Original Paper

Thermochemical study of the liquid systems $BaO-B_2O_3$ and $CaO-B_2O_3$[1])

Franz Müller and Suat Demirok
Institut für Gesteinshüttenkunde, Rheinisch-Westfälische Technische Hochschule, Aachen (FRG)

The integral molar enthalpy of mixing of the liquid mixtures $BaO-B_2O_3$ and $CaO-B_2O_3$ was measured calorimetrically in the composition range from about 30 to 100 mol% B_2O_3 at temperatures of 1551 and 1725 K, respectively, and the partial molar enthalpy of mixing of the component oxides was obtained by the method of intercepts. The curves representing the functional dependence of the integral and partial enthalpy of mixing on composition are composed of three distinct sections separated one from the other by "singularities" (points of inflection, maxima, etc.). The possible significance of this as well as the relationship between the thermochemical and structural properties of the liquid mixtures are discussed on the basis of information, reported for the structure of these mixtures in the literature.

Thermochemische Untersuchung der Schmelzen $BaO-B_2O_3$ und $CaO-B_2O_3$

Die integrale molare Mischungsenthalpie der Schmelzen $BaO-B_2O_3$ und $CaO-B_2O_3$ wurde im Bereich eines Stoffmengengehaltes von ungefähr 30 bis 100 % B_2O_3 bei 1551 bzw. 1725 K kalorimetrisch gemessen, und die partielle molare Mischungsenthalpie der Oxidkomponenten in den Schmelzen wurde nach der Abschnittsmethode bestimmt. Die Kurven, die den isothermen Verlauf der Mischungsgrößen als Funktion der Zusammensetzung darstellen, sind aus drei Abschnitten aufgebaut, die durch „Singularitäten" (Wendepunkte, Maxima usw.) deutlich voneinander getrennt sind. Die Bedeutung dieses Befundes sowie der Zusammenhang zwischen den thermochemischen und strukturellen Eigenschaften der Schmelzen werden an Hand von Informationen, die über die Struktur dieser Schmelzen in der Literatur vorliegen, erörtert.

1. Introduction

During the past decades there has been an increasing interest in the physicochemical properties of oxide melts, especially from the point of view of glass science and technology. Within the framework of these efforts, the investigation of the thermochemical properties of such melts by high temperature calorimetry has recently started in this laboratory. The results of preceding investigations referring to the liquid mixtures $CaO-B_2O_3$ [1] and Na_2O-SiO_2 [2] have already been, or are being published. In the present communication, the study of this type of mixtures is extended to the liquid system $BaO-B_2O_3$, in which the enthalpy of mixing has been determined in the range from 30 to 100 mol% B_2O_3 at 1551 K.

Further calorimetric measurements have been performed on the liquid mixture $CaO-B_2O_3$ at 1725 K in order to supplement the data already presented in a recent publication [1]. The aim of these measurements was the production of additional data so that the functional dependence of the enthalpy of mixing on composition may be established with greater accuracy.

In the solid state, the binary systems $BaO-B_2O_3$ and $CaO-B_2O_3$ exhibit remarkable similarities, but also interesting differences. According to the phase diagrams ($BaO-B_2O_3$: [3 to 7]; $CaO-B_2O_3$: [7 and 8], each system possesses four compounds ($3\,BaO \cdot B_2O_3$, $BaO \cdot B_2O_3$, $BaO \cdot 2\,B_2O_3$, and $BaO \cdot 4\,B_2O_3$; $3\,CaO \cdot B_2O_3$, $2\,CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$, and $CaO \cdot 2\,B_2O_3$); in both systems, the melting point of the compounds decreases systematically with increasing B_2O_3 content. However, in $BaO-B_2O_3$, a pyroborate corresponding to $2\,CaO \cdot B_2O_3$ does not exist; the tetraborate $BaO \cdot 4\,B_2O_3$ is found instead.

In view of these differences, it seems to be of interest to compare the thermochemistry of liquid $BaO-B_2O_3$ with that of liquid $CaO-B_2O_3$. In particular, it was hoped that the enthalpy-of-mixing data might throw some light on the stoichiometry of the borate species in these liquids.

2. Experimental

The measurements were performed by the drop method. Samples containing an intimate mechanical mixture of crystalline alkaline earth oxide AO (= BaO or CaO) and amorphous B_2O_3 at room temperature T_r (= 295 K) were dropped into the calorimeter operating at the temperature T_c (= 1551 and 1725 K, respectively). The overall process occur-

---

Received 18 October 1988.

[1]) Presented in German on 31 May 1988 at the 62nd Annual Meeting of the German Society of Glass Technology (DGG) in Würzburg (FRG).

