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Progress in the Polymer Chemistry of Borates

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Using a combined approach based on the symbiosis of macromolecular and colloid chemistry of polymers with inorganic chemistry, data on the low- and high-molecular-weight anionic metal oxoborates in the crystalline, amorphous, and vitreous states, in solution, in the melt, and in the gas phase are surveyed. An attempt is made on this basis to present an adequately logical and well-founded picture of their structure, to indicate a new method of study, and to facilitate the prediction of the properties of technical materials and the improvement of the technology of their manufacture. The entire wide variety of borates and many of their properties can be accounted for by the variation of the configurations and conformations of the macroanions in response to changes in external influences as a result of the flexibility of the B-O-B bonds by virtue of the O atoms being in a state intermediate between sp^2- and sp-hybridisation involving B atoms. The necessity to develop the polymer chemistry of compounds with the E-O-E linkages (E = B, Si, P, Al, etc.) is emphasised. It is noted that the chemistry of macroanions is in the forefront in this respect.
The bibliography includes 265 references.

CONTENTS

I. Introduction	203
II. Hydrated borates	204
III. Anhydrous oxoborates	211
IV. Conclusion	224

I. INTRODUCTION

The unity of the nature of organic, organoelemental, and inorganic polymers and the differences between them have already been discussed in a review,[1] where the inadequate development of this problem in relation to polymers of the last type was noted. The number of new publications on this topic can be literally measured in single figures.[2,3] This is clearly inconsistent with the abundance and importance of inorganic polymers in nature and technology.[4-8] The ideas developed in a monograph by Korshak et al.[9] stimulated at an earlier stage the consideration of certain aspects of the macromolecular physics and chemistry of boron oxides and hydrogen oxoborates.[1] This review is devoted to polymeric metal oxoborates† (henceforth referred to simply as borates).

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†The fluoro-, peroxo-, and other borate systems as well as inorganic polymers with B–O–E linkages in the macroanions (E = Si, Al, P, etc.), i.e. the corresponding boroelementoxanes,[10] will not be considered here. We note only that the use of the principles of macromolecular chemistry will permit an approach to the synthesis of such polymers and materials based on them.[11-16]

The characteristic features of the electronic structure of boron are responsible for the presence of the BO_3 and BO_4 sp^2- and sp^3-hybrids in the structures of borates and also for the possibility of their interconversions.[17] This complicates the structure of borates compared with, for example, phosphates[18] or silicates.[19] The elucidation of the structures of many borates has been scarcely reflected in their terminology, particularly in the trivial names of natural compounds. Although stereoregular crystalline linear (chain and cyclochain) borate polyanions can be fully described, according to IUPAC recommendations,[20] with the aid of stereochemical definitions and designations adopted by IUPAC for polymers,[21] in practice such terminology is not being used. Since the existing nomenclature for polymers[20-22] refers solely to linear single-stranded and quasi-single-stranded structures, the present review has retained mainly the traditional terminology of the chemistry of borates, in particular, the prefixed "phyllo" and "tekto" are used to designate two- and three-dimensional structures respectively.[23] Since the term "polyanion" has a dual significance in the chemistry of borates—it is frequently used to designate both intrinsically polymeric (chain, layer, and network) and isolated ("island") anions with a low degree of polymerisation, in the present review the latter are referred to as oligoanions[24] and the former as macroanions. The macroanions are in their turn subdivided into linear (poly-), layer (phyllo-), and network (tekto-). Instead of terms of the type "basic structural blocks",[25] "basic structural units",[26] etc., the term "constitutional repeat units" (CRU) [27] (it is also referred to as the elementary unit[28]), taken from the chemistry of macromolecular compounds, is used. The symbol "∞" has been replaced by the designation "n" used in the chemistry of macromolecular compounds.

The oligoanions are subdivided, as usual, into triborate, tetraborate, pentaborate, etc. anions. In order to reflect their wide variety, caused by the different combinations of BO_3 and BO_4 for the same number of boron atoms, it is most convenient to employ the nomenclature of complex compounds.[29] The review includes data on oxoborates published up to 1985, including data on new oligoanions with $n = 12$ [30] and $n = 16$,[31] on the heptaborate CRU,[32] etc., for example, the structure $CaO.2B_2O_3.0.5H_2O$,[33] which have not been included in any of the previous reviews.[34] Data on anhydrous crystalline[26] and vitreous[7,35] borates, etc. have also been supplemented.

II. HYDRATED BORATES

1. Crystalline Compounds

The fundamental principles governing the formation of structures[25] are described below taking into account the postulates of the chemistry of macromolecular compounds:

1. The simplest groups in the structures are BO_3 and BO_4.
2. The monomeric and dimeric anions are made up only of BO_3 groups or only BO_4 groups.
3. As a result of oligocondensation, the monomeric anions tend to form reactive anionic preoligomers, in which the degree of polymerisation of the simplest groups BO_3 (BO_4), functioning as structural fragments (subunits[20]) of the oligoanions, is $n \geq 3$.
4. The oligoanions specified in paragraph 3 can be modified by grafting to them side branches consisting of boron–oxygen and other element–oxygen groups.
5. Both monomeric and oligomeric anions (including modified anions) can polymerise via polycondensation (sometimes with ring opening) to macroanions functioning at the given stage of structural organisation as the CRU of the macroanions.#
6. In the structures of hydrated borates there is a possibility of the coexistence of the macroanions with mono-, di-, and oligo-anions.
7. In the hydrated borates, the oxygen atoms capable of being protonated are usually (but not always) protonated in the following sequence: initially the terminal oxygen ions (with formation of hydroxy-groups), next the oxygen atoms of the BO_4 sp^3-hybrid, then the oxygen atoms of the BO_3 sp^2-hybrid, and finally the hydroxy-group (with formation of water molecules).

The water in the crystalline hydrated borates can be present both in the molecular form (five classes of such water are distinguished)[36] and in the form of protons and hydroxyls, the hydrogen bonds playing an important role in the formation of the structures under these conditions. As the water content diminishes, the degree of polycondensation and the degree of cross-linking of the boron–oxygen anions increase.[36]

Fig. 1 presents the known varieties of the borate mono-, di-, and oligo-anions in the fully hydrated form. Partly dehydrated forms have also been detected in real borates. Some of the oligomers illustrated in Fig. 1 (*D*, *a*; *G*; *H*) have so far been detected in a modified form and as CRU of the macroanions. Examples of similar modified CRU are presented in Fig. 2.

Fig. 3 illustrates the "pentamer trimer" (i.e. a tripentaborate—not a pentadecaborate), found in the structure of natural ammonioborite,[37] and also the oligoanion $[B_{16}O_{24}.(OH)_{10}]^{10-}$ in which there are two heptaborate anions held by the BO_3 triangles.[31] The last example can also be regarded as an exception to the 7th of the principles quoted above; in the presence of water molecules, non-protonated oxygen bound to boron is present in the structure.

Starting with triborates ($1BO_3 + 2BO_4$), stereoisomers begin to appear. The triborate ring is a component of almost all oligoanions [the central O atom in the structure of the hexamers is coordinated to three B atoms at once and the charge of the hexamers is not equal to the number of B(IV) atoms as in other oligoanions, where it is smaller by unity]. One of the varieties of the tetraborate compounds is an exception.

The stereochemical similarity of borates to organic compounds has already attracted the attention of investigators[38] and Fig. 3*b* demonstrates their ability to form "chelate" complexes which constitute the basis of many coordination polymers.[39]

Examples of borates in the macroanions of which the residues of mono- and oligo-anions behave as CRU are given in Tables 1 and 2. Figs. 4 and 5 represent the fragments of certain macroanions included in the above Tables.

The set of data presented reveals the wide variety of macroanions, the origins of which are discussed in Section IV. In the light of ideas about the functionality of monomers in polycondensation,[76] the tendency towards the formation of predominantly heterocyclochain and layer polyboroxane macroanions, the possibility of their successive cross-linking, and also the possibility of the formation of

#The macroanions are capable of forming still higher forms of supermolecular (more precisely, "superionic") structural organisation, for example, formations of the spherulite type.

statistical and block-copolymers with B–O–E linkages (E = Si, Al, P, etc.) were already considered previously.[1] The possibility of the modification of the structures illustrated in Fig. 1 by the grafting of various side branches and the formation of the CRU shown in Fig. 2 also follows from the same pre-conditions. This type of transformation occurs likewise in the case where the polycondensation of the oligoanions is accompanied by the opening of the ring, as happens, for example, in the conversion of borax into kernite in accordance with the scheme shown in Fig. 6.[25]

It is noteworthy that polyborates [for example, hydroboracite (III) and colemanite (IV) in Table 1] frequently give rise to superionic formations of the type of spherulites,[77] despite the views of Frenkel'.[6]

Since boron absorbs effectively slow neutrons and hydrogen absorbs fast neutrons,[78] hydrated borates and binding compositions based on them[79,80] are promising as materials for protection against neutron radiation. The mechanical indices (density, hardness, etc.) increase almost linearly on passing from the monoanionic to the di- and oligo-anionic structures and further to polymers, reaching a maximum for network macroanions.[81] The latter also contain the maximum amount of boron but the hydrogen content is then reduced to a minimum. This means that chain or layer macroanions have the optimum properties. An idea about the necessary ratio of the components can be gained from the data in Tables 1 and 2. On the other hand, the conditions in the synthesis of the binding materials must be close to those in the synthesis of single crystals (see the original communications quoted in the Tables). Clearly polycrystalline and even amorphous polymers, formed by borates at 323–523 K,[17] are suitable for the preparation of technical binders, phylloanions being usually produced under hydrothermal conditions.[82] It is useful to employ for this purpose

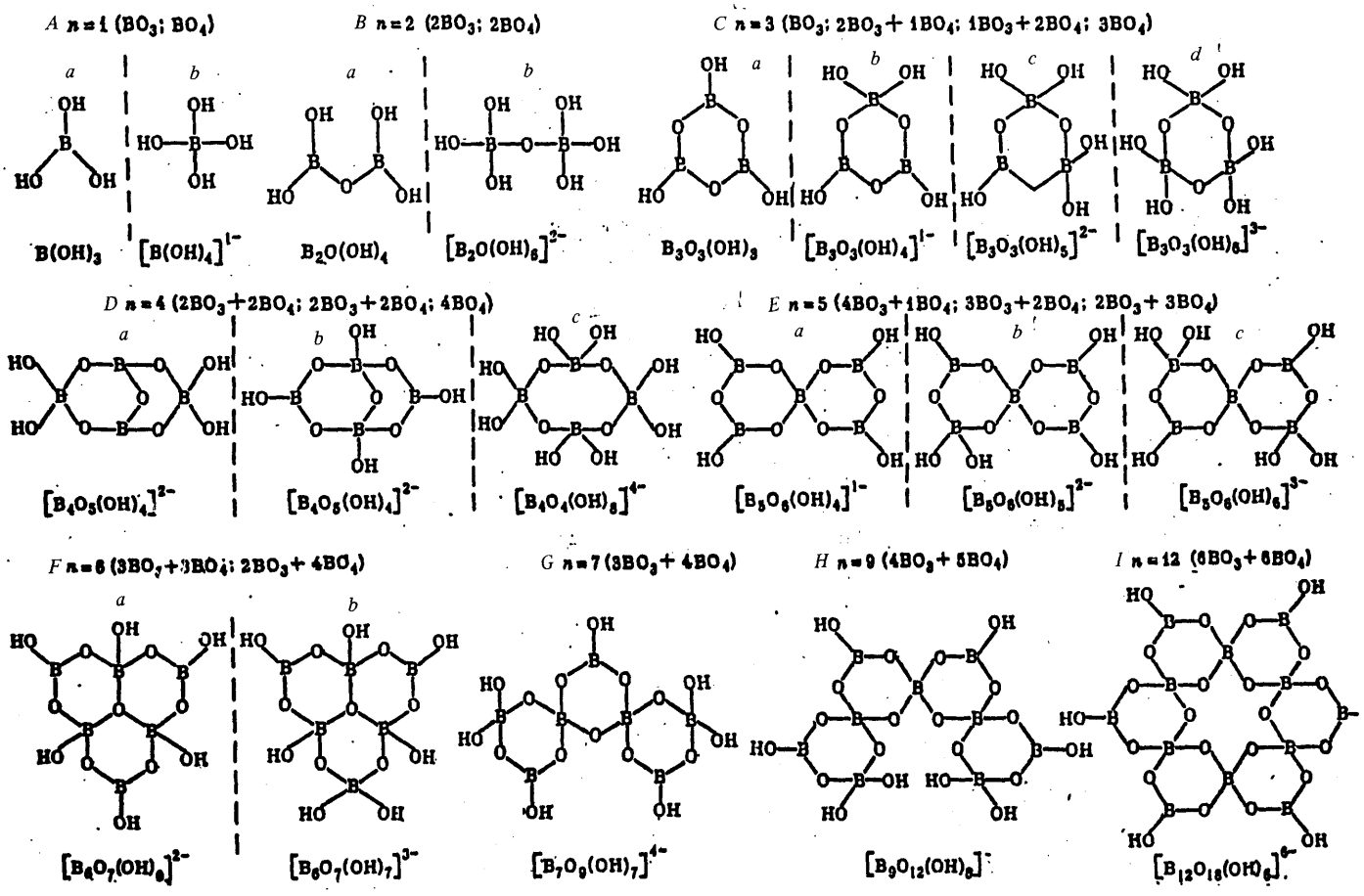


Figure 1. Borate monomers, dimers, and preoligomers with $n \geq 3$ in the fully hydrated form; their residues occur as the "usual" CRU of macroanions (Table 1) and subunits of modified (combined) CRU (Fig. 2).

the experience gained in the chemistry of macromolecular compounds in carrying out the polycondensation reactions[83] and to invoke the mechanochemical reactions[84] which are already employed in the practical synthesis of borates.[85]

Hydrated borates, for example calcium borates, are manufactured on an industrial scale.[86] The B_2O_3 content in the polymeric borates is higher than in the monomeric and oligomeric borates and for this reason, in the manufacture of calcium borates, the half-finished product $CaO.B_2O_3.6H_2O$ with the monoanion $[B(OH)_4]^-$ [34] is nowadays subjected to polycondensation in the course of the so called "drying" (Ref.86, p.115) and is converted into the commercial product $CaO.B_2O_3.2H_2O$ (43% B_2O_3). Commercial preparations with a higher B_2O_3 content can be obtained under conditions where the degree of polymerisation of the boron–oxygen anions is increased further.

