METAL BORATES

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I. Introduction

The chemistry of metal borates is surprisingly intricate. Early work was essentially of a synthetic nature, and it was the development of spectroscopic and X-ray crystallographic techniques that demonstrated the complexity of boron systems. During the past decade, crystal structures of metal borates have been determined at a rapid rate, and several novel types of borate anions have come to light. Concurrently, great advances in the understanding of the nature of borate ions in solution have been made through use of Raman, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopic techniques.

This review is concerned with the hydrated metal borates, their interactions in solution, and their synthesis. Section III outlines the known structures of the hydrates and includes details of a few anhydrous borates to show the relationship of their basic structural units to those of the partially and completely hydrated forms. Section IV re-

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views the work on polyborate ions in solution and the effect that cations have on their equilibria. Section V is a brief account of the properties of some metal borates. Literature up to July 1979 is included.

Because of the great volume of literature on boron–oxygen compounds, it has been necessary to be highly selective in the choice of material for inclusion. Thus the properties of boric acid, and formation of sulfatoborates, perborates, arsenatoborates, metal borate–organic complexes, glasses, and melts are omitted. The chemistry of the lanthanide and actinide borates has not been considered; although these borates represent a current active field of research, an account of their properties would necessitate a large extension of the text. Data on all these aspects of borate chemistry are reviewed in Mellor's "Comprehensive Treatise of Inorganic and Theoretical Chemistry" (*60, 307, 392*).

II. Nomenclature

For many years, confusion has arisen over the ambiguous naming of metal borates. Typically, borates of the type $M_2B_4O_7$ or $M_2O \cdot 2B_2O_3$ have been referred to as both tetraborates and diborates. With more structural data available, the use of such names is obviously misleading. The silver borate $Ag_2O \cdot 4B_2O_3$ has been labeled a tetraborate but its structure shows that it is built up of triborate (a B_3O_3 skeleton) and pentaborate (a B_5O_6 skeleton) units. In this article, formulas are written either as the empirical ratio of oxides or as the structural formulas where appropriate. Thus borax, $Na_2B_4O_7 \cdot 10H_2O$, appears either as $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ (or in its abbreviated form 1:2:10) or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$.

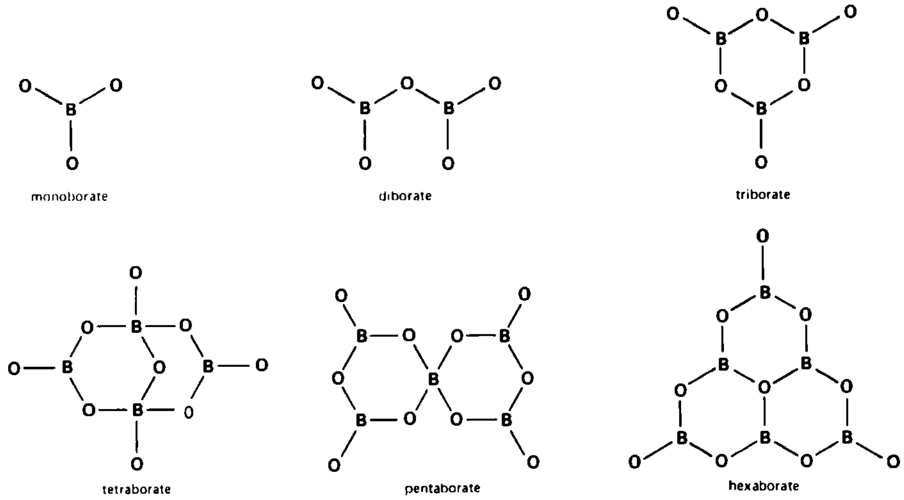
III. Structural Characteristics of Metal Borates

The ability of boron to coordinate to three and four oxygen atoms enables a wide range of theoretical structural entities to be formulated. An interesting history of early postulates in which only three-coordinate boron was considered has been outlined by Bokii and Kravchenko (*56*). Several authoritative reviews of the structural chemistry of borates have been published (*56, 77, 173, 182, 381, 408, 429*), but the most recent and reliable is that by Christ and Clark (*80*). In their paper they have considered structures determined from X-ray or neutron diffraction studies of single crystals, rather than include interpretations of spectroscopic or dehydration characteristics of borates. They have also amended the rules affecting formation of hydrated polyborate ions originally proposed by Christ in 1960 (*77*) and classified the borate structures using a shorthand notation describing the size of a boron–oxygen ring and the number of trigonal to tetrahedrally coordinated boron atoms; the space available does not permit an adequate description of this system. The arrangement of neighboring ions in anhydrous borates and glasses has been discussed in terms of the "structon theory" (*181, 182*).

The most common units found in borate structures are shown in Fig. 1. Many of the known borate structures can be rationalized by assigning appropriate charges, protons, or hydroxyl groups (which change the coordination of boron from trigonal to tetrahedral) to these basic units. Thus the BO_3 unit can become BO_3^{3-}, $B(OH)_3$, or $B(OH)_4^-$, respectively. Polymerization by elimination of one water molecule between two hydrated units results in chain formation, and further water elimination gives sheets or networks. These operations are illustrated in Fig. 2 for the triborate ring unit.

A. Hydrated Metal Borates

Table I lists many of the known hydrated borate structures, except for those containing silicon. The compounds are arranged according to structural similarity under the classification of Christ and Clark (*80*)


monoborate diborate triborate

tetraborate pentaborate hexaborate

Fig. 1. Basic units of borate structures. All trigonally coordinated boron atoms shown can theoretically become tetrahedrally coordinated.

TABLE I

STRUCTURES OF METAL BORATES

Structural formula	References	Structural formula	References
Isolated $B(OH)_3$ and BO_3^{3-}			
$B(OH)_3$	Sassolite (*446*)	$Al_5O_6(BO_3)$	(*388*)
α-Li_3BO_3	(*393*)	$CaAlO(BO_3)$	(*364*)
$Mg_3(BO_3)_2$	(*39*), Kotoite (*354*)	$LiCdBO_3$	(*205*)
$Ca_3(BO_3)_2$	(*418*)	$LiMnBO_3$	(*59*)
$AlBO_3$	(*420*)	$FeCoO(BO_3)$	(*421*)
Tl_3BO_3	(*332*)	$Mg(Mg_{0.5}Ti_{0.5})O(BO_3)$	Warwickite (*300*)
$Zn_3(BO_3)_2$	(*32, 138*)	$Mg_2MnO_2(BO_3)$	Pinakiolite (*300*)
$Ni_3(BO_3)_2$	(*326*)	$Mg_5O(OH)_5(BO_3)nH_2O$	Wightmanite (*300*)
$FeBO_3$	(*112*)	$Al_6(OH)_3(BO_3)_5$	Jeremejevite (*159*)
$Mn_3(BO_3)_2$	(*58*), Jimboite (*355*)	$Mg_3(OH)F(BO_3)$	Fluoborite (*404*)
$Co_3(BO_3)_2$	(*39*)	$Be_2(OH)(BO_3)$	Hambergite (*452*)
$Mg_3F(BO_3)_3$	(*66*)	$Ca_{12}Mg_4(CO_3)_4Cl(OH)_2(BO_3)_7 \cdot H_2O$	Sakhaite (*316*)
BO_2^- chain			
$LiBO_2$	(*449*)	$Sr(BO_2)_2$	(*46*)
$Ca(BO_2)_2$	(*275*)		
Isolated $B(OH)_4^-$ and BO_4^{5-}			
$LiB(OH)_4$	(*178*)	$Sr[B(OH)_4]_2$	(Monoclinic) (*228*)
$NaB(OH)_4 \cdot 2H_2O$	(*44*)	$Sr[B(OH)_4]_2$	(Triclinic) (*321*)
α-$CsB(OH)_4 \cdot 2H_2O$	(*459*)	$Ba[B(OH)_4]_2$	(*227*)
α-$Ca[B(OH)_4]_2$	(Monoclinic) (*320*)	$Ba[B(OH)_4]_2 \cdot H_2O$	(*253*)
α'-$Ca[B(OH)_4]_2$	(Orthohombic) (*457*)	$Ba[B(OH)_4]_2 \cdot 2H_2O$	(*322*)
β-$Ca[B(OH)_4]_2$	Frovolite (*122*)	$Na_2Cl[B(OH)_4]$	Teepleite (*128, 130*)
$Ca[B(OH)_4]_2 \cdot 2H_2O$	(*425, 426*), Hexahydroborite (*384*)	$CuCl[B(OH)_4]$	Bandylite (*89, 129, 130*)
$Mn_3(OH)_2(PO_4)[B(OH)_4]$	Seamanite (*301*)	$MgCa_2(CO_3)_2[B(OH)_4]_2 \cdot 4H_2O$	Carboborite (*437*)
$Mg_3(OH)_2(SO_4)[B(OH)_4]_2$	Sulfoborite (*190*)	$MgAlBO_4$	Sinhalite (*125*)
$Ca_2(AsO_4)[B(OH)_4]$	Cahnite (*334*)		
Chain $BO(OH)_2^-$			
$Ca[BO(OH)_2]_2$	Vimsite (*383*)		
Network BO_2^-			
γ-HBO_2	Cubic metaboric acid-I (*447*)		

	Isolated $B_2O_4(OH)^{3-}$ and $B_2O_5^{4-}$		
$Mg_2(OH)[B_2O_4(OH)]$	Ascharite, szaibelyite (*406*)	$Co_2B_2O_5$	(*40*)
$Mn_2(OH)[B_2O_4(OH)]$	Sussexite (*406*)	$Sr_2B_2O_5$	(*31*)
$Na_4B_2O_5$	(*219*)	$CaMgB_2O_5$	Mg kurchatovite (*438, 440*)
$Mg_2B_2O_5$	(*43*), Saunite (*405*)	$CaMnB_2O_5$	Mn kurchatovite (*439*)
	Isolated $B_2O(OH)_6^{2-}$		
$Ca[B_2O(OH)_6] \cdot 2H_2O$	Pentahydroborite (*120, 122*)	$Mg[B_2O(OH)_6]$	Pinnoite (*235, 328*)
	Isolated $B_3O_3(OH)_3$ and $B_3O_6^{3-}$		
$B_3O_3(OH)_3$	α-Metaboric acid III (*330*)	$Na_3B_3O_6$	(*276*)
$Ba_3(B_3O_6)_2$	(*297*)	$K_3B_3O_6$	(*361*)
	Isolated $B_3O_3(OH)_4^-$ and $B_3O_5(OH)_2^{3-}$		
$Na[B_3O_3(OH)_4]$	Ameghinite (*104*)	$Na_3[B_3O_5(OH)_2]$	(*94*)
	Chain $B_3O_4(OH)$ and sheet $B_3O_5^-$		
$B_3O_4(OH)(OH_2)$	β-Metaboric acid-II (*448*)	CsB_3O_5	(*242*)
LiB_3O_5	(*218*)		
	Isolated $B_3O_3(OH)_5^{2-}$ and $B_3O_4(OH)_4^{3-}$		
$Ca[B_3O_3(OH)_5] \cdot H_2O$	Meyerhofferite (*79, 85*)	$CaMg[B_3O_3(OH)_5]_2 \cdot 6H_2O$	Inderborite (*250*)
$Ca[B_3O_3(OH)_5] \cdot 2H_2O$	(*85, 86*)	$Zn[B_3O_3(OH)_5] \cdot H_2O$	(*324*)
$Ca[B_3O_3(OH)_5] \cdot 4H_2O$	Inyoite (*83, 85*)	$K_3[B_3O_4(OH)_4] \cdot 2H_2O$	(*319*)
$Mg[B_3O_3(OH)_5] \cdot 5H_2O$	Inderite (*92, 343*)	$Rb_3[B_3O_4(OH)_4] \cdot 2H_2O$	(*458*)
	Kurnakovite (*91, 339*)	$Ca_2Cl[B_3O_4(OH)_4]$	Solongoite (*441*)
	Chain $B_3O_4(OH)_3^{2-}$		
$Ca[B_3O_4(OH)_3] \cdot H_2O$	Colemanite (*81, 85*)	$CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$	Hydroboracite (*344*)
	Sheet $B_3O_5(OH)^{2-}$		
$Ca[B_3O_5(OH)]$	(*85, 88*), Fabianite (*224*)		
	Isolated $B_3O_3(OH)_6^{3-}$		
$Ca_3[B_3O_3(OH)_6]_2 \cdot 2H_2O$	Nifontovite (*121*)		
	Network $B_3O_6^{3-}$		
$Cu_3(B_3O_6)_2$	(*284*)	$Ca_3(B_3O_6)_2$	(*280*)

(*table continues*)

TABLE I (Continued)