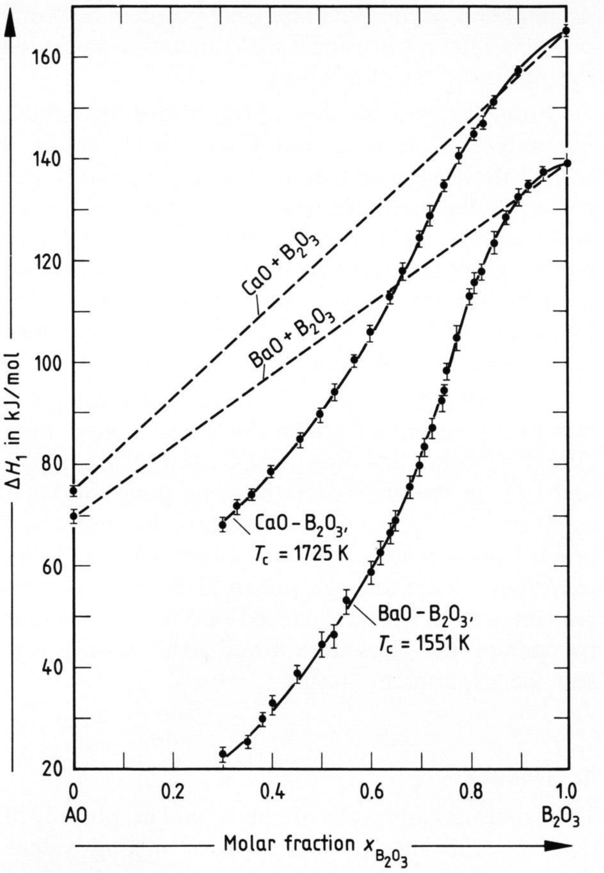


Figure 1. Enthalpy increments $H(T_c)-H(T_r)$ (see equation (1)), measured by heating $BaO(c.) + B_2O_3(gl.)$ and $CaO(c.) + B_2O_3(gl.)$ mixtures of defined composition x in the calorimeter from room temperature T_r = 295 K to the calorimetric temperature T_c which was kept at 1551 K in the measurements on the $BaO-B_2O_3$ system and at 1725 K in the measurements on the $CaO-B_2O_3$ system; ---: mechanical mixture $(1-x)\,AO(c.) + x\,B_2O_3(l.)$.

ring in the calorimeter may formally be described as follows (c. = crystalline, l. = liquid, gl. = glass):

$$(1-x)\,AO(c., T_r) + x\,B_2O_3(gl., T_r) \longrightarrow \text{mixture}(l., T_c),\ \Delta H_1\,. \quad (1)$$

At the fixed temperatures T_r and T_c, the enthalpy change $\Delta H_1 = H(T_c)-H(T_r)$ associated with this process is measured as a function of composition given by the molar fraction, x, of B_2O_3. For $x = 0$ and $x = 1$, the enthalpy change obviously refers to

$$AO(c., T_r) \longrightarrow AO(c., T_c)\,,\ \Delta H_2\,, \quad (2)$$

$$B_2O_3(gl., T_r) \longrightarrow B_2O_3(l., T_c)\,,\ \Delta H_3\,, \quad (3)$$

respectively. The integral molar enthalpy of mixing, $\Delta_m H$, for a liquid mixture of composition x and at temperature T_c is obtained by linear combination of equations (1 to 3):

$$(1-x)\,AO(c., T_c) + x\,B_2O_3(l., T_c) \longrightarrow \text{mixture}(l., T_c)\,,\ \Delta_m H,$$
$$\Delta_m H = \Delta H_1-(1-x)\,\Delta H_2-x\,\Delta H_3\,. \quad (4)$$