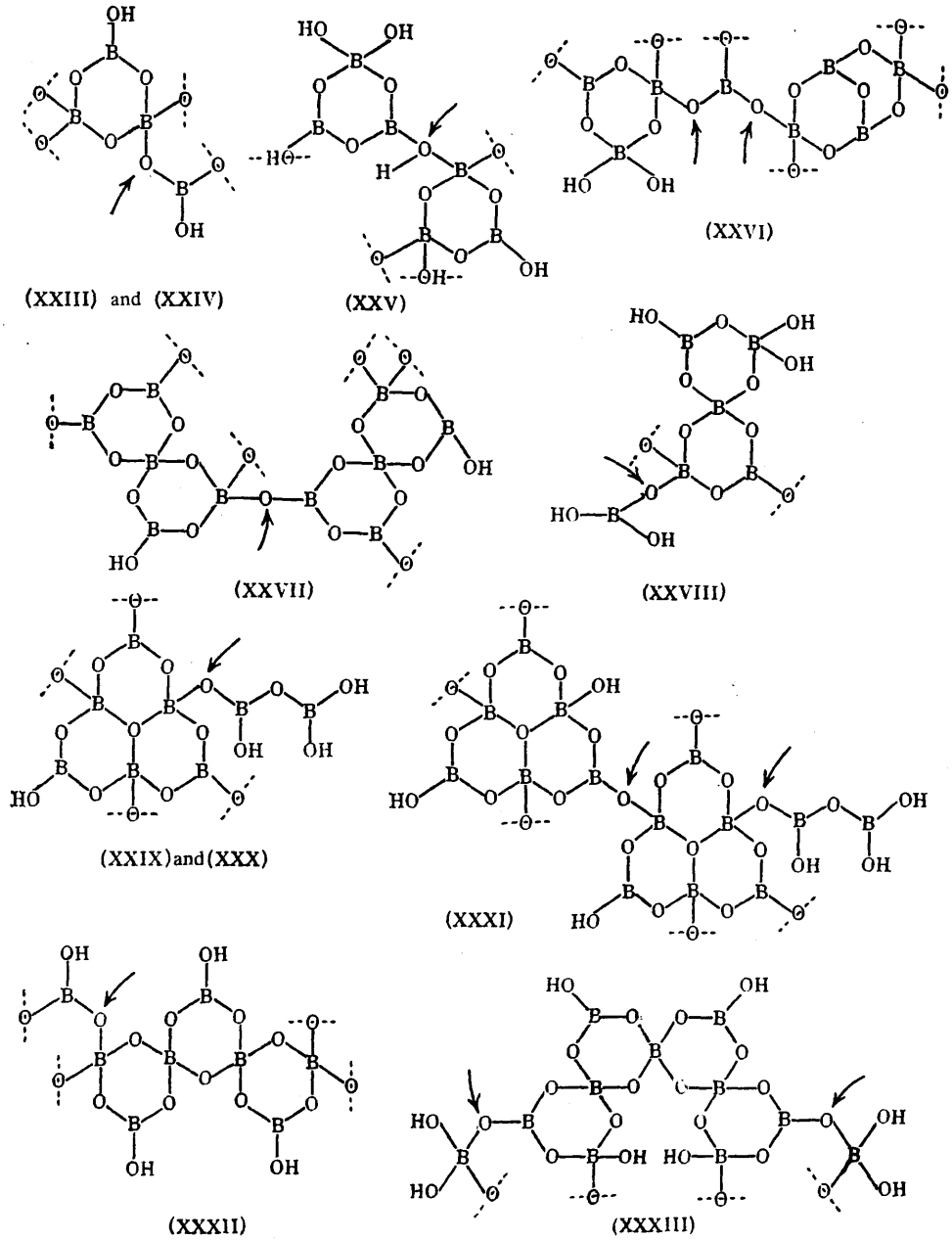


Figure 2. Examples of modified CRU in the macroanions of hydrated borates (the numerals correspond to those adopted in Table 2 for specific compounds); the arrows indicate the sites of grating of subunits; the connecting oxygen atoms shared with neighbouring CRU are indicated by dashed lines (see the footnote to Table 2).

The adhesive, binding, and film-forming properties of borates,[87,88] which are characteristic of polymers and are considered in the next Section, are also of practical interest.

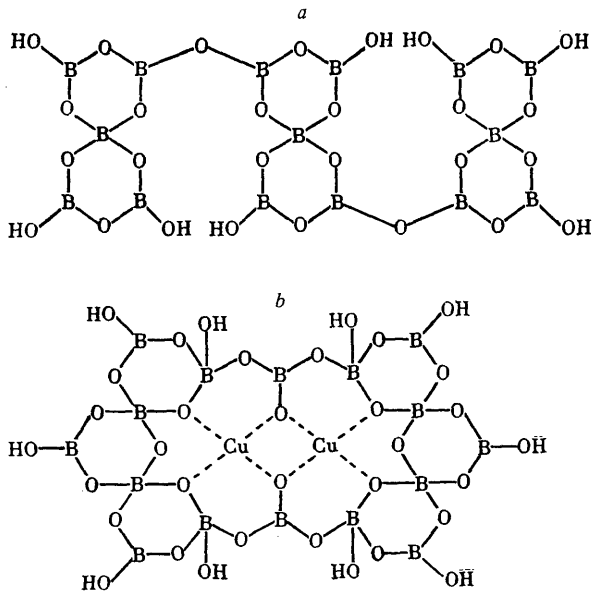


Figure 3. The tripentaborate oligoanion (*a*) in natural ammonioborite $(NH_4)_3[B_{15}O_{20}(OH)_8].4H_2O$ and the oligoanion with $n = 16$ (*b*) as part of the "chelate" oligoanion in synthetic $Na_6\{Cu_2[B_{16}O_{24}(OH)_{10}]\}.12H_2O$.

2. Solutions of Oxoborates

The water-soluble borates of Group Ia *s* elements have been most thoroughly investigated. On dissolution in water, their macroanions are degraded as far as the formation of mono-, di-, and oligo-anions with $n = 3–5$.[1] The regions in which some of them predominate in solution are shown in Fig. 7.[34,82]

It is striking that the structures made up wholly of BO_4 tetrahedra (for example, the network HBO_2-I macromolecules[1]) hydrolyse very slowly, in contrast to structures containing also the BO_3 triangles (for example, the cyclochain HBO_2-II macromolecules[1]), which makes it possible to isolate them from the mixture.[89] Consequently the resistance of borate macroanions to hydrolysis can be increased by filling with electrons the unoccupied *p* orbitals of the BO_3 sp^2-hybrids by their interaction with electron density donors, for example, with phosphates,[7,15] or by exposing them to UV [13] or ionising [90] radiation and by similar procedures.

Highly concentrated solutions in the $M_xO_y–B_2O_3–H_2O$ systems (M = metal),[87,88] obtained on heating or hydrothermal treatment, exhibit adhesive, binding, and film forming properties. Concentrated solutions in the $M_2O–B_2O_3–SiO_2–H_2O$ system have the same properties.[91] In the latter case even a very small content of boron compounds in compositions made up of oxygen compounds induces qualitative changes in the structures and properties of the statistical and block-copolymers formed.[91]

As already mentioned,[1] true solutions of borate polymers can be most readily obtained in non-aqueous solvents—either organic such as nitrobenzene in which they swell [92] or in "water removing" inorganic solvents of the type of H_2SO_4.[93] It has been suggested that in the latter case dissolution is

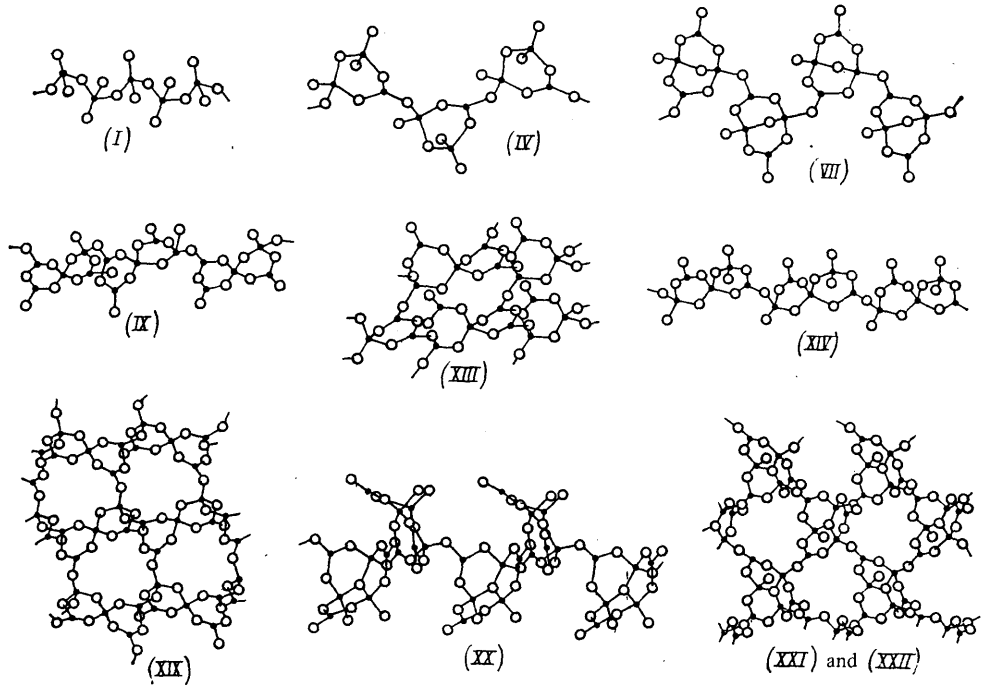
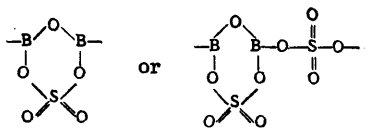


Figure 4. Fragments of the macroanions of certain borates presented in Table 1; the hydrogen atoms in the hydroxy-groups have been omitted for simplicity; here and henceforth the small filled circles denote boron and the larger open circles denote oxygen.

accompanied either by complex formation[94] or by polymer-analogue transformations with formation of CRU of the type[95]



The formation of a complex between $B(OH)_3$ and iron salts in solutions has also been noted.[96]

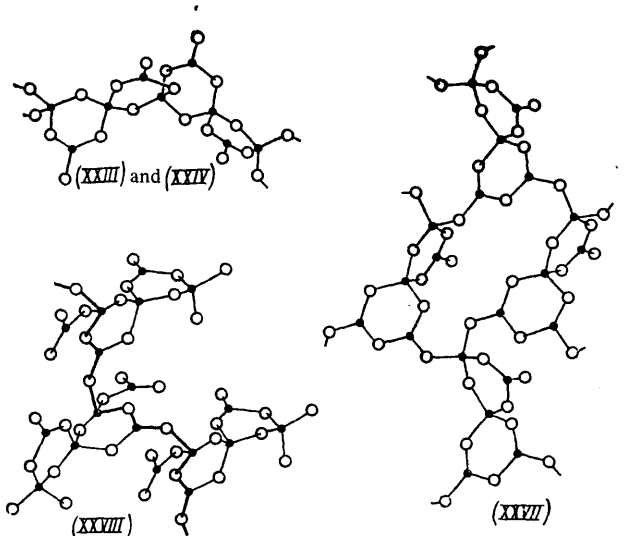


Figure 5. Fragments of the macroanions of certain borates presented in Table 2.

The set of data presented above provides a key to the understanding of the genesis of natural borate ores and the determination of the necessary conditions for the preparation of their synthetic analogues.

In nature at $T < 323$ K, mono-, di-, and oligo-borates are produced in the primary sedimentation period, undergoing various kinds of changes in the subsequent post-sedimentation period. As a result of polycondensation in accordance with the scheme[38]

$$[B_xO_y(OH)_z]^{(2y+z-3x)-} \xrightarrow[-qHOH]{t^\circ} [B_xO_{y+1}(OH)_{z-2}]^{(2y+z-3x)-}_{q+1},$$

accompanied under suitable conditions by ring opening (Fig. 6), the grafting of side groups, and similar processes, the primary sedimentation borates are usually converted into secondary, post-sedimentation borates, as a rule chain or layer borates, following a change in thermodynamic conditions in deep layers.[82]

In order to obtain a synthetic borate with a particular structure, it must be deposited from a solution containing definite mono- or oligo-anions. On the other hand, as can be seen from the data in Fig. 7, each of them exists predominantly within narrow temperature, pH, and concentration ranges, in the presence (see Section IV) of particular metal cations, and, finally, within a limited time interval (on "ageing" of the solutions). This greatly complicates the separation of borate homologues, which requires the application of many sophisticated technological methods and special procedures.[34,86,97–99] On the other hand, if the solution contains borate homologues of several varieties at once, then non-crystalline variable-composition amorphous borates are deposited from such a solution.

3. Amorphous Systems—Behaviour on Heating

Apart from the procedure noted above, amorphous borates are also formed in the course of the dehydration of crystalline hydrated borates (at a temperature ensuring the removal of the most strongly bound OH groups from the structures), yielding the so called amorphous powders.[77] The conversion of the amorphous borates into crystalline anhydrous compounds on further heating is accompanied by an effect which has been called the "borate rearrangement" (BR).[77]

In contrast to the usual crystallisation, whose rate is limited by the rate of removal of energy from the system, BR has an explosive (chain) exothermic character and occurs always at a reproducible temperature specific to each borate

Table 1. Examples of polymeric hydrated crystalline borates with the "usual" CRU (see also Figs. 1 and 4).

CRU[a] of macroanions	Initial monomer or preoligomer	Form and formula of macroanions	Examples of specific compounds (the trivial names are also quoted for the natural borates)	Refs.	Designation
Monoborate	$[B(OH)_4]^{1-}$	Chain $[B^{IV}O(OH)_3]^{n-}_n$	Wimsite $Ca[BO(OH)_3]_{2n}=CaO\cdot B_2O_3\cdot 2H_2O$	[40]	(I)
Triborate	$[B_3O_3(OH)_4]^{1-}$	Cyclochain $[B^{III}_2B^{IV}O_4(OH)_3]^{n-}_n$	$Tl[B_3O_4(OH)_3]_n\cdot 0{,}5H_2O=Tl_2O\cdot 3B_2O_3\cdot 3H_2O$	[41]	(II)
		Cyclochain $(B^{III}B^{IV}_2O_4(OH)_3]^{2n-}_n$	Hydroboracite $CaMg[B_6O_8(OH)_6]_{2n}\cdot 3H_2O = CaO\cdot MgO\times$ $\times 3B_2O_3\cdot 6H_2O$	[42]	(III)
	$[B_3O_3(OH)_5]^{2-}$		Colemanite $Ca[B_3O_4(OH)_3]_n\cdot H_2O=2CaO\cdot 3B_2O_3\cdot 5H_2O$	[43]	(IV)
		Layer $[B^{III}B^{IV}O_5(OH)]^{3n/n-}_{n/n}$	Fabianite $Ca[B_3O_3(OH)]_{n/n}=2CaO\cdot 3B_2O_3\cdot H_2O$ (mono lin.)	[44]	(V)
			$Ca[B_3O_3(OH)]_{n/n}=2CaO\cdot 3B_2O_3\cdot H_2O$ (orthorhomb.)	[45]	(VI)
Tetraborate[b]	$[B_4O_5(OH)_4]^{2-}$	Cyclochain $[B^{III}_2B^{IV}_2O_5(OH)_2]^{2n-}_n$	$Na_2[B_4O_5(OH)_2]_n=Na_2O\cdot 2B_2O_3\cdot H_2O$	[46]	(VII)
Pentaborate	$[B_5O_6(OH)_4]^{1-}$	Cyclochain $[B^{III}_4B^{IV}O_7(OH)_2]^{n-}_n$	Larderellite $NH_4[B_5O_7(OH)_2]_n\cdot H_2O=2NH_4OH\cdot 5B_2O_3\cdot 3H_2O$	[47]	(VIII)
		Cyclochain $[B^{III}_3B^{IV}_2O_7(OH)_3]^{2n-}_n$	Escurite $Na_2[B_5O_7(OH)_2]_n\cdot 2H_2O=2Na_2O\cdot 5B_2O_3\cdot 7H_2O$	[48]	(IX)
		Layer $[B^{III}_3B^{IV}_2O_8(OH)]^{3n/n-}_{n/n}$	Nasinite $Na_2[B_5O_8(OH)]_{n/n}\cdot 2H_2O=2Na_2O\cdot 5B_2O_3\cdot 5H_2O$	[49]	(X)
	$[B_5O_6(OH)_5]^{2-}$		$K_2[B_5O_8(OH)]_{n/n}\cdot 2H_2O=2K_2O\cdot 5B_2O_3\cdot 5H_2O$	[50]	(XI)
		Ditto in combination with monomeric $B(OH)_3$ located in the plane of the layers[c]	Gowerite $Ca[B_5O_8(OH)]_{n/n}B(OH)_3\cdot 3H_2O=CaO\cdot 3B_2O_3\cdot 5H_2O$	[51]	(XII)
			p- and A-Witchites $Sr_2[B_{10}O_{16}(OH)]_{2n/n}\cdot B(OH)_3\cdot H_2O = 4SrO\times$ $\times 11B_2O_3\cdot 7H_2O$	[52, 53]	(XIII)

Table 1 (cont'd).