Structural formula	References	Structural formula	References
Isolated $B_3O_3(OH)_4 \cdot OB(OH)_3^{3-}$			
$Ca_2[B_3O_3(OH)_4 \cdot OB(OH)_3]Cl \cdot 7H_2O$	Hydrochloroborite *(80)*		
Isolated $B_3O_3(OH)_5 \cdot OB(OH)_3^{4-}$			
$Ca_2[B_3O_3(OH)_5 \cdot OB(OH)_3]$	Uralborite *(367)*		
Isolated $B_4O_5(OH)_4^{2-}$ and $B_4O_7(OH)_2^{4-}$			
$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$	Borax *(267, 302)*	$Mn[B_4O_5(OH)_4] \cdot 7H_2O$	*(42)*
$Na_2[B_4O_5(OH)_4] \cdot 3H_2O$	Tincalonite *(143)*	$Rb_2Sr[B_4O_5(OH)_4]_2 \cdot 8H_2O$	*(191)*
$K_2[B_4O_5(OH)_4] \cdot 2H_2O$	*(277)*	$(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$	*(41)*
$Mg[B_4O_5(OH)_4] \cdot 7H_2O$	Hungchaoite *(424)*	$Ca_2Mn_2(OH)_4[B_4O_7(OH)_2]$	Roweite *(299)*
Chain $B_4O_6(OH)_2^{2-}$			
$Na_2[B_4O_6(OH)_2] \cdot 3H_2O$	Kernite *(82, 90, 144)*	$Na_2[B_4O_6(OH)_2]$	*(289)*
Network $B_4O_7^{2-}$			
$Li_2B_4O_7$	*(236, 306)*	CdB_4O_7	*(183)*
ZnB_4O_7	*(283)*		
Isolated $B_4O_6(OH)_6^{6-}$			
$Ca_4Mg(CO_3)_2[B_4O_6(OH)_6]$	Borcarite *(443)*		
Isolated $B_5O_6(OH)_4^{-}$			
$NaB_5O_6(OH)_4$	*(288)*	$K[B_5O_6(OH)_4] \cdot 2H_2O$	*(29, 451)*, Santite
$Na[B_5O_6(OH)_4] \cdot 3H_2O$	Sborgite *(294)*	$Cs[B_5O_6(OH)_4] \cdot 2DMSO$	*(131)*
β-$NH_4[B_5O_6(OH)_4] \cdot 2H_2O$	*(290)*	$(NH_4)_3[B_5O_6(OH)_3 \cdot OB_5O_6(OH)_2 \cdot OB_5O_6(OH)_3] \cdot 4H_2O$	Ammonioborite *(293)*
Isolated $B_5O_6(OH)_6^{3-}$			
$NaCa[B_5O_6(OH)_6] \cdot 5H_2O$	Ulexite *(142)*		
Chain $B_5O_7(OH)_2^{-}$			
$NH_4[B_5O_7(OH)_2] \cdot H_2O$	Larderellite *(291)*		

Chain $B_5O_7(OH)_3^{2-}$			
$Na_2[B_5O_7(OH)_3] \cdot 2H_2O$	Ezcurrite (*70*)		
Chain $B_5O_7(OH)_4^{3-}$			
$NaCa[B_5O_7(OH)_4] \cdot 3H_2O$	Probertite (*347*)		
Sheet $B_5O_8(OH)^{2-}$			
$Na_2[B_5O_8(OH)] \cdot 2H_2O$	Nasinite (*95*)	$K_2[B_5O_8(OH)] \cdot 2H_2O$	(*274*)
$Na_4[B_5O_8(OH) \cdot OB_5O_7(OH)] \cdot 2H_2O$	Biringuccite (*93*)		
Sheet $B_5O_8(OH)^{2-}$ + isolated $B(OH)_3$			
$Ca[B_5O_8(OH) \cdot B(OH)_3] \cdot 3H_2O$	Gowerite (*225*)	$Sr_2[B_5O_8(OH)]_2B(OH)_3 \cdot H_2O$	Veatchite (*87, 346*)
Sheet $B_5O_8(OH)_2^{3-}$			
$Na_3[B_5O_8(OH)_2] \cdot H_2O$	(*287*)	$Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]$	Heidornite (*80*)
Chain $B_5O_7(OH)_3 \cdot OB(OH)_2^{3-}$			
$HKMg_2[B_5O_7(OH)_3 \cdot OB(OH)_2]_2 \cdot 4H_2O$	Kaliborite (*97*)		
Isolated $B_6O_7(OH)_6^{2-}$			
$Mg[B_6O_7(OH)_6] \cdot 2H_2O$	Aksaite (*108, 167*)	$Co[B_6O_7(OH)_6] \cdot 7H_2O$	(*380*)
$Mg[B_6O_7(OH)_6] \cdot 3H_2O$	(*107, 139*)	$Ni[B_6O_7(OH)_6] \cdot 5H_2O$	(*378*)
$Mg[B_6O_7(OH)_6] \cdot 4H_2O$	(*106*)	$Ni[B_6O_7(OH)_6] \cdot 7H_2O$	(*380*)
$Mg[B_6O_7(OH)_6] \cdot 4.5H_2O$	Macallisterite (*105*)	$K_2Co[B_6O_7(OH)_6]_2 \cdot 4H_2O$	(*379*)
$Na_6Mg[B_6O_7(OH)_6]_4 \cdot 10H_2O$	Rivadavite (*109*)		
Chain $B_6O_8(OH)_4^{2-}$			
$Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4H_2O$	Aristarainite (*140*)		
Sheet $B_6O_9(OH)_2^{2-}$			
$Sr[B_6O_9(OH)_2] \cdot 3H_2O$	Tunellite (*84*)		
Sheet $B_6O_9(OH) \cdot OB_2O(OH)_3^{2-}$			
$Sr[B_6O_9(OH) \cdot OB_2O(OH)_3]$	Strontioborite (*67*)		
$Ca[B_6O_9(OH) \cdot OB_2O(OH)_3]$	(*455*)	$SrCa[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB_2O(OH)_3] \cdot 5H_2O$	Strontioginorite (*223*)
Isolated $B_6O_7(OH)_6 \cdot OAsO_3^{5-}$			
$Ca_4Mg[B_6O_7(OH)_6 \cdot OAsO_3]_2 \cdot 14H_2O$	Teruggite (*103*)		

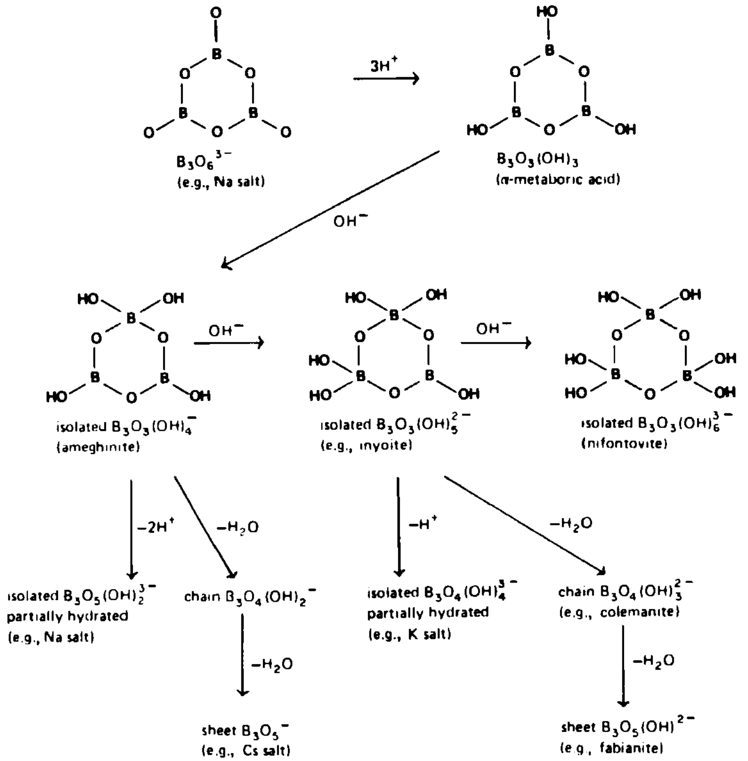


FIG. 2. Structural transformations of the triborate unit. (The use of protons and hydroxyl groups is schematic and does not represent chemical reaction.)

and include some anhydrous borates that are obvious extensions of the hydrated forms.

Of recent interest has been the determination of structures containing "partially hydrated" polyborate ions such as found in $Na_3B_3O_5(OH)_2$ (*94*), K_3 or $Rb_3[B_3O_4(OH)_4] \cdot 2H_2O$ (*319, 458*), and roweite ($Ca_2Mn_2(OH)_4[B_4O_7(OH)_2]$) (*299*), in which oxygen atoms arranged tetrahedrally around boron atoms are protonated and the triangular oxygens are not.

The most common ion of the triborate unit is $B_3O_3(OH)_5^{2-}$, and it is usually found associated with calcium and magnesium. Triborates of calcium $Ca_2B_6O_{11} \cdot xH_2O$ have been reviewed (*85*). Modification of triborate groups with attachment of a side tetrahedron leads to B_4 species. Uralborite, $Ca_2[B_3O_3(OH)_5 \cdot OB(OH)_3]$, is an example (*367*) and should be written as shown rather than with the ambiguous shorter formula of $Ca_2[B_4O_4(OH)_8]$. Christ and Clark (*80*) have doubted the proposed structure of $Mg[B_3O_3(OH)_4 \cdot OB(OH)_2] \cdot 6H_2O$ for $Mg[B_4O_4(OH)_6] \cdot 6H_2O$ (*6*) on the grounds that particular bond distances are too short to permit such a formulation.

The tetraborate unit $B_4O_5(OH)_4^{2-}$ was first found in borax (*302*) and is also present in the "octaborates" $M_2^{I}M^{II}B_8O_{14} \cdot 12H_2O$ (*149*). The polymerization of these ions to give, e.g., kernite, is not a simple elimination of water but involves the breaking of a B–O bond. The resulting polymeric ion consists of six-membered rings each possessing one trigonal and two tetrahedral borons, and the rings are joined by sharing tetrahedral boron atoms (*82, 90, 144*). The structure of the calcium borate $Ca_2[B_8O_{13}(OH)_2]$ has been reported as containing tetraborate units (*442*). Most tetraborates have their structure based on a double ring system, but borcarite $Ca_4Mg(CO_3)_2[B_4O_6(OH)_6]$ provides the one example so far of an eight-membered ring B_4O_4 (*443*) in which all the boron atoms are tetrahedrally coordinated in the partially hydrated unit.

The hexaborate anions have a unique structure, in that the central oxygen atom is coordinated to three borons. This arrangement was first found in the structure of tunellite (*84*).

A basic unit that has not been mentioned here is the nonaborate. This has mutually linked six-membered rings (Fig. 3) and has been reported in the form of a modified sheet in preobrazheskite $HMg_3[B_9O_{12}(OH)_4 \cdot (O_2B(OH)_2)_2]$ (*348*).

B. ANHYDROUS METAL BORATES

The structural chemistry of anhydrous metal borates is also complex; but, unlike the hydrated analogs, polyborate ions can be composed of dissimilar basic units.

The isolated, planar BO_3^{3-} ion (orthoborate) occurs in many of these

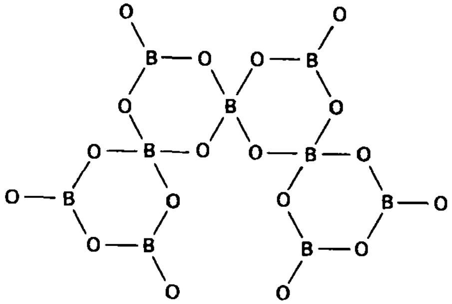


FIG. 3. The basic unit found in preobrazheskite (*348*).

compounds. In addition to the examples given in Table I, many compounds containing rare-earth elements have been examined. X-Ray crystallographic data on many of these borates have related $M^{III}BO_3$ to the calcite, aragonite, and vaterite polymorphs of $CaCO_3$. The low- and high-temperature forms of lanthanum borate $LaBO_3$ (*5, 47*) and lutetium borate $LuBO_3$ (*22*) possess these isolated BO_3^{3-} anions, as do the more recently determined structures of

$Li_3M_2(BO_3)_3$ where M = Eu (*18*), Nd (*10*), and Pr (*13*),
$Li_6M(BO_3)_3$ where M = Yb (*11*) and Ho (*19*),
$M_3Nd(BO_3)_4$ where M = Ga (*34*) and Al (*179*), and
$Sr_3M_2(BO_3)_4$ where M = Pr (*325*), La (*14*), Nd (*7*), and Er (*9*)

The so-called metaborates of empirical formula BO_2^- can take several forms. The infinite linear $(BO_2)_n^{n-}$ ion is found in the low-temperature form of $LiBO_2$ (*449*), $Ca(BO_2)_2$ (*275*), and $Sr(BO_2)_2$ (*46*). At high temperatures and pressures, the lithium compound possesses a sphalerite-like structure with boron in four-coordination (*278*). The triborate isolated $B_3O_6^{3-}$ group is found in the barium (*297*), sodium (*276*), and potassium (*361*) compounds, and the framework $B_3O_6^{3-}$ group, in which all the boron atoms are tetrahedral, exists for a high-pressure calcium metaborate phase (*280*) and copper metaborate (*284*). Two other anhydrous calcium metaborates are known to give the series

CaB_2O_4-I	chain BO_2^- (*275*)
CaB_2O_4-II	chain $B_2O_4^{2-}$ (*368, 450*)
CaB_2O_4-III	network $B_6O_{12}^{6-}$ (*279*)
CaB_2O_4-IV	network $B_3O_6^{3-}$ (*280*)

The relation between these polymorphs has been summarized (*280*). Thallium metaborate (*413*) and the rare-earth metaborates $Sm_2(B_2O_4)_3$, $Gd_2(B_2O_4)_3$ (*17*), and EuB_2O_4 (*269*) have the $B_2O_4^{2-}$ chains found in CaB_2O_4-II. In addition to the isolated and framework $B_3O_6^{3-}$ groups, the chain polymer of $B_3O_6^{3-}$ (two tetrahedral and one trigonal boron atoms) is present in the lanthanum metaborate LaB_3O_6 (*444*). A new type of structure has been found for the metaborates $CoM(BO_2)_5$, where M = Sm (*15*), La (*16*), Nd (*2*), and Ho (*12*). In these compounds, the boron unit consists of infinite chains of $B_5O_{10}^{5-}$ with each composed of three BO_4 tetrahedra and two BO_3 triangles. Neodymium aluminum metaborate $NdAl_{2.07}[B_4O_{10}]O_{0.6}$ (*335*) has endless chains of $B_2O_5^{4-}$. Zinc metaborate $Zn_4O(BO_2)_6$ has an unusual structure with all boron atoms tetrahedrally coordinated and situated at the vertices of a Federow's truncated octahedron to form a framework resembling the anion of sodalite (*57*).

