 2). These include the Inder region of Kazakhstan, the Stassfurt district of eastern Germany, northern Iran, and Yugoslavia. Numerous existing deposits in western United States, western Turkey, and in South America are not currently in production due to various economic reasons (16).

3. Boron Oxides

3.1. Boric Oxide. Boric oxide, B_2O_3, formula wt 69.62, is the only commercially important oxide. It is also known as diboron trioxide, boric anhydride, or anhydrous boric acid. B_2O_3 is normally 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 contains ca 1 wt % moisture as a surface layer of boric acid. The reaction with water:

$$B_2O_3\ (\text{glass}) + 3\ H_2O \longrightarrow 2\ B(OH)_3$$

is exothermic, $\Delta H^\circ = -75.94$ kJ/mol (-18.15 kcal/mol) B_2O_3 (17).

Boric oxide is an excellent Lewis acid. It coordinates even weak bases to form four-coordinate borate species. Reaction with sulfuric acid produces $H[B(HSO_4)_4]$ (18). At high (>1000°C) temperatures molten boric oxide dissolves most metal oxides and is thus very corrosive to metals in the presence of oxygen.

Molten boric oxide reacts readily with water vapor above 1000°C to form metaboric acid in the vapor state.

$$B_2O_3\ (\text{glass}) + H_2O(g) \longrightarrow 2\ HBO_2(g)$$

A value of$\Delta H_{298} = -199.2 \pm 8.4$ kJ/mol (-47.61 ± 2.0 kcal/mol) has been calculated for this reaction, which is of considerable economic importance to glass manufacturers because B_2O_3 losses during glass (qv) processing are greatly increased by the presence of water. For this reason anhydrous borates or boric oxide are often preferred over hydrated salts, eg, borax or boric acid for glass manufacture. The presence of MgO has been found to reduce volatilization of B_2O_3 from glass charges (19).

The physical properties of vitreous boric oxide (Table 3) are somewhat dependent on moisture content and thermal history. Much of the older physical data has been revised following development of more reliable techniques for sample preparation (23,24). 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. Removal of residual water causes the density to decrease and softening point at 6×10^6 Pa·s (6×10^7 P) to increase. At 0.28 wt% of water the density of boric oxide is 1.853, softening point 240–275°C; nearly anhydrous B_2O_3, having 20 ppm water has 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

Table 3. **Physical Properties of Vitreous Boric Oxide**

Property	Value	Reference
vapor pressure[a], 1331–1808 K	$\log P = 5.849 - \dfrac{16960}{T}$	20
heat of vaporization, ΔH_{vap}, kJ/mol[b]		
1500 K	390.4	21
298 K	431.4	21
boiling point, extrapolated	2316°C	17
viscosity, log η, mPa·s(= cP)		
350°C	10.60	22
700°C	4.96	22
1000°C	4.00	22
density, g/mL		
0°C	1.8766	
18–25°C	1.844	
18–25°C[c]	1.81	
500°C[d]	1.648	22
1000°C[d]	1.528	22
index of refraction, 14.4°C	1.463	
heat capacity (specific), J/(kg·K)[b]		
298 K	62.969	17
500 K	87.027	17
700 K	132.63	17
1000 K	131.38	17
heat of formation[e], ΔH_f, kJ,[b] 298.15 K	-1252.2 ± 1.7	17

[a] P is in units of kPa; T is in K. To convert kPa to torr, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

[c] Well-annealed.

[d] Quenched.

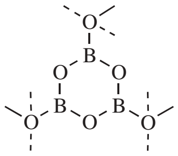
[e] For $2\,B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3$ (glass).

content. Boric oxide becomes pourable on heating to about 500°C. The viscosity of boric oxide with temperature is given below.

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 historical debate over the molecular structure of vitreous and molten boric oxide may never be completely resolved because of its amorphous nature (26). There are only trigonal borons in the solid glass and these are believed to have a branched network of planar boroxol $(\text{–BO–})_3$ rings (**1**). The three exocyclic oxygens, outside the ring, form bridges to neighboring rings or to planar BO_3 groups (27,28). 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 (24) that above

800°C the liquid consists of discrete, but strongly associated, small molecules, conceivably the same monomeric B_2O_3 units observed in the vapor state (29).



(**1**)

Two crystalline forms of boric oxide have been prepared, and the structures of both materials have been determined by x-ray diffraction (18). The phase relationships between the liquid and crystalline forms have also been developed (30). The more common hexagonal crystal phase, B_2O_3-I or α-form ($d = 2.46$ g/mL, mp $= 455 - 475$°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 (31). For the transformation $B_2O_3{-}\mathrm{I} \longrightarrow B_2O_3$ (glass), $\Delta H^\circ = +18.24$ kJ/mol (4.36 kcal/mol) (17). However, vitreous B_2O_3 does not crystallize in the absence of seed crystals or increased pressure. Crystallization of B_2O_3 can be induced by prolonged heating of melt with <18 wt % water below 235°C or in the presence of 5 wt % water and addition of crystalline B_2O_3 seed at 250°C. Crystals do not form at any temperature from melt containing <1 wt % water. Crystalline B_2O_3 can also be made by prolonged heating of boric acid seeded with boron phosphate at 220 to 260°C (32). A second dense monoclinic crystalline phase, B_2O_3-II or β-form ($d = 2.95$ g/mL, mp $= 510$°C) can be obtained at 400°C and >2.23 GPa (>22,000 atm). The crystal lattice of B_2O_3-II consists of a highly compact network of BO_4 tetrahedra where the four apical oxygens are shared by either two or three boron atoms. The acidic character associated with trigonal BO_3 groups is thus masked in B_2O_3-II. Although this material is thermodynamically unstable under ordinary conditions, it reacts very slowly with Lewis bases such as water and fluoride ion.

In the United States a high (99% B_2O_3) purity grade is produced by fusing refined, granular boric acid in a glass furnace fired by oil or gas. The molten glass is solidified in a continuous ribbon as the melt flows over chill-rolls. The amorphous solid product is crushed, screened, and packed in sacks or drums with moisture-proof liners. The price of this product has increased 11% since the mid-1980s and more than doubled since 1977. The carload (>36 metric tons) price in January 1990 was $2780–2950/t (fob plant) depending on mesh size and packaging (33). Boric oxide is no longer commercially produced by mixing borax and sulfuric acid in a fusion furnace. There is no commercial source of crystalline boric oxide (B_2O_3).

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 phosphate. It also is a powerful Lewis acid solvent for dissolving metal oxides, has a low surface tension, and readily wets metal surfaces. Boric oxide can be used as a solvent for metal reductions such as $2\,CuO + C \longrightarrow CO_2 + 2\,Cu$, for growing crystals of garnet, refractory oxides, and preparation of lead titanate, barium titanate, and calcium zirconates from the corresponding oxides.

The uses of boric oxide relate to its behavior as a flux, an acid catalyst, or a chemical intermediate. The fluxing action of B_2O_3 is important in preparing many types of glass, glazes, frits, ceramic coatings, and porcelain enamels (qv).

Boric oxide is used as a catalyst in many organic reactions. It also serves as an intermediate in the production of boron halides, esters, carbide, nitride, and metallic borides.

3.2. Boron Monoxide and Dioxide.

High temperature vapor phases of BO, B_2O_3, and BO_2 have been the subject of a number of spectroscopic and mass spectrometric studies aimed at developing theories of bonding, electronic structures, and thermochemical data (1,34). Values for the principal thermodynamic functions have been calculated and compiled for these gases (35).

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 (187 and 120 kcal/mol) were calculated for the respective B=O and B−B bond energies (36).

Two noncrystalline solid forms of BO have been prepared (1,34). Several polymeric $(BO)_n$ or $(B_2O_2)_n$ structures have been proposed for these materials. Although conclusive structural evidence is unavailable, the presence of B−B bonds appears likely. The low temperature form is a white, water-soluble powder produced at 220°C by vacuum-dehydration of tetrahydroxydiborane(4), [13675-18-8]$B_2(OH)_4$, that can be prepared from tetrakis(dimethylamino)diborane(4)[1630-79-1] (37). This product is irreversibly converted to an insoluble, light brown modification on heating above 500°C. The latter material was also prepared by reduction of B_2O_3 by boron at 1330°C, by carbon, or by boron carbides at 1250°C (38). Both BO polymorphs are strong reducing agents that decompose slowly in water to yield hydrogen gas and boric acid.

$$B_2O_3 + C \longrightarrow B_2O_2 + CO$$

$$5\,B_2O_3 + B_4C \longrightarrow 7\,B_2O_2 + CO$$

3.3. Lower Oxides.

A number of hard, refractory suboxides have been prepared either as by-products of elemental boron production (1) or by the reaction of boron and boric acid at high temperatures and pressures (39). It appears that the various oxides represented as B_6O, B_7O, $B_{12}O_2$, and $B_{13}O_2$ may all 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 (39). A study has been made of the mechanical properties of this material, which exhibits a hardness comparable to that of boron carbide (40). At temperatures above 1000°C, $B_{12}O_2$ gradually decomposes to B(s) and B_2O_2(g).

4. Boric Acid

The name boric acid is usually associated with orthoboric acid, which is the only commercially important form of boric acid and is found in nature as the mineral sassolite. Three crystalline modifications of metaboric acid also exist. All these forms of boric acid can be regarded as hydrates of boric oxide and formulated as $B_2O_3 \cdot 3H_2O$ for orthoboric acid and $B_2O_3 \cdot H_2O$ for metaboric acid.

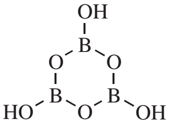
4.1. Forms of Boric Acid. Orthoboric acid, $B(OH)_3$, formula wt, 61.83, crystallizes from aqueous solutions as white, waxy plates that are triclinic in nature; sp $gr^{14}{}_4$, 1.5172. Its normal melting point is 170.9°C, however, when heated slowly it loses water to form metaboric acid, HBO_2, formula wt, 43.82, which may exist in one of three crystal modifications. Orthorhombic HBO_2-III or α-form ($d = 1.784$ g/mL,mp = 176°C) forms first around 130°C and gradually changes to monoclinic HBO_2-II or β-form ($d = 2.045$ g/mL,mp = 200.9°C). Water-vapor pressures associated with these decompositions follow. To convert kPa to mm Hg, multiply by 7.5.

	Vapor pressure of H_2O over $B(OH)_3$	
Temperature, °C	and HBO_2-III, kPa	and HBO_2-II, kPa
25	0.048	0.16
100	8.4	16
130	39.9	62.5
150	102	143

At temperatures above 150°C, dehydration continues to yield viscous liquid phases beyond the metaboric acid composition (39). The most stable form of metaboric acid, cubic HBO_2-I or γ-form ($d = 2.49$ g/mL, mp = 236°C) crystallizes slowly when mixtures of boric acid and HBO_2-III are melted in an evacuated, sealed ampul and held at 180°C for several weeks (41).

The relationships between condensed phases in the B_2O_3–H_2O system are shown in Figure 1 (42). There is no evidence for stable phases other than those shown. B_2O_3 melts and glasses containing less than 50 mol% water have mechanical and spectroscopic properties consistent with mixtures of HBO_2 and vitreous B_2O_3.

Vapor phases in the B_2O_3 system include water vapor and $B(OH)_3(g)$ at temperatures below 160°C. Appreciable losses of boric acid occur when aqueous solutions are concentrated by boiling (43). At high (600–1000°C) temperatures, $HBO_2(g)$ is the principal boron species formed by equilibration of water vapor and molten B_2O_3 (44). At still higher temperatures a trimer $(HBO_2)_3(g)$ (**2**) is formed.



(**2**)

The crystal structure of orthoboric acid consists of planar sheets made up of hydrogen-bonded, triangular $B(OH)_3$ molecules. The stacking pattern of the molecular layers is completely disordered, 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 (45). The structures of all three forms of metaboric acid are also known (46). The basic structural unit of

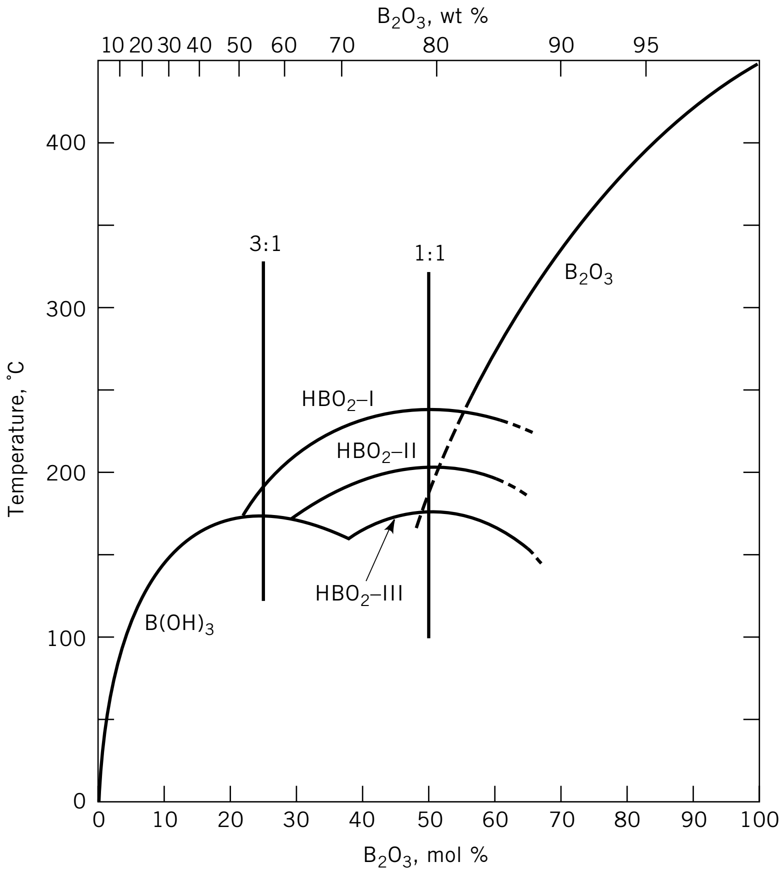


Fig. 1. Solubility diagram for the system $H_2O–B_2O_3$ (42). Courtesy of *The American Journal of Science*.

HBO_2-III is the trimeric ring (**2**) and consists of only planar trigonal BO_3 units. Metaborate-I has only tetrahedral BO_4 structural units and HBO_2-II contains both trigonal and tetrahedral borons in a ratio of 2:1. The HBO_2-III trimer may persist to some extent in the vapor phase, but infrared spectra indicate that monomeric O=B−OH species predominate in gaseous metaboric acid (47).

4.2. Properties. The standard heats of formation of crystalline orthoboric acid and the three forms of metaboric acid are $\Delta H_f^\circ = -1094.3$ kJ/ mol (−261.54 kcal/mol) for $B(OH)_3$; −804.04 kJ/mol (−192.17 kcal/mol) for HBO_2-I; −794.25 kJ/mol (−189.83 kcal/mol) for HBO_2-II; and −788.77kcal/mol (188.52 kcal/mol) for HBO_2-III (48). Values for the principal thermodynamic functions of $B(OH)_3$ are given in Table 4 (17).