CRU[a] of macroanions	Initial monomer or preoligomer	Form and formula of macroanions	Examples of specific compounds (the trivial names are also quoted for the natural borates)	Refs.	Designation
Pentaborate	$[B_5O_6(OH)_6]^{3-}$	Cyclochain $[B_2^{III}B_3^{IV}O_7(OH)_4]_n^{3n-}$	Probertite $NaCa[B_5O_7(OH)_4]_n \cdot 3H_2O = Na_2O \cdot 2CaO \cdot 5B_2O_3 \times 10H_2O$	[54]	(XIV)
		Layer $[B_2^{III}B_3^{IV}O_8(OH)_3]_{nn}^{3nn-}$	Heydornite $Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]_{nn}$[d]	[55]	(XV)
			$Na_3[B_5O_8(OH)_2]_{nn} \cdot H_2O = 3Na_2O \cdot 5B_2O_3 \cdot 4H_2O$[d]	[56]	(XVI)
			$Li_3[B_5O_6(OH)_3]_{nn}$=II=$3Li_2O \cdot 5B_2O_3 \cdot 2H_2O$ (orthorhomb.)[e]	[57]	(XVII)
		[f]Network $[B_2^{III}B_3^{IV}O_9]_{nnn}^{3nnn-}$	Hilgardite $Ca_3[B_5O_9]_{nnn} \cdot Cl \cdot H_2O = 3CaO \cdot CaCl_2 \cdot 5B_2O_3 \times 2H_2O$(monoclin.)[g]	[58]	(XVIII)
			$Na_3[B_5O_9]_{nnn} \cdot H_2O = 3Na_2O \cdot 5B_2O_3 \cdot 2H_2O$	[59]	(XIX)
Hexaborate	$[B_6O_7(OH)_6]^{2-}$	Cyclochain $[B_3^{III}B_3^{IV}O_6(OH)_4]_n^{3n-}$	Aristarainite $Na_2Mg[Ba_6O_6(OH)_4]_{3n} \cdot 4H_2O = Na_2O \cdot MgO \times 6B_2O_3 \cdot 8H_2O$	[60]	(XX)
		Layer $[B_3^{III}B_3^{IV}O_6(OH)_3]_{nn}^{3nn-}$	Nobleite $Ca[B_6O_8(OH)_3]_{nn} \cdot 3H_2O = CaO \cdot 3B_2O_3 \cdot 4H_2O$	[61]	(XXI)
			Tanellite $Sr[B_6O_8(OH)_2]_{nn} \cdot 3H_2O = SrO \cdot 3B_2O_3 \cdot 4H_2O$	[61]	(XXII)

[a]The CRU of the macroanions[27] may not be identical with the stereorepeating unit.[21] Thus the CRU in wimsite I is $-\overset{OH}{\underset{OH}{B}}-O-$, while the stereorepeating unit is in essence a diborate unit consisting of two BO_4 tetrahedra.[40]

[b]See also Table 2 [(XXIII) and (XXXIV)].

[c]The monomeric $B(OH)_3$ groups in gowerite are located in each layer, while in p- and A-witchites they are located in alternate layers. In the structures of the latter the two-layer arrangements made up of identical phylloanions differ only by their relative dispositions; whereas the first layers are identical, the second in A-witchite is a mirror image of the second layer of p-witchite in the plane perpendicular to the c axis.[62]

[d]Although compounds (XV) and (XVI) have the same initial preoligomer $[B_5O_6(OH)_6]^{3-}$, its polycondensation can occur with participation of different OH groups, so that ultimately the end groups in compound (XV) consist of two different triangles with one OH group in each, while those in compound (XVI) consist of two OH groups in one of the tetrahedra.

[e]The synthesis under a pressure of about 100 MPa results in the formation of $Li_3[B_5O_8(OH)_2]$-I (tetragonal), in the anionic network of which it is possible to distinguish helical strips made up of triborate rings ($1BO_3 + 2BO_4$).[63] Sections through the deformation electron density of this borate[64] indicate the covalent character of the boron–oxygen bonds in the BO_3 and BO_4 groups and also in the B–O–B bridges, whereas the Li–O bonds are significantly ionic.

[f]The tektoanion is anhydrous and contains no functional OH groups, being a product of a later stage of the three-dimensional polycondensation of the preoligomer $[B_5O_6(OH)_6]^{3-}$. The zeolite-like boron–oxygen skeleton formed has large cavities in which water molecules are accommodated and in the case of compound (XVIII) also chlorine, so that the borates (XVIII) and (XIX) constitute, as it were, an intermediate stage on the way to the fully anhydrous systems—see (LXII) and (LXIII) in Table 3. Having the same CRU, the macroanions of (XVIII) and (XIX) nevertheless consist of different stereorepeating units: in compound (XVIII) the identity period along the boron–oxygen chains in the network is 0.63 nm, while in compound (XIX) it is 1.12 nm, i.e. corresponds to 2CRU.

[g]The triclinic modification of hilgardite has the same tektoanion.[65]

(somewhat below melting point T_m), and is accompanied by a marked contraction, an increase in the density and hardness of the substance, so that, on the basis of physical properties, it is difficult to put forward the hypothesis that before and after BR one is dealing with a substance having the same chemical composition.[77] It has been established[100–103] that, above the temperature of the BR exothermic effect, the specimens consist as a rule of a mixture of two borates, for one of which the modulus $m = B_2O_3/M_xO_y$ is higher and for the other lower than for the initial borate—in the limit it is made up of B_2O_3 ($m = \infty$) and monomeric (dimeric) borates with a minimum modulus if the newly formed borates are thermodynamically unstable. From the standpoint of the chemistry of macromolecular compounds, this resembles very closely the solid-phase polycondensation[104] or polymerisation[105] reactions. Both reactions proceed at an appreciable rate over a narrow temperature range below T_m, are autocatalytic, their rate has a high temperature coefficient, and their activation energy is also high. Bearing in mind that at the instant of the occurrence of the BR amorphous borates already lack the OH functional groups[100–103]§ (although the isolation of low-molecular-weight anionic products in the chemistry of silicates is also attributed to polycondensation processes as an alternative to ionic polymerisation[107]), it is more likely that the BR represents a kind of unusual solid-phase polymerisation process. It is noteworthy that, in the course of the BR, a fundamental change in the structures of the CRU of the macroanions frequently takes place. For example, colemanite, (IV) in Table 1, is converted after the BR into a mixture of $Ca[(BO_2)_2]_n$, (XXXV) in Table 3, and $Ca_2[B_8O_{14}]_{nnn}$, (LXXVI) in Table 4,[102] while hydroboracite, (III) in Table 1, is converted into a mixture of $Ca[(BO_2)_2]_n$

§Certain iron borates are exceptions.[106]

Table 2. Examples of polymeric hydrated crystalline borates with modified (combined) CRU (see also Figs. 2 and 5).

Initial monomers and oligomers whose grafting results in the formation of the subunits in the CRU	Form and formula of macroanion[a]	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$(2BO_3 + 2BO_4)$[b]	Cyclochain $[B^{III}B^{IV}_2O_5(OH)\cdot B^{III}O(OH)]^{n-}_n$	Kernite $Na_2[B_4O_6(OH)_2]_n\cdot 3H_2O = Na_2O\cdot 2B_2O_3\cdot 4H_2O$ $Tl_2[B_4O_6(OH)_2]_n\cdot 2H_2O = Tl_2O\cdot 2B_2O_3\cdot 3H_2O$	[66] [67, 68]	(XXIII) (XXIV)
$(1BO_3+2BO_4)+(2BO_3+1BO_4)$	Layer[c] $[B^{III}B^{IV}_2O_4(OH)_2\cdot B^{III}_2B^{IV}O_5(OH)_2]^{nn-}_{nn}$	$Mg[B_6O_7(OH)_5]_{2nn} = MgO\cdot 6B_2O_3\cdot 5H_2O$	[69]	(XXV)
$(2BO_3 + 2BO_4)$[d] $+ 1BO_3 + (1BO_3 + 2BO_4)$	Network $[B^{III}_2B^{IV}_2O_7\cdot B^{III}O_{1,5}B^{III}B^{IV}_2O_{4,5}\times$ $\times(OH)_2]^{4nnn-}_{nnn}$	$Ca_2[B_6O_{12}(OH)_2]_{nnn} = CaO\cdot 2B_2O_3\cdot 0,5H_2O$	[33]	(XXVI)
$(3BO_3+2BO_4)+(3BO_3+2BO_4)$	Layer $[B^{III}_2B^{IV}_2O_5(OH)\cdot B^{III}_2B^{IV}_2O_5(OH)]^{4nn-}_{nn}$	Biringuchite $Na_4[B_{10}O_{16}(OH)_2]_{nn}\cdot 2H_2O = 2Na_2O\cdot 5B_2O_3\cdot 3H_2O$	[70]	(XXVII)
$(2BO_3+3BO_4)+1BO_3$	Cyclochain $[B^{III}_2B^{IV}_{2,5}(OH)_3\times$ $\times B^{III}O_{0,5}(OH)_2]^{2n-}_n$	Caliborite $HKMg_2[B_6O_8(OH)_5]_{2n}\cdot 4H_2O = K_2O\cdot 4MgO\cdot 12B_2O_3\cdot 19H_2O$	[71]	(XXVIII)
$(3BO_3+3BO_4)+2BO_3$	Layer $[B^{III}_3B^{IV}_2O_{9,5}(OH)\cdot B^{III}_2O_{1,5}(OH)_2]^{2nn-}_{nn}$	Strontioborite $Sr[B_8O_{11}(OH)_4]_{nn} = SrO\cdot 4B_2O_3\cdot 2H_2O$ $Ca[B_8O_{11}(OH)_4]_{nn} = CaO\cdot 4B_2O_3\cdot 2H_2O$	[72] [73]	(XXIX) (XXX)
$(3BO_3+3BO_4)+(3BO_3+3BO_4)+2BO_3$	Layer $[B^{III}_3B^{IV}_2O_9(OH)_2\cdot B^{III}_3B^{IV}_2O_{9,5}(OH)\times$ $\times B^{III}_2O_{1,5}(OH)_2]^{4nn-}_{nn}$	Strontioginorite $(Sr, Ca)_2[B_{14}O_{20}(OH)_6]_{nn}\cdot 5H_2O =$ $= 2(Sr, Ca)O\cdot 7B_2O_3\cdot 8H_2O$	[74]	(XXXI)
$(3BO_3+4BO_4)+1BO_3$	Cyclochain[e] $[B^{III}_3B^{IV}_4O_{11}(OH)_2\cdot B^{III}O(OH)]^{4n-}_n$	$Tl_4[B_8O_{12}(OH)_4]_n\cdot H_2O = Tl_2O\cdot 2B_2O_3\cdot 2H_2O$	[68, 32]	(XXXII)
$(4BO_3+5BO_4)+1BO_4+1BO_4$	Layer $\{B^{III}_4B^{IV}_5O_{14}(OH)_4\cdot[B^{IV}O(OH)_2]_2\}^{7nn-}_{nn}$	Preobrazhenskite $HMg_2[B_{11}O_{16}(OH)_8]_{nn} = 6MgO\cdot 11B_2O_3\cdot 9H_2O$	[75]	(XXXIII)

[a] In order to maintain a unified treatment, on passing to the CRU of the anhydrous borates (see Section III), the subunits in the CRU and the CRU in the macroanions are distinguished in Fig. 2 with respect to the connecting oxygen atoms[35] and not the boron–oxygen bonds.[25,34] For this reason, whereas the formulae of the CRU are identical, those of the subunits differ somewhat from those adopted in the literature.[25,34]

[b] The initial preoligomer is illustrated in Fig. 1 (*D*, *b*); the formation of the polyanion is illustrated schematically in Fig. 6.

[c] A characteristic feature of the phylloanion of this borate is the grafting of side branches ($2BO_3 + 1BO_4$) to the main chain of the hydroboracite type—see (III) and (IV) in Table 1, as well as the cross-linking of these chains into layers via B–OH–B bridges[69] and not B–O–B bridges as is usually the case. Since two oxygen atoms (at the sites corresponding to grafting and cross-linking) are tricoordinate (with 2B and 1 H), the charge of the CRU does not agree with the number of B^{IV} atoms in it and is in fact equal to only −1 and not −3 [cf. also with (XX)–(XXII) in Table 1 and (XXIX)–(XXXI) in the present Table].

[d] The initial preoligomer is illustrated in Fig. 1 (*D*, *a*).

[e] The CRU of the polyanion of the given borate can be regarded also as the dimer of the CRU of compound (XXIV) in the present Table.

and $Mg_2\{[B_4O_7]_{nnn}\}_2$, (XLIX) in Table 3,[101] and preobrazhenskite, (XXXIII) in Table 2, is converted into a mixture of $Mg_2\{[B_4O_7]_{nnn}\}_2$ and $Mg_2B_2O_5$ with a dimeric anion (on further heating, the former melts incongruently decomposing into the same compound $Mg_2B_2O_5$ and B_2O_5, which are in fact the final products of the thermal transformation of preobrazhenskite[103]). In the polymer chemistry of phosphates, this type of opening and transformation of the rings is attributed to heterolytic cleavage and the formation of zwitter-ions, the polymerisation proceeding subsequently in accordance with an ionic mechanism (Ref. 5, p. 91). As regards borates, it is known only (in relation to the so called calcium "octaborates", which are in fact tetraborates[108]), that although neither they themselves nor their dehydration products are electrically conducting, nevertheless electrical conductivity appears at the temperature of the BR [109] despite the fact that T_m is higher by 100 °C. However, electrical conductivity can be manifested also on homolytic cleavage of the rings accompanied by the appearance of radicals. EPR studies on the BR as well as its initiation by different methods might throw light on this question. Hitherto BR has been initiated mainly thermally, although in the chemistry of macromolecular compounds the radiation, mechanochemical, and other methods are used for the initiation of solid-phase polymerisation.[105]¶

The examples presented demonstrate differences in the structures of hydrated and anhydrous borates even when these contain the same cations and show that it is useful to consider separately these genetically interrelated compounds.

¶ Phenomena analogous to the BR effect are not a unique feature of borates. They occur also in the thermal transformations of aluminosilicates, for example, kaolinite (which consists of alternating polysiloxane and polyaluminoxane phylloanions[4] and is a component of natural clays), into mullite and silicon dioxide.[110] The latter are ingredients in the compositions of ceramic materials whose polymer-colloidal nature and composition are complex.[6,111]

III. ANHYDROUS OXOBORATES

1. Crystalline Compounds

The main methods for the preparation of crystalline anhydrous oxoborates are the BR considered above (for amorphous powders), synthesis from solutions or melts under normal and increased pressures, and also heat treatment of vitreous borates below T_m. In the last case, the process resembles the BR as regards its chain character (induction period, autoacceleration) the physical properties (density and hardness) of the crystals obtained from the amorphous powders and vitreous systems being identical.[77]

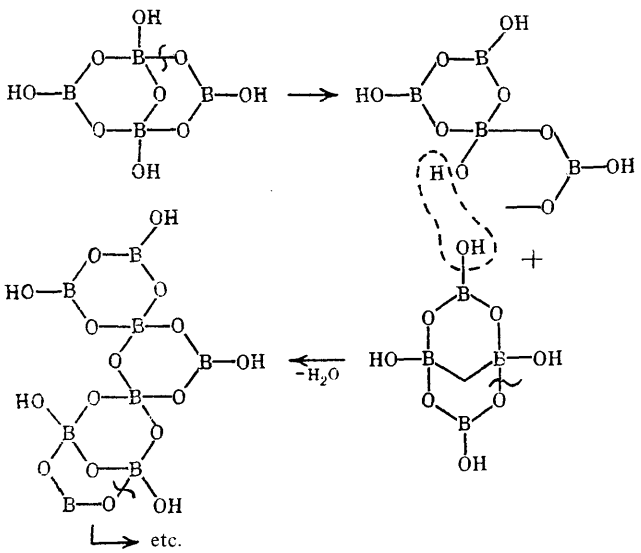


Figure 6. Schematic representation of the polymerisation reaction of borax to give kernite.[25]

The main principles governing the formation of the structures[26] are described below taking into account the postulates of the chemistry of macromolecular compounds.

1. The simplest groups in the structures are BO_3 and BO_4.

2. The monomeric and dimeric anions are made up only of BO_3 or only BO_4.

3. The simplest groups (subunits) can function as the CRU of the macroanions, which are usually formed as a result of the linking of the vertices of the BO_3 triangles and BO_4 tetrahedra via the *p*-bridges >B–O–B<, >B–O–B–, or –B–O–B–.†

4. Oligoanions with $n \geq 3$ can exist in the structures of anhydrous borates, but such oligoanions are more common as the CRU of the macroanions with a structure specific to anhydrous borates.