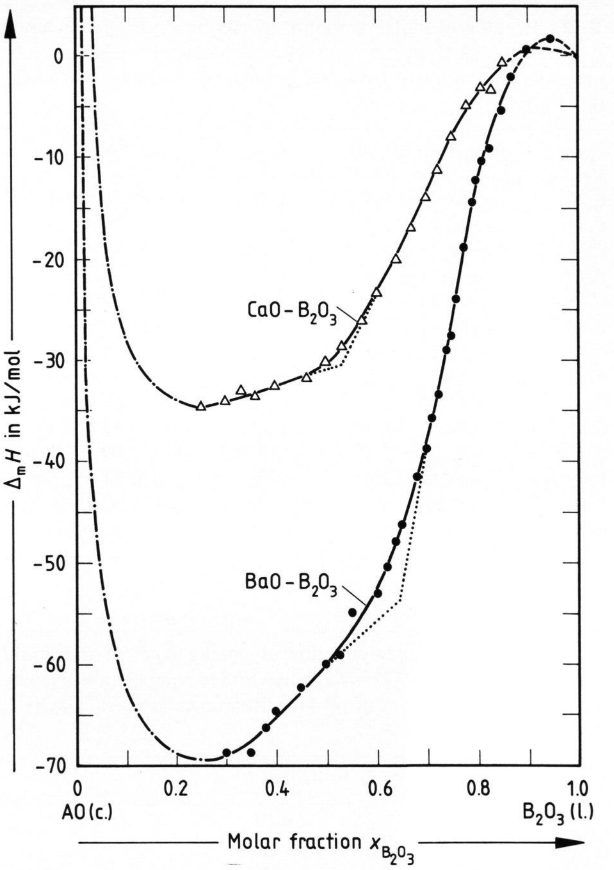


Figure 2. Integral molar enthalpy of mixing $\Delta_m H$ of the liquid mixtures of B_2O_3 with BaO and CaO at 1551 and 1725 K, respectively, as a function of composition x; reference states: BaO(c.), CaO(c.), and B_2O_3(l.).

The calorimetric measurements were carried out in the Setaram HT 1500 calorimeter (Setaram, Lyon (France)) under an argon atmosphere. The experimental set-up and procedure of measurement were similar to those used in the authors' recent work on the mixtures $CaO-B_2O_3$ [1] and Na_2O-SiO_2 [2].

In the majority of measurements samples without any platinum cover were used; in these cases, the calorimeter was calibrated by dropping spheres of pure platinum at room temperature into the calorimeter at the operating temperature. In addition, some measurements were made by using samples encapsulated in 10 μm platinum foil, and then calibrations were carried out using corundum spheres also encased in 10 μm platinum foil. Results obtained by both methods of measurement and calibration agreed well. The heat effects of the calibration runs were calculated on the basis of the enthalpy data for platinum and corundum recommended by Barin et al. [9 and 10]. The reproducibility of the calibration was about 2 %.

B_2O_3 was prepared by heating boric acid (p.a., Merck, Darmstadt (FRG)) in a platinum dish over a gas burner until bubbling subsided. Then the melt was exposed to vacuum, and its temperature peri-

Table 1. Integral molar enthalpy of mixing $\Delta_m H$ of the liquid system $BaO-B_2O_3$ at 1551 K as a function of composition given by the molar fraction x of B_2O_3. Reference states: BaO(s.), B_2O_3(l.) (s. = solid)

$x_{\mathrm{B\,203}}$	$\Delta_m H$ in kJ/mol	$x_{\mathrm{B\,203}}$	$\Delta_m H$ in kJ/mol
0.30	−68.96 ± 1.9	0.71	−35.76 ± 3.3
0.35	−68.84 ± 2.3	0.725	−33.30 ± 4.7
0.38	−66.43 ± 2.0	0.74	−28.85 ± 2.7
0.40	−64.74 ± 2.4	0.75	−27.44 ± 3.6
0.45	−62.44 ± 2.5	0.76	−24.18 ± 4.1
0.50	−60.19 ± 3.0	0.775	−18.70 ± 4.4
0.525	−59.18 ± 2.3	0.80	−12.22 ± 3.4
0.55	−54.79 ± 4.2	0.81	−10.3 ± 2.9
0.60	−53.04 ± 3.3	0.825	− 9.05 ± 5.0
0.62	−50.39 ± 3.0	0.85	− 5.37 ± 3.4
0.64	−47.98 ± 2.5	0.875	− 2.10 ± 3.2
0.65	−46.18 ± 3.4	0.90	+ 0.29 ± 3.5
0.68	−41.60 ± 3.1	0.92	+ 1.20 ± 4.1
0.70	−38.73 ± 4.0	0.95	+ 1.81 ± 3.8

Table 2. Integral molar enthalpy of mixing $\Delta_m H$ of the liquid system $CaO-B_2O_3$ at 1725 K as a function of composition given by the molar fraction x of B_2O_3. Reference states: CaO(s.), B_2O_3(l.)

$x_{\mathrm{B\,203}}$	$\Delta_m H$ in kJ/mol
0.25[2]	−34.64 ± 3.5
0.29	−34.10 ± 2.1
0.33[2]	−33.04 ± 2.3
0.36	−33.82 ± 1.9
0.40[2]	−32.63 ± 2.2
0.46	−31.92 ± 2.5
0.50[2]	−30.75 ± 3.0
0.53	−28.71 ± 3.2
0.57[2]	−26.10 ± 3.1
0.60	−23.32 ± 2.6
0.64	−19.98 ± 2.3
0.667[2]	−16.81 ± 2.6
0.70	−13.91 ± 1.9
0.72	−11.34 ± 4.1
0.75[2]	− 7.97 ± 2.7
0.78	− 4.80 ± 3.2
0.81	− 3.22 ± 2.5
0.83[2]	− 3.34 ± 2.2
0.85	− 0.59 ± 2.7
0.90[2]	+ 0.99 ± 2.3

[2] Taken from [1].

odically changed between about 1150 and 1500 K in order to expel traces of water [11]. The anhydrous B_2O_3 glass, still enclosed in the reaction vessel, was transferred to a glove box where an argon atmosphere free of H_2O and CO_2 was maintained. Here, the glass was pulverized in a ball mill and stored in a desiccator.