The solubility of boric acid in water (Table 5) increases rapidly with temperature. The heat of solution is somewhat concentration dependent. For solutions having molalities in the range 0.03–0.9 m, the molar heats of solution fit the empirical relation (49):

$$\Delta H = \left[22062 - 222\, m + 979\, e^{-1230\, m}\right] \text{kJ/mol}$$

Table 4. **Thermodynamic Properties of Crystalline Boric Acid, $B(OH)_3$**[a]

Temperature, K	C°_p,J/(kg·K)[b]	S°, J/K[b]	$H^\circ - H^\circ_{298}$, J/mol[b]
0	0	0	−13393
100	35.92	28.98	−11636
200	58.74	61.13	−6866
298	81.34	88.74	0
400	100.21	115.39	9284

[a] Ref. 44.

[b] To convert J to cal, divide by 4.184.

Table 5. **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		

[a] Melting point.

[b] Boiling point.

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 decreased by lithium and sodium chlorides. Basic anions and other nucleophiles, notably borates and fluoride, greatly increase boric acid solubility by forming polyions (44).

Boric acid is quite soluble in many organic solvents (Table 6). Some of these solvents, eg, pyridine, dioxane, and diols, are known to form boric acid complexes.

Dilute aqueous solutions of boric acid contain predominantly monomeric, undissociated $B(OH)_3$ molecules. The acidic properties of boric acid relate to behavior as a base acceptor, ie, as a Lewis acid, rather than as a proton donor. For the reaction

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

an equilibrium constant of 5.80×10^{-10} at 25°C has been reported (50). However, calculated pH values based on this constant deviate considerably from measured ones as the boric acid concentration is increased, as shown in Table 7. 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 $B_3O_3(OH)_4^-$ [17927-69-4] appears to be the most important of these complex ions (52).

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 $B(OH)_4^-$ and/or polyborate anions. More than one

Table 6. **Solubility of Boric Acid, Borax Decahydrate, and Borax Pentahydrate in Organic Solvents**

Solvent	Temperature, °C		Solubility, wt %	
			$B(OH)_3$	$Na_2B_4O_7 \cdot 10H_2O$
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]		
n-propanol	25	59.4[a]		
n-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	ca 14.6[a]		
pyridine	25	ca 70[a]		
aniline	20	0.15		
acetic acid, 100%	30	6.3		

[a] Solubility values are in g/L.

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 to that of carboxylic acids, and such solutions may be titrated using strong base to a sharp phenolphthalein end point. Normally titrations of boric acid are carried out following addition of mannitol or sorbitol, which form stable chelate complexes with $B(OH)_4^-$ in a manner typical of polyhydroxy compounds. Equilibria of the type:

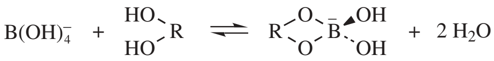
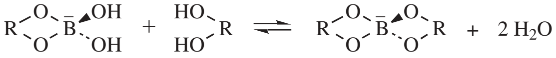


Table 7. **Observed and Calculated pH Values for Boric Acid**[a]

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

[a] Ref. 51.

and



have been exploited in other applications besides analytical determinations of boric acid (53). Ion-exchange resins containing polyols have been developed that are highly specific for removing borates from solution (54). A number of aliphatic and aromatic diols have been patented as extractants for borates and boric acid (55).

Boric acid and fluoride ion react to form a series of fluroborates where OH^-; is displaced by F^-; (see FLUORINE COMPOUNDS, INORGANIC, FLUOROBORIC ACID AND FLUOROBORATES). Stepwise formation of the ions fluorotrihydroxyborate[32554-53-3], $BF(OH)_3^-$, difluorodihydroxyborate[32554-52-2], $BF_2(OH)_2^-$, and trifluorotrihydroxyborate[18953-00-9], $BF_3(OH)_3^-$, proceeds rapidly in acidic solutions, but tetrafluoroborate[14874-70-5], BF_4^-, forms slowly (56). A fluorosubstituted polyborate, $B_3O_3F_6^{3-}$ [59753-06-9], has also been identified (52).

Alcohols react with boric acid with elimination of water to form borate esters, $B(OR)_3$. A wide variety of borate salts and complexes have been prepared by the reaction of boric acid and inorganic bases, amines, and heavy-metal cations or oxyanions (44,45). Fusion with metal oxides yields anhydrous borates or borate glasses.

4.3. Manufacture.

The majority of boric acid is produced by the reaction of inorganic borates with sulfuric acid in an aqueous medium. Sodium borates are the principal raw material in the United States. European manufacturers have generally used partially refined calcium borates, mainly colemanite from Turkey. Turkey uses both colemanite and tincal to make boric acid.

When granulated borax or borax-containing liquors are treated with sulfuric acid, the following reaction ensues:

$$Na_2B_4O_7 \cdot xH_2O + H_2SO_4 \longrightarrow 4\,B(OH)_3 + Na_2SO_4 + (x-5)\,H_2O$$

In the United States boric acid is produced by United States Borax & Chemical Corp. in a 103,000 B_2O_3 metric ton per year plant by reacting crushed kernite ore with sulfuric acid. Coarse gangue is removed in rake classifiers and fine gangue is removed in thickeners. Boric acid is crystallized from strong liquor, nearly saturated in sodium sulfate, in continuous evaporative crystallizers, and the crystals are washed in a multistage countercurrent wash circuit.

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 by cooling the filtrate.

A unique liquid–liquid extraction process for manufacturing boric acid from sodium borate brines has been operated at Searles Lake, Trona, California, by the North American Chemical Co. since 1962. Both potassium sulfate and sodium sulfate are produced as coproducts in this process.

Boric acid crystals are usually separated from aqueous slurries by centrifugation and dried in rotary driers heated indirectly by warm air. To avoid overdrying, the product temperature should not exceed 50°C. Powdered and impalpable boric acid are produced by milling the crystalline material.

The principal impurities in technical-grade boric acid are the by-product sulfates, <0.1 wt %, and various minor metallic impurities present in the borate ores. A boric acid titer is not an effective measure of purity because overdrying may result in partial conversion to metaboric acid and lead to $B(OH)_3$ assays above 100%. High purity boric acid is prepared by recrystallization of technical-grade material.

4.4. Uses. Boric acid has a surprising variety of applications in both industrial and consumer products (6,57). It serves as a source of B_2O_3 in many fused products, including textile fiber glass, optical and sealing glasses, heat-resistant borosilicate glass, ceramic glazes, and porcelain enamels (see ENAMELS, PORCELAIN AND VITREOUS). It also serves as a component of fluxes for welding and brazing (see SOLDERS AND BRAZING FILLER METALS; WELDING).

A number of boron chemicals are prepared directly from boric acid. These include synthetic inorganic borate salts, boron phosphate, fluoborates, boron trihalides, borate esters, boron carbide, and metal alloys such as ferroboron [11108-67-1].

Boric acid catalyzes the air oxidation of hydrocarbons and increases the yield of alcohols by forming esters that prevent further oxidation of hydroxyl groups to ketones and carboxylic acids (see HYDROCARBON OXIDATION).

The bacteriostatic and fungicidal properties of boric acid have led to its use as a preservative in natural products such as lumber, rubber latex emulsions, leather, and starch products.

NF-grade boric acid serves as a mild, nonirritating antiseptic in mouthwashes, hair rinse, talcum powder, eyewashes, and protective ointments (see DISINFECTANTS AND ANTISEPTICS). Although relatively nontoxic to mammals (58), boric acid powders are quite poisonous to some insects. With the addition of an anticaking agent, they have been used to control cockroaches and to protect wood against insect damage (see INSECT CONTROL TECHNOLOGY).

Inorganic boron compounds are generally good fire retardants (59). Boric acid, alone or in mixtures with sodium borates, is particularly effective in reducing the flammability of cellulosic materials. Applications include treatment of wood products, cellulose insulation, and cotton batting used in mattresses (see FLAME RETARDANTS).

Because boron compounds are good absorbers of thermal neutrons, owing to isotope ^{10}B, the nuclear industry has developed many applications. High purity boric acid is added to the cooling water used in high pressure water reactors (see NUCLEAR REACTORS).

4.5. Analytical Methods. Boric acid is such a weak acid that it cannot be accurately determined by direct alkali titration. Howevr, it can be transformed into a relatively strong acid by adding polyols such as glycerol or mannitol. The resulting ester complexes are much stronger acids and can be titrated accurately (60).

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

5. Solutions of Boric Acid and Borates

5.1. Polyborates and pH Behavior. Whereas boric acid is essentially monomeric in dilute aqueous solutions, polymeric species may form at concentrations above 0.1 *M*. The conjugate base of boric acid in aqueous systems is the tetrahydroxyborate [15390-83-7] anion sometimes called the metaborate anion, $B(OH)_4^-$. This species is also the principal anion in solutions of alkali metal (1:1) borates such as sodium metaborate, $Na_2O \cdot B_2O_3 \cdot 4H_2O$ (61). Mixtures of $B(OH)_3$ and $B(OH)_4^-$ appear to form classical buffer systems where the solution pH is governed primarily by the acid:salt ratio, ie,$[H^+] = K_a[B(OH)_3]/[B(OH)_4^-]$. This relationship is nearly correct for solutions of sodium or potassium (1:2) borates, eg, borax, where the ratio $B(OH)_3$:$B(OH)_4^- = 1$, and the pH remains near 9 over a wide range of concentrations. However, for solutions that have pH values much greater or less than 9, the pH changes greatly on dilution as shown in Figure 2 (62).

This anomalous pH behavior results from the presence of polyborates, which dissociate into $B(OH)_3$ and $B(OH)^-;_4$ as the solutions are diluted. Below pH of about 9 the solution pH increases on dilution; the inverse is true above pH 9. This is probably because of the combined effects of a shift in the equilibrium concentration of polymeric and monomeric species and their relative acidities. At a Na_2O:B_2O_3 mol ratio equal to 0.41 at pH 8.91, or K_2O:B_2O_3 mol ratio equal to 0.405 at pH 9 the pH is independent of concentration. This ratio and the pH associated with it have been termed the isohydric point of borate solutions (63).

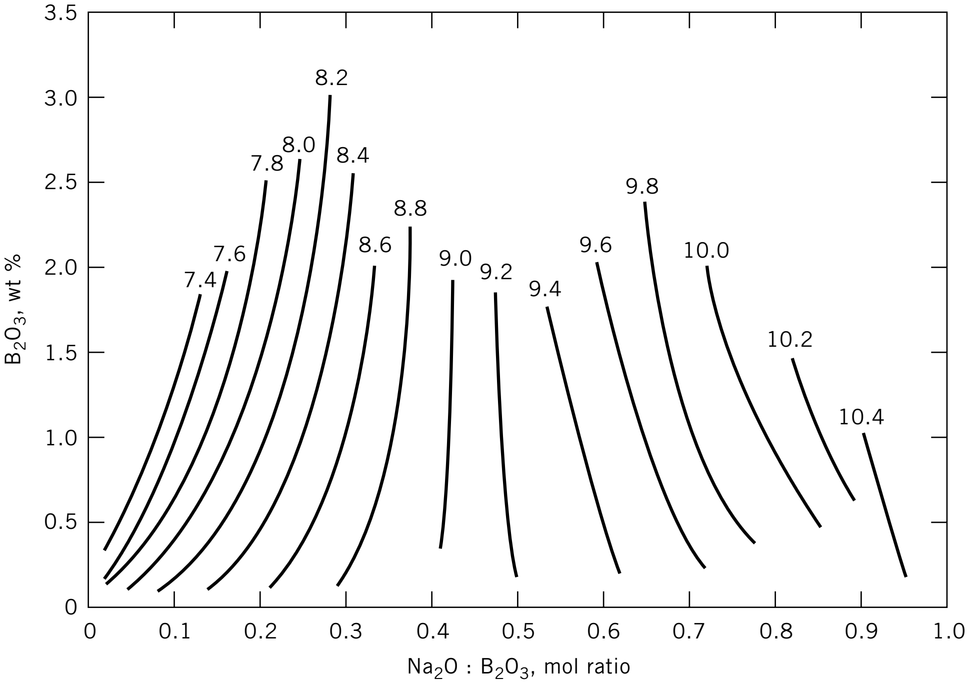


Fig. 2. Values of pH in the system Na_2O–B_2O_3–H_2O at 25°C (62).

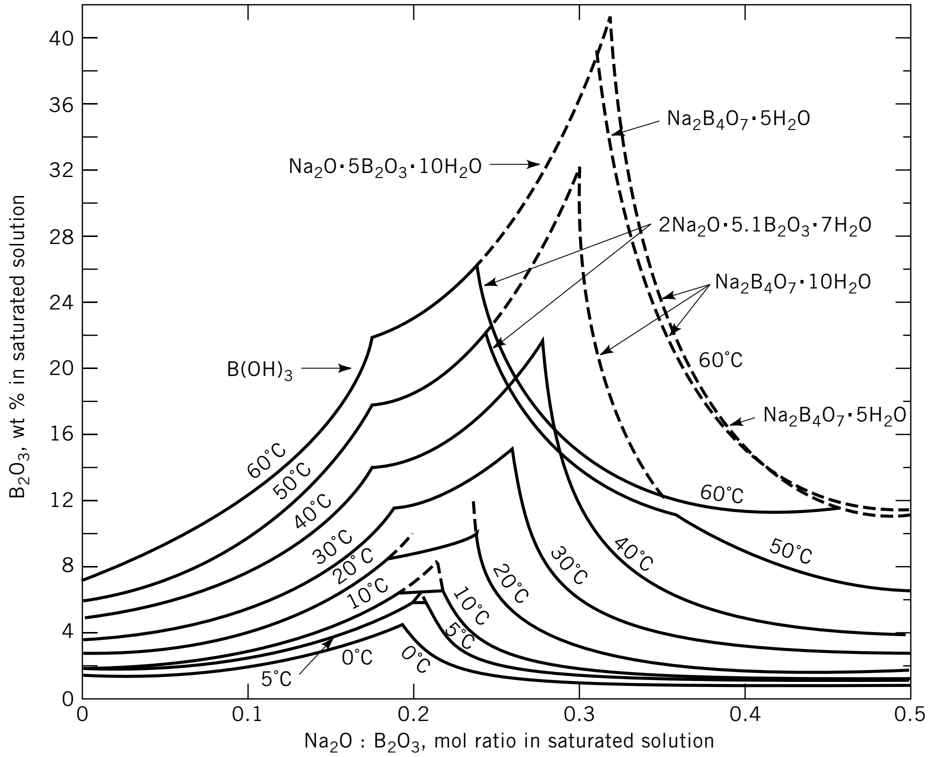


Fig. 3. Solubility isotherms for the system $Na_2B_4O_7$–B_2O_3–H_2O at 0–60°C. The compound $2Na_2O \cdot 5.1B_2O_3 \cdot 7H_2O$ (Suhr's borate) usually does not appear because it crystallizes very slowly in the absence of seed.

The presence of metal salts, particularly those containing alkaline-earth cations and/or halides, cause some shifts in the polyborate equilibria. This may result from direct interaction with the boron–oxygen species, or from changes in the activity of the solvent water (64).