5. A decrease of M_xO_y/B_2O_3 (i.e. an increase of the modulus m) and an increase of the size of the metal cations (to a lesser extent) lead to an increase of the degree of polymerisation and of the density of the cross-linking of the macroanions (and also of the ratio BO_3/BO_4 for $M_xO_y/B_2O_3 \lesssim 1$), while an increase of the charge of the cations M^{y-} induces the opposite tendency.

6. Each O atom is usually linked to two B atoms (the ratio $BO_3/BO_4 = m - 1$ is valid for such compounds having the composition $nM_xO_y.mB_2O_3$ when $m > 1$), but terminal (non-bridging) oxygen ions and transitional (bridging) oxygen atoms with hybrid coordinations with respect to boron of 3 and even 4 can be encountered.#

7. The phyllo- and tekto-anions of the anhydrous M^+ and M^{2+} borates exhibit a tendency towards twinning, frequently with formation of interpenetrating polymer networks (IPN).

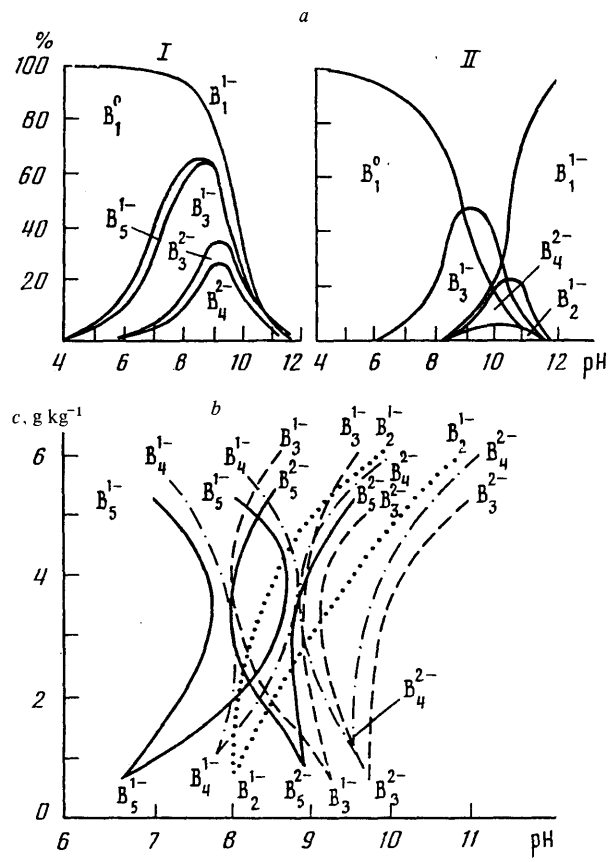
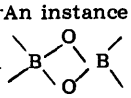


Figure 7. Borate homologues in aqueous solutions (B_n^{m-} is an abbreviated designation of the corresponding borates presented in Fig.1): *a*) the fraction of the corresponding borate as a function of the pH of the solution at a boron concentration $c = 0.4$ M and $T = 298$ K (I) and also at $c = 0.6$ M and $T = 393$ K; the regions where they predominate as a function of the pH and the boron concentration c in the range 1–6 g kg^{-1} according to the data of Farmer[34] and Ozol[82]).

†An instance of the polymerisation of the BO_4 tetrahedra via  bridges is known—see (XCIX) in Table 4 and the corresponding remark in the same Table.

#See Figs. 9–12.

Fig. 8 presents the known varieties of the mono-, di-, and oligo-anions in the fully ionised (cationic) form. Specific examples of such borates are not considered here, as for hydrated borates in Section II. We shall only note that the pentaborate (Fig. 8, *D*), which is not mentioned in the monograph of Leonyuk and Leonyuk,[26] has been discovered in the structure $Bi_3O[B_5O_{11}] = 3Bi_2O_3.5B_2O_3$,[112] while the oligomer (Fig. 8, *E*) has been found in the structure $Pb_6.[B_{10}O_{21}] = 6PbO.5B_2O_3$.[113] The latter is not in fact a decaborate and consists of a modified (combined) oligoanion (two tetraborates grafted to one another via two BO_3 triangles).

Fig. 9 presents examples of the "usual" CRU in the macroanions of anhydrous crystalline borates and Table 3 lists the corresponding specific compounds.

Fig. 10 presents modified (combined) CRU and Table 4 the corresponding borates.

The fragments of the macroanions of certain borates quoted in Tables 3 and 4 are illustrated in Figs. 11 and 12. Fig. 13 demonstrates the formation of IPN.

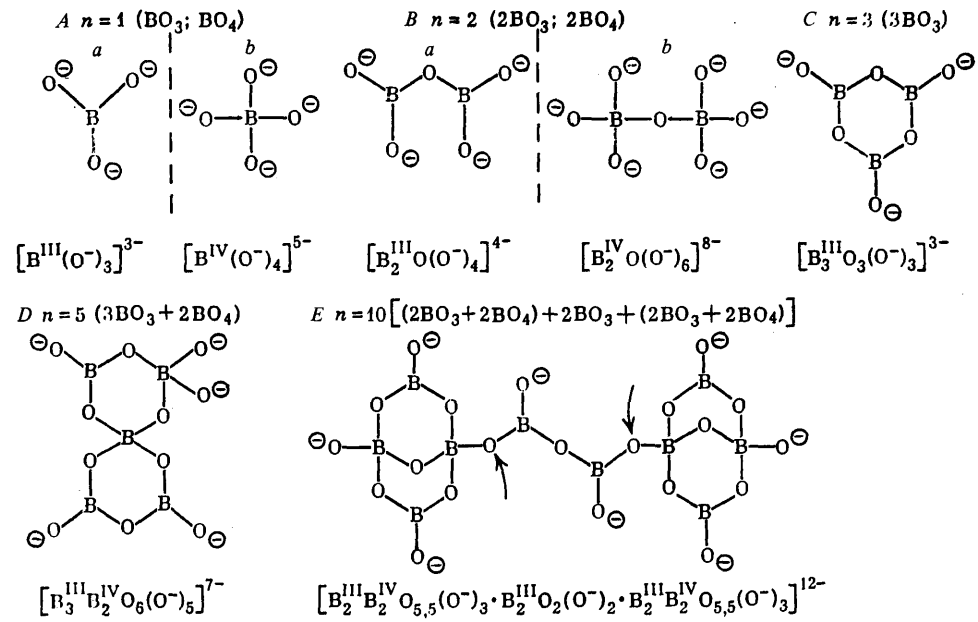


Figure 8. The monoanions, dianions, and oligoanions of anhydrous crystalline borates in the fully ionised (cationic) form.

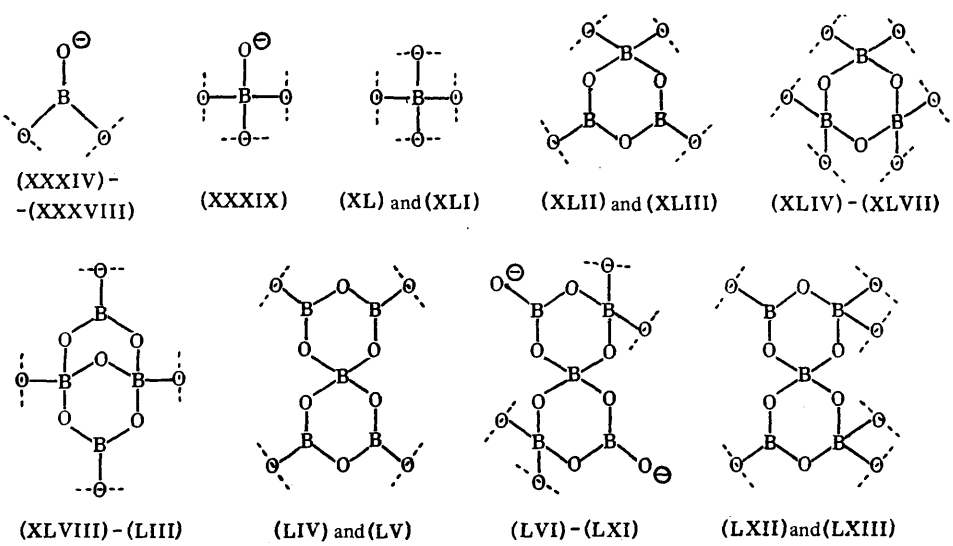


Figure 9. Examples of the "usual" CRU in the macroanions of anhydrous crystalline borates (the Roman numerals correspond to those adopted in Table 3 for specific compounds).

From the standpoint of the chemistry of macromolecular compounds, it is evident that, when the individual BO_3 (or BO_4) groups are linked predominantly by covalent bonds to other elementoxane groups (SiO_4, PO_4, AlO_4, etc.), forming the corresponding macroanions with the linkages B–O–E (for example, in the chain polyanions of calcium[175] or strontium[176] aluminoborates), then they are no longer isolated[26] and enter, in the form of subunits of a new kind, into the composition of the corresponding CRU in inorganic polyborelementoxanes, which are not considered here. Conversely, compounds of the type $La_2O_3.B_2O_3.2MoO_3$ and $La_2O_3.B_2O_3.2WO_3$ [compounds (XXXVII) and (XXXVIII) in Table 3], in the structure of which discrete MoO_4 and WO_4 tetrahedra are not in contact either with one another or with the chain polyboroxane polyanion, are not copolymers (inorganic polyboroelementoxanes) from the standpoint of the chemistry of macromolecular compounds, i.e. are not boromolybdates and borotungstates,[26] since the polyanions contain only B–O–B linkages. These compounds should be regarded rather as mixtures of a polyborate with a monomolybdate or

Table 3. Examples of polymeric anhydrous crystalline borates with the "usual" CRU (see also Figs. 9 and 11).

CRU[a] of macroanions	Initial monomer or preoligomer	Form and formula of macroanion	Examples of specific compounds	Refs.	Designation
Monoborate	BO_3	Chain $[B^{III}O(O^-)]_n^{n-}$	$Li[BO_2]_n=\alpha\text{-}Li_2O\cdot B_2O_3$	[114]	(XXXIV)
			$Ca[(BO_2)_2]_n=CaO\cdot B_2O_3$—I	[115]	(XXXV)
			$Eu[(BO_2)_3]_n=EuO\cdot B_2O_3$	[116]	(XXXVI)
			$La_2[(BO_2)_3]_n\cdot[MoO_4]_3=La_2O_3\cdot B_2O_3\cdot 2MoO_3$	[117]	(XXXVII)
			$La_2[(BO_2)_3]_n\cdot[WO_4]_3=La_2O_3\cdot B_2O_3\cdot 2WO_3$	[117]	(XXXVIII)
	BO_4	Layer[b] $[B^{IV}O_{3.5}(O^-)]_{nn}^{2nn-}$	$NdAl_3O_{0.5}[(BO_{2.5})_4]_{nn}=Nd_2O_3\cdot 2Al_2O_3\cdot 4B_2O_3$	[118]	(XXXIX)
		Network $[B^{IV}O_2]_{nnn}^{nnn-}$	$Li[BO_2]_{nnn}=\gamma\text{-}Li_2O\cdot B_2O_3$	[119]	(XL)
			$Zn_4O[(BO_2)_6]_{nnn}=4ZnO\cdot 3B_2O_3$[a]	[120]	(XLI)
Triborate	$2BO_2^e+1BO_4$	Network $[B_2^{III}B^{IV}O_5]_{nnn}^{nnn-}$	$Cs[B_3O_5]_{nnn}=Cs_2O\cdot 3B_2O_3$	[121]	(XLII)
			$Li[B_3O_5]_{nnn}=Li_2O\cdot 3B_2O_3$	[122]	(XLIII)
	$3BO_4$	Network[d] $[B_2^{IV}O_5]_{nnn}^{3nnn-}$	$Ca_2[(B_3O_6)_2]_{nnn}=CaO\cdot B_2O_3$—IV	[123]	(XLIV)
			$Sr_2[(B_3O_6)_2]_{nnn}=SrO\cdot B_2O_3$—IV	[124]	(XLV)
			$Cu_2[(B_3O_6)_2]_{nnn}=CuO\cdot B_2O_3$	[125]	(XLVI)
			$Pd_2[(B_3O_6)_2]_{nnn}=PdO\cdot B_2O_3$	[126]	(XLVII)
Tetraborate[e]	$2BO_2+2BO_4$	Network (two IPN)[f] $\{[B_2^{III}B_2^{IV}O_7]_{nnn}^{3nnn-}\}_2$	$Li_4\{[B_4O_7]_{nnn}\}_2=Li_2O\cdot 2B_2O_3$	[127]	(XLVIII)
			$Mg_2\{[B_4O_7]_{nnn}\}_2=MgO\cdot 2B_2O_3$	[128]	(XLIX)
			$Mn_2\{[B_4O_7]_{nnn}\}_2=MnO\cdot 2B_2O_3$	[129]	(L)
			$Zn_2\{[B_4O_7]_{nnn}\}_2=ZnO\cdot 2B_2O_3$	[130]	(LI)
			$Cd_2\{[B_4O_7]_{nnn}\}_2=CdO\cdot 2B_2O_3$	[131]	(LII)
			$Fe_2\{[B_4O_7]_{nnn}\}_2=FeO\cdot 2B_2O_3$	[132]	(LIII)
Pentaborate	$4BO_2+1BO_4$	Network (two IPN)[g] $\{[B_4^{III}B^{IV}O_8]_{nnn}^{nnn-}\}_2$	$K_2\{[B_5O_8]_{nnn}\}_2=\alpha\text{-}K_2O\cdot 5B_2O_3$	[133]	(LIV)
			$K_2\{[B_5O_8]_{nnn}\}_2=\beta\text{-}K_2O\cdot 5B_2O_3$	[134]	(LV)
	$2BO_2+3BO_4$	Layer $[B_2^{III}B_3^{IV}O_8(O^-)_2]_{nn}^{3nn-}$	$LaCo[B_5O_{10}]_{nn}=La_2O_3\cdot 2CoO\cdot 5B_2O_3$	[135]	(LVI)
			$NdCo[B_5O_{10}]_{nn}=Nd_2O_3\cdot 2CoO\cdot 5B_2O_3$	[136]	(LVII)
			$SmCo[B_5O_{10}]_{nn}=Sm_2O_3\cdot 2CoO\cdot 5B_2O_3$	[137]	(LVIII)
			$HoCo[B_5O_{10}]_{nn}=Ho_2O_3\cdot 2CoO\cdot 5B_2O_3$	[138]	(LIX)
			$YCo[B_5O_{10}]_{nn}=Y_2O_3\cdot 2CoO\cdot 5B_2O_3$	[139]	(LX)
		Layer $[B_2^{III}B_3^{IV}O_9]_{nnn}^{3nnn-}$	$LaMg[B_5O_{10}]_{nn}=La_2O_3\cdot 2MgO\cdot 5B_2O_3$	[140]	(LXI)
			$Eu_2[B_5O_9]_{nnn}\cdot Cl=3EuO\cdot EuCl_3\cdot 5B_2O_3$	[141]	(LXII)
			$Eu_2[B_5O_9]_{nnn}\cdot Br=3EuO\cdot EuBr_3\cdot 5B_2O_3$	[141]	(LXIII)

[a] The CRU of the macroanions[27] may not be identical with the stereorepeating units; for example, the stereorepeating units in compounds (XXXIV)–(XXXVIII) are made up of two BO_3 triangles.

[b] When the tetrahedra are joined together into chains, the stereorepeating unit is $2BO_4$, when the chains are joined up to form a layer, rings consisting of six BO_4 are produced, and when the layers alternate, the $\rightarrow B-O^-$ terminal bonds in the layers are alternately directed to one side or another of the layer, so that overall a structure similar to micas is formed.[4]

[c] The tetrahedra in the tektoanion of this borate are linked in such a way that a "Chinese lantern" with six "windows" (rings made up of $4BO_4$) and eight "windows" (rings made up of $6BO_4$) is produced.

[d] Although the borates (XLIV) and (XLV) have identical CRU, they differ from compounds (XLVI) and (XLVIII) in the way that the CRU are joined together in space.