The network $B_4O_7^{2-}$ tetraborate ion consisting of two tetrahedral and two trigonal boron atoms is found in the Li (*236, 306*), Zn (*283*), and Cd (*183*) compounds. Other "tetraborates" do not necessarily contain the tetraborate group but are composed of pentaborate and triborate units giving the empirical unit $B_8O_{14}^{4-}$. The sodium borate $Na_2O \cdot 2B_2O_3$ has a three-dimensional network constructed from this combination of units and has one nonbridging oxygen atom (*240*). Its potassium analog is formed from tetraborate and triborate groups linked by planar BO_3 triangles (*239*). The borates $Ag_2O \cdot 4B_2O_3$ (*233*), $BaO \cdot 2B_2O_3$ (*45*), and $BaO \cdot 4B_2O_3$ (*245*) possess linked pentaborate and triborate groups, while the strontium and lead (*46, 232, 329*) $MO \cdot 2B_2O_3$ compounds have all the boron atoms tetrahedrally coordinated and an oxygen common to three tetrahedra. The structure of calcium tetraborate has recently been reported as containing a network of $B_8O_{14}^{4-}$ ions (*454*).

Compounds with empirical formulas that suggest the presence of triborate or hexaborate groups are found to be composites. Thus, the calcium borate $Ca_2B_6O_{11}$ has a symmetric pentaborate unit connected to a framework by additional boron tetrahedra (*453*). The low-temperature form of sodium borate, α-$Na_2O \cdot 3B_2O_3$, consists of two separate interpenetrating frameworks of alternating pentaborate and tetraborate groups as shown in Fig. 4 (*241*), while the high-temperature modification is formed from linked pentaborate, triborate, and BO_4 groups (*238*). Cesium enneaborate $Cs_2O \cdot 9B_2O_3$ (*244*) has two independent networks of linked but different triborate units.

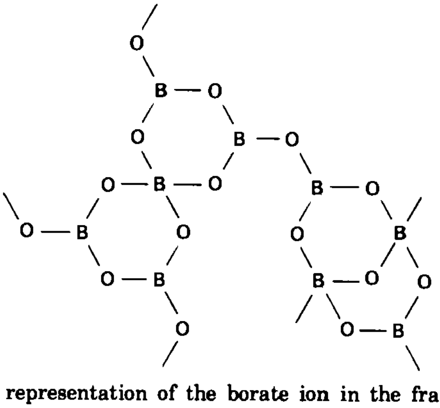


FIG. 4. Schematic representation of the borate ion in the framework structure of α-$Na_2O \cdot 3B_2O_3$ (*241*).

Potassium pentaborate exists in three forms, of which two have been studied crystallographically. The high-temperature α (*237*) and low-temperature β (*234*) forms consist of two separate three-dimensional interlocking networks of pentaborate groups $B_5O_8^-$ differing only in close packing of the matrices. The mineral hilgardite $Ca_2B_5O_9Cl \cdot H_2O$, despite being a hydrate, similarly has a structure based on a network of pentaborate groups with six extra-annular oxygen atoms of $B_5O_9^{3-}$ shared with other groups (*141*). Another type of pentaborate ion is found in the bismuth borate $Bi_3O(B_5O_{11})$, but in this case, the $B_5O_{11}^{7-}$ ion is isolated (*419*).

The largest isolated borate anion found so far in an anhydrous borate belongs to the lead borate $6PbO \cdot 5B_2O_3$ (*246*). The ion $B_{10}O_{21}^{12-}$ is built up from two tetraborate groups linked by two BO_3 triangles. Pentapotassium enneakaidecaborate $5K_2O \cdot 19B_2O_3$ (*243*) possesses four types of units with interconnected pentaborate, triborate, BO_4 tetrahedra, and BO_3 triangles.

Anhydrous aluminum borates have rings incorporating aluminum atoms. The aluminate $2SrO \cdot Al_2O_3 \cdot B_2O_3$ consists of a six-membered ring of two AlO_4 tetrahedra and one BO_3 triangle (*305*). $3Li_2O \cdot Al_2O_3 \cdot 2B_2O_3$ has infinite chains of $Al_2(BO_3)_4^{6-}$ in which the rings are formed by two AlO_4 tetrahedra and two BO_3 triangles, interlinked in one direction by two other BO_3 triangles (*8*).

C. Boron–Oxygen Bond Lengths

Wells (*433*) has quoted ranges for the boron–oxygen bond lengths of trigonally and tetrahedrally coordinated boron as

$$BO_3\text{:}\quad 1.28 \rightarrow 1.43\ \text{Å, average } 1.365\ \text{Å;}$$

$$BO_4\text{:}\quad 1.43 \rightarrow 1.55\ \text{Å, average } 1.475\ \text{Å.}$$

The isolated ion $B_3O_6^{3-}$ found as sodium (*276*) and potassium (*361*) compounds has an exocyclic B—O length of 1.28 and 1.33 Å respectively and an endocyclic B—O length of 1.433 and 1.398 Å respectively. The short $BO_2—O^-$ bond is characteristic for nonbridging atoms attached to rings in anhydrous borates; its value in $Na_2O \cdot 2B_2O_3$ is 1.295 Å (*240*). In isolated BO_3^{3-} ions, the B–O distance is typically 1.37 Å, but a notable exception is found in $Pr_2Sr_3(BO_3)_4$ (*325*) where three of the triangles have an average B—O length of 1.46 Å and the fourth is as low as 1.23 Å; this has not been explained.

Boron–oxygen bond lengths in tetrahedrally coordinated boron vary from about 1.4 to 1.55 Å; synthetic $Ca[B_3O_3(OH)_5] \cdot 2H_2O$ possesses these extremes (*85*). Long B–O bonds are also found if an oxygen is coordinated to three boron atoms, as for example in aristarainite $Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4H_2O$, where the distance is 1.517 Å (*140*).

Related boron structures exhibit similar bond distances. The structure of sodium perborate has been recently refined (*74*). It consists of the cyclic anion $[(HO)_2B \cdot (O_2)_2 \cdot B(OH)_2]^{2-}$ with two peroxy bridges. The terminal groups have a B—OH length of 1.442 Å and the ring B—O distance is 1.495 Å. The boron atom in boron triethanolamine $B(OC_2H_4)_3N$ is tetrahedrally surrounded by oxygen and nitrogen atoms, with a B—O length of 1.431 Å (*127*). Potassium boromalate (*282*) has a tetrahedral arrangement about the boron atom with the oxygens directly bonded to malic acid; the B–O bond lengths average 1.438 and 1.508 Å.

Hückel theory has been used to correlate bond lengths in planar BO_3 triangles with π-bond order (*98*), but with the marked deviation from predicted values for $B_3O_6^{3-}$, the treatment is of limited applicability. Other studies have similarly related π-electron charge density with the geometry of borates (*360, 395*). The results indicate that the bond order in boron tetrahedra is slightly lower than unity, and slightly greater than unity in BO_3 triangles; the π-electron charge on boron does not vary significantly among borate structures.

D. Structure Elucidation by Spectroscopic Techniques

Numerous NMR (*61, 194–196, 331, 445*), Raman (*63–65, 222, 434*), and IR (*252*) studies of borate glasses and melts have been made and related to the structural units found in crystalline borates, and to the species such as $B_3O_{4.5}$, $B_8O_{13}^{2-}$, and $B_4O_7^{2-}$ postulated by Krogh-Moe (*231*) in his investigations into the melting-point depression of sodium borate melts. Borate glass structures have been recently reviewed (*164, 338*) and will not be discussed here.

In the examination of crystalline borates, caution has been exercised over the structural interpretations of spectroscopic studies. Certain features pertaining to the boron coordination and water/hydroxyl entities can be deduced, but absolute configurations of molecules require more exacting techniques.

The sodium tetraborates, borax (the decahydrate) and tincalconite (the pentahydrate), have been studied by proton (*33, 281*), boron-11 (*101, 111*), and sodium-23 (*102, 111*) magnetic resonance, and the data is compatible with X-ray studies. Similar agreement with crystal structures has been found with the ^{11}B NMR of the hexaborate ion in tunellite (*100*) and pentaborates (*26, 254*). Wegener *et al.* (*192, 430*) measured the proton magnetic resonance of several potassium borates and have differentiated between water of crystallization and hydroxide groups. The BO_2^- chain in crystalline calcium metaborate $Ca(BO_2)_2$ has been observed by ^{11}B NMR (*229*), as has the BO_3^{3-} triangle in $Sr_3(BO_3)_2$ (*327*). The relative merits of NMR techniques for borate structure determination have been reviewed (*62, 230*).

Infrared spectroscopy is the favored technique for characterizing borates, and several compilations of data have been made (*171, 333, 417, 423, 431, 432*). The intense absorption at about 970 cm^{-1} is characteristic of tetrahedrally coordinated boron, as measured for the magnesium borates $MgO \cdot B_2O_3 \cdot nH_2O$ (*153*), and bands at 700 to 900 and 1200 to 1500 cm^{-1} can correspond to triangular boron coordination. Absorptions in the region 400 to 700 cm^{-1} have been attributed to chain structures (*423*).

With the many crystal structures now known, more reliance can be put on speculative interpretations of IR spectra. The "octoborates" $M^I_2O \cdot M^{II}O \cdot 4B_2O_3 \cdot 12H_2O$ have spectra identical to borax and accordingly are assigned the anion structure $B_4O_5(OH)_4^{2-}$ (*155, 157, 158*). In the lead borate system, species such as $B_5O_9(OH)^{4-}$, $B_4O_5(OH)_4^{2-}$, $B_5O_7(OH)_3^{2-}$, and $B_3O_3(OH)_4^-$ are claimed (*385, 386*).

Raman spectroscopy has seldom been used for elucidating structures of crystalline solids. However, with IR, it has proved valuable for observing isostructural rare-earth borates (*110*) and for measurement of phonon coupling in the zinc borate $Zn_4O(BO_2)_6$ (*304*).

IV. Aqueous Solutions of Metal Borates

The mode of dissolution of metal borates in aqueous solution is complex. Hydrolysis of the borate anion can result in completely different boron species that are stable only under particular conditions of pH, temperature, and concentration.

The parent acid, H_3BO_3, functions as a weak acid in aqueous solution, possessing an ionization constant of about 6×10^{-10} at 25°C in dilute solution. As its concentration increases, the ionization constant increases markedly. Kolthoff (*220*) investigated this effect by electrical conductivity and emf measurements, obtaining values of 4.6×10^{-10} and 408×10^{-10} for boric acid concentrations of 0.1 *M* and 0.75 *M* respectively at 18°C. These results were attributed to the formation of tetraboric acid.

Other studies into the apparent ionization constant of boric acid and interpretation of data are given by Sprague (*392*). Of greater relevance to metal borate synthesis and stability is the variation in polyborate ions in solution with pH and concentration.