5.2. Solubility Trends. Formation of polyborates greatly enhances the mutual solubilities of boric acid and alkali borates. Solubility isotherms in the system Na_2O–B_2O_3–H_2O are shown in Figure 3. When borax, $Na_2B_4O_7 \cdot 10H_2O$, 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 in the solution greatly increases. Polymerization decreases the concentrations of $B(OH)_3$ and $B(OH)_4^-$ in equilibrium with the solid phases, thus permitting more borax or boric acid to dissolve.

Sodium borate solutions near the Na_2O:B_2O_3 ratio of maximum solubility can be spray-dried to form an amorphous product with the approximate composition $Na_2O \cdot 4B_2O_3 \cdot 4H_2O$ commonly referred to as sodium octaborate (65). This material dissolves rapidly in water without any decrease in temperature to form supersaturated solutions. Such solutions have found application in treating cellulosic materials to impart fire-retardant and decay-resistant properties (see CELLULOSE).

5.3. The Polyborate Species. From a series of very rigorous pH studies, a series of equilibrium constants involving the species $B(OH)_3$, $B(OH)_4^-$,

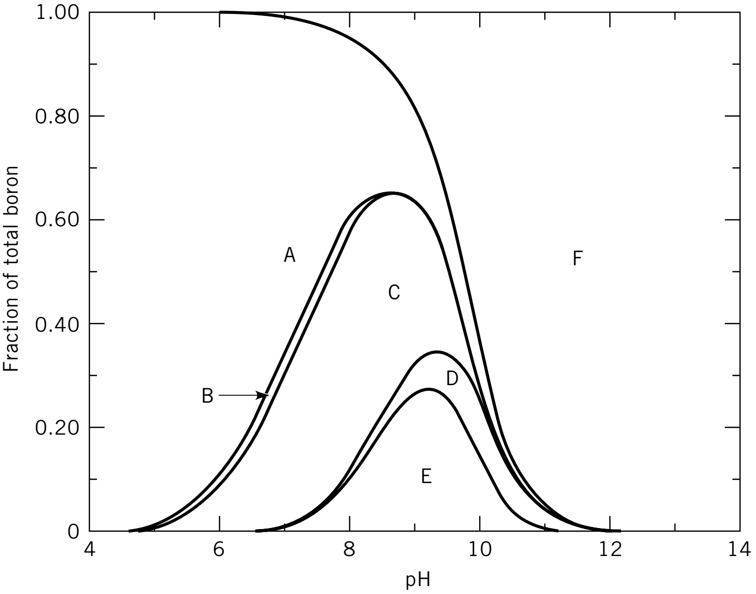
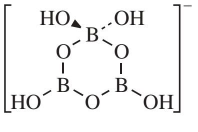


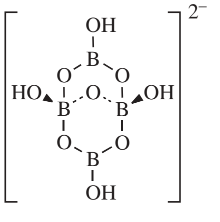
Fig. 4. Distribution of boron in A, $B(OH)_3$; B, $B_5O_6(OH)_4^-$; C, $B_3O_3(OH)_4^-$; D, $B_3O_3(OH)_5^{2-}$; E, $B_4O_5(OH)_4^{2-}$; F, $B(OH)_4^-$; where total B_2O_3 concentration is 13.93 g/L. At a given pH, the fraction of the total boron in a given ion is represented by the portion of a vertical line falling within the corresponding range (66).

and the plyions $B_3O_3(OH)_5^{2-}$ [12344-78-4], $B_3O_3(OH)_4^-$ [12344-77-3], $B_5O_6(OH)_4^-$ [12343-58-7], and $B_4O_5(OH)_4^{2-}$ [12344-83-1] have been calculated (65). The relative populations of these species as functions of pH are shown in Figure 4. It is clear that species containing three, four, and five borons are significant at intermediate pH values. The ratio between the total anionic charge and the number of borons per ion increases with increasing pH.

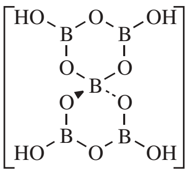
The polyions postulated in solution all have known structural analogues in crystalline borate salts. Investigations of the Raman (67) and ^{11}B nmr (68) spectra of borate solutions have confirmed the presence of three of these species: the triborate (**3**), $B_3O_3(OH)_4^-$, tetraborate (**4**), $[B_4O_5(OH)_4^{2-}]$, and pentaborate (**5**) $B_5O_6(OH)_4^-$, polyanions. Skeletal structures were assigned based on coincidences between the solution spectra and those solid borates for which definitive structural data are available (52). These same ions have been postulated to be present in alkali metal borate glasses as well. A rapid equilibrium exists among the various polyborate species in aqueous solutions.



(**3**)



(**4**)



(**5**)

6. Borates

6.1. Sources and Supplies.

A limited number of geographic regions on earth contain borate deposits. The two main producers and regions are Borax in California and Etibank in Turkey. Other minor producers exist in the Andes region of northern Chile and Argentina, Bolivia, Peru, California, Russia, and China (69).

Borax. Borax is the world's leading supplier of refined borates, distinguished from other producers by its integrated approach to mining, refining, and distribution. The Borax Group is includes mining and refining facilities in the United States, Argentina, and France; shipping terminals in the United States, the Netherlands, France, and Spain; corporate, sales, or technical offices in the United States, the United Kingdom, Argentina, Belgium, Brazil, Germany, Spain, France, Italy, Japan, and Singapore; and warehouses in Austria, Germany, Russia, and the Ukraine. Borax is owned by world's largest mining company, Rio Tinto. The company's headquarters are in Valencia, California, with regional headquarters in England and Singapore.

Borax operates California's largest open-pit mine in Boron, about 90 m (144.81 km) northeast of Los Angeles. The mine produces approximately one million tons of borates annually, enough to satisfy nearly half the world's demand. At an onsite refinery, the company employs two separate processes to refine ore: the boric acid process and the refined borax process. The boric acid process uses kernite as feedstock: the refined borax process uses a combination of borax ore and kernite ore that has been converted to borax.

This primary deposit consists of borax and kernite. These ores are interbedded with montmorillonite-illite clays, which are overlain with claystones containing ulexite and minor colemanite. The ulexite and colemanite are currently being stockpilled in the ore extraction process. All kernite ore is kept separte from the borax and borax/kernite blended ores.

The company's refinery and shipping terminal in the Port of Los Angeles in Wilimington, California, currently produces special quality grades of borates and boric acid, other enhanced borates, and a range of speciality products that fall under the general categories of flame retardants, agricultural products, pest control products, and wood preservatives.

Under its Borax Argentina division, the company runs mining and refining operations in the Salta Province of northern Argentina. Ores mined include borax from Tincalayu, hydroboracite from Sijes, and ulexite from Salar Diablillos and Cauchari. The annual combined production from these operations combined is less than 100,000 tons of borates. The majority of product mined by Borax Argentina supplies South American markets, and the remainder, mainly hydroboracite, is shipped to Spain for use in ceramic frits and glases.

IMC Chemicals Inc. IMC chemicals Inc. (IMCC), formerly North American Chemical Co. (NACC), is a subsidiary of IMC Global Inc. The IMC chemicals business unit is responsible for the soda ash–boron buisness. IMC is the second largest producer of boron products in North America. The feed for the Searles Lake operations come from two salt horizons saturated with brines extracted by solution mining (continuous and selective crystallization and precipitation of different salts). The brines contain bicarbonate, borate, chloride, carbonate, Potassium,

Table 8. **Scope and Size of Etibank Operations**

Location	Approximate number of mines	Main Boron minerals	Approximate concentrate capacity × 10^3 t
Kirka	1 open-pit	tincal	600
Kestelek	1 open-pit	colemanite	100
Bigadic	3 open-pit	colemanite	400
	2 underground ulexite		120
Emet	2 open-pit	colemanite	500

and sulfate ions. The total B_2O_3 production level is about 60,000 tons per year including borax pentahydrate, borax decahydrate, boric acid, and anhydrous boric acid production.

In addition to the Searles Lake operation, IMCC also has an Italian associate (Societa Chimica Larderello) based in Tuscany, which produces high specification boric acid and speciality products using imported colemanite and ulexite as fedback.

Fort Cady Minerals Corp. Mining operatiions are located in Barstow, California. Borates are mined using a solution mining process where a dilute acid solution is injected into the colemanite ore body to create a high purity calcium borate. The annual capacity of this operation is ~4000 tons/year.

American Borate Co. American Borate Company (ABC) operates an underground mine in Death Valley, California. The colemanite and ulexite ore is extracted by means of a froth flotation and calcining operation to produce 15,000–20,000 tons/year of mineral concentrate. The majority of these concentrates are exported to Asia, primarily for textile fiberglass manufacturing.

Etibank. The second largest supplier of borates in the world and the largest supplier of calcium borates is state-owned Etibank in Turkey. Etibank consists of mines in several locations, including Kirka, Kestelek, Bigadic, and Emet (see Table 8).

Etibank controls an estimated 60% of the discovered borate reserves in the world and currently produces around 400,000 tons/year of B_2O_3. (see Table 9). It is estimated that the majority of the product — colemanite, colemanite concentrates, and some ulexite — is exported. This high export volume accounts for one-quarter of Turkey's overall mineral exports. The generally accepted method of distribution is through various agents.

Argentina. The total borate production in Argentina is estimated at approximately 245 × 10^3 t. Most producers are small mining companies, which make crude ulexite concentrates. Aside from the Borax operations in argentina,

Table 9. **Feedback, Main Products, Capacity, and B_2O_3 content of Etibank**

Minerals processed	Products	Capacity, ×10^3 t	Grade B_2O_3, %
tincal	tincal concentrate	600	32.0
	borax pentahydrate	320	47.8
	anhydrous borax	60	68.87
colemanite and concentrates	borax decahydrate	50	36.47
	boric acid	135	56.25
	borax pentahydrate	5	47.75

the other main producers are S.R. Minerals and Ulex S.A. It was estimated that S.R. Minerals produced 30,000 t in 1997 from their Loma Blanca mine. Ulex S.A. produces 10,000 t/yr of concentrated colemantic and hydroboracite. The majority of their production is exported.

Chile. There are various producers of borates in Chile, including Quiborax Boroquimica and Sdad Boroquimica, who mine ulexite reserves from salars in the north of the country. Although most production is consumed locally for applications like agriculture, a substantial amount of product is exported. The total borate production in 1995 was estimated at 212×10^3 t; of this, 250 t of borax and 30,100 of boric acid were exported.

Bolivia. Like Chile, Bolivia has a number of relatively small producers who mainly exploit ulexite reserves. Most 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. In 1996, an estimated 4100 t of ulexite, 4400 t of boric acid, and 200 t of borax were exported. The total production capacity is estimated to be around 13,000 t.

Peru. The main production of borates in Peru originates from Cia Minera Ubinas and Quimica Oquendo, both owned by the Collorabia group in Italy. Like their South American competitors, they mine Ca 180,000 t of ulexite during the nonwinter months. The ore is used to produce both a crude washed ulexite and boric acid.

Former Soviet Union. Although thers are numerous borate deposits in this area, only one is a significant producer of borates. JSC Bor in Russia mines datolite in the city Dalnergorsk, producing datolite concentrate and refined borates, including calcium borates, borax, boric acid and sodium perborate. Bor is the only Russian producer to export borates, mostly to Japan.

China. Like the South American countries, Chinab 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 szaibelyte. However, ulexite, pinnoite, hydroboracite, and borax are also mined in Qinghai. The Chinese products are generally a lower quality than the refined products produced by in the United States. The annual Chinese production is estimated at around 100,000 tons/year (70).

7. Sodium Borates

7.1. Disodium Tetraborate Decahydrate (Borax Decahydrate).

Disodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$, formula wt, 381.36; monoclinic; sp gr, 1.71; specific heat 1.611 kJ/(kg · K) [0.385 kcal/(g°C] at 25–50°C (70); heat of formation, −6.2643 MJ/mol (−1497.2 kcal/mol) (71); exists in nature as the mineral borax. Its crystal habit, nucleation, and growth rate are sensitive to inorganic and surface active organic modifiers (72).

The solubility–temperature curves for the $Na_2O{-}B_2O_3{-}H_2O$ system are given in Figure 5 (Table 10). The solubility curves of the penta- and decahydrates 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 the reverse occurs below this temperature. This transition temperature may be lowered in solutions of inorganic salts, eg, 49.3°C in

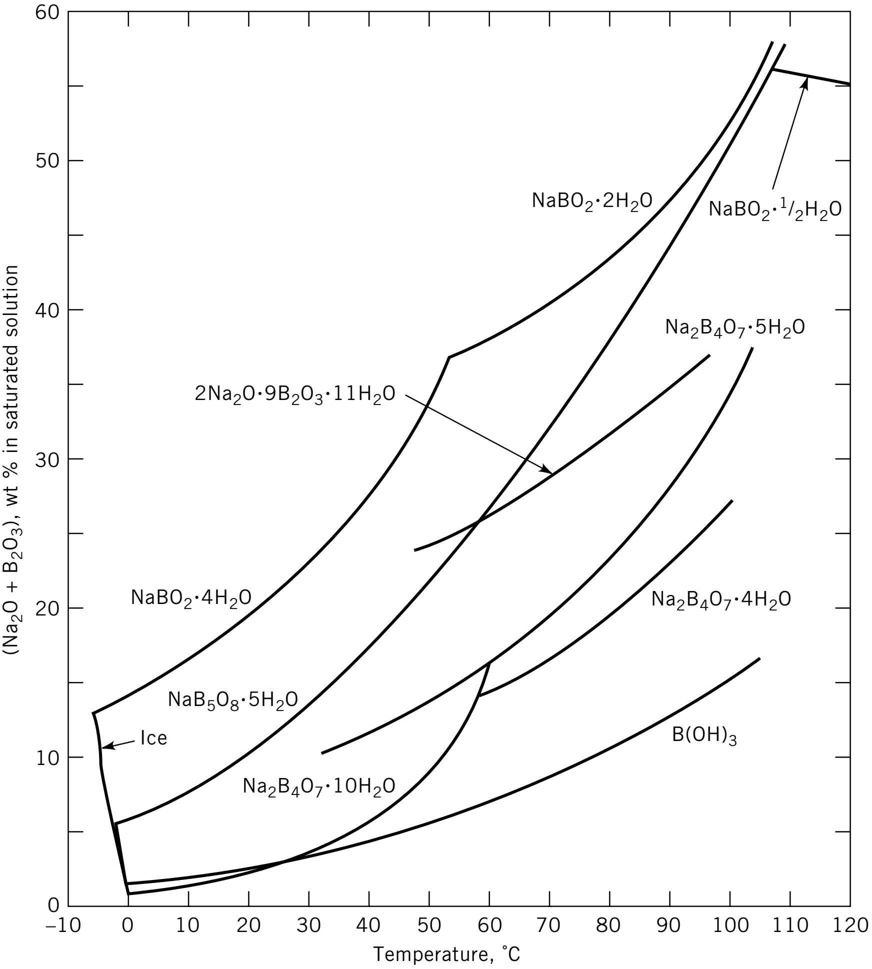


Fig. 5. Solubility–temperature curves for boric acid, borax, sodium pentaborate, and sodium metaborate (73). Courtesy of The American Chemical Society.

solutions saturated with sodium sulfate and 39.6°C with sodium chloride. Heats of solution for borax have been determined (68,75) and the manufacturer quotes a value of about 283 kJ/kg (67.6 kcal/mol) (33).