[e] As in Section II, the "kernite-like" CRU have been classified as modified units—see compounds (LXX) and (LXXI) in Table 4.

[f] Although the borate (XLVIII) has the same CRU, it differs from compounds (XLIX)–(LIII) in the stereorepeating units.

[g] The borates (LIV) and (LV) differ in the disposition of the CRU relative to the double rotational axes (in one case the axes pass near the ends of the pentaborate groups and in the other they pass virtually through their centres).

tungstate just as compounds (XII) and (XIII) in Table 1 are mixtures of phylloborates with monoborate.

It is seen from the data presented that the macroanions of anhydrous crystalline borates are more complex and varied than the hydrated macroanions (see also, Section IV). Modified CRU, distinguished by a great variety, are encountered among them more frequently. The macroanions themselves have a three-dimensional structure and more rarely two- and mono-dimensional structures. Network macroanions then tend to form IPN. All these factors prevent a stereoregular packing of the macroanions, greatly hindering the formation of polymeric single crystals of anhydrous borates. This requires the maintenance of a series of special conditions, including prolonged isothermal treatment, the introduction of seeds, etc.[26] When polymeric borate melts are cooled in the usual way, they pass to a vitreous state.

2. Vitreous Oxoborates

Many borates, including the borates of all the Group IA and IIA elements, zinc and cadmium (Group IIB), thallium (Group IIIA), lanthanum (IIIB), lead (Group IVA), and bismuth (Group VA),[7] tellurium (Group VIA),[177] and other elements, let alone binary and more complex borates, have been obtained in a vitreous state. In contrast to the crystalline borates, the vitreous borates are non-equilibrium systems, i.e. in any specific borate glass one of the many structures characteristic of melts having the same composition is fixed.

Table 5 makes it possible to compare the boundaries of the glass formation regions in certain borate systems[177,178] with data concerning the crystalline compounds existing in these regions.[179] It is easily seen that all the compounds with known structures are in this instance the polymers listed

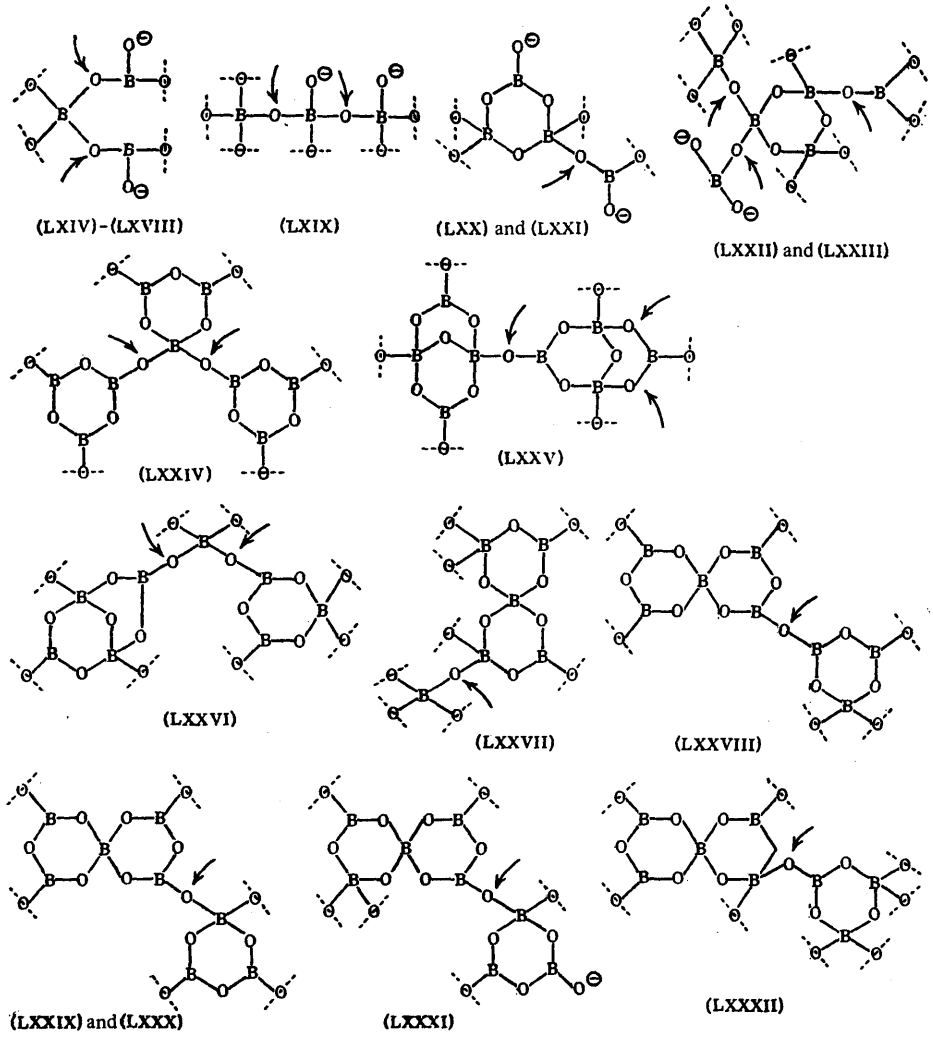


Figure 10. Examples of modified (combined) CRU in the macroanions of anhydrous crystalline borates in Table 4 (the notation is analogous to that adopted in Figs. 2 and 9); for the CRU of the macroanions (XCVI)–(XCVIII), the numerals opposite the connecting oxygen atoms sp^2-hybridised with respect to boron represent the fraction of such atoms contributed by neighbouring CRU.

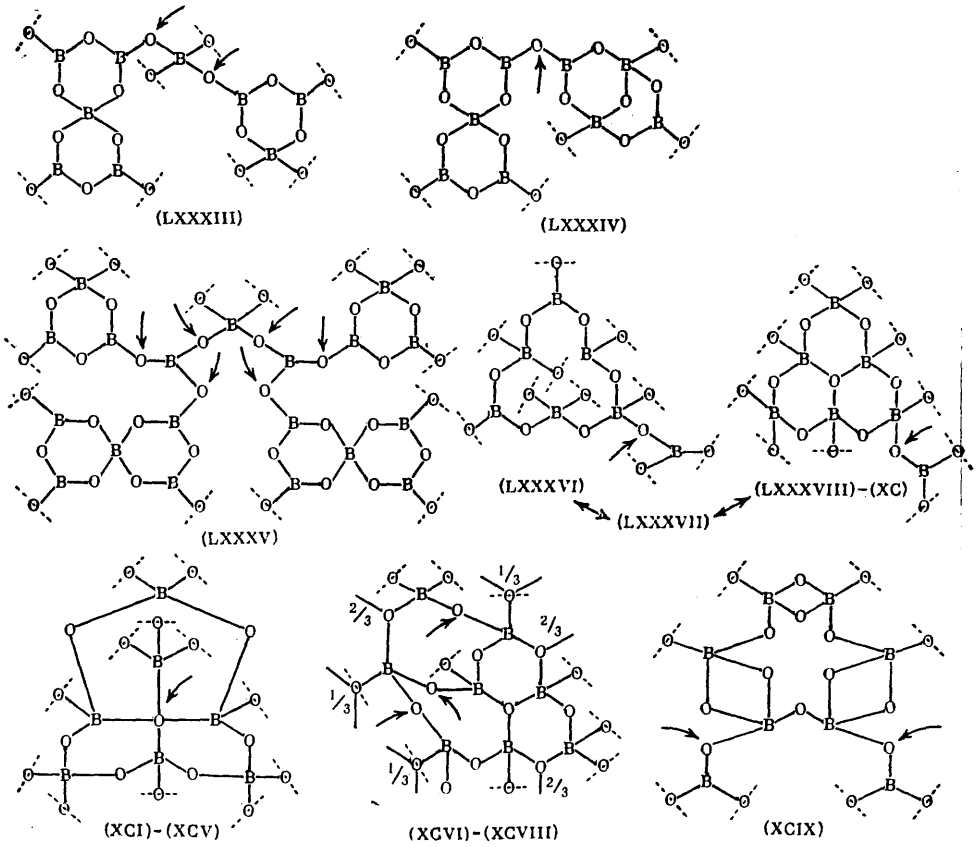


Figure 10 (contd.).

in Tables 3 and 4. This suggests that the structures which have not so far been elucidated also have a polymeric structure (or at least an oligomeric structure with $n \geq 5$).

The glass formation regions are usually bounded by compositions forming optically homogeneous glasses (these boundaries depend on the experimental conditions—the volume of the melt and the rate of its cooling). Polymeric borates can also form optically inhomogeneous glasses. In one case these are liquating glasses,[181,182] the appearance of which is a consequence of the immiscibility, with phase inversion, characteristic of colloidal polymer systems.[183] In another these are partly crystallising glasses, whose formation may be caused by the crystallisation of chain polyanions with a simple configuration or by the formation of rigid networks of the type of boracites. In the latter case, the fraction of flexible B–O–B bonds diminishes as the transitional O atoms undergo a change from a state involving *sp*-hybridisation to states involving sp^2- and sp^3-hybridisation with B atoms (the –O– bridges are replaced by $\overset{|}{\underset{/\backslash}{O}}$ and even $-\overset{|}{O}-$), i.e. the configurational-conformational statistics of the polymers is impoverished. However, the low-molecular-weight anionic fraction, especially monomeric borates, crystallises most readily, even under conditions where the melts are subjected to intense cooling. In other words, the tendency of a particular substance towards glass formation is determined not only and not so much by kinetic as by structural factors.[184] Among them, the leading role is due to the presence in the structure of atoms or groups of atoms connected by directional bonds[184]§ and such structures should possess fairly pronounced flexibility, ensuring a definite set of conformations and configurations (see Section IV).

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§The latter agrees with all the criteria of the polymeric structure of matter.[1,185]

The fact that glasses are formed in boron oxide–zinc oxide (cadmium, lead, and bismuth oxide) systems when the B_2O_3 content is less than 50 mole % suggests that the above elements are incorporated into the macroanionic network of the glass with formation of B–O–E linkages.[7] In particular, this has been confirmed for the $PbO–B_2O_3$ system by NMR data[7] and for the $ZnO–B_2O_3$ system by the results of the EPR study of the mechanodegradation of the corresponding

Table 4. Examples of polymeric anhydrous crystalline borates with modified (combined) CRU (see also Figs. 10 and 12).

Grafted groups (CRU subunits)	Form and formula of macroanion	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$1BO_3+1BO_4+1BO_3$	Cyclochain[a] $[B^{III}O(O^-)\cdot B^{IV}O_2\cdot B^{III}O(O^-)]_n^{2n-}$ Layer[b] $[B^{III}O(O^-)\cdot B^{IV}O_2\cdot B^{III}O(O^-)]_{nn}^{2nn-}$	$La[B_3O_6]_n=La_2O_3\cdot 3B_2O_3$ $Nd[B_3O_6]_n=Nd_2O_3\cdot 3B_2O_3$ $Sm[B_3O_6]_n=Sm_2O_3\cdot 3B_2O_3$ $Gd[B_3O_6]_n=Gd_2O_3\cdot 3B_2O_3$ $Bi[B_3O_6]_{nn}=Bi_2O_3\cdot 3B_2O_3$	[142] [143] [144] [144] [145]	(LXIV) (LXV) (LXVI) (LXVII) (LXVIII)
$1BO_4+1BO_4+1BO_4$	Layer[c] $[B^{IV}O_2\cdot B^{IV}O_{1.5}(O^-)\cdot B^{IV}O_{1.5}(O^-)]_{nn}^{2nn-}$	Yohachidolite $CaAl[B_3O_7]_{nn}=2CaO\cdot Al_2O_3\cdot 3B_2O_3$	[146]	(LXIX)
$(1BO_3+2BO_4)+1BO_3$[r]	Cyclochain $[B^{III}B_2^{IV}O_6(O^-)\cdot B^{III}O(O^-)]_n^{4n-}$	Calciborite $Ca_2[B_4O_8]_n=CaO\cdot B_2O_3$—II $Ag_4[B_4O_8]_n=Ag_2O\cdot B_2O_3$	[147] [148]	(LXX) (LXXI)
$3BO_4+1BO_4+1BO_3+1BO_3$	Network $[B_3^{IV}O_6\cdot B^{IV}O_2\cdot B^{III}O_{1.5}\cdot B^{III}O_{0.5}(O^-)_2]_{nnn}^{3nnn-}$	$Ca_2[B_6O_{12}]_{nnn}=CaO\cdot B_2O_3$—III $Sr_2[B_6O_{12}]_{nnn}=SrO\cdot B_2O_3$—III	[149] [124]	(LXXII) (LXXIII)
$3BO_3+(2BO_3+1BO_4)+3BO_3$	Network (two IPN) $\{[B_3^{III}O_{4.5}\cdot B_2^{III}B^{IV}O_5\cdot B_3^{III}O_{4.5}]_{nnn}^{nnn-}\}_2$	$Cs_2\{[B_9O_{14}]_{nnn}\}_2=\beta\text{-}Cs_2O\cdot 9B_2O_3$	[150]	(LXXIV)
$(2BO_3+2BO_4)+(1BO_3+2BO_4)+1BO_3$	Network $[B_2^{III}B_2^{IV}O_7\cdot B^{III}B_2^{IV}O_{5.5}\cdot B^{III}O_{1.5}]_{nnn}^{4nnn-}$	$K_4[B_8O_{14}]_{nnn}=K_2O\cdot 2B_2O_3$	[151]	(LXXV)
$(2BO_3+2BO_4)+1BO_4+(2BO_3+1BO_4)$	Network $[B_2^{III}B_2^{IV}O_7\cdot B^{IV}O_2\cdot B_3^{III}B^{IV}O_5]_{nnn}^{4nnn-}$	$Ca_2[B_8O_{14}]_{nnn}=CaO\cdot 2B_2O_3$—II	[152]	(LXXVI)
$(2BO_3+3BO_4)+1BO_4$	Network $[B_2^{III}B_2^{IV}O_9\cdot B^{IV}O_2]_{nnn}^{4nnn-}$	$Ca_2[B_8O_{11}]_{nnn}=2CaO\cdot 3B_2O_3$	[153]	(LXXVII)
$(4BO_3+1BO_4)+(2BO_3+1BO_4)$	Network (two IPN)[e] $\{[B_4^{III}B^{IV}O_8\cdot B_2^{III}B^{IV}O_5]_{nnn}^{3nnn-}\}_2$	$Na_4\{[B_6O_{13}]_{nnn}\}_2=\alpha\text{-}Na_2O\cdot 4B_2O_3$ $Ag_{3.4}Na_{1.6}\{[B_6O_{13}]_{nnn}\}_2=0{,}6\ Ag_2O\cdot 0{,}4\ Na_2O\cdot 4B_2O_3$ $Ba_2\{[B_6O_{13}]_{nnn}\}_2=BaO\cdot 4B_2O_3$	[154] [155] [156]	(LXXVIII) (LXXIX) (LXXX)
$(3BO_3+2BO_4)+(2BO_3+1BO_4)$	Layer $[B_2^{III}B_2^{IV}O_{6.5}\cdot B_2^{III}B^{IV}O_{4.5}\times$ $\times(O^-)]_{nn}^{4nn-}$	$Na_2[B_2O_{14}]_{nn}=\alpha\text{-}Na_2O\cdot 2B_2O_3$	[157]	(LXXXI)
$(3BO_3+2BO_4)+(1BO_3+2BO_4)$	Network $[B_3^{III}B_2^{IV}O_{6.5}\cdot B^{III}B_2^{IV}O_{6.5}]_{nnn}^{4nnn}$	$Ba_2[B_8O_{14}]_{nnn}=BaO\cdot 2B_2O_3$	[158]	(LXXXII)
$(4BO_3+1BO_4)+1BO_4(2BO_3+1BO_4)$	Layer (2 layers)[f] $\{[B_4^{III}B^{IV}O_8\cdot B^{IV}O_2\cdot B_2^{III}B^{IV}O_5]_{nn}^{3nn-}\}_2$	$Na_6\{[B_6O_{13}]_{nn}\}_2=\beta\text{-}Na_2O\cdot 3B_2O_3$	[159]	(LXXXIII)
$(4BO_3+1BO_4)+(2BO_3+2BO_4)$	Network (two IPN)[g] $\{[B_4^{III}B^{IV}O_8\cdot B_2^{III}B_2^{IV}O_7]_{nnn}^{3nnn-}\}_2$	$Na_6\{[B_6O_{12}]_{nnn}\}_2=\alpha\text{-}Na_2O\cdot 3B_2O_3$	[160]	(LXXXIV)
$1BO_4+2\cdot[(4BO_3+1BO_4)+1BO_3+$ $+(2BO_3+1BO_4)]$	Network $[B^{IV}O_4\cdot 2(B_4^{III}B^{IV}O_8\cdot B^{III}O_{1.5}\times$ $\times B_2^{III}B^{IV}O_5)]_{nnn}^{8nnn-}$	$K_6[B_{19}O_{31}]_{nnn}=5K_2O\cdot 19B_2O_3$	[161]	(LXXXV)
$(3BO_3+3BO_4)+1BO_3$	Network[h] $[B_2^{III}B_3^{IV}O_{10.5}\cdot B^{III}O_{1.5}]_{nnn}^{3nnn-}$	$Li_4Cl[B_7O_{12}]_{nnn}=\gamma\text{-}3Li_2O\cdot 2LiCl\cdot 7B_2O_3$ $Li_5Cl[B_7O_{12.5}]_{nnn}=4Li_2O\cdot 2LiCl\cdot 7B_2O_3$[i]	[162] [163]	(LXXXVI) (LXXXVII)

Table 4 (cont'd).