A. Boron Species in Aqueous Solution

1. *Monomeric Boric Acid and Borate Ion*

The presence of monomeric H_3BO_3 and $B(OH)_4^-$ in aqueous solutions has been confirmed by spectroscopic techniques. Infrared (*126, 415–417*) and Raman (*176, 247*) spectra of boric acid solutions show similar absorptions to crystalline H_3BO_3 (*176*), for which a planar BO_3 arrangement has been found (*446*). The monoborate ion $B(OH)_4^-$ has similarly been identified by vibrational spectroscopy (*119, 161, 176*); its expected tetrahedral structure has been confirmed by comparison of its spectra with that of teepleite $NaB(OH)_4 \cdot NaCl$ (*213, 342*) and bandylite $Cu[B(OH)_4]_2 \cdot CuCl$ (*342*), which are known to contain monomeric tetrahedral BO_4 units.

2. *Polyborate Ions*

The formation of polymeric boron ions in solution is well established. The significant increase in solubility in terms of B_2O_3 in aqueous mixtures of borax and boric acid relative to the individual components is explained by such polyborate formation. The comprehensive reviews by Nies (*307*) and Sprague (*392*) reveal that, despite the many investigations over the last 50 years, the identity of the borate ions involved has still not been completely resolved.

a. Potentiometric investigations. Of the techniques available for studying polyborate equilibria, potentiometry has received greatest attention. However, interpretation of data from the sodium hydroxide–boric acid system has led to conflicting postulated species, e.g.,

$B_5O_8^-$ and $B_4O_7^{2-}$ (*389, 390*)

BO_2^-, $HB_2O_4^-$, $B_4O_7^{2-}$, and $HB_4O_7^-$ (*255*)

$B_5O_8^-$, BO_2^-, $HB_2O_4^-$, $B_4O_7^{2-}$, and $HB_4O_7^-$ (*256*)

$B_5O_8^-$, HBO_2, and HB_2O_4 (*73*)

HBO_2, BO_2^-, $B_5O_8^-$, and $B_4O_7^{2-}$ (*268*)

A phenomenon resulting from polyborate formation is that at a certain ratio M_2O/B_2O_3 the pH of the metal borate solution is unaffected by dilution. For M = Na, this mole ratio is 0.412 and the solution pH is 8.91 (*286*). This composition was called the isohydric point and the related data used to fit a model based on the presence of $HB_5O_9^{2-}$ species (*71*); in this early paper (1949) it was claimed that tetracoordinated boron atoms cannot exist in aqueous solution. More recent studies (*54, 55, 72*) have shown that the isohydric reaction involves hydrolysis of $HB_5O_9^{2-}$:

$$HB_5O_9^{2-} + 6H_2O \rightleftharpoons 3H_3BO_3 + 2BO(OH)_2^- \qquad pK = 4.53$$

The extensive investigations by Ingri *et al.* (*185–189*) provided the first reliable quantitative description of borate equilibrium, and several of the postulated species have subsequently been verified by vibrational spectroscopy. Ingri proposed that the polyborates in solution would possess structural units similar to those in crystalline metal borates, i.e., $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_3^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ (see Section III for details of structures). At this point it should be noted that potentiometry cannot afford information on "degrees of hydration" and that previously described species such as $B_5O_8^-$ can be considered as identical to $B_5O_6(OH)_4^-$:

$$B_5O_8^- + 2H_2O \rightleftharpoons B_5O_6(OH)_4^-$$

$$HBO_2(aq) + H_2O \rightleftharpoons H_3BO_3$$

$$B_4O_7^{2-} + 2H_2O \rightleftharpoons B_4O_5(OH)_4^{2-}$$

Ingris' potentiometric titrations at 25°C in 3 *M* $NaClO_4$ indicated that at boron concentrations less than 0.025 *M* only H_3BO_3 and $B(OH)_4^-$ are present; at higher concentrations, $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ (*189*), and at the upper concentration range of 0.4 to 0.6 *M* boron, either $B_4O_5(OH)_3^-$ or $B_5O_6(OH)_4^-$ are the predominant polymeric species (*185*). Figure 5 illustrates the distribution of boron species over a range of pH at 25°C.

The presence of certain neutral salts increases the acidity of boric acid as determined potentiometrically (*187, 358, 375, 391, 422*), and the effect has been attributed to the hydration energies of ions (*375, 391, 422*). In 3 *M* KBr solutions containing up to 0.4 *M* boron, H_3BO_3, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$ were consistent with experimental results, but in the presence of $NaClO_4$, NaBr, or LiBr, the inclusion of $B_3O_3(OH)_5^{2-}$ improved the solution analysis (*187*).

Later investigations in alkali metal chloride and sulfate media suggested that $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ were the major polymeric species, with $B_5O_6(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ being present in small concentrations (*391*). This same study included systems at temperatures up to

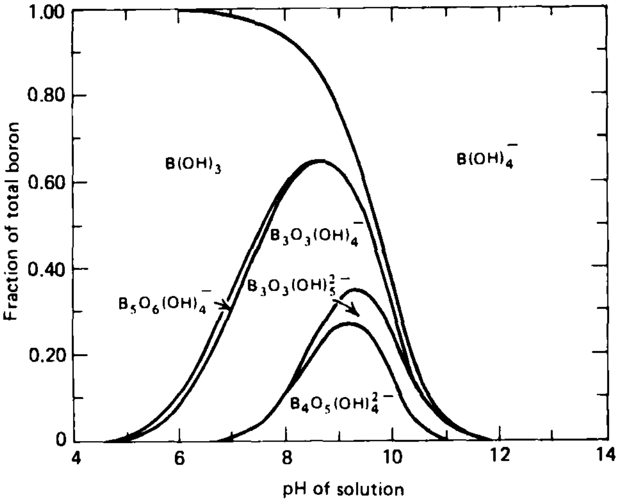


Fig. 5. Variation in the distribution of boron species with solution pH at 25°C. Total boron concentration is 0.4 *M* (*188*).

90°C (Table II). Other work has gone beyond this temperature range (50–290°C, Ref. *295*), and new species are postulated: in 1 *M* KCl solutions, boron at high concentrations can exist as $B_2(OH)_7^-$ [equivalent to $B_2O(OH)_5^-$] and $B_3(OH)_{10}^-$ [$B_3O_3(OH)_4^-$] with lesser amounts of either $B_4(OH)_{14}^{2-}$ [$B_4O_5(OH)_4^{2-}$] or $B_5(OH)_{18}^{3-}$ [$B_5O_6(OH)_6^{3-}$].

b. Other studies. Recent investigations by a variety of methods have not yet clarified the situation. Solution pH techniques in concentrated solution have indicated that boron is present mainly as $B_5O_6(OH)_4^-$ (*303*), as $B_3O_3(OH)_4^-$ (*23*), or as $B_3O_3(OH)_5^{2-}$ and $B_3O_3(OH)_4^-$ (*357*); no evidence for the formation of monoborate ions possessing a greater charge than $B(OH)_4^-$ was found by using a lead amalgam electrode (*362*). Ion exchange analysis suggests $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, $B_4O_5(OH)_3^-$, and $B_5O_6(OH)_4^{2-}$ (*30*). Infrared and ion exchange studies indicate the presence of $B_5O_6(OH)_4^-$ at pH 7.5 to 8.5, $B_4O_5(OH)_4^{2-}$ at pH 9.2, and $B(OH)_4^-$ at pH > 10 (*126*). Cryoscopic measurements based on the depression of freezing point of sodium sulfate decahydrate yield two sets of equilibria involving either $B_4O_5(OH)_4^{2-}$ or a combination of trimeric and pentameric anions (*193*).

c. Spectroscopic techniques. Nuclear magnetic resonance studies of ^{11}B in solutions of boric acid and metaborates $MB(OH)_4$ are consistent with the presence of H_3BO_3 and tetrahedral $B(OH)_4^-$ in dilute solution (*99, 160, 175, 180, 315, 387, 428*). In aqueous pentaborate solutions two

TABLE II

FORMATION CONSTANTS OF BORATE IONS AND pH FOR THEIR MAXIMUM CONCENTRATIONS[a]

		At 25°C			At 90°C		
	Salt media	Formation constant	Optimum pH	Maximum % concentration	Formation constant	Optimum pH	Maximum % concentration
$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$	3 *M* KCl	1.76×10^{-9}			2.93×10^{-9}		
	3 *M* NaCl	2.73×10^{-9}			5.53×10^{-9}		
	5 *M* NaCl	3.83×10^{-9}			16.5×10^{-9}		
$3H_3BO_3 \rightleftharpoons B_3O_3(OH)_4^- + 2H_2O + H^+$	3 *M* KCl	1.81×10^{-7}	8.1	46	9.94×10^{-8}	7.9	28
	3 *M* NaCl	2.78×10^{-7}	7.8	43	2.38×10^{-7}	7.8	42
	5 *M* NaCl	6.98×10^{-7}	7.6	44	5.15×10^{-7}	7.5	42
$3H_3BO_3 \rightleftharpoons B_3O_3(OH)_5^{2-} + H_2O + 2H^+$	3 *M* KCl	4.60×10^{-18}	9.8	2	8.13×10^{-18}	9.7	2
	3 *M* NaCl	8.63×10^{-17}	9.7	11	1.78×10^{-17}	9.5	1
	5 *M* NaCl	9.19×10^{-16}	9.6	27	4.35×10^{-17}	8.4	2
$4H_3BO_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 3H_2O + 2H^+$	3 *M* KCl	1.73×10^{-15}	9.3	26	2.87×10^{-15}	8.8	30
	3 *M* NaCl	5.85×10^{-15}	8.9	27	1.93×10^{-15}	8.7	9
	5 *M* NaCl	2.24×10^{-14}	8.7	24	4.78×10^{-15}	8.2	4
$5H_3BO_3 \rightleftharpoons B_5O_6(OH)_4^- + 5H_2O + H^+$	3 *M* KCl	1.75×10^{-7}	6.9	3	6.25×10^{-7}	7.1	12
	3 *M* NaCl	1.83×10^{-7}	6.7	2	9.58×10^{-8}	6.6	1
	5 *M* NaCl	3.65×10^{-7}	6.3	2	3.94×10^{-7}	6.4	3

[a] Constants determined in 0.4 *M* boron solutions; concentrations expressed as percent of total boron. Data from Spessard (*391*).

resonances were observed (*298*) and the variation in their relative intensities with concentration were interpreted as indicating:

$$OH^- + H_3BO_3 \overset{fast}{\rightleftharpoons} B(OH)_4^-$$

$$2H_3BO_3 + B(OH)_4^- \overset{fast}{\rightleftharpoons} B_3O_3(OH)_4^- + 3H_2O$$

$$4H_3BO_3 + B(OH)_4^- \overset{slow}{\rightleftharpoons} B_5O_6(OH)_4^- + 6H_2O$$

The two resonances were believed to arise from $B_5O_6(OH)_4^-$ and the rapid exchange among H_3BO_3, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$. At 80 MHz a third signal appeared at high boron concentrations, attributed to another polyborate species (*387*). Aqueous solutions of sodium tetraborate display a single resonance at 14 MHz (*298*) and 80 MHz (*387*). Other qualitative studies have also indicated the presence of polyborate ions in concentrated solution (*99, 175*).

Vibrational spectroscopy has proved to be the most useful technique yet for identifying which boron species are present in solution. Close agreement between solution spectra and those of crystalline borates of known structure have confirmed the presence of hitherto postulated polyborate ions. Details of the IR spectra of the $Na_2O-B_2O_3-H_2O$ system at 26°C with absorptions assigned to polyborate species are shown in Table III (*416, 417*). In a more recent study (*126*), the major ions in 0.5 *M* boron solution were identified as $B_5O_6(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B(OH)_4^-$.

Recent laser Raman investigations (*271, 285, 318*) have led to simi-

TABLE III

INFRARED SPECTRA OF SODIUM BORATE SOLUTIONS[a]

Mole ratio $B_2O_3:Na_2O$	pH	Absorption bands (cm^{-1})					Frequency assignment
1	11	940	1125	1230		1430	$B(OH)_4^-$
1.5	11	950	1120	1200	1330	1430	$B_3O_3(OH)_5^{2-}$
1.7	10.5	960		1220	1330	1430	$B_3O_3(OH)_5^{2-}$
2	9		1010	1200	1330	1430	$B_4O_5(OH)_4^{2-}$
2.3	8.5		1020	1150	1335	1420 1450	$B_4O_5(OH)_4^{2-}$
2.9	8		1020	1200	1330	1450	$B_3O_3(OH)_4^-$
3.5	7.5		1020	1185	1330	1450	$B_5O_6(OH)_4^-$
4.6	6.5		1020	1100	1340 1180	1440	$B_5O_6(OH)_4^-$
5	6.5		1115	1210	1370	1450	$B_5O_8(OH)_4^-$

[a] From Valyashko and Vlasova (*417*).

lar conclusions on the state of boron in solution at various pH. No evidence for $B_3O_3(OH)_5^{2-}$ was found. The frequencies assigned to the borates are given in Table IV. The relative intensities of absorptions measured by Maya (*285*) were used to calculate equilibrium constants; the derived values compared favorably with those determined by Ingri by potentiometric titration (*187*):

	Maya (*285*)	Ingri (*187*)
$3H_3BO_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O$	pK = 6.6	pK = 6.7
$5H_3BO_3 \rightleftharpoons B_5O_6(OH)_4^- + H^+ + 5H_2O$	pK = 6.9	pK = 6.6
$4H_3BO_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O$	pK = 15.6	pK = 14.7

3. *Rate of Formation of Polyborate Ions*

"Temperature-jump" techniques have been employed to investigate the mode of formation of polyborates (*27*). The reaction

$$H_3BO_3 + OH^- \rightleftharpoons B(OH)_4^-$$

was too fast to measure (predicted rate 10^{10} mol^{-1} sec^{-1}), but overall rate constants for the formation of $B_3O_3(OH)_4^-$ and $B_5O_6(OH)_4^-$ were obtainable:

$$2H_3BO_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \qquad k = 2.8 \times 10^3\ mol^{-2}\ sec^{-1} \text{ at pH } 7.4$$

$$2H_3BO_3 + B_3O_3(OH)_4^- \rightleftharpoons B_5O_6(OH)_4^- + 3H_2O \qquad k = 2 \times 10^2\ mol^{-2}\ sec^{-1} \text{ at pH } 7.4$$

The former value agrees well with the value of 3.5×10^3 found in pressure-jump measurements (*317*).