The pH of a borax solution increases slightly with increasing concentration (Table 11) and drops slightly with increasing temperature. The vapor pressures of aqueous saturated borax solutions at various temperatures are (75,76):

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

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

Compound	CAS Registry Number	Solubility, wt% anhydrous salt, at °C 0	10	20	25	30	40	50	60	70	80	90	100
$Li_2O\cdot 5B_2O_3\cdot 10H_2O$[a]	[37190-10-6]							20.88	24.34	27.98	31.79	36.2	41.2
$Li_2O\cdot 2B_2O_3\cdot 4H_2O$	[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
$Li_2O\cdot B_2O_3\cdot 16H_2O$[b]	[41851-38-1]	0.88	1.42	2.51	3.34	4.63	9.40						
$Li_2O\cdot B_2O_3\cdot 4H_2O$	[15293-74-0]						7.40	7.84	8.43	9.43	10.58, 9.75	11.8, 9.7	13.4, 9.70[c]
$Na_2O\cdot 5B_2O_3\cdot 10H_2O$	[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
$Na_2O\cdot 2B_2O_3\cdot 10H_2O$	[1303-96-4]	1.18	1.76	2.58	3.13	3.85	6.00	9.55	15.90				
$Na_2O\cdot 2B_2O_3\cdot 4.67H_2O$[d]	[12045-88-4]								16.40	19.49	23.38	28.37	34.63
$Na_2O\cdot 2B_2O_3\cdot 4H_2O$[e]	[12045-87-3]								14.82	17.12	19.88	23.31	28.22
$Na_2O\cdot B_2O_3\cdot 8H_2O$[f]	[10555-76-7]	14.5	17.0	20.0	21.7	23.6	27.9	34.1					
$Na_2O\cdot B_2O_3\cdot 4H_2O$	[16800-11-6]								38.3	40.7	43.7	47.4	52.4
$K_2O\cdot 5B_2O_3\cdot 8H_2O$	[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
$K_2O\cdot 2B_2O_3\cdot 4H_2O$	[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
$K_2O\cdot B_2O_3\cdot 2.5H_2O$	[27516-44-5]		42.3	43.0	43.3	44.0	45.0	46.1	47.2	48.2	49.3	50.3	
$Rb_2O\cdot 5B_2O_3\cdot 8H_2O$	[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[g]
$Cs_2O\cdot 5B_2O_3\cdot 8H_2O$[h]	[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[i]
$(NH_4)_2O\cdot 2B_2O_3\cdot 4H_2O$	[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	
$(NH_4)_2O\cdot 5B_2O_3\cdot 8H_2O$	[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	

[a] Incongruent solubility below 37.5 or 40.5°C.

[b] Transition point to tetrahydrate, 36.9 or 40°C.

[c] At 101.2°C.

[d] Commonly known as the five hydrate(74), transition point to decahydrate, 60.7°C, 16.6% $Na_2B_4O_7$.

[e] Transition point to decahydrate, 58.2°C, 14.55% $Na_2B_4O_7$.

[f] Transition point to tetrahydrate, 53.6°C, 36.9% $Na_2B_2O_4$.

[g] At 102°C.

[h] Dicesium tetraborate pentahydrate [12228-83-0], $Cs_2O\cdot 2B_2O_3\cdot 5H_2O$, anddicesium diborate heptahydrate [66634-85-3], $Cs_2O\cdot B_2O_3\cdot 7H_2O$, also exist. The former has incongruent solubility; the latter has a solubility of 36.8 wt% anhydrous salt at 18°C.

[i] At 101.65°C.

Table 11. **pH of Aqueous Borate Solutions**

	Concentration, wt %						
Compound	0.1	0.5	1.0	2.0	4.0	10.0	15.0
$Na_2B_4O_7{\cdot}10H_2O$	9.2	9.2	9.2	9.2	9.3[a]		
$Na_2B_8O_{13}{\cdot}4H_2O$			8.5	8.5	8.1	7.6	7.3
$NaB_5O_8{\cdot}5H_2O$			8.5	8.4	8.1	7.6	7.3
$NaBO_2{\cdot}4H_2O$	10.5	10.8	11.0	11.2	11.4	11.8	11.9
$NaBO_2{\cdot}2H_2O$	10.6	10.9	11.1	11.3	11.5	11.8	12.0
$K_2B_4O_7{\cdot}4H_2O$	9.2	9.1	9.1	9.2	9.3		
$KB_5O_8{\cdot}4H_2O$		8.4	8.4	8.3	7.9	7.6	
$NH_4B_5O_8{\cdot}4H_2O$	8.5	8.4	8.3	8.2	7.8	7.3	

[a] Saturated solution, 4.71 wt %.

To convert from kPa to mm Hg, multiply by 7.5. Values for the specific heat of aqueous borax solutions as a function of weight percent decahydrate are (75):

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

To convert from kJ/(kg · K) to cal/(g · °C), divide by 4.184. The solubilities of borax in organic solvents are given in Table 6.

If borax has been previously warmed to 50°C, it dehydrates reversibly into the pentahydrate and water vapor. The equilibrium vapor pressure for this transition at various temperatures is (76, 77): 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); 59°C, 17.7 kPa (133.0 mm Hg). If the decahydrate has not been warmed above 50°C, it develops a vapor pressure of only 0.213 kPa (1.6 mm Hg) at 20°C. In this case, when placed over P_2O_5, it does not form the crystalline pentahydrate but decomposes gradually to form an amorphous product having about 2.4 molecules water content.

Heats of dehydration per mole of water vapor are (76) decahydrate to pentahydrate, 54.149 kJ (12.942 kcal), and decahydrate to tetrahydrate, 54,074 kJ (12.924 kcal). Borax stored over a saturated sucrose–sodium chloride solution maintains exactly 10 moles of water and can thus be used as an analytical standard. Commercial borax tends to lose water of crystallization if stored at high temperature or in dry air.

A single-crystal x-ray diffraction study has shown that the borate ion present in borax has the formula $[B_4O_5(OH)_4]^{2-}$ (4), the sodium ions occupying two unique sites, and eight moles of water of crystallization and two moles of water existing as hydroxyl groups. The formula is best represented as $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ (78). The same borate ion (4) exists in the pentahydrate, explaining the ready interconversion of the penta- and decahydrates (79). Slow dehydration of borax results in the loss of eight moles of water between 50 and 150°C.

Rapid heating of either borax decahydrate or pentahydrate causes the crystal to dissolve before significant dehydration, and at about 140°C, puffing occurs from rapid vaporization of water to form particles having as high as 90% void volume and very low bulk density (80).

7.2. Disodium Tetraborate Pentahydrate (Borax Pentahydrate).

Although referred to as borax pentahydrate, well-formed crystals actually contain not five but 4.67 moles of water, $Na_2B_4O_7\cdot 4.67H_2O$ or $Na_2O\cdot 2B_2O_3\cdot 4.67H_2O$. This structure has been confirmed by an x-ray single crystal analysis that showed that two of the three water of crystallization sites are only partially filled (73). The structural formula is best represented as $Na_2[B_4O_5(OH)_4]\cdot 2.67H_2O$; formula wt, 286.78; trigonal; rhombohedral crystal shape; sp gr, measured 1.880, crystallographic 1.912; specific heat, 1.32 kJ/(kg·K) [0.316 kcal/(g·°C)] (70); heat of formation, −4.7844 MJ/mol (−1143.5 kcal/mol) (71). It is found in nature as a fine-grained mineral, tincalconite, formed by dehydration of borax.

Solubility data in water are given in Figure 5 and in Table 10, solution pH in Table 11, and the solubility in organic solvents is given in Table 6. Heats of solution in water have been determined (70,75). The pentahydrate, in contact with its aqueous solution, is metastable with respect to the tetrahydrate (kernite) at temperatures above 58.2°C and metastable to borax decahydrate below 60.6–60.8°C. Kernite can be slowly crystallized from a near saturate solution heated near the boiling point for several days.

Pentahydrate is reversibly converted to an amorphous dihydrate, at 88°C and 0.26 kPa (2 mm Hg) or by boiling with xylene (75,77). The heat of dehydration for the pentahydrate to tetrahydrate has been calculated to be 53.697 kJ (12.834 kcal) per mole of water (76). Thermogravimetric analyses show that 2.75 moles of water are lost on heating to 140°C. Like borax, pentahydrate puffs when heated rapidly to give a product having a bulk density of 0.042 g/mL (81).

A single-crystal x-ray structure determination has shown that the borate ion in the pentahydrate and in borax are identical (79).

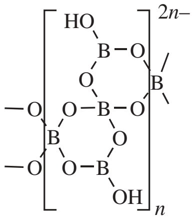
7.3. Disodium Tetraborate Tetrahydrate.

Disodium tetraborate tetrahydrate, $Na_2B_4O_7\cdot 4H_2O$ or$Na_2O\cdot 2B_2O_3\cdot 4H_2O$, formula wt, 273.27; monoclinic; sp gr, 1.908; specific heat, ca 1.2 kJ/(kg·K) [0.287 kcal/(g·°C)] (62); heat of formation, −4.4890 MJ/mol (−1072.9 kcal/mol) (71); exists in nature as the mineral kernite and has a structural formula $Na_2[B_4O_6(OH)_2]\cdot 3H_2O$. The crystals have two perfect cleavages and when ground, form elongated splinters.

The water solubility of kernite is shown in Figure 5 and in Table 10. Kernite is the stable phase in contact with its solutions from 58.2°C to ca 95°C (73). Its rate of crystallization is, however, much slower than that of the 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 over P_2O_5 in vacuum or by heating at 100–120°C, forming a crystalline dihydrate, metakernite, which reverts to kernite at 60% relative humidity (76).

The structure of kernite consists of parallel infinite chains of the $[B_4O_6(OH)_2]_n^{2n-}$ ion (**6**) composed of six membered rings (82). The polymeric nature of the anion is consistent with the slow rate of dissolution and crystallization observed for kernite.



(**6**)

7.4. Disodium Tetraborate (Anhydrous Borax). Disodium tetraborate, $Na_2B_4O_7$ or $Na_2O \cdot 2B_2O_3$, formula wt, 201.21; sp gr (glass), 2.367, (α-crystalline form), 2.27; heat of formation (glass),−3.2566 MJ/mol (−778.34 kcal/mol), (α-crystalline form),−3.2767 MJ/mol (−783.2 kcal/mol) (17); exists in several crystalline forms as well as a glassy form (75). The most common α-crystalline form that melts congruently at 742.5°C is obtained by dehydrating borax hydrates and is the stable form above 600–700°C (75). A large amount of heat capacity data has been reported (17,83). Anhydrous borax glass dissolves in water more slowly than the hydrated forms. Heats of solution have been measured (71), and the manufacturer lists a value of −213.8 kJ/kg (−51.1 kcal/kg) (33). The solubilities of finely divided crystalline disodium tetraborate at 25°C expressed as weight percent $Na_2O \cdot 2B_2O_3$ 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 as 161 kJ/mol (38.5 kcal/mol) of $Na_2O \cdot 2B_2O_3$ (75,84). The heat of fusion has been reported as 81.2 kJ/mol (19.4 kcal/mol) (17).

A single-crystal x-ray diffraction study has shown that the borate anion in anhydrous borax is polymeric in nature and is formed via oxygen bridging of triborate and pentaborate groups (85). The chemistry of anhydrous borax has been reviewed (75,86).

7.5. Disodium Octaborate Tetrahydrate. The composition of a commercially available sodium borate hydrate, 66.3 wt% B_2O_3, POLYBOR (65), corresponds quite closely to that of a hypothetical compound, disodium octaborate tetrahydrate, $Na_2B_8O_{13} \cdot 4H_2O$ or $Na_2O \cdot 4B_2O_3 \cdot 4H_2O$. This product dissolves rapidly in water without the temperature decrease, which occurs when the crystalline borates dissolve, and easily forms viscous supersaturated solutions at elevated temperatures. The solution pH decreases as the concentration increases

(Table 11). The solubility of the product is shown compared with that of borax (33):

		Concentration, B_2O_3 in saturated solutions, wt %	
Temperature, °C	Solubility, POLYBOR, wt %	POLYBOR	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 Pentahydrate. Sodium pentaborate pentahydrate, $NaB_4O_8 \cdot 5H_2O$ or$Na_2O \cdot 5B_2O_3 \cdot 10H_2O$; formula wt, 295.11; monoclinic; sp gr, 1.713; exists in nature as the mineralsborgite[12272-01-4]. Heat capacity, entropy, and other thermal measurements have been made at 15–345 K (87).

Sodium pentaborate can easily be crystallized from a solution having a Na_2O:B_2O_3 mol ratio of 0.2. Its water solubility (Fig. 5 and Table 10) exceeds that of borax and boric acid. Its pH decreases with solution concentration (Table 11). It is stable in contact with its own solution between 2 and 59.5°C. When a saturated pentaborate solution is agitated for some time at temperatures near boiling, the compound $2Na_2O \cdot 9B_2O_3 \cdot 11H_2O$, also known as Taylors borate, sp gr, 1.903; crystallizes very slowly if seed is present. Pentaborate pentahydrate, which is metastable to Taylors 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 (75).

Crystalline sodium pentaborate pentahydrate is stable in the atmosphere. When heated in vacuum, it is stable to 75°C; however, above 75°C, four of its five H_2O molecules are lost (75).

A single-crystal x-ray diffraction study gives a structural formula of $Na_2[B_5O_6(OH)_4] \cdot 3H_2O$ and contains the pentaborate ion analogous to that found in the corresponding potassium compound (88).

7.7. Sodium Metaborate Tetrahydrate. Sodium metaborate tetrahydrate, $NaBO_2 \cdot 4H_2O$ or $Na_2O \cdot B_2O_3 \cdot 8H_2O$; 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 and 53.6°C. At temperatures above 53.6°C, the dihydrate, $NaBO_2 \cdot 2H_2O$, becomes the stable phase. The water solubility of sodium metaborate is given in Figure 5 and in Table 10 and the pH with concentration is given in Table 11.

Heat capacity data for metaborate solutions have been reported (89). The solubility of sodium metaborate tetrahydrate in methanol at 40°C is 26.4 wt% (62).

The relative humidity over a saturated solution of the tetrahydrate at 14–24°C is 90 ± 1%, and the humidity over mixtures of the tetra- and dihydrates is 42% at 22°C; 43% at 24.8°C; 45% at 27.0; and 39% at 91.3°C (90). The heat of hydration for the dihydrate to tetrahydrate conversion has been calculated as 52.51 kJ (12.55 kcal) per mole of water (90). The thermogravimetric curve shows a loss of 0.5 moles of water at 130°C; two moles at 140°C; three moles at 280°C; and the last at temperatures up to 800°C (91).