Grafted groups (CRU subunits)	Form and formula of macroanion	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$6BO_4+1BO_3$	Network $[B^{IV}_6O_{11,5}\cdot B^{III}O_{1,5}]^{snnn-}_{nnn}$	α-Boracite $Mg_6Cl[B_7O_{13}]_{nnn}$=α-5MgO·MgCl$_2$·7B$_2$O$_3$ $Fe_{2,4}Mg_{3,6}Cl[B_7O_{13}]_{nnn}$ = 5(Fe, Mg)O·(Fe, Mg)Cl$_2$·7B$_2$O$_3$ $Ni_3Br[B_7O_{13}]_{nnn}$=5NiO·NiBr$_2$·7B$_2$O$_3$	[164] [164] [165]	(LXXXVIII) (LXXXIX) (XC)
$7BO_4$	Network $[B^{IV}_7O_{12}]^{snnn-}_{nnn}$	β-Boracite $Mg_6Cl[B_7O_{13}]_{nnn}$=β-5MgO·MgCl$_2$·7B$_2$O$_3$ $Mg_3Br[B_7O_{13}]_{nnn}$=5MgO·MgBr$_2$·7B$_2$O$_3$ $Co_3I[B_7O_{13}]_{nnn}$=5CoO·CoI$_2$·7B$_2$O$_3$ $Cu_3Br[B_7O_{13}]_{nnn}$=5CuO·CuBr$_2$·7B$_2$O$_3$ $Cd_3S_{0,9}[B_7O_{13}]_{nnn}$=5CdO·CdS·7B$_2O_3$	[166] [167] [168] [168] [169]	(XCI) (XCII) (XCIII) (XCIV) (XCV)
$6BO_4+2BO_4$	Network $[B^{IV}_6O_{10,5}\cdot B^{IV}_2O_{2,5}]^{snnn-}_{nnn}$	$Eu_2[B_8O_{14}]_{nnn}$=EuO·2B$_2$O$_3$ $Sr_2[B_8O_{14}]_{nnn}$=SrO·2B$_2$O$_3$ $Pb_2[B_8O_{14}]_{nnn}$=PbO·2B$_2$O$_3$	[170] [171] [171]	(XCVI) (XCVII) (XCVIII)
$6BO_4+2BO_3$	Layer[j] $[B^{IV}_6O_{12}\cdot 2B^{III}O_{1,5}]^{snn-}_{nn}$	$Na_4Zn_2MnB_{6,97}O_{11}$=3Na$_2$O·6ZnO·3MnO·7B$_2$O$_3$[k]	[172]	(XCIX)

[a]When two CRU are joined together, a modified tetraborate ring is formed in the chain—see Fig. 12 (LXIV)–(LXVII).

[b]When the CRU are joined together, "windows" consisting of rings made up of ($4BO_3$ + $4BO_4$) are produced in the layer.

[c]When the CRU are joined together, two forms of "windows" consisting of rings made up of $4BO_4$ and $6BO_4$ are produced in the layer.

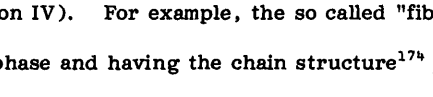
[d]"Kernite-like" CRU—see also (XXIII) and (XXIV) in Table 2.

[e]As can be seen from Fig. 10, compound (LXXVIII) differs from compounds (LXXIX) and LXXX) by the different ways in which the triborate subunit is joined to the pentaborate subunit in the CRU.

[f]Two layers are cross-linked by oxygen bridges (between the pentaborate subunits of the CRU and the BO_4 tetrahedra).

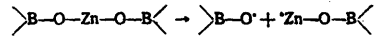
[g]Thus the metastable low-temperature β-form, having the same overall composition as the α-form, undergoes changes both in the steric structure of the macroanions and in the structure of the CRU subunits.

[h]The borate (LXXXVII) has a structure transitional between those of (LXXXVI) and (LXXXVIII). Whereas in compound (LXXXVI) the site of the 13th oxygen atom (at the centre of the ring) is unoccupied, in compound (LXXXVIII) it is fully occupied, while in compound (LXXXVII) it is partially occupied.

[i]If subsequent refinement confirms the interpretation of Bondareva et al.[172], it will be necessary to recognise the possibility of the anion polymerisation not only via B–O–B bridges but also via  B bridges. In this connection one should note that the initial interpretation of the structure of the borate (XCVII) also assumed such a possibility,[173] but subsequently it was regarded as incorrect.[26,171] However, there is no fundamental prohibition of such polymerisation (see also Section IV). For example, the so called "fibrous" *W*-form of silicon dioxide, polymerising from the gas phase and having the chain structure[174] , i.e. the SiO_4 tetrahedra are in this case also joined together via their edges, is known in the chemistry of silicates. However, this product is unstable and after isothermal treatment is gradually transformed into the usual three-dimensional varieties of silicon dioxide (initially, at 473–1073 K, into tridymite and at higher temperatures into cristobalite), where the tetrahedra in the network are joined together in the usual way—via vertices (Si–O–Si) bridges—although different CRU are in fact produced.

[j]Boron is not present solely as part of the composition of the purely borate macroanion and part of it participates in the form of BO_3 triangles together with the ZnO_4 tetrahedra in the construction of the "cationic" part of the structure.[172]

glasses.[186] In the latter case the mechanodegradation of the macroanions involves precisely the B–O–Zn linkages, which are weaker¶ than the B–O–B linkages:[186]



As already mentioned, consideration of such copolymers is outside the framework of this review. The above results[186] have attracted attention primarily because of the very fact of the detection of radicals in the mechanical breakdown of borate glasses, since in low-molecular-weight compounds the dissociation of chemical bonds with formation of radicals does not occur under such an influence,[84] i.e. the phenomenon of mechanodegradation is characteristic of polymers alone.[84] Together with polymer-analogue transformations, the

¶In the terminology of the chemistry of glass,[187] zinc behaves in this instance as a modifier-intermediate.

exchange interaction of the macromolecules, etc. it is a specific chemical property of macromolecular compounds. The macromolecular nature of the substance is also manifested in a series of specific physical properties. These include the capacity for fibre and film formation, adhesion (binding) properties, orientation effects in electric, magnetic, and mechanical fields (in the last case up to crystallisation on stretching), and the ability to pass to the highly elastic state (non-Newtonian flow of melts and solutions, dissolution with preliminary swelling, immiscibility in the plastic state, characteristic features of the change in heat capacity at a low temperature, the presence of a spectrum of relaxation times, etc.[188-190] A number of similar properties have also been shown by vitreous borates.[1,7,184,191-193] The effect associated with the orientation of the structure of the sodium borate glass on vitrification in weak (0.07 and 0.8 T) magnetic fields may serve as one of the new examples of this kind.[194] Similar effects have been observed for organic polymers and diamagnetic liquid crystals and, when the number of elementary units in molecules of such substances is of the order of 10^6–10^8, orientation is already achieved at a magnetic induction $B \approx 0.1$ T.[194]

Overall, the concept of the presence in the structure of a covalently bound element–oxygen "network" is nowadays virtually generally accepted for borate (and other oxides) glasses,[1,7,35,184,187,191-193] etc. In this case the term "network" includes the concept of macroionic element–oxygen chains or segments of these chains (including highly branched chains), two-dimensional layers, and also intrinsically three-dimensional networks and their fragments. Although the discussion concerning the structure of the last features is still continuing,[195,196] as regards vitreous borates,[35] there are numerous experimental data demonstrating the presence in such a "network" of CRU analogous to those shown in Figs. 9 and 10 together with the corresponding metal cation clusters. However, for thermodynamic and kinetic reasons, these CRU are frequently different for crystals and glasses of the same composition, for example,

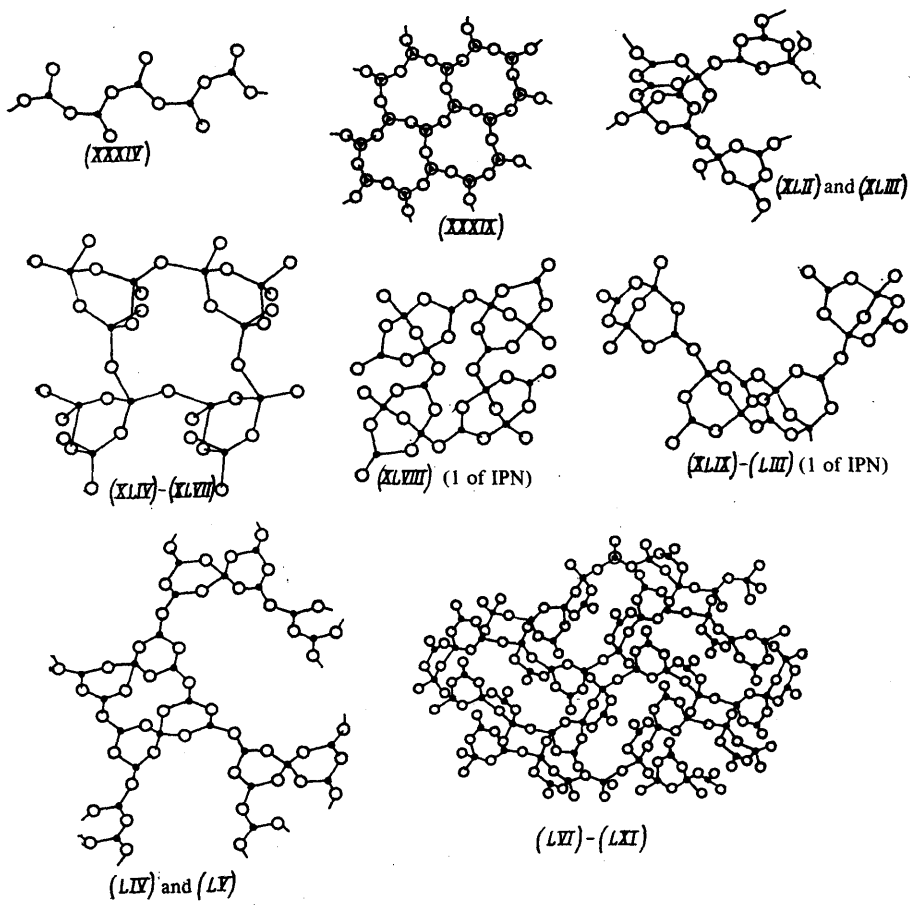


Figure 11. Fragments of the macroanions of certain borates in Table 3.

the $SrO.2B_2O_3$ CRU are not the same in the crystalline and vitreous states.[35] At the same time, the presence in the "network" of borate glasses of CRU analogous to (XXXIV) to (XXXVIII), (XLII) and (XLIII), (XLVIII)–(LIII), and (LIV) and (LV) in Fig. 9 and (LXXVIII) and (LXXXI) in Fig. 10, as well as the CRU subunits (LXXIV) and (LXXV) in the same figure can now be regarded as established.[35] Evidently, BO_3 and BO_4 can also function as independent CRU of the network and its fragments. The idea of a covalently-bound macroionic network in vitreous borates would be incomplete if one disregarded the possibility of its further differentiation already at the polymer–colloidal level of structural organisation (see the next Section).[181–183]

In contrast to the abbreviations Δ and *T* (or *t*) adopted for BO_3 and BO_4 in the crystal chemistry of borates,[25,26] in the chemistry of vitreous borates[35] a more far-reaching

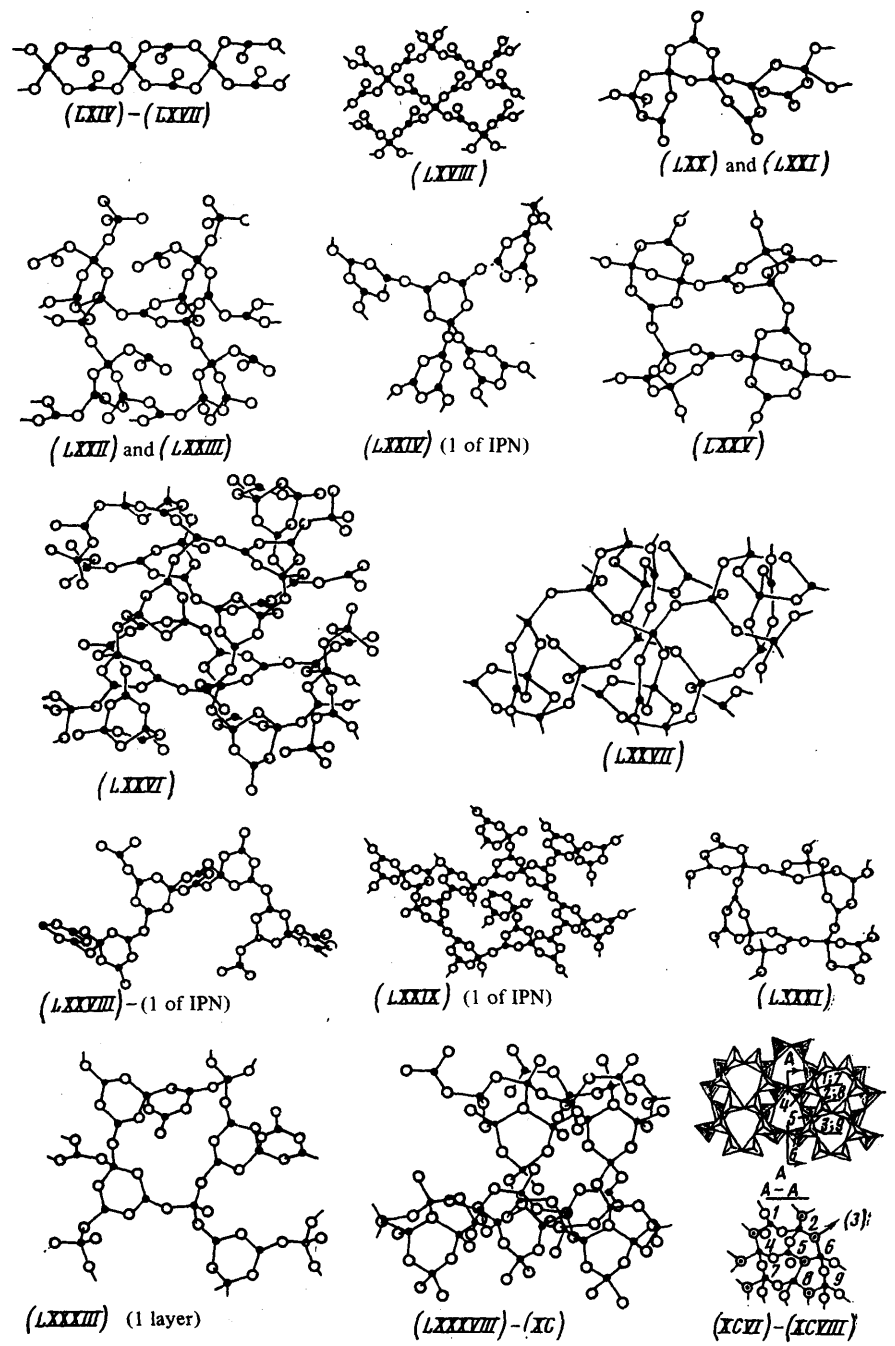


Figure 12. Fragments of the macroanions of certain borates in Table 4 [the A–A view for the clinographic (XCVI)–(XCVIII) projection—cf. with the planar representation of the corresponding CRU in Fig. 10].

gradation has been adopted in the abbreviations for borate groups together with a terminology based on chemical composition and not structure (Table 6). Here it is easy to put $BO_3 = a$, $BO_3' = b$, $BO_3'' = b''$, $BO_3''' = b'''$, $BO_4 = c$, etc. At the same time the term "diborate" for what is actually a tetraborate CRU and the term "tetraborate" for the modified CRU (LXXVIII) in Fig. 10 are unjustified. The use of double Greek prefixes to designate heterochain CRU with identical n ("di-triborate", "di-pentaborate") is also not entirely apt—it implies the dimerisation of the CRU.