Slow changes in borate species have been observed by IR spectroscopy (*415, 417*). Absorptions by borate solutions prepared by the addi-

TABLE IV

ASSIGNED FREQUENCIES (cm^{-1}) OF RAMAN SPECTRA OF POLYBORATE IONS IN AQUEOUS SOLUTION[a]

$B_3O_3(OH)_4^-$		$B_4O_5(OH)_4^{2-}$		$B_5O_6(OH)_4^-$	
From (*271*)	From (*285*)	From (*271*)	From (*285*)	From (*271*)	From (*285*)
430 w (dp)		385 w (dp)		525 s (p)	527 (p)
458 w (dp)		447 w (dp)			763 (p)
490 w (dp)		565 s (p)	567 (p)	917 w	914 (dp)
609 s (p)	613 (p)				
995 w	995 (p)				

[a] s, sharp; w, weak; p, polarized; dp, depolarized. From Maeda *et al.* (*271*).

tion of sodium hydroxide to boric acid, or hydrochloric acid to borax, indicated that over a period of 1 month, the structure of the solution altered, eventually reaching the equilibria appropriate for stable boron species at that pH. Borax solutions at pH 9 to 9.5 provided a spectrum that changed little with time. It is proposed that the relative concentration of four-coordinate boron increases with pH and that the rate of transformation is affected more by cleavage of bridging bonds, B—O—B, than by the conversion of trigonal to tetrahedral boron coordination.

B. SOLUBLE METAL BORATE COMPLEXES

Until recently, very little had been reported on the important area of metal borate complexation in aqueous solution. The effect of salts on the ionization of boric acid (*358, 375*) has been mentioned above, and subsequent research suggests that complexation of borate with, for example, calcium ions can account for the enhanced acidity of H_3BO_3. Literature on cationic complexes of boron was reviewed in 1970 (*376*).

Potentiometric, cryoscopic, and conductometric measurements of the reaction between Fe^{3+} and $B_4O_7^{2-}$ have revealed the presence of $FeB_4O_7^-$ (*373*), and in oxalate media, the cationic complexes $FeBO_2^{2+}$ and $Fe(BO_2)_2^+$ were assumed to be present (*370*). The instability constant for $FeBO_2^{2+}$ was estimated as 3.12×10^{-9} by spectrophotometric techniques (*68*). The appearance of IR absorption bands at 1260, 1105, 860, and 815 cm^{-1} was attributed to the formation of an iron borate complex during oxidation of elemental iron in borate solutions (*118*).

Instability constants for the formation of $Al(BO_2)_2^+$, $AlBO_2^{2+}$, and $Al(BO_2)_6^{3-}$ have been evaluated (*374*), although the reliability of the results is in question. Other metals that have been examined in borate solutions include lead (*372*), cobalt (*270, 371*), zinc, and cadmium (*369*), providing evidence for $Pb(BO_2)_3^-$, $PbBO_2^+$, $Co(BO_2)_4^{2-}$, $Ni(BO_2)_3^-$, $Zn(BO_2)_4^{2-}$, and $Cd(BO_2)_4^{2-}$. Silver is believed to form a weak neutral complex $AgBO_2$ (*177*).

The interaction between sodium and alkaline-earth metal ions and borate has attracted recent attention, particularly from the point of view of association of ions in seawater. Several studies (*69, 114, 168, 169, 340*) have shown that the boron content of seawater ($4-5 \times 10^{-4}$ *M*) is too low to support appreciable concentrations of polyborate species. The increase in acidity of boric acid in the presence of metal ions results from ion-pair formation:

$$Na^+ + B(OH)_4^- \rightleftharpoons NaB(OH)_4^0$$

$$M^{2+} + B(OH)_4^- \rightleftharpoons MB(OH)_4^+$$

Measurement of association by density (*427*) and potentiometric (*69, 133, 340*) methods are consistent with this scheme. Dissociation constants over the temperature range 10–50°C (where T is the absolute temperature) are (*340*)

$$\begin{aligned} \mathrm{p}K\ \mathrm{NaB(OH)_4^0} &= 0.22 \text{ at } 25^\circ\mathrm{C} \\ \mathrm{p}K\ \mathrm{MgB(OH)_4^+} &= 1.266 + 0.001204T \\ \mathrm{p}K\ \mathrm{CaB(OH)_4^+} &= 1.154 + 0.002170T \\ \mathrm{p}K\ \mathrm{SrB(OH)_4^+} &= 1.033 + 0.001738T \\ \mathrm{p}K\ \mathrm{BaB(OH)_4^+} &= 0.942 + 0.001850T \end{aligned}$$

and the calculated value for the apparent ionization constant of boric acid in seawater was found to be 1.86×10^{-9} (*69, 340*). The same data were used to indicate that 44% of the borate ions present in seawater are complexed with sodium, magnesium, and calcium (*69*).

C. HETEROGENEOUS SYSTEMS

The first comprehensive list of solubility data on borates was compiled by Teeple in 1929 (*407*). Since then, several hundred aqueous systems have been examined, covering most combinations of reactants over a range of temperatures. Of particular interest is the mode of dissolution of borates and the conditions under which they can be synthesized.

1. *Dissolution of Borates*

Most borates dissolve in strong acid (e.g., HCl, HNO_3) solution with formation of the weaker boric acid. For colemanite, hydroboracite, ulexite, and inyoite (calcium-, magnesium-, and sodium-containing minerals) the rate of solution increases with acid concentration but passes through a maximum as a protective layer of allegedly mainly boric acid encompasses the borate sample (*184*). In alkalis (Na_2CO_3 or NaOH), the solution rates are affected by the solubility of protective films of carbonate (*200*) and solution rates of metal oxides (*273*). The influence of solubility of by-products of dissolution on solution rates has also been observed in studies on the effect of anions (*199*) and cations (*198*) of magnesium and calcium minerals; ferric ions substantially accelerate borate decomposition (*198*). More recent work on the solubility rates of boric acid in aqueous metal chloride solutions (*365*) and anhydrous borax in aqueous/organic media (*136*) or metal nitrate/chloride solutions (*137*) has shown that dissolution rates increased with increasing water activity and are affected by surface sorption of cations.

The mode of dissolution of metal borates was followed by Svarcs *et al.* in the late 1950s using cryoscopic and electrical conductivity techniques (*207–209*). The mobilities of anions at 25°C in aqueous solutions of alkali metal borates were found to be 39–40 mho · cm², decreasing to 15 in 3% H_3BO_3. This latter value was interpreted as indicating formation of pentaborate ions. Calcium, strontium, and barium metaborates decompose in aqueous solution to give boric acid. However, the mobility of anions in borate $MB_6O_{10} \cdot xH_2O$ ($M = Mg, Ca, Sr$) was measured as 34 mho · cm² and 10.25 in 3% H_3BO_3; the proposed mechanism for hydrolysis was as follows

$$MB_6O_{10} \rightleftharpoons M^{2+} + B_6O_{10}^{2-}$$

$$M^{2+} + B_6O_{10}^{2-} + 3H_2O \rightleftharpoons M^{2+} + B_4O_7^{2-} + 2H_3BO_3$$

$$M^{2+} + B_4O_7^{2-} + 2H_3BO_3 + 3H_2O \rightleftharpoons M^{2+} + 2BO_2^- + 4H_3BO_3$$

$$M^{2+} + 2BO_2^- + 4H_3BO_3 + 3H_2O \rightleftharpoons M^{2+} + 6H_3BO_3$$

Other papers by the same authors (*208, 399, 400, 403*) discuss the partial and complete hydrolysis of many borates and give details of various resulting boron species.

The relationship between the composition and structure of borates and their decomposition in aqueous solution has been reviewed (*78, 226, 414, 417*). Borates of the alkali and alkaline-earth metals give an alkaline reaction in solution, as the borates formed by hydrolysis possess a lower boron-to-metal ratio than in the initial material (*414*).

The pH of an aqueous solution brought into contact with borates can determine the decomposition products both in solution and in the solid phase (*414*). Conversely, pH plays an important role in the synthesis of metal borates precipitated from aqueous media.

2. *Synthesis of Borates*

Valyashko and Gode (*414*) have summarized the conditions necessary for formation of borates of sodium, potassium, ammonium, calcium, and magnesium. The effect of varying the cation is to alter the type of borate that is stable in contact with the aqueous solution. The stability ranges for solid phases in the sodium and calcium systems are shown in Table V.

TABLE V

STABILITY RANGES FOR SODIUM AND CALCIUM BORATES[a]

Solid phase	pH Range for stable solid phase at 25°C	
	$Na_2O-B_2O_3-H_2O$ System	$CaO-B_2O_3-H_2O$ System
H_3BO_3	Up to 6.2	Up to 5.5
$CaO \cdot 3B_2O_3 \cdot 4H_2O$		5.5–7.4
$Na_2O \cdot 5B_2O_3 \cdot 10H_2O$	6.2 → 7.2	
$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	7.2 → 13.7	
$2CaO \cdot 3B_2O_3 \cdot 13H_2O$		7.4 → 9.6
Metaborates	Over 13.7	Over 9.6

[a] From (*414*).

The pH ranges over which the solid phases are stable agree reasonably well with the stability ranges of the polyborate ions $B_5O_6(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_5^{2-}$ outlined in Section IV,A; thus it can be expected that to precipitate a borate of a particular structure, it should be prepared from a solution containing those same borate ions.

The effect of calcium ions on polyborate equilibria is significant, but it is only recently that the detailed analysis of the ionic species in the $CaO-B_2O_3-H_2O$ system has been made (*133, 377*).

A general observation is that the tendency for precipitation of borates possessing a small polyborate ring increases with pH. Further, higher temperatures lead to products of increased B_2O_3/M_xO ratio and lower hydration.

The effect of neutral salts (e.g., NaCl) on the composition of borates precipitated from, or in equilibrium with, aqueous solutions doubtless arises from a reduction in water activity, metal borate complexation, and a shift in polyborate equilibria (Sections IV,A, B). The "indifferent or inert component" method has frequently been used for the synthesis of borates. Potassium and sodium chlorides can be used to enhance the precipitation of specific nickel (*48*), aluminum (*51*), iron (*49*), and magnesium (*151*) borates. In the $K_2O-B_2O_3-H_2O$ system at 25°C (*248*), the presence of potassium chloride results in a reduced boric acid crystallization curve, lower borate solubilities, lower pH, and an extended $B_2O_3:K_2O$ range over which the pentaborate crystallizes.

Hence the synthesis of borates is governed by the concentration of cations (whether "neutral" or active), pH, and temperature. These parameters affect the nature of boron ions in solution that are directly related to the composition of precipitated species.

V. Preparation and Properties of Metal Borates

This section briefly outlines the preparation and properties of the major metal borates, with particular emphasis on their hydrates. Recent and comprehensive reviews of the various group metal borates are found in Mellor (*60, 307*), from which additional data and references covering the entire field can be obtained. For brevity, the borates are referred to in terms of the mole ratio $M_2O:B_2O_3:H_2O$ or $M_2O:B_2O_3$ of their composition.

A. ALKALI METAL, AMMONIUM, AND SILVER BORATES

These have been reviewed by Nies (*307*), and the commercially important borates have been reviewed by Doonan and Lower (*113*).