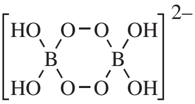
Sodium metaborate absorbs CO_2 from the atmosphere, forming borax and sodium carbonate. Crystals of the tetrahydrate melt in its water of crystallization at about 54°C. The solid-state structure of the tetrahydrate, $Na[B(OH)_4]\cdot 2H_2O$, consists of discrete tetrahedral $B(OH)^{-};_{4}$ groups (92).

7.8. Sodium Metaborate Dihydrate. Sodium metaborate dihydrate, $NaBO_2\cdot 2H_2O$ or $Na_2O{\cdot}B_2O_3\cdot 4H_2O$; formula wt, 101.83; triclinic; sp gr, 1.909; can be prepared by heating a slurry of the tetrahydrate above 54°C, by crystallizing metaborate solutions at 54–80°C, or by dehydrating the tetrahydrate in vacuum. Large crystals can be grown by heating the solid in its mother liquor for several days. The dihydrate is the stable phase in contact with its saturated solution between 53.6 and 105°C. At higher temperatures a hemihydrate, $NaBO_2\cdot 0.5H_2O$, is formed (75).

The water solubility for the dihydrate is shown in Figure 5 and in Table 10 and solution pH with concentration is given in Table 11. The solubility of the dihydrate inethanol is 0.3 wt % at boiling, and in methanol it is 17.8% at 22°C, 19.5% at 40°C, and 24.6% at 60°C (62).

The dihydrate loses water slowly at room temperature. Its heat of dehydration to $NaBO_2\cdot 0.5H_2O$ has been calculated as 58.1 kJ/mol (13.9 kcal/mol) of H_2O (90). Sodium metaborate dihydrate reacts with atmospheric CO_2 to produce sodium carbonate and borax. The melting point is 90–95°C, compared to 54°C for the tetrahydrate. Some crystallographic work has been done (93).

7.9. Sodium Perborate Hydrates. Peroxyborates are commonly known as perborates, written as if the perborate anion were BO_3^-. X-ray crystal structure has shown that they contain the dimeric anion $[(HO)_2B(O_2)_2B(OH)_2]^{2-}$ (**7**) (94). Three sodium perborate hydrates, $NaBO_3\cdot xH_2O$ ($x = 1$, 3, and 4), are known. Only the mono- and tetrahydrate are of commercial importance, primarily asbleaching agents (qv) in laundry products.



(**7**)

Sodium perborate tetrahydrate, $NaBO_3\cdot 4H_2O$ or $Na_2B_2(O_2)_2(OH)_4\cdot 6H_2O$, is triclinic; heat of formation, −2112 kJ/mol (−504.8 kcal/mol) (crystal), −921 kJ/mol (−220.2 kcal/mol) (1*M* soln); and contains 10.4 wt % active oxygen. It melts at 63°C by dissolving in its own water of hydration and on heating to 250°C decomposes rapidly and completely to oxygen and sodium metaborate. In water its decomposition, 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 pH. The solubility in water is 2.5 wt% $NaBO_3 \cdot 4H_2O$ at 20°C and 3.6 wt% at 29°C (95). The solubility is enhanced by certain polyhydroxy compounds which form complexes with borates, such as tartaric acid, citric acid, mannitol, glycerol, and most significantly, by alkali polyphosphates. Dilute solutions contain the monoperoxyborate anion, $B(OH)_3(OOH)^-$. More concentrated solutions contain this anion plus $B(OH)_2(OOH)_2^-$, $B(OH)(OOH)_3^-$, $B(OOH)_4^-$, and polyperoxyborate anions (96).

Commercial preparation of sodium perborate tetrahydrate is by reaction of a sodium metaborate solution, from sodium hydroxide and borax pentahydrate, and hydrogen peroxide followed by crystallization of tetrahydrate (97). The trihydrate and monohydrate can be formed by reversible dehydration of the tetrahydrate.

Sodium perborate trihydrate, $NaBO_3 \cdot 3H_2O$ or $Na_2B_2(O_2)_2(OH)_4 \cdot 4H_2O$, triclinic, contains 11.8 wt% active oxygen (98). It has been claimed to have better thermal stability than the tetrahydrate but has not been used commercially. The trihydrate can be made by dehydration of the tetrahydrate or by crystallization from a sodium metaborate and hydrogen peroxide solution in the present of trihydrate seeds. Between 18 and 50°C the trihydrate is more stable but slower to crystallize than the tetrahydrate. Below 15°C the trihydrate is spontaneously converted into the tetrahydrate.

Sodium perborate monohydrate, $NaBO_3 \cdot H_2O$ or $Na_2B_2(O_2)_2(OH)_4$, 16.0 wt% active oxygen, is commercially prepared by dehydration of the tetrahydrate. The monohydrate has the same peroxyborate anion (**7**), as the higher hydrates and is the anhydrous sodium salt of this anion. Further dehydration results in decomposition of the peroxyborate.

7.10. Analysis.

The alkali metal and ammonium borates are analyzed for M_2O and B_2O_3 content by dissolving the compound in water, titrating the M_2O content with dilute HCl and determining the B_2O_3 content by complexation with excess mannitol followed by titration with dilute NaOH (99). The B_2O_3 content for calcium borates and other borates of low water solubility is determined by extraction into acid solution followed by mannitol complexation and titration with dilute base. The commercial hydrates are often overdried, leading to apparent B_2O_3 assays over 100%.

Borate reacts with curcumin [458-37-7], $C_{21}H_{20}O_6$, in the presence of a mineral acid to give a colored 1:2 borc acid: curcumin complex that has been used to determine microamounts of boron. Carminic acid [1260-17-9], $C_{22}H_{20}O_{13}$, (100) and azomethine-H (101) also form a colored complex useful for low level detection of borates. Boron compounds give a characteristic green color when burned in a flame.

Methods for analysis of industrial borate chemicals have been reviewed (103).

Crude (Mineral) Borates.

The titrimetric determination of B_2O_3 in crude borates — such as tincalconite, kernite, colemanite, or 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 Pacific Coast Borax Company (now U.S. Borax Inc.)(102).

The procedure is based on the fact that barium borate, formed by the addition of barium carbonate to boric acid, is quite soluble. It acts as a buffer solution to cause precipitation of the hydroxides of heavy metals.

The sample is first finely ground to <100 mesh. It is digested in HCl and neutralized by NaOH using methyl red as the indicator. Saturated bromine water is added to oxidize Fe(II) to Fe(III). Excess bromine is removed by boiling. Barium carbonate is added. The hydroxides of heavy metals are removed by filtering. The sample is acidified using HCl and boiled to remove carbon dioxide. It is neutralized with NaOH to a boric acid solution using methyl red as the indicator. Mannitol (or glycerol) is then added, and the resulting solution is titrated with NaOH solution using phenolphalein as the indicator.

7.11. Manufacturing, Production and Processing. Both sedimentary and metamorphic borate mineral deposists are exploited, although sedimentary deposits are by far the larger sources. Ore extraction is typically accomplished using conventional surface and underground mining tehniques. Solution mining has also been employed, albeit on a small scale. Sedimentary sodium borate minerals borax and kernite, the sedimentary calcium mineral colemanite, the sedimentary calcium–sodium mineral ulexite, and the metamorphic mineral datolite are the principal ore types exploited around the world.

In nearly all end uses, borates are either dispersed in low concentrations (eg, detergents, agricultural products) or incorporated into products from which borate seperation would be difficult (eg, ceramics, fiberglass). Because borates cannot easily be recycled, nearly all borates used in commerce are obtained from virgin sources located in remote desert regions.

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

Commercial borate ores fall into basic types: sodium borates, which are relatively soluble in water; and calcium or sodium–calcium borate ores, which are relatively insoluble in water. Because of these intrinsic properties, sodium borate ores are often used to produce refined borate products (various forms of sodium borates and boric acid) whereas calcium and sodium–calcium borate ores are often used to supply mineral borates.

Most large-scale borate extraction is performed using conventional surface mining techniques. Overburden material is drilled, blasted, and stripped away using large shovels and haul trucks to expose the ore body. Once the ore is exposed, it is blasted to loosen it. Electric or hydryaulic shovels load the ore into trucks with capacities as large as $\geq$200 tons. The haul trucks carry the ore to crushers for size reduction. mine ore can range in size from a few millimetres to $\geq$2 m in diameter. Crushers reduce the particle size to prepare the ore for sale or refining.

Some commercial uses for borates, such as insulation fiberglass and ceramic glazes, do not typically require high purity feedstocks. For these limited uses, raw or upgraded minerals can provide the borate source. Few ores are of high enough grade to be used directly, but ore is upgraded using gravity or magnetic separation techniques. Gravity separation takes advantage of the differences in specific gravity between the borate salts and the surrounding clay matrix. Magnetic separation takes advantage of the weakly magnetic properties of the clays impurities. Borate recovery from these separation processes is often relatively poor, but the cost of the processing is low.

Most commercial applications of borates require the use of refined borates. The feedstock to the refineries can be raw or upgraded ore. The refining process includes four steps: dissolution, purification, recrystallization, and drying.

Refining processes for sodium borate ores take advantage of their highly soluble nature. In the first step of refining, crushed ore is dissolved in hot water using agitation and steam. Dissolution produces a hot, saturated salt solution containing sodium borates and a suspension of insoluble of insolube matter.

Either sodium- or calcium-containing borate minerals may be used to produce boric acid. The first step in refining is essentially the same; however, sulfuric or some other mineral acid is added to assist dissolution and to convert the borate mineral to soluble boric acid and sodium or calcium sulfate, which is typically discarded because of its low value. In boric acid production, dissolution also results in a hot, saturated salt solution containing boric acid along with a suspension of insoluble matter.

Impurities present in the borate solutions typically consist of insoluble clays or other minerals (and, in the case of boric acid production, either insoluble sodium or calcium sulfate). Impurity removal is accomplished by passing the solution through a series of screens, settling tanks, and filters.

Following particular removal, the saturated borate solution is cooled in vacuum crystallizers to produce a slurry of pure sodium borate or boric acid crystals. As the solutions enter the crystallizers, a vacuum is applied, causing the solution to boil. As the saturated solutions cools, crystals form. The conditions used in the vacuum crystallizers determine the form of refined borate product generated. Sodium borates are typically crystallized into forms containing either 5 or 10 molecules of water of hydration. In the industry, these hydrated forms of sodium borates are classified as pentahydrate, or 5 mol and decahydrate, or 10 mol sodium borates.

The crystal slurry is dewatered in centrifuges or belt filters, generating a moist cake of sodium borate or boric acid crystals. These crystals may be washed to remove soluble impurities and fine particulates. The final step in refining involves drying in steam or gas-fired dryers to drive off remaining moisture. Heated air is passed countercurrent to the flow of borate salt crystals, removing free moisture and producing a dry, flowable granular product.

The finished product is stored in silos or warehouses to await shipment. Because the final product is white, contamination from rust, dirt, or other material is readily apparent. Storage is normally fully enclosed to ensure a contaminant-free product.

High value, speciality borates are commonly produced from 5-mol, 10-mol, or boric acid products. High purity borates are produced by redissolving and recrystallizing the commercial-gradeproducts. Low water or anhydrous forms of borates are produced by dehydrating or melting the commercial-grade products to drive off waters of hydration.

7.12. Shipment. Because there are so few primary sources of borates, and because of the wide diversity of end uses and end-use locations, distribution of finished products is of critical importance. This is as true today as it was centuries ago when traders carried borates to Europe along the same trade routes used by Marco Polo or in the late 1800s when the famous Twenty Mule Team carried borates out of Death Valley to the nearest railhead.

Today, borates are moved by virtually all available forms of transportation. Bulk, intercontinental shipments are made in ocean-going vesels with capacities of $\geq$ 40,000 tones. 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 aganist supply interruptions. The major producers maintain worldwide networks of sales representatives, agents and distributors to interact with customers and ensure reliable supplies and service.

7.13. Grades, Specifications, and Quality Control. The major mineralization in the borax deposit in borax deposit in Boron, California is ulexite ($Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$), kernite ($Na_2O \cdot 2B_2 \cdot O_3 \cdot 4H_2O$), and borax ($Na_2O \cdot 2B_2O_3 \cdot 10H_2O$). Currently only the borax are present in a one-to-one ratio with an average ore grade of 23% B_2O_3.

While both minerals are salts, their aqueous solubility requires different refining methods. Borax at an average ore grade of 23% is fed to the sodium borate plant, where it is dissolved in hot water, clarified, and crystallized (under controlled conditions) to yield Neobor ($Na_2O \cdot 2B_2O_3 \cdot 5H_2O$) and borax. Kernite at an average B_2O_3 content of 29% is either hydrated to form borax and is fed to the sodium borate plant or is processed with sulfuric acid, clarified, filtered, and crystallized to form boric acid. Both Neobor and boric acid are fused to their anhydrous forms, Dehybor ($Na_2B_4O_7$) and boric oxide (B_2O_3) in separate plants.

Quality control starts at the ore mining stage. After an ore block is mapped, samples are taken and tested for mineralization type and selected impurities. On the basis of these determinations, the various ores are blended and crushed in several stages to yield plant feeds.

After crushing and blending, feedstocks are tested for B_2O_3 content and various impurities to ensure a consistent plant feed. Both liquid and solid samples are assayed during processing to ensure optimum recovery and a high quality product. To ensure consistent quality, both of the fusing plants are fed directly from production with minimal testing.

Specifications for the maximum allowable impurity levels for borate products are given in Table 12. Where maximum levels are not set, typical values are given. Typical levels of impurities generally fall well below the maximum specification. Both borax decahydrate and pentahydrate are sometimes overdried in manufacture and may give higher than theoretical assays.

7.14. Economic Aspects. The pie chart in Figure 6 demonstrates the end-use makeup of the estimated 1.2×10^6 t global market for borates.

7.15. Health and Safety. Cases of industrial intoxication on exposure to inorganic borates have not been reported (104). There is a large body of literature on the toxicology of boric acid and borax (105). Acute oral LD_{50} in the rat is 3000–4000 mg/kg for boric acid and 4500–6000 mg/kg for borax (58). These values are comparable to sodium chloride, LD_{50} 3750 mg/kg. Ingested boric acid is excreted rapidly in the urine with a half-life of 21 h (106). Chronic ingestion studies (high dosage level and repeated exposure) indicates some reproductive toxicity in animals, but adequate evidence for these effects in humans is lacking (107). Studies

Table 12. **Maximum Impurity Specifications for Borates[a], wt %**

Chemical	Grade[b]	Cl^-	SO_4^{2-}	Fe_2O_3	Na^+	Ca^{2+}	Heavy metalsas Pb	H_2O insolubles
$Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$	T	0.07	0.06	0.003				0.02
	SQ[c]	0.4[d]	1.0[d]	2.8[d]		50[d]	10[d]	10[d]
$Na_2O{\cdot}2B_2O_3{\cdot}5H_2O$	T	0.05	0.08	0.004				
$NaBO_2{\cdot}4H_2O$	T	0.1	0.1	0.003		0.002[e]	0.0005[e]	0.002[e]
$NaBO_2{\cdot}2H_2O$	T	0.1	0.1	0.007		0.003[e]	0.0005[e]	0.002[e]
$K_2O{\cdot}2B_2O_3{\cdot}4H_2O$	T	0.05	0.05	0.0014	0.10	0.002[e]	0.0005[e]	0.002[e]
$KB_5O_8{\cdot}4H_2O$	T	0.05	0.05	0.003	0.10		0.0005[e]	
$(NH_4)_2O{\cdot}2B_2O_3{\cdot}4H_2O$	T	0.05	0.05	0.0014	0.0026[e]			
$NH_4B_5O_8{\cdot}4H_2O$	T	0.05	0.05	0.0014			>0.0001[e]	
	SQ	0.4[d]	1[d]	5[d]			2[d]	10[d]

[a] Ref. 33.