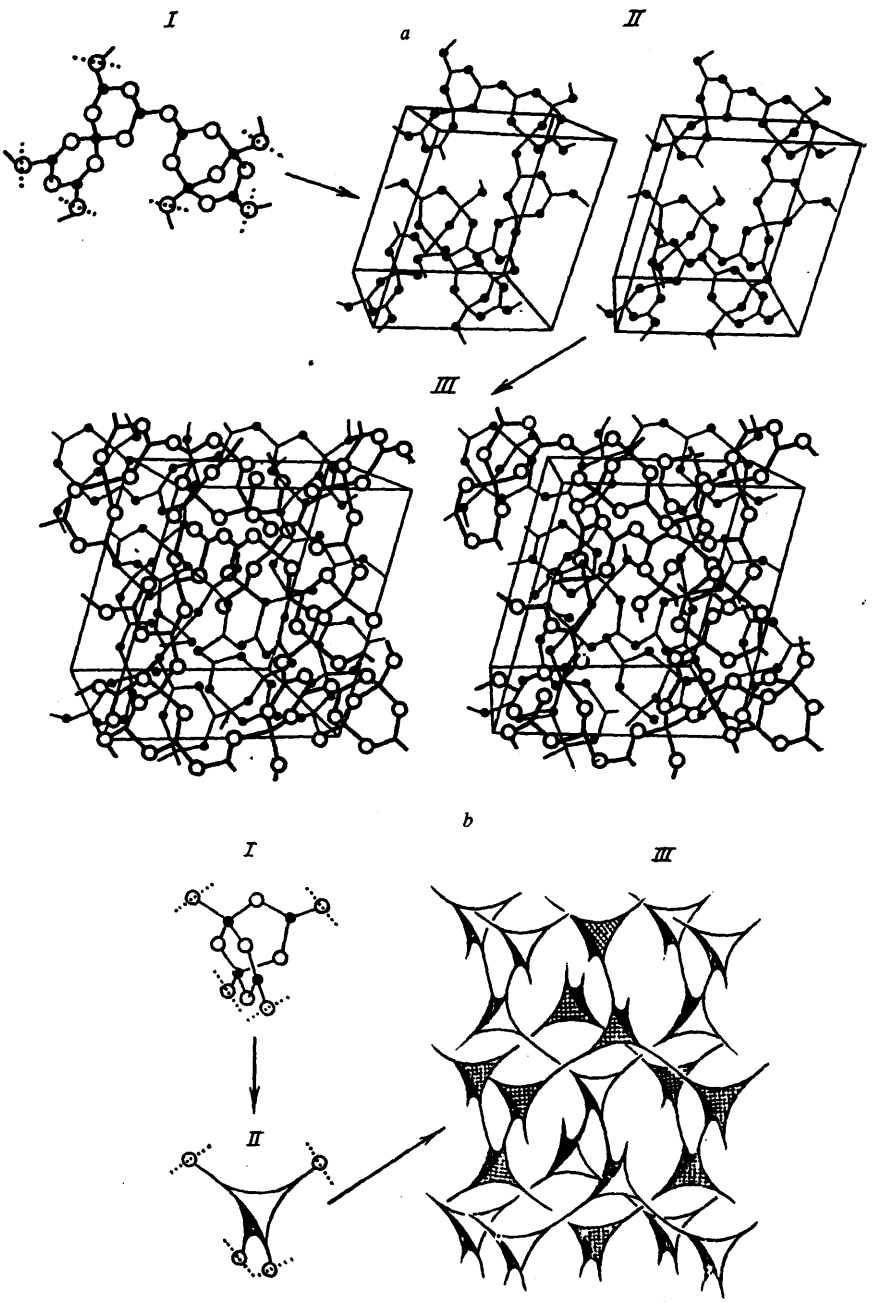


Figure 13. Examples of the formation of the IPN from the macroanions of anhydrous borates: *a*) for the borate (LXXXIV) in Table 4 [stereopairs based on "spherical" models were used: *I*) CRU; *II*) network made up of CRU *I*; *III*) IPN made up of two networks *II*]; *b*) for the borate (XLIX) in Table 3 [a simplified clear model was used: *I*) CRU; *II*) its conventional representation; *III*) IPN made up of two networks *II*].

Here it will be more convenient to invoke ordinal Latin prefixes or, even better, the nomenclature of complex compounds.[29]

In considering vitreous borates, one cannot bypass the question of the so called "borate anomaly" (BA)—the changes in the properties of borates which are non-additive in terms of composition.[35,197] The extrema and inflections in the "composition–property" relations are located predominantly in the regions corresponding to the compositions $2M_2O.5B_2O_3$ and $M_2O.5B_2O_3$ (28.6 and 16.7 mole % M_2O) and for certain properties also when the M_2O content is 4 to 5 mole.[197] Among the different models of the structural

Table 5. Comparative analysis of certain vitreous and crystalline anhydrous borates (see also Table 7).

M_xO_y in the M_xO_y–B_2O_3 system	Limits of glass formation region, mole % M_xO_y (Refs.177, 178)		Crystalline compounds (Ref.179) formed at atmospheric pressure[a] in different composition ranges (mole % M_xO_y)										
	lower	upper	50	46.2	40	37.5	33.3	28.6	25	20.8	20	16.7	10
Li_2O[b]	0	50	α-(XXXIV)	—	—	—	(XLVIII)	?	(XLIII)	—	?	—	?
Na_2O	0 (67)[a]	30 (72)[a]	α-Trimer (Ref.26) β-?	—	?	—	α-(LXXXI) β, γ-?	?	α-(LXXXIV) β-(LXXXIII) γ-?	—	α-(LXXVIII) β-?	α, β, γ-?	α, β, γ-?
K_2O	0	37	Trimer (Ref.26)	—	—	—	(LXXV)	—	?	(LXXXV)	?	α-(LIV) β-(LV)	?[d]
MgO	43.0	44.2	?	α-(XXXVIII) β-(XCI)[e]	?	—	(XLIX)	—	—	—	—	—	—
CaO	27.1	41.1	Phase I (XXXV)	—	(LXXVII)	—	Phase I-? II-(LXXVI)	—	?	—	—	—	—
SrO	24.2	43.0	Phase I-?[f]	—	—	—	(XCVII)	—	?	—	—	—	—
BaO	17.0	39.8	α-? β-Trimer (Ref.26)	—	—	—	(LXXXII)	?	—	—	(LXXX)	—	—
Tl_2O	0	44.5	?	—	—	—	α, β, γ-?	—	?	—	?	?	—
La_2O_3	19.0	28.2	(XXXVII)[g] (XXXVIII)	—	—	—	—	—	(LXIV)	—	—	—	—
ZnO[h]	44.0	63.6 (79.6)	α, β-?	?	—	—	(LI)	—	?	—	—	—	—
CdO	18.9	55.0 (85.4)	—	(XCV)[i]	?	—	(LII)	—	—	—	—	—	—
PbO[h]	20.0	76.5	?	—	—	—	(XCVIII)	—	—	—	—	—	—
Bi_2O_3	22.0	65.3 (85.0)	—	—	—	Pentomer (Ref.112)	—	—	(LXVIII)	—	?	—	—

[a]The macroanions listed in Tables 3 and 4; the literature references are given to the monoanions and oligoanions; ?—the compound is known but its structure has not been elucidated; dash—there is no information about the formation of compounds; α-, β-, and γ- as well as phase I, II—the compound exists in different polymorphic modifications.

[b]Compounds belonging to the Li_2O–$LiCl$–B_2O_3 system are also present in the glass formation region; see compounds (LXXXVI) and (LXXXVII) in Table 4.

[c]The Na_2O–B_2O_3–CO_2 system (effect involving the retention of CO_2 in the structure of borate glasses containing more than 67 mole % Na_2O [180]).

[d]It is appropriate to make a comparison with the structure of caesium borate of the same composition—see compound (LXXIV) in Table 4.

[e]The MgO–$MgCl_2$–B_2O_3 system.

[f]Isostructural with $CaO.B_2O_3$-I according to some data.[26]

[g]The La_2O_3–B_2O_3–MoO_3 and La_2O_3–B_2O_3–WO_3 systems.

[h]For the last four systems, there is a possibility of the incorporation of Zn, Cd, Pb, and Bi into the structure of macroanions in the vitreous state, i.e. the formation of the corresponding copolymers.[7]

[i]The CdO–CdS–B_2O_3 system.

[j]The compound $6PbO.5B_2O_3$, consisting of oligoanions with $n = 10$, is also present in the glass formation region[113] (see Fig.8, *E*).

changes occurring under these conditions, Tarasov's model[184,199] with certain modifications, illustrated in Fig. 14 (here N_4 is the fraction of BO_4 according to NMR data), is thought to be outstanding.[198]

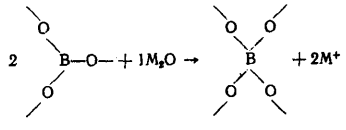
Table 6. The system of notation adopted in the chemistry of vitreous borates.[35]

Borate groups			Names of groups	Symbolic representation[a]
Fig.8	Fig.9	Fig.10		
A, a	—	—	Orthoborate	b'''
B, a	—	—	Pyroborate	b''_2
C	—	—	Cyclic metaborate	b_3
—	(XXXIV)—(XXXVIII)	—	Chain metaborate	b_∞
—	—	Subunit (LXXIV)	Boroxole ring[b]	a_3
—	(XLII) и (XLIII)	—	Triborate	a_2c
—	—	Subunit (LXXXI)	Triborate with one cyclic (non-bridging) oxygen ion	abc
—	—	Subunit (LXXV)	Di-triborate	ac_2
—	(XLVIII)—(LIII)	—	Diborate	a_2c_2
—	(LIV) и (LV)		Pentaborate	a_4c
—	—	Subunit (LXXXI)	Di-pentaborate	a_5c_2
—	—	(LXXVIII)	Tetraborate	a_6c_2

[a]Here *a* represents the BO_3 triangle with all the bridging (connecting) oxygen atoms, *b*, *b''*, and *b'''* represent similar triangles with one, two, and three terminal (non-bridging) oxygen ions, and *c* is the BO_4 tetrahedron with all the bridging (connecting) oxygen atoms [as in the CRU (XL) and (XLI) in Fig. 9]. For example, the CRU (XLII) and (XLIII) in Fig. 9 can be represented by the abbreviated formula a_2C.

[b]This is also the CRU in the layer network of vitreous B_2O_3 [1,35] (although it has been suggested[204] that the model in Fig. 15*c* agrees best with experimental data in this case).

According to this model, as the M_2O/B_2O_3 ratio increases, the (B_2O_3) macromolecules, which are initially of the parquet type (Fig. 14*a*), are cross-linked to form a three-dimensional network (Fig. 14*b*) via the reaction[35]



Next follows the accumulation in the network of non-connecting BO_4' groups, i.e. the terminal $\equiv B-O^-M^+$ groups (Fig. 14*c*) with retention of the maximum density of cross-links attained in the region of x = 25 mole % M_2O. After this, the completion of the "accumulation" of BO_4' is accompanied simultaneously by the degradation of the cross-links between the layers (Fig. 14*d*). The latter then involves bonds between cyclochains in the layer, including the termination of the cyclochains themselves (Fig. 14*e*). Finally, in the composition $M_2O.B_2O_3$, the small Li^+ ions are distributed freely at the terminal O atoms after the degradation of the polyboroxane layers into strips and chains and the capacity for their formation is retained (Fig. 14*f'*). Under these conditions, as in the case of B_2O_3,[1] the CRU in the $Li_2O.B_2O_3$ chains in the vitreous and crystalline states are not identical, since in the former state N_4 = 33.3% while in the latter N_4 = 0. The larger Na^+ and K^+ ions break up the chain into segments as far as the formation of the corresponding cyclic trimers. The capacity for glass formation is then lost (Fig. 14*f''*). Tarasov's model agrees with NMR data and explains satisfactorily a number of the changes in the properties of the vitreous borates.[7,184,200–202] At the same time it can be supplemented by taking into account the idea that some of the boroxole rings in the $(B_2O_3)_C$ structure are opened,[1,203] particularly on passing to melts (Fig. 15).[204] This is the reason for the larger set of CRU in the network and in the fractions of low-molecular-weight anionic groups in borate glasses.[35,200,205]

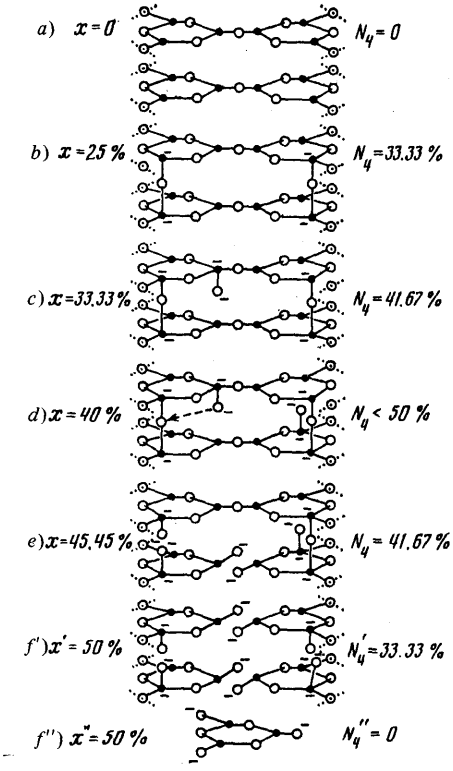


Figure 14. Tarasov's model for the cross-linking-degradation reactions of a network of borate glasses with M_2O contents in the range x = 0–50 mole % (according to Tarasov[184,199]).

This type of model does not exhaust the entire wide variety of mechanisms of the change in the long-range polymeric order in borate glasses (and the BA effect associated with it). For example, the interconversions of the one-, two-, and three-dimensional macroanions and their CRU can change as a result of hydrolysis (the properties of the glasses synthesised *in vacuo* and in air differ[197]). The fraction of the $\equiv B-OH$ end groups (the changes in N_4 are not recorded by NMR) corresponding to 20% mole % M_2O can amount to only 0.002–0.004,[206] but this is not small, because even 0.01–0.1% of cross-linking (destructuring) agents are capable of influencing the course of macromolecular reactions.[189] Since vitreous borates are polyelectrolytes,[207] certain extrema (for example the solubility minimum) can be induced by passage

through the isoelectric point (p*I*).[208] Since acid–base interactions are a fundamental concept in the chemistry of glass,[209] it is to be expected that additional structure-forming oxygen can be introduced into the glass network not only with M_2O (see Fig.14) but also directly from the atmosphere as N_4 is varied.[210,211] From the standpoint of the chemistry of macromolecular compounds, it is also not immaterial in what way the glass network has been formed: (a) by the fusion (congruent or incongruent) of the polymeric single crystal; (b) by the introduction of M_2O into the polymer $(B_2O_3)_C$ (Fig.14); (c) by synthesis from a charge containing monomeric $B(OH)_3$. In the latter case a series of macroanionic reactions, including polycondensation, BR effects (Section II), etc. take place. For example, a mixture of $Li_2O.B_2O_3$, $Li_2O.2B_2O_3$, and $Li_2O.4B_2O_3$ is formed at 873–1173 K from a mixture of H_3BO_3 and Li_2CO_3.[212] Although the exchange interaction[15] can lead to the formation of an equilibrium melt, it remains probable that different conformations of the macroanions, a distribution of their molecular weights, etc. will be observed under different cooling conditions in glasses with identical overall compositions.† Finally, changes in the structural organisation already at the polymeric-colloidal level can exert an appreciable influence on the properties of glasses,[181–183] as will be shown in the next Section.