1. Lithium Borates

Solubilities of lithium borates in the system $Li_2O–B_2O_3–H_2O$ at 10–80°C (*341*), 100°C (*35*), and up to 400°C (*36*) have shown the presence of compounds with $Li_2O:B_2O_3:H_2O$ mole ratios of 1 : 1 : 1, 1 : 1 : 4, 1 : 1 : 16, 1 : 2 : 2, 1 : 2 : 3, 2 : 1 : 1, 2 : 5 : 7, and 1 : 5 : 10.

a. Metaborates. The two principal borates are the 1 : 1 : 4 and 1 : 1 : 16 compounds, having the structural formulas $LiB(OH)_4$ and $LiB(OH)_4 \cdot 6H_2O$ respectively. Their IR and Raman spectra are recorded (*210, 272*), and recent studies (*115, 116*) on their thermal decomposition show that the higher hydrate loses water in four stages: the first H_2O molecule of $LiB(OH)_4 \cdot 6H_2O$ is lost at 30–50°C, the next five at 50–120°C, and the hydroxyl water at 120–160°C and at temperatures higher than 165°C. The transition point between the two hydrates in water is 36.9°C.

b. Tetraborates. The lithium borate $Li_2O \cdot 2B_2O_3 \cdot 3H_2O$ is the most stable borate of the 1 : 2 : x series. In contact with aqueous solutions, it is stable from −3 to 150°C, and can be dehydrated to afford the 1 : 2 : 2, 1 : 2 : 1, and anhydrous 1 : 2 : 0 compounds.

c. Pentaborates. Lithium pentaborate $Li_2O \cdot 5B_2O_3 \cdot 10H_2O$ has a congruent solubility above 40.5° or 37.5°C, and is stable in its aqueous solution up to 140°C, whereupon the 1 : 5 : 2 borate is formed. The "decaborate" $2Li_2O \cdot 5B_2O_3 \cdot 7H_2O$ loses two water molecules at 160°C and becomes anhydrous at 220°C (*35*).

2. *Sodium Borates*

Numerous studies have been made into the phase equilibria in the $Na_2O-B_2O_3-H_2O$ system at 0–100°C (e.g., *135, 216, 217, 308*), and more recently at 150° (*96*). A partial phase diagram for this system covering the range of mole ratio Na_2O/B_2O_3 to 0.5 in solution is shown in Fig. 6. Over 25 borates of sodium in the absence of other cations have been identified (*307*).

a. Metaborates. The borates of composition 1 : 1 :x, where x = 12, 8, 4, and 1, have been isolated and found to be stable in contact with highly alkaline solutions at −3 to 11.5°C, 11.5–53.6°C, 53.6–105°C, and above 105°C, respectively. The thermal decomposition (*397*) and IR (*211*) of the 1 : 1 : 8 compound are consistent with its structural formula of $NaB(OH)_4 \cdot 2H_2O$ (*44, 210*). The 1 : 1 : 4 borate is prepared by heating a slurry of the tetrahydrate above 54°C, crystallization from hot metaborate solutions, or dehydration of 1 : 1 : 8 *in vacuo*; it loses its water slowly at room temperature. Aqueous solutions of sodium metaborates absorb carbon dioxide from the atmosphere to form borax and sodium carbonate.

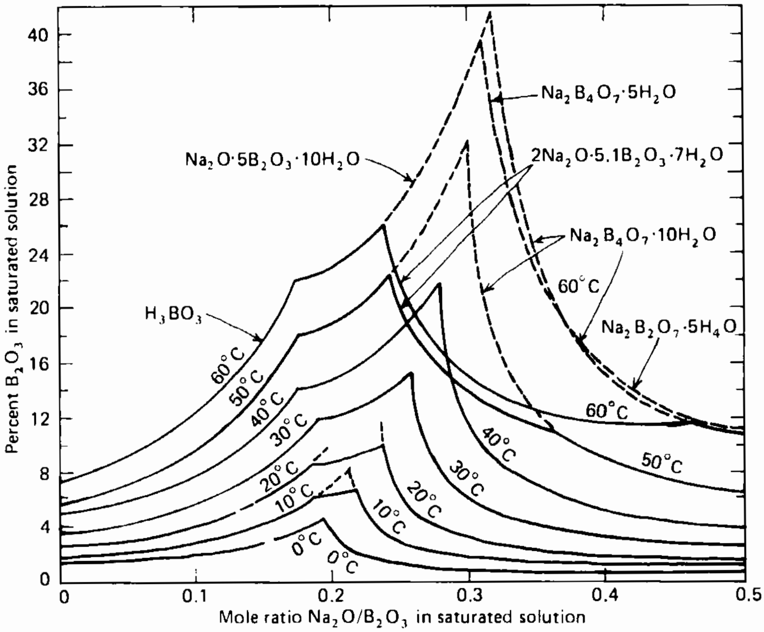


FIG. 6. Solubility isotherm for the system $Na_2O-B_2O_3-H_2O$. From Doonan and Lower (*113*).

b. Tetraborates. The decahydrate $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ exists in nature as borax and is commercially the most important of the borates. Its crystal structure shows the borate ion to be $B_4O_5(OH)_4^{2-}$ (*267, 302*). Borax crystallizes from aqueous solution at temperatures up to 60.7°C as monoclinic prisms, but its crystal habit can be changed by the addition of various substances. The dehydration of borax has been extensively studied. In aqueous solution it dehydrates to the pentahydrate above 60°C. One of the latest investigations (*314*) reports the appearance of a single DTA endothermic peak commencing at 115°C and ending at 238°C, with a minimum at 145°C. Dehydration was complete at 350–450°C, and at 245°C, the rate of dehydration followed the equation

$$\log(b - m) = -8.5 \times 10^{-4}t + C$$

where m is the amount of water lost in t minutes, b is the quantity of water initially present, and C is a constant. Aqueous solutions of borax have a pH of about 9.0, which is almost invariable with small additions of acid or alkali.

The pentahydrate $Na_2O \cdot 2B_2O_3 \cdot 5H_2O$ has the same polyborate ion as borax. It crystallizes from aqueous solution above 60°C but is also unstable with respect to kernite in solution above 40°C. In accord with its structure, $Na_2[B_4O_5(OH)_4]3H_2O$, the first three water molecules are lost at a temperature of 140 or 150°C, with the anhydrous product formed at over 400°C.

In kernite $Na_2O \cdot 2B_2O_3 \cdot 4H_2O$, the borate anion contains parallel infinite chains of $[B_4O_6(OH)_2]^{2-}$. The formation of this ion by B–O bond cleavage (Section III,A) accounts for its slow rate of crystallization and dissolution in aqueous media. Kernite is the stable phase in contact with its solutions from 58 to 95°C.

c. Pentaborates. Ezcurrite $2Na_2O \cdot 5.1B_2O_3 \cdot 7H_2O$, nasinite $2Na_2O \cdot 5B_2O_3 \cdot 5H_2O$, and biringuccite $2Na_2O \cdot 5B_2O_3 \cdot 3H_2O$ are "dibasic" pentaborates and are stable phases in the $Na_2O–B_2O_3–H_2O$ system at 40–94°C, 90–195°C, and 195–240°C, respectively. The most common sodium pentaborate is the 1:5:10 compound, also known as the mineral sborgite. It is stable in contact with its own solution between 2 and 59.5°C, but at temperatures near boiling the 2:9:11 salt is deposited. The 1:5:10 borate has the structural formula $Na[B_5O_6(OH)_4] \cdot 3H_2O$ (*294*).

3. *Potassium Borates*

a. Metaborates. The solubilities in the potassium metaborate–water system are shown in Table VI. Omitted from this table are the

TABLE VI

THE POTASSIUM METABORATE–WATER SYSTEM[a]

Temperature (°C)	Wt % $K_2O \cdot B_2O_3$ in solution	Solid phase[b]
−20	27.1	Eutectic α-1:1:8 and ice
−18	26.6	α-1:1:8
11	39.0	α-1:1:8
24	43.8	Transition α-1:1:8 to 1:1:2⅔
0	35.5	1:1:2⅔ (metastable)
30	44.4	1:1:2⅔
180	68.8	1:1:2⅔
195	73.0	Transition 1:1:2⅔ to 1:1:⅔
200	73.1	1:1:⅔
237	73.4	1:1:⅔
250	74.0	Transition 1:1:⅔ to 1:1:0

[a] From Nies (*307*).

[b] The solid phase is expressed as the mole ratio $K_2O:B_2O_3:H_2O$.

1:1:9 and β-1:1:8 metaborates that are stable at 0°C. The 1:1:2⅔ borate loses two water molecules at 177–253°C and the remainder at 253–309°C (*460*), consistent with its structure $K_3[B_3O_4(OH)_4] \cdot 2H_2O$ (*319*). Further evidence for this structure was obtained by the appearance of IR absorptions appropriate for trigonal and tetrahedral boron atoms (*212*).

b. Tetraborates. Potassium tetraborate tetrahydrate $K_2O \cdot 2B_2O_3 \cdot 4H_2O$ has a structure similar to that of borax, i.e., $K_2[B_4O_5(OH)_4] \cdot 2H_2O$ (*277*). Two of its water molecules are lost at 112–195°C, the third at 195–220°C, and the last at 240–420°C (*398*). The trihydrate 1:2:3 is stable in solution from 50 to over 100°C, and the di- and monohydrates can be prepared from the tetrahydrate at 90 and 140–200°C respectively.

c. Pentaborates. The 2:5:5 compound is known as Auger's potassium borate. It has the structural formula $K_2[B_5O_8(OH)] \cdot 2H_2O$ (*274*) and is stable in solution at temperatures down to 28°C. Its dehydration at 140 and 300–400°C affords the 2:5:3 and 2:5:1 compounds. The major pentaborate of potassium is the α-1:5:8, with the formula $K[B_5O_6(OH)_4] \cdot 2H_2O$ (*29, 451*). It is stable over a wide range of temperatures, and on dehydration loses water of crystallization at 120–170°C, eventually yielding the anhydrous form at 440°C (*398*). Recently, the β-1:5:8 compound has been isolated from the α form at 149°C (*38*).

The hydrolysis of trimethyl borate with water in the presence of potassium alkoxides has afforded polyborates of composition 1 : 12 : 7, 1 : 5 : 4, 1 : 3 : 4, 2 : 5 : 5, and 1 : 2 : 2 (*172*). Infrared (*174*) and NMR (*172*) studies have indicated that these products contain water only in the form of hydroxyl groups.

4. *Rubidium Borates*

a. Metaborates. The rubidium metaborates of composition $Rb_2O \cdot B_2O_3 \cdot xH_2O$ have been isolated from the system Rb_2O–B_2O_3–H_2O. The 1 : 1 : 8 compound is stable in contact with its solution from −19 to 20°C. At higher temperatures, the 1 : 1 : 2⅔ (isomorphous with the potassium salt) compound crystallizes out (*461*) and there is evidence for the 1 : 1 : 0.5 and 1 : 1 : ⅔ compounds. The latter is stable in solution from 190 to 220°C, above which temperature the anhydrous salt is formed.

b. Tetraborates. The regions of stability in aqueous solutions for rubidium tetraborates are:

1:2:5	20–104°C
1:2:3	104–172°C
1:2:2	172–244°C
1:2:1	244–320°C

The same derivatives can be obtained by dehydrating the 1 : 2 : 5 compound in air.

c. Pentaborates. The pentaborates of rubidium, $Rb_2O \cdot 5B_2O_3 \cdot xH_2O$, have been the subject of recent investigations (*37*). In the aqueous system at 100°C, the α-1 : 5 : 8, β-1 : 5 : 8, 1 : 5 : 4, 2 : 5 : 6, and 2 : 5 : 5 pentaborates were detected. Thermogravimetric analyses showed that the α-1 : 5 : 8 compound dehydrates continuously, dehydration of the 1 : 5 : 4 compound gives the 1 : 5 : 2 and 1 : 5 : 1 compounds, and the 2 : 5 : 3 and 2 : 5 : 1 compounds are obtained from heating the 2 : 5 : 5 and 2 : 5 : 6 forms.

5. *Cesium Borates*

a. Metaborates. Four hydrates of cesium metaborate have been identified. The α-1 : 1 : 8 form, the crystal structure of which shows the formula α-$CsB(OH)_4 \cdot 2H_2O$ (*459*), is stable in aqueous solution at 50 to 78°C. Below 50°C, the β form is stable, and above 78°C, the 1 : 1 : 2 compound is the stable phase (*214, 215*). The latter compound can be prepared from the β-1 : 1 : 8 form by dehydration over phosphorous pentoxide.

b. Tetraborates. The transition point in aqueous solution between the cesium tetraborates 1 : 2 : 5 and 1 : 2 : 2 is 111°C (*214*). Three water molecules are lost on heating the 1 : 2 : 5 compound in air between 105 and 165°C, and the remainder between 230 and 400°C.

c. Pentaborates. The known cesium pentaborates are represented by the 1 : 5 : 8 and 2 : 5 : 7 compositions. Thermal dehydration of the former borate yields the 1 : 5 : x (x = 4, 3, 2, 1) compounds.

The cesium borates obtained by hydrolysis of trimethyl borate in organic media in the presence of $CsOC(CH_3)_3$ have been studied by IR (*132*) and tentatively assigned the formulas $Cs[B_{12}O_{13}(OH)_{11}]$, $Cs[B_4O_4(OH)_5]$, $Cs[B_5O_6(OH)_4]$, $Cs[B_3O_3(OH)_4]$, and $Cs_3[B_5O_6(OH)_6]$.