[b] T = technical and SQ = special quality.

[c] Also contains 10 ppm phosphate.

[d] Values are ppm.

[e] Maximum values are not set. These are typical values.

indicate no evidence of carcinogenic (108) or mutagenic activity (109). Boric acid and borax are poorly absorbed through healthy skin and do not cause skin irritation. A permissible exposure limit (PEL) of 10 mg/m^3 of sodium borate dust has been adopted by OSHA in the United States (110).

Sodium metaborate hydrates are more alkaline than borax and greater care is required in handling. The metaborate material is harmful to the eyes and can cause skin irritation. Gloves, goggles, and a simple dust mask should be used when handling sodium metaborate powder.

Boron in the form of borate is an essential micronutrient for the healthy growth of plants and is present in the normal daily human diet at an estimated level of 3–40 mg as boron. It is not a proven essential micronutrient for animals (111).

The handling of boric acid and borax is generally not considered dangerous. There are no fire risks associated with the storage or use of inorganic borates, and they are not explosive.

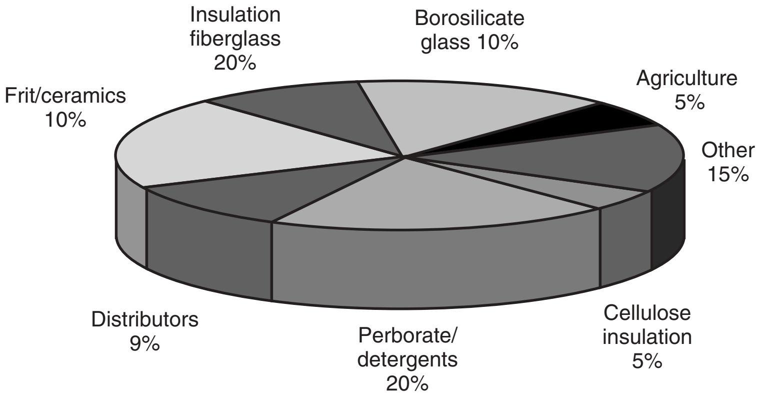


Fig. 6. End-use makeup of the global market for borates.

7.16. Uses. The single largest end use for borate is insulation fiberglass or glass wool. Insulation fiberglass accounts for 20% of the total world B_2O_3 demand and >30% of the total demand in North America. Of the estimated half million tons of borates used for insulation fiberglass production in 1996. 60% was used in Norh America, 30% in Europe, and 10% in other regions of the world.

The second largest end use is perborate and cleaning products, accounting for just under 20% of world demand. Much of this use category consists of perborate, which is included in the formulations of various soapers. Approximately 95% of the perborate demand originates in Europe with the remainder arising mostly from North America. Conversly, the demand for cleaning products is approximately 90% from North America and the remainder from Europe.

The third largest end use for borates is textile fiberglass, accounting for roughly 15% of world borate demand. More than half of the world's textile fiberglass producers are in North America, another 25% in Europe, and 20% in Asia.

Another 10% of the world's borates end up in ceramics and frits. The leading market is Europe with more than half of that production taking place in Spain and Italy. Producers in Asia and South America each account for another 15% of borate use in ceramics and frits.

The final catchall category, "other uses," accounts for an additional 15% of global demand for borates. Most end uses for these categories are relatively minor applications such as cellulose and adhesives. Therefore, these manufacturers have a small annual tonnage requirement.

Borosilicate glass accounts for 10% of B_2O_3 world demand; >70% of this demand arises from North America and Europe. Cellulose insulation is the smallest of the end use categories and accounts for only 2% of world demand, 80% of which comes from producers in North America.

Disodium Tetraborate Decahydrate. In the United States, nearly all the refined borax is used for household cleaning products. Small amounts are used as fertilizers and herbicides. USP-grade borax is used in cosmetic and toilet goods, in which purity is demanded. Special quality-grade borax is used in electrolytic capacitors, in nuclear applications, and as a laboratory chemical.

Disodium Tetraborate Pentahydrate. Refined pentahydrate consumed in the United States is used in insulation fiber glass, glass, fertilizers, and herbicides. Smaller amounts are used in antifreeze (see ANTIFREEZES AND DEICING FLUIDS), ceramic glazes, and cleaning agents. About 40% of the pentahydrate produced in the United States is exported (112). A large-scale application of this chemical is in the preparation of perborate bleaches.

Disodium Tetraborate. In the United States, anhydrous borax finds most application in the glass industry for enamels, borosilicate glass, and fiber glass insulation. It is also used as an antifreeze additive and as an algicide in industrial water.

Disodium Octaborate Tetrahydrate. Commercially available products, having the approximate composition of a hypothetical disodium octaborate tetrahydrate, have found application in wood (qv) preservatives, fertilizer sprays, insecticides, herbicides, and fire retardants. In many applications the large water solubility of these products is an asset.

Disodium octaborate tetrahydrate (TIM-BOR) is registered for a variety of pests including termites, wood destroying beetles, and carpenter ants. This same compound is also used to control fly larvae in manure piles and is marketed as POLYBOR 3 for this application.

Disodium octaborate tetrahydrate is also used to protect wood from wood destroying fungi and pests. Whereas it has mainly been used for this application in New Zealand, it is being introduced into the United States for this use.

Sodium Metaborate Tetrahydrate and Dihydrate. The sodium metaborates are components in textile finishing, sizing and scouring compositions, adhesives, and detergents. They are also used in many photographic applications. In agriculture they are used in both herbicides and fertilizer sprays. The dihydrate is less affected by heat.

8. Other Alkali Metal and Ammonium Borates

8.1. Dipotassium Tetraborate Tetrahydrate.

Dipotassium tetraborate tetrahydrate, $K_2B_4O_7 \cdot 4H_2O$ or $K_2O \cdot 2B_2O_3 \cdot 4H_2O$, formula wt, 305.49; orthorhombic; sp gr, 1.919; is much more soluble than borax in water. Solubility data are given in Table 10; pH with concentration is given in Table 11.

Phase relationships in the system K_2O–B_2O_3–H_2O have been described and a portion of the phase diagram is given in Figure 7. The tetrahydrate,

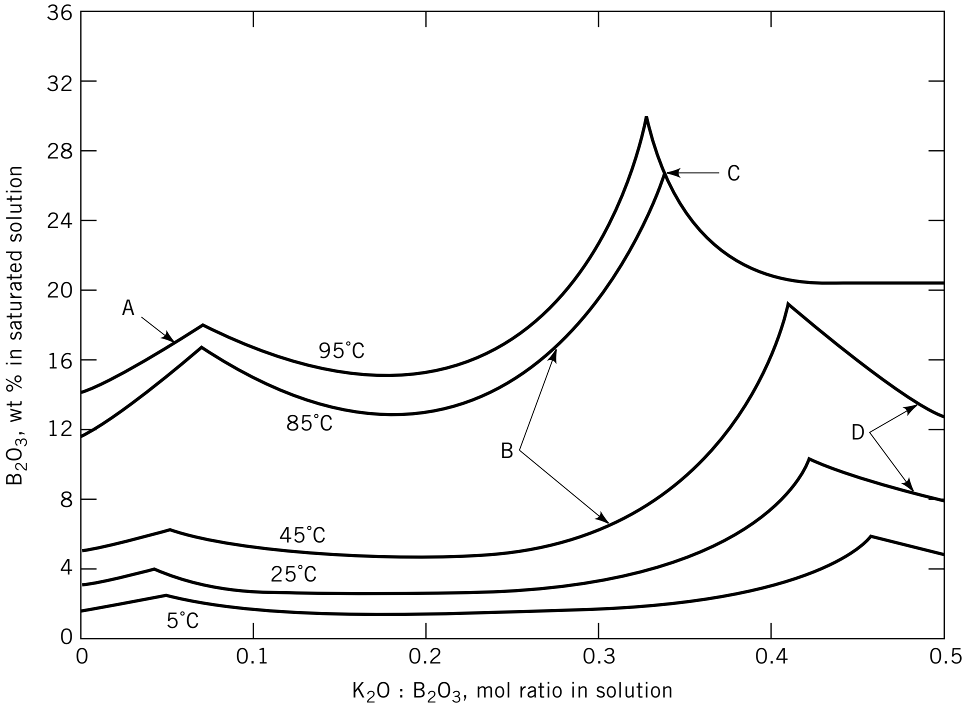


Fig. 7. Solubility isotherms for the K_2O–B_2O_3–H_2O system at temperatures from 5 to 95°C where A, B, C, and D represent the solid phases $B(OH)_3$, $K_2O \cdot 5B_2O_3 \cdot 8H_2O$, $2K_2O \cdot 5B_2O_3 \cdot 5H_2O$, and $K_2O \cdot 2B_2O_3 \cdot 4H_2O$, respectively (113).

which can be dried at 65°C without loss of water of crystallization, begins to dehydrate between 85 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/mol (20.7 kcal/mol) of H_2O. Thermogravimetric curves indicate that two moles of water are lost between 112 and 140°C, one more between 200 and 230°C and the last between 250 and 290°C (114).

Single-crystal x-ray studies have shown that the borate ion in the potassium compound is identical to that found in borax (4) and has the structural formula $K_2[B_4O_5(OH)_4] \cdot 2H_2O$ (115).

8.2. Potassium Pentaborate Tetrahydrate. Potassium pentaborate tetrahydrate, $KB_5O_8 \cdot 4H_2O$ or $K_2O \cdot 5B_2O_3 \cdot 8H_2O$; formula wt, 293.20; orthorhombic prisms; sp gr, 1.74; heat capacity, 329.0 J/(mol · K) [78.6 cal/(mol · K)] at 296.6 K; is much less soluble than sodium pentaborate (Tables 10 and 11). Heat capacity measurements on the solid have been made over a broad temperature range (87).

The tetrahydrate is stable under normal conditions of storage. Its heat of dehydration has been calculated as 110.8 kJ/mol (26.5 kcal/mol) between 106.5 and 134°C (114). Its thermal stability is highly dependent on the partial pressure of atmospheric water. It is stable when heated in a vaccum up to 105°C; in an atmosphere saturated with water at 90°C, it is stable up to 170°C.

The solid-state structural formula is $K[B_5O_6(OH)_4] \cdot H_2O$ (116), which is analogous to that found in sodium pentaborate (5).

8.3. Diammonium Tetraborate Tetrahydrate. Diammonium tetraborate tetrahydrate, $(NH_4)_2B_4O_7 \cdot 4H_2O$ or $(NH_4)_2O \cdot 2B_2O_3 \cdot H_2O$; formula wt, 263.37; monoclinic; sp gr, 1.58; is readily soluble in water (Table 10). The pH of solutions of diammonium tetraborate tetrahydrate is 8.8 and independent of concentration. The compound is quite unstable and exhibits an appreciable vapor pressure of ammonia. Phase relationships have been outlined and the x-ray crystal structure formula is $(NH_4)_2[B_4O_5(OH)_4] \cdot 2H_2O$ (117).

8.4. Ammonium Pentaborate Tetrahydrate. Ammonium pentaborate tetrahydrate, $NH_4B_5O_8 \cdot 4H_2O$ or $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$; formula wt, 272.13; sp gr, 1.567; heat capacity, 359.4 J/(mol · K) [85.9 cal/(mol · K)] at 301.2 K; exists in two crystalline forms, orthorhombic (α) and monoclinic (β). The α-form, which crystallizes as the kinetic product, is the commercial form of ammonium pentaborate tetrahydrate and the β-form is the thermodynamic product but is slow to crystallize. Its heat capacity has been measured over a broad temperature range (87). Solubility data are given in Table 10 and pH data in Table 11.

Ammonium pentaborate tetrahydrate is very stable in respect to ammonia loss. On heating from 100 to 230°C, it loses 75% of its water content but less than 1% of the 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 to give boric oxide (118).

The pentaborate is shown by x-ray data to contain the $[B_5O_6(OH)_4]^-$ ion (5), analogous to that found in the sodium and potassium compounds. The α-form has the structural formula $NH_4[B_5O_6(OH)_4] \cdot 2H_2O$ and the β-form $NH_4[B_5O_8] \cdot 4H_2O$ (119).

8.5. Lithium Borates. Two lithium borates are of minor commercial importance, the tetraborate trihydrate and metaborate hydrates.

Dilithium tetraborate trihydrate, $Li_2B_4O_7 \cdot 3H_2O$ or $Li_2O \cdot 2B_2O_3 \cdot 3H_2O$, has a density of 1.88 g/mL. It crystallizes with difficulty from a supersaturated solution of lithium hydroxide and boric acid, which on standing forms a gelatinous deposit that is converted to hydrate crystals after boiling for several hours. The trihydrate is stable up to 180°C, then the compound dehydrates becoming anhydrous up to about 320°C, and fuses at 890°C.

Lithium metaborate octahydrate, $LiBO_2$ $8H_2O$ or $Li_2O \cdot B_2O_3 \cdot 16H_2O$, hexagonal; $d = 1.825$ g/mL; has the structural formula $Li[B(OH)_4 \cdot 6H_2O$ (120). On heating to 70°C six waters are lost; the last two waters are lost between 140 and 280°C (121).

The octahydrate is the stable solid phase in contact with its solution below 36.9°C. Above this temperature lithium metaborate dihydrate, $LiBO_2 \cdot 2H_2O$ or $Li_2O \cdot B_2O_3 \cdot 4H_2O$, becomes the stable solid phase. Dihydrate crystals are orthorhombic having a density of 1.825 g/mL and a structural formula $Li[B(OH)_4]$. In solution above 150°C a hemihydrate, $LiBO_2 \cdot 1/2H_2O$, forms and the anhydrous salt crystallizes above 225°C.

8.6. Manufacture. Potassium tetraborate tetrahydrate may be prepared from an aqueous solution of KOH and boric acid having a B_2O_3:K_2O ratio of about 2 or by separation from a KCl–borax solution (122). Potassium pentaborate is prepared in a manner analogous to that used for the tetraborate, but the strong liquor has a B_2O_3:K_2O ratio near 5.

Ammonium tetraborate tetrahydrate is prepared by crystallization from an aqueous solution of boric acid and ammonia having a B_2O_3:$(NH_4)_2O$ ratio of 1.8:2.1. Ammonium pentaborate is similarly produced from an aqueous solution of boric acid and ammonia having 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 (123). A process for the production of ammonium pentaborate by precipitation from an aqueous ammonium chloride–borax mixture has been patented (124).