Table 7. The phase separation regions and parameters in certain borate glass forming systems.[181]

M_xO_y in the M_xO_y–B_2O_3 system	Critical temperature, K	Critical composition (c_C), mole % M_xO_y	Liquidus temperature at c_C, K	Minimum temperature[a] T_{min}, K	Concentration range[b] for liquation at T_{min}, mole % M_xO_y
Li_2O[c]	726	4.5	1003	293	2–6 [224]
MgO	—	—	1415	1415	1.0–49.3
CaO	—	—	1248	1248	0.9–27.0
SrO	—	—	1213	1213	0–21.0
BaO	1423	6.9	1151	1151	0.7–16.3
Tl_2O_3	933 and 778[d]	48.2 and 4.1	809	873[e]	37.0–52.0
La_2O_3	—	—	1409	1409	1.5–21.5
ZnO	—	—	1235	1235	2.6–50.0
CdO	—	—	1253	1253	0.5–37.0
PbO	1060	9.4	1015	853	0.5–18.7
Bi_2O_3	—	—	982	982	2.0–19.0

[a] In the range investigated.

[b] Like the boundaries of the glass formation regions (Table 5), these boundaries depend on the method of observation and can differ from the data quoted here.[213] In particular, the electron paramagnetic probe method,[214] for example, EPR for Cu^{2+} and other ions,[215] reveals the presence in the optically transparent borate glasses of the region of the so called "EPR immiscibility".[216] In order to eliminate the latter, for example, in the K_2O–BaO–B_2O_3 system, the K_2O content should be ten times greater than that required for the elimination of opalescence.[216]

[c] A "pseudophase" structure,[224,225] resembling structures of the phason type, known in the colloid chemistry of polymers[183] and intermediate between the classical one- and two-phase structures, has been discovered in alkali metal borate systems with Na_2O and K_2O.

[d] The system has two critical points—the upper point in the region of stable liquation and lower point in the region of metastable liquation.

[e] The temperature at which the region of liquating compositions is widest.

†Effects similar to BA (as well as BR) are not a unique feature of borates and are manifested also in phosphate, inverted silicate, and other oxide glasses.[197]

3. Oxoborate Melts

Melts of low-molecular-weight anionic borates are typical ionic liquids: they expand with increase of temperature and their viscosity falls, while on cooling they readily crystallise without passing to a vitreous state. On the other hand, monophase and multiphase glasses, polycrystalline sitalls, and polymeric single crystals can be obtained from melts of macroanionic borates (i.e. glass-forming melts) when the composition and conditions are varied.

Table 7 indicates the regions and parameters of phase separation in certain borate glass forming systems.[181] The table shows that phase separation is manifested for low contents of M_xO_y in B_2O_3. The latter does not exhibit microheterogeneities other than thermal density fluctuations.[217]# The characteristic LAX [220] and light scattering[221] "flash" on passing to a melt is gradually abolished and the state usual for thermal density fluctuations obtains. The content of M_xO_y less than 25 mole % in the melt is apparently insufficient for the formation of the structure, illustrated in Fig.14b, throughout the bulk of the melt. New CRU, stabilised by the metal cations, arise in the B_2O_3 matrix (Fig.15). These CRU form individual blocks in the B_2O_3 matrix (this is indicated by the low-frequency branch of the Raman spectra[200,222]) connected to the CRU of the matrix via B–O–B linkages. Ultimately the "network" is found to be made up of CRU blocks of different chemical nature. In the colloid chemistry of polymers[183] such systems (of the type of network polyblock polymers or IPN)§ are treated as multicomponent polymer mixtures as regards phase separation. Phase separation in such mixtures proceeds via binodal (nucleation and growth) and spinodal mechanisms. The phase decomposition mechanism is known[183] to influence the morphology of the polymeric-colloidal structures formed.

The nucleation and growth mechanism	Spinodal mechanism
1. The composition of the second phase remains constant and invariant in time (equilibrium phase).	1. Before the attainment of equilibrium, there is a continuous change in composition.
2. The interface between the growing phase and the matrix is sharp.	2. The interface is diffuse and only gradually becomes sharp.
3. There is a distinct tendency towards a statistical distribution of the sizes and positions of the particles of the equilibrium phases.	3. A definite regularity arises in the sizes and distribution of the segregated phases.
4. The particles of the segregated phases tend to become spherical and only weakly interconnected.	4. The separated phases are usually non-spherical and are highly interconnected.

#We have in mind a preparation obtained from an evacuated melt. The presence of H_2O entails, according to low-angle X-ray diffraction (LAX) data,[217] the appearance of 25–30 nm heterogeneities, which is correlated with electron-microscope observations[218] and is reflected in a change of the rheological properties[219] (the appearance of a yield point and a decrease of viscosity). A decrease of viscosity is characteristic of only low (<0.3 mole %) H_2O contents, while an increase of the water content to >0.5 mole % inhibits such decrease.

§A characteristic feature of macromolecular networks is the presence of rings in the latter and also a globular supermolecular organisation.[223] This is probably valid also for macroanionic networks.

The rheological, electrical, optical, diffusion, and chemical properties of borate melts and glasses, their glass points, densities, thermal expansion coefficients, capacity for crystallisation, etc. depend in their turn on the character of the phase distribution.[181,182] Hence the importance of taking into account the polymeric-colloidal aspect in synthesising vitreous materials with specified properties becomes clear.

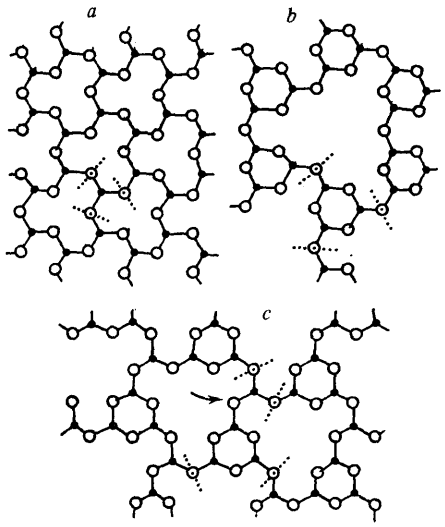


Figure 15. Quasi-crystalline models for the B_2O_3 melt:[204] *a*) $[BO_{1.5}]_{nn}$; *b*) $[B_3O_{4.5}]_{nn}$; *c*) $[B_3O_{4.5}.BO_{1.5}]_{nn} = [B_4O_6]_{nn}$; the last model agrees best with the experimental data.

Together with features which they have in common with polymer mixtures, systems of the type of network polyblock polymers and IPN are also characterised by features such as the presence of chemical and real spinodal curves. For systems with an upper consolute point (UCP), the latter passes below the chemical spinodal curve, so that the region of unstable states under the real spinodal curve can be altogether inaccessible.[183] In the region between the chemical and real spinodal curves lie dissipative systems of the phason type, which are intermediate between the classical one- and two-phase systems. These apparently include also the so called "pseudophases" [224] and "modulated structures" [225] observed in borate melts and glasses. On ultracentrifugation of the melts,[182,226] the compositions of the separated phases correspond to those expected on the basis of the phase diagrams. Numerous examples of the practical applications of phase separation in glasses, including the so called precondition for the formation of sitalls,[228] are known.[227] The heat treatment of borate glasses designed to convert them into sitalls is carried out at 1023–1173 K (Ref. 228, p. 410). If polycrystalline sitalls are obtained in the presence of not less than 10^{12} prenuclear centres in 1 cm^3 of the volume, then the synthesis of polymeric single crystals requires the directional growth of one or several nuclei (see the original communications quoted in Tables 3 and 4). In general, the rate of growth changes from 2 [$PbO.2B_2O_3$—(XCVIII) in Table 4] to approximately 3000 μm s^{-1} [$Li_2O.2B_2O_3$—(XLVIII) in Table 3 [229]].

4. Oxoborates in the Gas Phase

Above the UCP, the glass-forming melts are homogenised evidently as a consequence of the decrease of the molecular weight and of the degree of polymerisation with increase of temperature. The presence of M_xO_y [230,231] as well as H_2O [1,232] in the B_2O_3 melt promotes its thermal degradation with transfer to the gas phase of low-molecular-weight anionic metal oxoborates[233–239] or of the low-molecular-weight fraction of hydrogen oxoborates.[1] Graft copolymerisation of the latter with various oxide substrates[11–13] makes it possible to achieve the chemical moulding of joints and coatings,[240–243] which has an advantage over the traditional technology in that it is possible to avoid laborious operations involving the processing of a macroanionic substance, since the synthesis of the polymer is combined with its moulding. As a consequence of the heterodiffusional character of the polymer formation reaction,[244] reactions of this type made it possible to achieve a gradient anisotropy of properties (refractive index, coefficient of thermal expansion, etc.) with respect to thickness. Special procedures for the formation of boron–oxygen monomers in the gas phase are also used in establishing a refractive index gradient in the manufacture of articles for fibre and integrated optics.[245,246]

IV. CONCLUSION

The question arises how one can account for the wide variety of borate macroanions which can be different for borates having identical chemical compositions. It is known that the unique nature of the macroanions and macromolecules is determined by the following criteria: (1) chains (layers, networks) of atoms or groups of atoms (CRU) linked by directional, predominantly covalent,¶ bonds can be discovered in their structure by one method or another;[1,185] the capacity for the formation of such chains (layers, networks) is determined by the structure of the electron shells of the corresponding atoms, i.e. by their position in the Periodic System of the Elements;[6,184] (2) the set of their properties does not change appreciably with decrease (increase) in the size of the chain (layer, network) by one or several CRU.[1,27] Such chains (layers, networks) are to some extent flexible due to the retention of the rotational degrees of freedom of the constituent units,[248] which is achieved in polyelementoxane macroanions as a result of a

¶It has been suggested[247] that a given chain (layer, network) is polymeric provided that the degree of covalence of the bonds between the atoms in it is not less than 50% (52, 65, 68, 71% respectively for Al–O, Si–O, B–O, and P–O) or in the case of magnesium–oxygen polymers it can even be as low as 43%. Apart from electronegativity, the decrease of the entropy of a particular element with increase of the degree of polymerisation, i.e. of the number of covalently bound atoms, can serve as a measure of the degree of covalence of bonds.[247]

change in the bond length and valence angles in the E–O–E *p*-bridges (E = Si, B, P, Al, etc.).[184,191] This ensures a fairly large set of conformations in the given macroanions (a physical change in the steric form) and configurations (. change in form accompanied by a chemical reaction, i.e. by at least one transposition of bonds or valence angles). Hence one can understand not only the ability of the macroanions to pass to the vitreous (and for linear and layer macroanions also the highly elastic) state[184,191] but also their ability, familiar in crystal chemistry,[249] to "become adjusted" to the cationic component of the structure, i.e. their ability to alter, as the nature of the cations is altered [or, for the same cation, when the conditions of synthesis are changed—see, for example, (LXXXIII) and (LXXXIV) in Table 4], their configuration at all levels of the structural hierarchy—from CRU (including the formation of the "bow-shaped" configurations  and bridges of the type  [249]) to a superanionic organisation (the formation of IPN). In anhydrous compounds the requirements for the flexibility of the macroanion are enhanced, as increase in degree of hydration entails the appearance of the possible coordination of the cations not only to the  end groups or the connecting  groups but also to the oxygen of water with subsequent damping [?bonding (Ed.of Translation)] via hydrogen bonds to the anion.[36,250]

As a result of the non-directional nature of the ionic bond, the cations always tend to become surrounded by the maximum number of counter-ions. For this reason, in the structural† sense, cationic constructions constitute a conservative, rigid base of substances with element–oxygen macroanions.[249] On the other hand, the macroanions are a component of the structure of such substances, which is variable and responds to a change in the nature of the cation and external conditions. Their configurational and conformation statistics are determined by O atoms in a state intermediate between the sp^2- and sp-hybridisations with atoms of other elements[251] and ultimately determines both the wide variety of borates, silicates, phosphates, and similar compounds and many of their properties.

This justifies the assumption that the development of the chemistry of these substances, which are widely distributed in nature and are used in technology, will be determined by the advances in their polymer chemistry. The *chemistry of macroanions*, which, in contrast to the macromolecular chemistry of carboatomic compounds, is still an inadequately developed albeit a promising field of polymer chemistry, comes to the fore for such substances. For the development of this field, it appears useful to employ a combined approach the necessity for which has been noted at the XXIInd Conference on the Chemistry and Macromolecular Compounds.[252] Its essential feature is as follows: since the unity of the material world is manifested in inorganic polymers, in order to reflect it adequately it is essential to achieve the symbiosis of various chemical disciplines, in the first place the macromolecular and colloid chemistry of polymers with inorganic chemistry. In this sense the present review (as well as the previous review[1]) should be regarded as an attempt at a practical realisation of this type of approach to borates and an attempt to present on this basis a sufficiently logical and well-founded picture of their structure, to demonstrate new ways of study, and to facilitate the prediction of the properties of technical materials and the improvement of the technology of their manufacture.

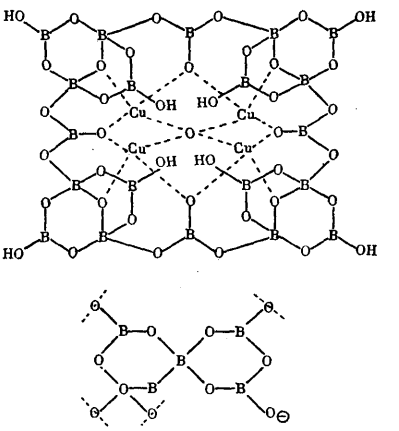
†But not in the chemical sense (for example, exchangeable cations).

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During the preparation of the manuscript for the press, a new monograph, devoted to inorganic polymers, was published.[253] Other publications[254,255] and the Russian translation of the IUPAC recommendations concerning the nomenclature of single-stranded and quasi-single-stranded inorganic polymers[256] attract attention in this connection. The choice of oxygen as a basis for the chemistry of non-carbon polymers has been justified[254] and a classification of the elements of the Periodic Systems in terms of their contributions to the structures of heteroatomic polymers has been developed.

During the same period, the family of oligoborates has been supplemented by a new representative $K_5H\{Cu_4O[B_{20}O_{32}\cdot(OH)_8]\}\cdot 33H_2O$,[257] where $n = 20$. Ghose[258] examined the stereoisomers of the hilgardite network [(XVIII) in Table 1] with stereorepeating units made up of 1-, 3-, and 4-CRU.

Fig. 9 may be supplemented by an example of a new pentaborate CRU ($3BO_3 + 2BO_4$) with a single terminal (non-bridging) O atom:



while Table 3 may be supplemented by the corresponding example of a layer macroanion $[B_3^{III}B_2^{IV}O_8(O^-)]_{nn}^{3nn-}$, whose presence in the $CaNa[B_5O_9]_{nn}$ has been established,[259] and by yet another representative of phylloborates belonging to the $LnCo[B_5O_{10}]_{nn}$ group, where Ln = Yb.[260] Table 4 should be supplemented by new examples of boracites: $Fe_3Cl[B_7O_{13}]_{nnn}$ [261] and $Cu_3I[B_7O_{13}]_{nnn}$.[262]

Thermodynamic calculations have been carried out on the regions corresponding to the existence of various boron–oxygen monomers in the B_2O_3–H_2O vapour–gas phase at T = 300–1500 K at atmospheric pressure.[263]

The section on vitreous borates can be supplemented by data from a new review.[264] Detailed data on alkaline earth metal borates are described in a new monograph.[265]

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