6. *Ammonium Borates*

The major ammonium borates are the tetraborate $(NH_4)_2O \cdot 2B_2O_3 \cdot 4H_2O$, and three pentaborates $(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$, larderellite $(NH_4)_2O \cdot 5B_2O_3 \cdot 4H_2O$, and ammonioborite $(NH_4)_2O \cdot 5B_2O_3 \cdot 5\frac{1}{3}H_2O$. The 1 : 5 : 8 compound exists as both rhombic (α) and monoclinic (β) forms, and, on heating to about 100°C, yields ammonioborite (*409*, *410*). Isothermal studies (*411*) on the $(NH_4)_2O-B_2O_3-H_2O$ system have indicated that over the temperature range 0–50°C, the 1 : 5 : 8 and 1 : 2 : 4 compounds are metastable phases with respect to the 1 : 5 : 5$\frac{1}{3}$ and a 1 : 2 : 2.5 borate. Crystal structure determinations of the 1 : 5 : x compounds show that they contain true pentaborate groups (Table I).

7. *Silver Borates*

The $Ag_2O-B_2O_3-H_2O$ system has been investigated over the temperature range 0–100°C, and the borates $Ag_2O \cdot 2B_2O_3 \cdot 2H_2O$ and $2Ag_2O \cdot 5B_2O_3 \cdot 5H_2O$ obtained as stable phases (*356*). The 1 : 2 : 2.5 compound can be prepared by addition of silver nitrate to sodium borate solutions (*206*).

B. GROUP II METAL BORATES

1. *Beryllium Borates*

The borate chemistry of beryllium is somewhat limited. The mineral hambergite $Be_2BO_3(OH)$ can be synthesized, and studies of the $BeO-B_2O_3-H_2O$ system under hydrothermal conditions have produced

$2BeO \cdot B_2O_3 \cdot 3H_2O$, $BeO \cdot B_2O_3 \cdot H_2O$, and $BeO \cdot 2B_2O_3 \cdot 1.2H_2O$ (*262, 359*).

2. *Magnesium Borates*

Many magnesium borate systems have been investigated; a few of the major studies are listed in Table VII. The main magnesium borates stable in contact with aqueous solutions are the 1 : 1 : 3 (pinnoite), 1 : 3 : x, 2 : 1 : 1, and 2 : 3 : 15 (inderite) compounds.

Pinnoite $MgO \cdot B_2O_3 \cdot 3H_2O$ has a structure represented by $Mg[B_2O(OH)_6]$ (*235, 328*). It is formed in the $MgO–B_2O_3–H_2O$ system over the temperature range 45–200°C, and can be synthesized by warming solutions containing borax with high concentrations of magnesium chloride; the formation temperature can be lowered to 25°C in saturated KCl solution (*151*). Pinnoite is unstable in water at room temperature, and on dehydration, it loses two water molecules at 140–300°C and the third at 300–600° (*1*).

The 1 : 3 : x compounds (x = 4.5, 5, 6, 7 and 7.5) separate from the $MgO–B_2O_3–H_2O$ systems at 25–200°C or from $MgO–B_2O_3–MgCl_2–H_2O$

TABLE VII

MAGNESIUM BORATE AQUEOUS SYSTEMS

Aqueous system	Temperature (°C)	Reference	Species in contact with solution, expressed as the mole ratio $MgO : B_2O_3 : H_2O$
$MgO–B_2O_3–H_2O$	25	(*28, 251*)	1:2:9, 1:3:7.5, 1:2:8.5, 2:3:15
	35	(*28*)	1:3:7.5, 2:3:15
	45	(*349*)	1:3:7.5, 1:1:3, 2:3:15
	70	(*349*)	1:3:7.5, 1:1:3
	83	(*28*)	1:3:7.5, 1:1:3
	100–200	(*313*)	1:3:6, 1:3:5, 1:3:4, 1:1:3, 1:2:2.5
	150	(*366*)	2:1:1, 1:2:2.5
	100–700	(*162*)	2:1:1
$MgO–MgCl_2–B_2O_3–H_2O$	25	(*28, 350*)	2:3:3, 3:1:11
	70	(*21*)	1:3:7.5, 1:3:5, 1:1:3, 2:1:3
	83	(*28*)	1:1:3, 2:1:1
$MgO–NaCl–B_2O_3–H_2O$	25	(*350*)	1:3:7.5, 2:3:13, 2:3:15
$MgCl_2–Na/KCl–KOH–B_2O_3–H_2O$	25	(*150*)	2:3:15 (Except at high NaCl concentration)

systems. Macallisterite $MgO \cdot 3B_2O_3 \cdot 7.5H_2O$ can also be prepared by the reaction between magnesium chloride and potassium borates at pH 5.6 (*152, 249*). The compounds with x = 5, 6, 7, and 7.5 possess isolated $B_6O_7(OH)_6^{2-}$ hexaborate ions (Table I). Their dehydration (*4, 124, 261, 312, 396*) and IR (*259, 312, 313, 394*) characteristics are well established.

Inderite $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ crystallizes at pH 7–9 in most magnesium systems below 70°C, although high concentrations of NaCl can limit its formation. A direct synthesis is the reaction of magnesium chloride with potassium borate at pH 7.9 (*146, 152*). Inderite has the structural formula $Mg[B_3O_3(OH)_5] \cdot 5H_2O$ (*92, 343*), and its thermal dehydration occurs in four stages with formation of the 2:3:1, 1:2:9, and 1:1:3 compounds (*3, 123, 124*).

The $2MgO \cdot B_2O_3 \cdot H_2O$ borate is known as ascharite. It can be prepared from the MgO–B_2O_3–H_2O system at temperatures of 150–450°C. The presence of magnesium chloride at a concentration of 25% extends its aqueous stability range down to 83°C. Ascharite is almost insoluble in water, and a solubility of 0.0085% B_2O_3 at 25°C has been reported (*456*). Its dehydration has been studied (*123, 165*).

3. *Calcium Borates*

Calcium borates are widespread in nature, and some are used for the commercial production of boric acid and its salts. As a result, extensive investigations have been made into their occurrence, decomposition, and dissolution in aqueous media. Some of the aqueous phase studies are given in Table VIII.

TABLE VIII

CALCIUM BORATE AQUEOUS SYSTEMS

Aqueous system	Temperature (°C)	Reference	Species in contact with solution, expressed as the mole ratio $CaO:B_2O_3:H_2O$
CaO–B_2O_3–H_2O	25	(*251*)	1:1:6, 1:3:4, 2:3:13
	30	(*204*)	1:1:6, 1:3:4, 2:3:13, 6:5:3
	45	(*352*)	1:1:4, 1:3:4, 2:3:9
	95	(*311*)	2:1:1
	200–400	(*170*)	2:1:1, 2:2:1, 2:3:1, 3:9:1
CaO–$MgCl_2$–B_2O_3–H_2O	25	(*350, 351*)	1:1:4, 1:1:6, 1:3:x, 2:3:9, 2:3:13
CaO–$NaCl$–B_2O_3–H_2O	25	(*350, 353*)	1:1:6, 1:3:4, 1:3:5, 2:3:13, $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$

a. Metaborates. The two common metaborates of calcium are the 1 : 1 : 4 and 1 : 1 : 6 compounds. They are formed in the $CaO-B_2O_3-H_2O$ system at a pH greater than 9.6, the 1 : 1 : 6 at temperatures of 30°C or less and the 1 : 1 : 4 at over 30°C. The presence of calcium (*154*) or magnesium (*350, 351*) chlorides extends the temperature range for 1 : 1 : 4 metaborate down to less than 20°C. Alternatively, these hydrates can be prepared from calcium chloride–sodium metaborate mixtures (*257*). The IR (*210*) and dehydration (*20, 462*) properties of the 1 : 1 : 6 and 1 : 1 : 4 borates are consistent with their structural formulas $Ca[B(OH)_4]_2 \cdot 2H_2O$ (*425, 426*) and $Ca[B(OH)_4]_2$ (*320, 457*) respectively. The 1 : 1 : 2 hydrate is formed by dehydrating the hexahydrate at 105°C (*266*), but unlike the higher hydrates, its structure is represented by the formula $Ca_2[B_3O_3(OH)_5 \cdot OB(OH)_3]$ (*367*). The structures of calcium metaborate minerals have been reviewed (*382*).

b. Borates $CaO \cdot 3B_2O_3 \cdot xH_2O$. The 1 : 3 : 4 compound (nobleite) is a stable phase in the $CaO-B_2O_3-H_2O$ system at a pH of 5.5 to 6.5 between 25 and 60°C. It dehydrates via formation of a 1 : 3 : 3 borate (*462*). The pentahydrate can be prepared by the reaction between calcium chloride, borax, and boric acid at 60°C (*147*); in nature it occurs as gowerite. The IR spectra of the tetrahydrate and pentahydrate have been recorded (*259*).

c. Borates $2CaO \cdot 3B_2O_3 \cdot xH_2O$. This series of borates has structures showing the stepwise polymerisation of isolated $B_3O_3(OH)_5^{2-}$ ions. The structures have been discussed by Christ and Clark (*85*) and are shown in Table I. The lowest member, 2 : 3 : 1, occurs in the $CaO-B_2O_3-H_2O$ system above 200°C (*170*) and is identical with the mineral fabianite. At elevated temperatures it is also formed by the hydrothermal reactions between the 2 : 3 : 7, 1 : 3 : 5, or 2 : 7 : 8 borates with boric acid. Colemanite, 2 : 3 : 5, is a commercially important borate; it exhibits interesting ferroelectric (*166*) and optical (*363*) properties. Meyerhofferite, 2 : 3 : 7, the synthetic 2 : 3 : 9, and inyoite, 2 : 3 : 13, are all structurally similar, possessing isolated $B_3O_3(OH)_5^{2-}$ ions. Meyerhofferite is formed by heating aqueous solutions of borax and sodium hydroxide with calcium chloride at 85°C (*156*). The 2 : 3 : 9 and 2 : 3 : 13 borates are stable species in the $CaO-B_2O_3-H_2O$ system and can be respectively prepared, for example, by reacting calcium chloride with ammonium pentaborate solutions or calcium iodate with borax solutions at 30°C (*435*). The effect of sodium chloride on the $CaO-B_2O_3-H_2O$ system is to widen the pH range for 2 : 3 : 13 compound formation, from 7.2–9.3 to 8.0–9.6. The thermal dehydration properties of colemanite, meyerhofferite, and inyoite have recently been reinvestigated (*221*).

4. *Strontium Borates*

The chemistry of strontium borates is restricted. Investigations (*203*, *258*) into the $SrO–B_2O_3–H_2O$ systems have revealed the presence of the stable species 1:1:4, 1:3:5, and 1:3:9 at 30°C; 1:1:4, 1:3:5, and 1:3:6 at 100°C; and 1:1:1 and 1:4:2 at 190°C.

Strontium metaborate $SrO \cdot B_2O_3 \cdot 4H_2O$ has been well characterized, the crystal structures of both monoclinic (*228*) and triclinic (*321*) forms indicating the formula $Sr[B(OH)_4]_2$. It is readily formed by reacting soluble strontium salts with sodium metaborate solutions at a pH in excess of 11.

The $SrO \cdot 3B_2O_3 \cdot 4H_2O$ compound, occurring as tunellite, can be synthesized from the reaction between ammonium pentaborate and strontium salts. It was the first borate to be identified as possessing the hexaborate anion (Section III,A). The pentahydrate, 1:3:5, is stable in the $SrO–B_2O_3–H_2O$ system within the temperature range 0–100°C. Several routes to its preparation have been reported (*206*), and its dehydration has recently been studied (*197*).

The strontium analog of colemanite, $2SrO \cdot 3B_2O_3 \cdot 5H_2O$, can be prepared from the reaction between strontium iodate and borax in water at 65°C (*436*). Like colemanite, it possesses ferroelectric properties.

5. *Barium Borates*

Very few studies of hydrated barium borates have been published.

The metaborates, 1:1:*x*, are the most common borates of barium. $BaO \cdot B_2O_3 \cdot 1\frac{2}{3}H_2O$ precipitates from a boiling solution of barium chloride and boric acid treated with sodium hydroxide to a pH of over 11.4 (*260*); it dehydrates completely at 300°C. The 1:1:4, 1:1:5, and 1:1:6 metaborates have the formula $Ba[B(OH)_4]_2 \cdot xH_2O$ (Table I). The tetrahydrate is stable at 30°C in the $BaO–B_2O_3–H_2O$ system (*202*) and can be separated from sodium borate/barium chloride solutions at pH 11; at a higher pH and in dilute solution, the pentahydrate crystallizes out.

$BaO \cdot 3B_2O_3 \cdot 4H_2O$ is a stable phase in the $BaO–B_2O_3–H_2O$ (*202*) and $BaCl_2–Na_2B_4O_7–H_2O$ (*201*) systems at 30°C, and is also formed by dehydration of the pentahydrate (*323*) or hexahydrate.