8.7. Economic Aspects. The potassium, lithium, and ammonium borates are low volume products. Annual production figures are in the range of hundreds of metric tons.

8.8. Health and Safety. Little toxicological data are available on borates other than boric acid and borax. Most water-soluble borates have the same toxicological effects as borax when adjusted to account for differences in B_2O_3 content.

8.9. Analytical Methods. *Sodium, Potassium, and Ammonium Borates.* Sodium, Potassium, and ammonium salts of borates are first dissolved in hot water. The solution is neutralized using hydrochloric acid (HCl). An excess amount of HCl is added to the solution. Carbon dioxide is removed by boiling. It is neutralized with NaOH to a boric acid solution using methyl red as the indicator. Mannitol (or glycerol) is then added, and the resulting solution is titrated with NaOH solution using phenolphthalein as the indicator. 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.

8.10. Uses. Dipotassium tetraborate tetrahydrate is used to replace borax in applications where an alkali metal borate is needed but sodium salts cannot be used or where a more soluble form is required. The potassium compound is used as a solvent for casein, as a constituent in welding fluxes, and a component in diazotype developer solutions. Potassium pentaborate tetrahydrate is used in fluxes for welding and brazing of stainless steels for nonferrous metals. Diammonium tetraborate tetrahydrate is used when a highly soluble borate is desired but alkali metals cannot be tolerated. It is used mostly as a neutralizing agent in the manufacture of urea–formaldehyde resins and as an ingredient in flameproofing formulations. Ammonium pentaborate tetrahydrate is used as a component of electrolytes for electrolytic capacitors, as an ingredient in flameproofing formulations, and in paper coatings.

9. Calcium-Containing Borates

9.1. Dicalcium Hexaborate Pentahydrate. Dicalcium hexaborate pentahydrate, $Ca_2B_6O_{11} \cdot 5H_2O$ or $2CaO \cdot 3B_2O_3 \cdot 5H_2O$; formula wt, 411.08; monoclinic; sp gr, 2.42; heat of formation, -3.469 kJ/mol ($-$ 0.83 kcal/mol)(125); exists in nature as the mineral colemanite. Its solubility in water is about 0.1% at 25°C and 0.38% at 100°C. Heats of solution have been determined in HCl (125). Colemanite is slowly formed on heating saturated solutions of inyoite, $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, or other higher hydrates. Colemanite decrepitates violently at 480°C losing all its water and forming an anhydrous very low bulk density powder (126).

The crystal structure of colemanite has been shown to contain $[B_3O_4(OH)_3]^{2n-}{;}_n$ polyanion chains. The structural relationships between colemanite and the other minerals of the series $2CaO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 1$, 5, 7, 9, 13), and structural changes accompanying the ferroelectric transition of colemanite have been outlined (127).

9.2. Sodium Calcium Pentaborate Octahydrate. Sodium calcium pentaborate octahydrate, $NaCaB_5O_9 \cdot 8H_2O$ or $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$; formula wt, 405.23; triclinic; sp gr, 1.95; exists in nature as the mineral ulexite. The compound can be prepared by seeding a solution of 110 g $CaB_2O_4 \cdot 6H_2O$, 40 g boric acid, 100 g borax, 450 g $CaCl_2$ and 2.5 L H_2O (111). Ulexite is slowly converted to $NaCaB_5O_9 \cdot 5H_2O$, probertite, when seed is added to a moistened sample at 80–100°C. When crystals of ulexite are heated, four moles of water are lost at 80–100°C, 8.5 more until 175°C, and the remaining 3.5 on heating to 450°C (128).

The x-ray crystal structure consists of isolated pentaborate polyanions and the structural formula is $NaCa[B_5O_8(OH)_6] \cdot 5H_2O$ (129). Some specimens of ulexite have fiber optic properties with surprisingly good resolution of projected images. The fiber is aligned along the *c*-axis with index of 1.529. Cladding results from random orientation of crystals about the fiber direction, producing a core-to-cladding index difference ranging from 0 to a maximum of $\gamma - \alpha = 0.038$ (130).

The solubility in water at 25°C is 0.5% as $NaCaB_5O_9$. Calcining at 200–500°C increases its solubility to 9–13 g/L.

9.3. Sodium Calcium Pentaborate Pentahydrate. Sodium calcium pentaborate pentahydrate, $NaCaB_5O_9 \cdot 5H_2O$ or $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$; formula wt 351.19; monoclinic; sp gr, 2.14; exists in nature as the mineral probertite. Probertite can be prepared by heating a mixture of two parts ulexite and one part borax to about 60°C (131) or by heating a borax and calcium metaborate solution at 105°C for eight days (76). The structural formula NaCa $[B_5O_7(OH)_4] \cdot 3H_2O$ has been determined from the crystal structure (132). By thermogravimetric analysis two moles of water are lost at 100°C, four more from 100° to 180°C, and slow loss of the last four up to 400°C.

9.4. Manufacture. The alkaline-earth metal borates of primary commercial importance are colemanite and ulexite. Both of these borates are sold as impure ore concentrates from Turkey, which is the principal world supplier. Colemanite and ulexite mining areas in Turkey are the Bigadic, Emet, and Kestelek regions. In 1986 Etibank run-of-mine production was about 793,000 t/yr of colemanite and 185,000 t/yr of ulexite. The concentrates produced are glass-grade material. The mining is both open-pit and underground.

At Hisarcik, in the Emet District, Etibank operates an open-pit mine and a colemanite concentrating plant. The production from this plant is relatively high in arsenic, about 3500 ppm. The ore consists of colemanite nodules, closely packed with shale. The presence of high concentrations of arsenic sulfides has been indicated. Plant capacity is about 184,000 t/yr as B_2O_3. At Espey, Etibank operates an underground mine, which was to be converted to an open-pit mine, that had a capacity of 25,000 t/yr as B_2O_3. A concentrating plant at Bigadic has a capacity of 132,000 t/yr as B_2O_3 (6,133).

Death Valley, California, has historically been a significant source of both colemanite and ulexite, but mining in the Death Valley National Monument has been forbidden as a result of environmental concerns. In 1986, the American Borate Co. ceased mining in Death Valley, but continues to market ore concentrate from inventory as well as borates and concentrates imported from Turkey.

9.5. Specifications and Shipping. The colemanite, which is to be used in the production of glass fibers, must conform to the purchasers' specifications on Fe and As. Colemanite is available in bags and bulk.

9.6. Uses. Colemanite, $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, is used in the production of boric acid and borax, as well as in several direct applications. It is a highly desirable material for the manufacture of the E-glass used in textile glass fibers and plastic reinforcement (where sodium cannot be tolerated). High As or Fe levels in the ore concentrate can limit its use in this application. Colemanite has seen limited application as a slagging material in steel manufacture. It is also used in some fire retardants and as a precursor to some boron alloys.

Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, and probertite, $NaCaB_5O_9 \cdot 5H_2O$, have found application in the production of insulation fiber glass and borosilicate glass as well as in the manufacture of other borates.

Borate Melts and Glasses. Like silicon oxide and lead oxide, boric oxide (B_2O_3) is a natural glass network-forming oxide having very 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 alkali metal borates to form a clear liquid melt. If these liquids are high (M_2O/B_2O_3 from 0 to 2 mol) in boric oxide content, they become viscous on cooling and form glasses.

Most of the interest in alkali metal borate glasses has centered on reports indicating the existence of maxima and minima in some of the physical properties

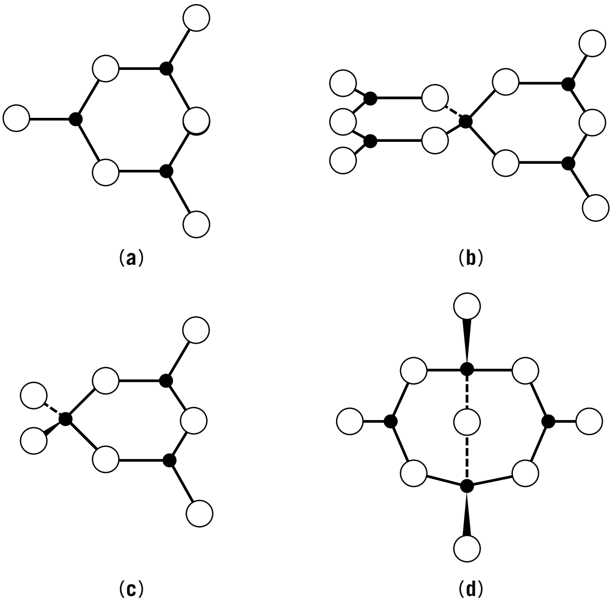


Fig. 8. The borate glass structural groups where • = boron; ○ = oxygen; (**a**) boroxol; (**b**) pentaborate; (**c**) triborate; and (**d**) diborate (135).

of the glasses, such as viscosity, density, and thermal expansion coefficient, that occur with increasing metal oxide content. This phenomenon has been called the boron oxide anomaly (134). Modern theory on borate glass structure, however, indicates that these property changes are not anomalous but are the result of well-defined structural changes in the glass at the molecular level. Four different borate structural groups have been theorized to be present in alkali borate glasses below 34 mol % M_2O (135). These groups are shown in Figure 8. The triborate and pentaborate groups always occur in pairs which are then referred to as tetraborate groups. The argument that pure vitreous B_20_3 consists of flat BO_3 triangles in the form of boroxol rings connected by BO_3 chains is strongly supported by boron nuclear quadrapole resonance spectroscopy (136). Addition of alkali oxide to boron oxide to form an alkali borate glass results in transformation of BO_3 triangles to BO_4 tetrahedra in a continuous manner. On addition of M_2O, up to 20 mol %, tetraborate groups are formed. Between 20 and 34 mol % M_2O, diborate groups form at the expense of the tetraborate groups. Infrared (135) and laser Raman (28) data on borate glasses and the analogous crystalline anhydrous borates support this reasoning. Changes in the physical properties of the glass with M_2O content represent compromises between the effect of adding more metal ions to the system and the effect of making the borate structural entities more rigid by converting trigonally coordinated borons to tetrahedrally coordinated borons.

Another widely studied phenomenon in alkali borate glasses is the mixed alkali effect, the nonlinear change in glass properties when a second kind of alkali oxide is added into the single-alkali glass. Models have been suggested to explain the mixed alkali effect (137), but a universally accepted model has not been developed as of this writing.

A number of 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 (75). The application of x-ray diffraction, nmr, Raman scattering, ir spectroscopy, and esr to structural analysis is available (26). Phase-equilibrium diagrams for a large number of anhydrous borate systems are included in a compilation (138), and thermochemical data on the anhydrous alkali metal borates have been compiled (17).

The largest single commercial use of borates is in fiber glass. There are two basic types of glass fibers: insulation (soda lime borosilicate glass) and textile (low alkali lime aluminosilicate glass) grades. Borax pentahydrate is the most common source of B_2O_3 for making insulation fiber glass. Textile or E-glass fiber requires low sodium formulations and for this reason boric acid or colemanite is commonly used. Only borates having low arsenic content are suitable for use in glass making. Smaller amounts of borates are consumed in heat-resisting (Pyrex or low thermal expansion) glass, sealing glass, glazes and enamels (frit), optical glass, nuclear waste storage glass, and in the making of vycor. The typical range of B_2O_3 content in commercial glasses is shown in Table 13. Borates are not generally used in container or flat glass.

Boron oxide, B_2O_3, can be added to a glass formulation from a variety of boron-containing compounds, but because the boron is taken into vitreous solution, it is often immaterial which source of boron is used. The choice of raw material is usually determined by consideration of the price per contained B_2O_3 unit, uniformity of composition, purity, hydration state, and compatibility of the cation in the finished glass. In addition, boron-containing raw materials are usually the only water-containing constituents in a glass batch and because the water must be removed in the melting furnace, the dehydration characteristics are important (137).

Boron oxide is added to borosilicate glass formulations to improve properties both in the finished glass and in the glass-making process (146). The benefits of B_2O_3 use in glass making are (*1*) creation of a low melting flux to dissolve refractory silica; (*2*) a lower liquidus temperature and inhibition of devitrification; (*3*) lower melt viscosity; (*4*) enhanced melt rate; and (*5*) improved draw qualities in fiber production. The benefits of B_2O_3 in the finished glass product

Table 13. **Borate Content in Commercial Glass**

Glass type	B_2O_3, wt %
fiber	
textile	6–13
insulation	3–7
heat resisting (pyrex)	12–15
sealing glass	8–30
porcelain enamel (frit)	11–13
vycor	20[a]

[a] This is the percent B_2O_3 in glass prior to acid leaching toform vycor.

are (*1*) improved chemical durability; (*2*) lower thermal expansion; (*3*) increased mechanical strength; (*4*) decreased devitrification tendency; (*5*) improved scratching hardness; and (*6*) enhanced refraction, color, and brilliance.

10. Other Metal Borates

Borate salts or complexes of 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 have achieved commercial importance.

In general, hydrated borates of heavy 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 having variable compositions. Crystalline products are generally obtained from slightly acidic solutions.

Anhydrous metal borates may be prepared by heating the hydrated salts to 300–500°C, or by direct fusion of the metal oxide with boric acid or B_2O_3. Many binary and tertiary anhydrous systems containing B_2O_3 form vitreous phases over certain ranges of composition (138).

10.1. Barium Metaborate. Three hydrates of barium metaborate, $BaO \cdot B_2O_3 \cdot xH_2O$, are known. The tetrahydrate (140) and pentahydrate (141) both contain the $B(OH)_4^-$ anion, and are properly formulated as $Ba[B(OH)_4]_2 \cdot xH_2O$, where $x = 0$ or 1. These compounds crystallize when solutions of barium chloride and sodium metaborate are combined at room temperature (142). The higher hydrate is favored when excess sodium metaborate is used. Saturated aqueous solutions contain 13.5 g/L of $BaO \cdot B_2O_3 \cdot 4H_2O$ at 25°C. Both forms dehydrate at temperatures above 140°C (143). Barium metaborate may also be prepared from barium sulfide formed by prior reduction of barium sulfate. The presence of sulfide impurities in the product may render it unsuitable for some applications (62). Crystals of a hydrate, $x = 1.67$ H_2O, form from a boiling solution having the B:Ba molar ratio <2. Dehydration of this hydrate at 300°C gives $BaO \cdot B_2O_3$ in which boron atoms are both triangularly and tetrahedrally coordinated (144).

Barium metaborate is used as an additive to impart fire-retardant and mildew-resistant properties to latex paints, plastics, textiles, and paper products (6).

10.2. Copper, Manganese, and Cobalt Borates. Borate salts of copper, manganese, and cobalt are precipitated when borax is added to aqueous solutions of the metal(II) sulfates or chlorides (145). However, these materials are no longer produced commercially.

10.3. Zinc Borates. A series of hydrated zinc borates have been developed for use as fire-retardant additives in coatings and polymers (59,146). Worldwide consumption of these zinc salts is several thousand metric tons per year. A substantial portion of this total is used in vinyl plastics where zinc borates are added alone or in combination with other fire retardants such as antimony oxide or alumina trihydrate.