6. *Zinc Borates*

The addition of alkali to solutions containing zinc salts with boron usually leads to formation of amorphous precipitates unless conditions are carefully controlled. Apart from the borate $ZnO \cdot B_2O_3 \cdot H_2O$ formed in aqueous solutions of borax and zinc nitrate, the best known zinc borates belong to the 2 : 3 : x series.

The $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ compound is the lowest hydrate under normal conditions and is prepared by the reaction between aqueous zinc sulphate and boric acid at temperatures above 70°C (*309*), or between zinc oxide and boric acid above 100°C (*310*). It retains its water up to 260°C. At lower temperatures, zinc salts react with borate solutions to give the 2 : 3 : 7 and 2 : 3 : 7.5 compounds. Alternatively, the borates can be formed according to the equation (*134*):

$$4NH_4OH + 2ZnSO_4 + 6H_3BO_3 \rightarrow 2ZnO \cdot 3B_2O_3 \cdot nH_2O + 2(NH_4)_2SO_4 + mH_2O$$

A crystal structure determination of the 2 : 3 : 7 compound shows it to have the structural formula $Zn[B_3O_3(OH)_5] \cdot H_2O$ (*324*).

A borate of composition 3 : 5 : 14 has been synthesized from zinc acetate and boric acid solutions (*336*), and the borates 1 : 5 : 4.5, 2 : 3 : 3, and 6 : 5 : 3 under hydrothermal conditions (*263*).

7. *Cadmium Borates*

Only a few borates of cadmium are known. Cadmium monoborate monohydrate $CdO \cdot B_2O_3 \cdot H_2O$ is formed in cadmium nitrate/borax solutions. The 1 : 2 : 5 borate precipitates from hot boric acid solutions containing cadmium acetate (*206*). Its dehydration occurs in three stages, with one water molecule lost at 100°C, three at 100–150°C, and the last at over 300°C.

Amorphous products were obtained in the reaction between alkali metal borates and cadmium chloride, analyzed as the 2 : 3 : 7 compound (*337*). More recently, a patent claiming the formation of $6CdO \cdot 7B_2O_3 \cdot (3\text{–}3.8)H_2O$ has appeared (*264*).

8. *Mercury Borates*

The mercury compounds $(PhHg)_2HBO_3$ (*296*), $Hg_3B_2O_6$ (*76*), and $Hg_4O(BO_2)_6$ (*75*) have been reported, but there is not conclusive evidence for hydrated borates.

9. *Double Metal Borates*

Table IX lists many of the known, well characterized hydrated double borates of general formula a $M^{I}_2O \cdot bM^{II}O \cdot cB_2O_3 \cdot dH_2O$. The structures of kaliborite, hydroboracite, inderborite, probertite, ulexite, $(NH_4)_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$, and $Rb_2O \cdot SrO \cdot 4B_2O_3 \cdot 12H_2O$ are

TABLE IX

TYPICAL DOUBLE-METAL BORATES

$(NH_4)_2O \cdot MgO \cdot 3B_2O_3 \cdot xH_2O$
$3Na_2O \cdot MgO \cdot 12B_2O_3 \cdot 22H_2O$, rivadavite
$Na_2O \cdot 2MgO \cdot 5B_2O_3 \cdot 30H_2O$
$K_2O \cdot MgO \cdot 3B_2O_3 \cdot 9H_2O$
$K_2O \cdot 4MgO \cdot 11B_2O_3 \cdot 18H_2O$, kaliborite
$K_2O \cdot 4MgO \cdot 11B_2O_3 \cdot 14H_2O$, heintzite
$K_2O \cdot MgO \cdot 3B_2O_3 \cdot 15H_2O$
$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$, hydroboracite
$CaO \cdot MgO \cdot 3B_2O_3 \cdot 11H_2O$, inderborite
$CaO \cdot 4SrO \cdot 5B_2O_3 \cdot 20H_2O$ (*148*)
$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$, probertite
$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$, ulexite
$Na_2O \cdot 2SrO \cdot 5B_2O_3 \cdot 16H_2O$
$K_2O \cdot SrO \cdot 4B_2O_3 \cdot 14H_2O$
$K_2O \cdot BaO \cdot 4B_2O_3 \cdot 14H_2O$
$K_2O \cdot 2ZnO \cdot 5B_2O_3 \cdot 10H_2O$
$(NH_4)_2O \cdot ZnO \cdot 6B_2O_3 \cdot 10H_2O$
$(NH_4)_2O \cdot 2ZnO \cdot 5B_2O_3 \cdot 10H_2O$
$K_2O \cdot CdO \cdot 6B_2O_3 \cdot 10H_2O$
$M_2O \cdot M'O \cdot 4B_2O_3 \cdot 12H_2O$
  $M = NH_4$, K; $M' = Ca$
  M = Rb, Cs; M′ = Ba (*155*), Sr, Ca

given in Table I. All the octaborates $M_2O \cdot M'O \cdot 4B_2O_3 \cdot 12H_2O$ are believed to possess the isolated $B_4O_5(OH)_4^{2-}$ ion on the basis of their IR similarity with borax. The preparation and properties of the tabled borates have been reviewed (*60*).

C. GROUP III METAL BORATE HYDRATES

1. *Aluminum Borates*

The hydrothermal reaction between aluminum oxide and boric acids yields the borates of empirical composition $Al_2O_3 \cdot 3B_2O_3 \cdot 7H_2O$ and $Al_2O_3 \cdot 2B_2O_3 \cdot (2.5{-}3)H_2O$ (*265*). By the "indifferent component method" (Section III,C) aluminum borates $Al_2O_3 \cdot B_2O_3 \cdot xH_2O$ ($x = 2$ to 6) are formed by mixing aluminum nitrate and borax solutions in the presence of sodium or potassium chloride (*51*). The thermal decomposition of the 1 : 1 : 3 compound has been studied (*52*). High-frequency conductometric titrations of solutions containing aluminum salts and alkali-metal tetraborates have detected the presence of $Al(OH)_2(BO_2)_nH_2O$ in solution (*50*).

2. *Thallium Borates*

The only recent authoratitive work on hydrated thallium borates is that by Touboul, who reviewed the field in 1971 (*412*). It is clear that insufficient data are available to rationalize the thallium borates, but there is definite evidence for the compounds 1 : 2 : 1, 1 : 2 : 3, 1 : 2 : 6, 1 : 5 : 8, 3 : 1 : x, and 2 : 5 : 5, which is stable up to 100°C.

D. GROUP IV METAL BORATE HYDRATES

Within this group, only lead and zirconium have borates of definite composition. The $PbO \cdot 2B_2O_3 \cdot 4H_2O$ compound is formed by evaporation of acetic acid from lead acetate–boric acid mixtures (*206*). It dehydrates in three stages: the first water molecule is lost at 50–95°C, two more between 130 and 170°C, and the remainder at over 300°C. The $PbO–B_2O_3–H_2O$ system has been studied at 50, 75, and 100°C (*385, 386*), and the compounds detected were 1:2:3 at 50°C; 4:5:2.5, 1:2:3, and 3:10:9 at 75°C; and 4:5:2.5, 1:2.5:2, and 3:10:9 at 100°C. Postulated structures for some of these borates are outlined in Section III,D.

The zirconium tetraborate $ZrO \cdot B_4O_7 \cdot 4H_2O$ is formed from the reaction between zirconyl chloride and boric acid at a temperature of 30°C at pH 4 (*25*). Its physicochemical properties have been studied (*24*).

E. TRANSITION-METAL BORATES

The borate chemistry of these elements is mainly restricted to the anhydrous compounds. Although this is an important area, space does not allow adequate coverage of the vast amount of pertinent literature.

1. *Chromium Borates*

The reaction products of the $Cr_2O_3–B_2O_3–K/NaNO_3–H_2O$ system are the chromium borates $2Cr_2O_3 \cdot 3B_2O_3 \cdot xH_2O$ ($x = 13$ and 18) (*145*). A basic borate $Cr(OH)(BO_2)_2 \cdot nH_2O$ has been detected by high-frequency conductometry (*50*).

2. *Manganese Borates*

The amorphous borate $2MnO \cdot 3B_2O_3 \cdot xH_2O$, prepared by mixing solutions of borax and manganous chloride, provides a useful starting material for the synthesis of other manganese borates. Treatment of this product with boric acid yields the 1:2:9 and 1:3:8 borates; boric acid and potassium or sodium chlorides give the 1:1:3 borate; and when it is dissolved in MOH ($M = K$ or NH_4), the double borates $M_2O \cdot MnO \cdot 6B_2O_3 \cdot 11H_2O$ are obtained (*53, 206*).

The thermal dehydration of the 1:1:3 (*52*) and, in particular, the hexaborates of general formula 1:3:x (*396*) have been studied intensely. Structurally, the 1:2:9 compound resembles borax and has been assigned the formula $Mn[B_4O_5(OH)_4] \cdot 7H_2O$ (*42*). On the basis of IR evidence, the hexaborates are believed to possess both tetrahedral and trigonal boron atoms (*402*).

3. *Iron Borates*

Most of the hydrated iron borates are formed under hydrothermal conditions. A recent study (*163*) of the $FeO–Fe_2O_3–B_2O_3–H_2O$ system over the temperature range 135–700°C detected the species $FeO \cdot 2B_2O_3 \cdot 2.5H_2O$, $FeO \cdot 3B_2O_3 \cdot 4.5H_2O$, $FeO \cdot 6B_2O_3 \cdot 5H_2O$, $FeO \cdot 2B_2O_3 \cdot 4.5H_2O$, $6FeO \cdot 7B_2O_3 \cdot H_2O$, $2FeO \cdot B_2O_3 \cdot H_2O$, and $Fe_2O_3 \cdot B_2O_3 \cdot nH_2O$ hydrates.

The borate $FeO \cdot 3B_2O_3 \cdot 8H_2O$ has been prepared at room temperature in an inert atmosphere from borax, boric acid, and ferrous sulfate (*401*). The $Fe_2O_3 \cdot B_2O_3 \cdot xH_2O$ borate is formed in the $Fe_2O_3–B_2O_3–Na/KCl–H_2O$ systems (*49, 145*).

The IR spectra (*402*) and thermal decomposition (*396*) of the $FeO \cdot 3B_2O_3 \cdot xH_2O$ borates have been measured. The anhydrous iron borates Fe_3BO_6 and $FeBO_3$ exhibit interesting magnetic and magneto-optical properties. In the last 10 years, well over 50 papers have been written on these borates, a few of which have been summarized by Bowden and Thompson (*60*).

4. *Cobalt Borates*

The only definite borate hydrates of cobalt are the $CoO \cdot 3B_2O_3 \cdot 8H_2O$ and $CoO \cdot 3B_2O_3 \cdot 10H_2O$ compounds. The octahydrate is prepared by evaporation of acetic acid from cobalt acetate–boric acid mixtures, or by mixing aqueous solutions of cobalt chloride, borax, and boric acid (*206*). The 1:3:7.5 borate can form as a solid solution and, in the presence of 3% boric acid, affords the decahydrate (*117*). The crystal structure determination of this 1:3:10 compound shows it to possess the hexaborate ion (*380*). The IR spectra (*402*) and thermal decomposition (*396*) of these compounds have been determined.

5. *Nickel Borates*

The borate $NiO \cdot B_2O_3 \cdot 8H_2O$ is prepared from nickel salt and borax solutions after digesting with boric acid. The decahydrate is formed from the octahydrate in boric acid at temperatures below 10°C; above 80°C the pentahydrate separates out (*206*). Both the octahydrate and decahydrate have the hexaborate ion $B_6O_7(OH)_6^{2-}$ (*378, 380*).

A 1 : 1 : 2 compound is obtained in the $NiCl_2$–$M_2B_4O_7$–MCl–H_2O (M = K or Na) system (*48*).

VI. Concluding Remarks

The structure determination of crystalline borates is well advanced, and it is hoped that the present enthusiasm will continue. There are many candidates for further investigation, particularly where spectroscopic or dehydration characteristics have suggested a particular boron anion. For example, the borate $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ loses its water at temperatures in excess of 260°C, implying that its formula water is in the form of hydroxyl groups.

Knowledge of the stability of various polyborate ions is lacking. It is known from structure determinations that the isolated $B_3O_3(OH)_5^{2-}$ is the most common ion of the triborates, but not why there are so few examples of $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_6^{3-}$. Further, why does borcarite have an eight-membered ring in preference to a tetraborate group?

Probably the most neglected field is that of metal borate complexation in solution. Early proposals of ionic species were based on rather dubious evidence, and a great deal of new experimental work is required. With more sophisticated spectroscopic instruments becoming available, both this phenomenon and the related topic of polyborate ions in solution will be easier to observe.

The lack of data on certain metal borate systems has been implied in Section V. Quite apart from thallium, zinc, and lead compounds, the range of known borates of barium and strontium is somewhat limited. There are no obvious reasons why the latter should not have stability ranges approaching those of calcium and magnesium borates. Clearly, more investigations are necessary in this area.

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