Zinc borate $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$ is formed when borax is added to aqueous solutions of soluble zinc salts at temperatures below about 70°C. An x-ray structure determination has indicated that this compound is orthorhombic and has a zinc triborate monohydrate structure, $Zn[B_3O_3(OH)_5]\cdot H_2O$ (2). Zinc borates $2ZnO\cdot 3B_2O_3\cdot 7H_2O$ and $ZnO\cdot B_2O_3\cdot 2H_2O$ lose water of hydration when heated from 130 to 250°C (59).

A different crystalline hydrate, $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$, equivalent to $4ZnO\cdot 6B_2O_3\cdot 7H_2O$, is produced when the reaction between zinc oxide and boric acid is carried out at temperatures of 90–100°C (147). This product has also been crystallized from solutions containing borax, zinc chloride, and sodium hydroxide (148). It is marketed by the United States Borax & Chemical Corp. under the trademark FIREBRAKE ZB, BOROGARD ZB, and under AMAX, Inc. as ZB-467.This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fireretardant additive for plastics and rubbers that require high processing temperatures. It is also used as an anticorrosive pigment in coatings. Zinc borates are also manufactured by Storey (UK) and Waardals (Norway).

Zinc borate $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$ has an acute oral toxicity in rats $LD_{50} > 10,000$ mg/kg body weight and acute dermal toxicity in rabbits $LD_{50} > 10,000$ mg/kg body weight. It is not a skin irritant and gives a negative response in the Ames mutagenicity test.

11. 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.

$$B(OH)_3 + H_3PO_4 \longrightarrow BPO_4 + 3\,H_2O$$

Complete dehydration requires temperatures above 1000°C.

The structure of boron phosphate prepared under normal atmospheric conditions consists of tetragonal bipyrimids analogous to the high cristobalite form of silica. Both the boron and phosphorus are tetrahedrally coordinated by oxygen. Similar silicalike structures are found for $BAsO_4$ and $TaBO_4$ (149). A quartzlike form of boron phosphate can be prepared by heating the common form to 500°C at 5.07 GPa (50,000 atm) (150).

The tri-, tetra-, penta-, and hexahydrates of boron phosphate have been reported. All of these decompose rapidly in water to give solutions of the parent acids. Anhydrous boron phosphate hydrolyzes in a similar fashion, though the reaction proceeds quite slowly for material that has been ignited at high temperatures.

The principal application of boron phosphate has been as a heterogeneous acid catalyst (151).

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 considerable portion of the B_2O_3–SiO_2–P_2O_5 system (152).

12. Environmental Concerns, General

Boron is present everywhere — in soil, water, plants, and animals — in trace amounts. Although scientists refer to "levels of boron" when addressing environmental, health, and safety issues, is important to note that the element boron does not exist by itself in nature. Rather, boron combines with oxygen and other elements to form boric acid, or inorganic salts called borates.

Concentrations of boron compounds large enough to mine are limited to only a few places on the planet. In fact, the vast majority are mined at one of two world-class deposits. Boron compounds are essential ingredients in many industrial processes including the manufacture of glass, ceramics, fiberglass insulation, detergents, flame retardants, and wood protection products.

Despite the millions of tons of industrial borates mined, processed, and distributed around the world every year, a far larger quantity of boron travels around the planet by way of natural forces. Rain, volcanic activity, condensation, and other atmospheric activities move at least twice as much boron as all commercial practices combined.

Boron was identified in the 1920s as one of the seven micronutrients essential to all plants. The element is integral to a plant's reproductive cycle: controlligg flowering, pollen production, germination, and seed and fruit development. Boron also acts as a fuel pump, aiding the transmission of sugars from older leaves yo new growth areas and root systems (153).

In some regions, heavy rainfall, geologic characteristics, or farming practices have leached boron from the soil, leaving too little to support plant and crop survival. Many crop plants — including canola, alfalfa, clover, corn, cotton, peanuts, apples, carrots, celery, table beets, and fruit and nut trees — are regularly treated with foliar or systemic boron supplements to enhance crop quality and yield.

On the other hand, high concentrations of boron can be harmful to some types of plants. Citrus trees, for instance, are particularly susceptible to boron toxicity.

Overall, agriculture relies heavily on boron supplementation to ensure an adequate food supply. Studies indicate that people in a wide variety of cultures consume about 1–3 mg of boron per day through a combination of foods and drinking water in their local diets (154). Although it has yet to be proved that humans need boron to live, there is almost universal agreement that boron is nutritionally important to maintaining optimal human health.

In summary, trace amounts of boron are enviornmentally ubiquitous, essential to plant life and nutritionally important to humans. However, as with any substance, the dose makes the poison. In other words, overexposure to boron compounds can be hazardous to plants, animls, and even people. Concentration of boron in the environment are discussed below (155).

12.1. Boron in Water.

Boron occurs naturally in seawater at an average concentration of 5 mg of boron per liter. Boron generally occurs in freshwater at concentrations of up to 1 mg/L, or one part per million (ppm) (156).

A boron concentration of 1 ppm is believed to be safe for all aquatic creatures. As context, 1 ppm is equivalent to a handful of borax in a body of water the size of an Olympic swimming pool.

Higher concentrations of boron in water — ranging from 10 to 1000 ppm — have been created in laboratory settings in order to measure boron toxicity and its effects. These lab studies show that extremely high levels of boron may have a negative impact on the reproductive systems of aquatic organisms. Zebrafish and rainbow trout – species with a heightened sensitivity to boron in their larval stages — are most often used in this reserch adverse. It is interesting to note that studies using zebra fish have shown that the fish exhibit adverse reproductive and developmental effects when exposed to enviornments where *not enough* boron is present, as well (157). Simply put, not enough boron is as harmful as too much.

12.2. Boron in Soil. The earth's soil can be categorized as low boron (<10 ppm boron) or high boron (on the order of 100 ppm boron). The average overall concentration of boron in all soil ranges from 10 to 20 ppm.

Because borates dissolve easily, their concentration in soil is greatly dependent on the physical and chemical characteristics of the soil, as well as the availability of water moving through it. As mentioned above, when natural boron levels have been depleted through leaching by rainwater or uptake by plants, soils are regularly treated with borates to encourage crop production.

Extremely high boron soils are rare. In fact, there are only two known deposits of borates on the planet: in California's Mojave Desert and in Turkey. Both deposists were formed over many millions of years as a result of precise geologic conditions that fostered high concentrations of borates becoming encapsulated in nonpermeable layers of clay.

12.3. Boron in Air. Relatively little information is available about how much boron is present in the air. Boron has been detected in measurable quantities in rain, snow, evaporation from seawater and hot springs, and industrial airborne dust.

In rain and snow, boron has been reported in concentrations ranging between 0.003 and 0.005 mg/L. On a global basis, boron moves through the atmoshere at a rate of 5–7 million tonnes per year.

13. Health and Safety Factors, General

This section introduces some of the effects of both overexposure and deficiency of boron. Boron compounds have relatively low acute toxicity — meaning that ingestion of small amounts is not likely to cause health problems. Laboratory studies show that very large doses of boron compounds can cause reproductive and developmental effects in animals. However, similar effects have *not* been observed in humans.

Although both humans and animals readily absorb boron compounds, the vast majority is excreated rapidly; in humans, 80–100 % of that elimination is through urination. Further, boron is not metabolized by animals or by humans. Boron compounds are poorly absorbed through intact skin in both humans and animals, although they can be absorbed through damaged skin. Boric acid and other boron compounds are used at a concentration of 5% in cosmetics and talc in the United States and Europe. Data also indicate that inhaling boron compounds does not pose a significant risk to animals or humans.

13.1. Effects in Humans.

Early literature reported the toxicity of boric acid when it was used as a medicinal treatment; that use has long since been discontinued. Accidental misuse resulting in poisoning and death occured in hospitals — most notably when a 30% solution of boric acid was mistaken for distilled water and used to make up baby formula for newborns and from repeated use of 100% boric acid powder on large areas of diaper rash.

Adults may display adverse health effects after ingesting ~3 g of boric acid. This amount represents 1000–3000 times more boron than an adult consumes each day in a normal healthy diet (158).

Of 784 cases of acute boric acid ingestion reported to the National Capital Poison Review Center and the Maryland Poison Center between 1981 and 1985, 88.3% were asmyptomatic. Among the remaining 11.7% less frequent symptoms included lethargy, headache, lightheadness, and rash. Although one death has been reported after a person injested about 30 g of boric acid, $\leq$88 g of boric acid has been ingested, by an adult, without undue harm (159).

A study of mine and refinery workers exposed to high levels ($\leq$14 mg/m^3) of borate dust measured only minor respiratory effects such as mild nose, eye, and throat irritation. No pulmonary or other health effects were observed in workers exposed to higher than average borate levels over time (160).

The reproductive performance of workers at a large mining – refining facility was also studied. The study measured the rate of births to the wives of workers after prolonged occupational exposure to boron compounds; 72% of the eligible workers took part in this study. The study found that these workers had more offspring than the national average; indicating no adverse effect on human reproduction (161).

13.2. Animal Studies: Acute Toxicity.

Boron compounds have been tested on numerous species, including 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 in two ways: *acute*. meaning a single high dose; and *chronic*, meaning repeated exposures over longer periods of time.

The commonly used figure for determining acute toxicity is the LD_{50}, which is the threshold at which the administered dose is lethal to at least half of the animals being tested. The oral LD_{50} for boric acid and most borates in rats ranges from 3.5 to 5.0 g per kilogram body weight. Oral LD_{50} refers to test results in which animals ingest such a dosage on a one-time basis (162).

Dermal toxicity for borate products has been determined to be >5 g/kg body weight. The extremely low dermal toxicity is due to the fact that borates do not penetrate intact skin. In fact, the permeability of human skin to borate products has been determined to be <1%.

A wide range of inhalation studies indicate that borates are not toxic by inhalation. Research shows that the toxic inhalation threshold for boron compounds is >2 mg/L for boron compounds. In other words, animals tested at this extremely high air concentration did not die; rather, they displayed the effect of being exposed to a high level of dust, but recovered after a short time outside the inhalation chamber.

In skin and eye studies, boron compounds were found to be mildly to moderately irritating, but insufficiently harmful to classify and label them as irritants. The finding makes sense, as borates and boric acid are used in cosmetics, talc, oral hygiene products, eyewashes, and contact lens solutions for humans. Finally, there is no evidence of skin sensitization in humans or animals as a result of boron exposure.

13.3. Animal Studies: Chronic Toxicity. Boron compounds have also been tested to determine their long-term or chronic toxic effects. The results of these studies are highlighted in the following paragraphs (162).

Numerous studies testing the effect of boron compounds on both bacteria and mammalian cells prove that they are not mutagenic (ie, do not cause genetic mutation), nor are boron compounds considered carcinogenic, or cancer-causing.

The main treatment-related effects of long-term exposure to high doses of boron compounds among animals are testicular atrophy and reduced fertility. Rats that ingested 58.5 mg boron/kg body weight per day for an extended period exhibited sterility with no viable sperm in males and decreased ovulation in females. In mice, 111 mg boron/kg body weight per day impaired male fertility but did not reduce female fertility.

High doses of boron compounds have also been shown to cause developmental effects in rats, mice, and rabbits. Symptoms of developmental toxicity (eg, decreased fetal body weight, skeletal defects, and circulatory system damage) were noted in pregnant animals at doses ranging from 13.3 to 87 mg boron/kg body weight per day. Maternal toxicity also occured at the higher exposure levels. The definitive rat developmental toxicity study of boric acid accepted today by all health and regulatory authorities demonstrated a no-effect level of 9.6 mg boron/kg body weight per day (163).

13.4. Essentiality. Another area of boron research concerns essentiality, or what role boron plays in maintaing and promoting health in animals and humans. To demonstrate born's nutritonal essentiality, researchers are working to show that insufficient boron in the diet results in adverse health effects — from those that severely interfere with an organism's quality of life to those that result in death. The World Health Organization has concluded that boron is probably essential to humans (164).

In humans, boron's importance in energy metabolism, bone health and strength, and brain function has been established. In animals, reserch is currently under way to measure boron's impact on reproduction and development. One study involving zebrafish has demonstrated that boron deficiency significantly reduces embryo survival rate, and that embryonic death begins very early in the post-fertilization period in the absence of sufficient boron (165).

Early results of another study indicate that insufficient boron results in pooor-quality embryos — some dead and most developing poorly and dying prematurely — in frogs (166). Although it is more difficult to effectively eliminate dietary boron in mammalian studies, essentiality research is also being conducted with rats and mice.

13.5. Safety. Boron is an ubiquitous element, essential to plants and a normal component of a healthy human diet. Although scientists create artificial levels of boron in laboratories to study the effects of over- and underexposure its distribution in the natural world poses little or no risk to plants, animals, or people.

Research on exposure to boron compounds proves that too much or too little boron triggers adverse health effects in a variety of plants and animals. These plant and animal studies also form the basis for determining safe levels of boron exposure for people.

13.6. Risk Assessments. Risk assessments are conducted to pinpoint safe levels of boron in the air, food, water, or other exposure sources. To make this assessment, reults of existing boron toxicity and exposure studies are subjected to complex calculations to produce a generally acceptable guideline for human intake of a substance.

For instance, a particular risk assessment of boron in the the United States determined that 18 mg of boron per day would be an acceptable daily intake from all sources (167). Given that average dietary intake of boron is $\sim$1.0 mg/day, and that the median boron level in United States drinking-water supplies is $<$0.10 mg boron/L, this and other risk assessments have concluded that boron exposure from all sources are not expected to pose any public health risk.

13.7. Occupational Safety. Safety standards are most important for the people exposed to higher than usual amounts of boron compounds, including workers at mining and refining facilities, and at industrial plants where borates and boric acid are used to manufacture other products. These standards are also important tools for the cadre of local, national, and international regulators entrusted with protecting human health and the enviornment.

Occupational exposure limits are set by federal and state agencies to control worker exposure to borate dust in industrial settings. These exposure limits range within 1–15 mg dust/m^3 air. The higher limits are consistent with the default values applied to “nuisance dusts” or materials that are not otherwise classified.

Within some industrial settings, there are areas of particularly high boron dust concentration. In these areas, personal protective equipment is required. The equipment can include respirators or dust masks, eye protection, gloves, and protective clothing.

13.8. Product Safety. Since the late nineteenth century, borate products have enjoyed an excellent reputation for safety and effectiveness when used as directed. Borates and boric acid are used to manufacture a wide range of products, including fiberglass insulation, heat-resistant glass, flame retardants, cosmetics, fertilizers, and household laundry detergents.

Some products that contain boron compounds — such as fertilizers, pesticides, and pharmaceutical products — are regulated by state and federal agencies. Moreover, most industrial borate and boric acid products are regulated under the federal Occupational Safety and Health Administration (OSHA) hazard communication standard. Therefore, these products require Material Safety Data Sheets (MSDSs) and proper labeling.

MSDs are standardized documents that list a comprehensive range of information, including chemical composition and characteristics, hazard identification, first aid measures, firefighting and accidental release measures, proper handling and storage guidance, exposure controls and personal protection recommendations, detail on toxicologic and ecologic information, disposal considerations, transport information, and regulatory information.

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