BaO and CaO were prepared from $BaCO_3$ and $CaCO_3$ (both p.a., Merck), respectively. The carbonates were decomposed and the oxide powders thus obtained were annealed overnight at about 1500 K. Both decomposition and annealing were performed in a platinum crucible in vacuum. Subsequent examination of the BaO and CaO powders by X-ray powder diffraction using Cu-K_α radiation indicated the purity of the substances.

From the fine powders of the oxides, two-phase mixtures $BaO + B_2O_3$ and $CaO + B_2O_3$ of fixed composition were prepared in the glove box: The corresponding amounts were intimately mixed in an agate mortar; the mixtures were compacted into pellets, and these were annealed at 650 K in vacuum in order to improve their mechanical stability. Prior to use in the calorimetric measurements, the pellets were stored in a desiccator in the glove box.

Samples were taken individually from the glove box to the calorimeter with the aid of a glass tube closed at its ends and protecting the sample from H_2O and CO_2 in the air. After the glass tube had been connected to the charging tube of the calorimeter by a ground glass joint, and this latter tube and the calorimeter had thoroughly been flushed using argon gas, the sample was introduced into the calorimeter by opening the glass tube towards the calorimeter, and the experiment started.

3. Results

The experimental results are presented graphically in figure 1. The integral enthalpy of mixing values obtained from the data of figure 1 are listed in tables 1 and 2 and are plotted versus composition in figure 2. In order to extract as much information as possible from the data represented in figure 2, the partial enthalpies of mixing of the component oxides have been determined by the method of intercepts (figures 3a and b), i.e. by drawing tangents to large-scale plots of the integral enthalpy of mixing.

Furthermore, the interaction parameter λ, defined by $\lambda \equiv \Delta_m H/(x\,(1-x))$, has been calculated (figure 4). Note that the plots of the interaction parameter versus composition also illustrate the experimental precision achieved in the calorimetric measurements.

4. Discussion

Both systems have S-shaped enthalpy-of-mixing curves (figure 1) which start out with positive values in the high B_2O_3 range, rise to a maximum of the order of 1 kJ/mol and fall sharply with decreasing B_2O_3 content. This trend in the liquid state of increasing stability with decreasing B_2O_3 contents parallels the thermal stability in the solid state, as is indicated by the melting points of the barium and calcium borates, see section 1. Hence, a minimum of enthalpy is expected on each curve, i.e., a maximum of stability, at about $x = 0.25$ where the compound $(3\,AO \cdot B_2O_3)$ with the highest thermal stability exists. Below about $x = 0.2$, a steep rise of the enthalpy-of-mixing curves is anticipated, as is suggested by the dashed lines. The end points of the curves on the axis of the ordinates are determined by the heat of fusion of the corresponding alkaline earth oxides (BaO: $\Delta_{fs}H = 26.6$, CaO: $\Delta_{fs}H = 79.5$ kJ/mol [12]).

Several significant features are evident from figures 2, 3a and b:

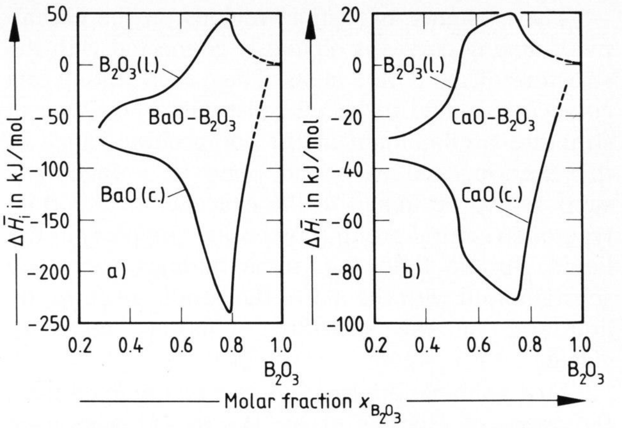
First, below about $x = 0.8$, the formation of the barium borate mixture is more exothermic than that of the corresponding calcium borate mixture. Qualitatively, this trend may be rationalized by means of a simple electrostatic model which relates the stability of liquid oxide mixtures to the ionic potential of the metal cations; for a cation of charge z_i and radius r_i the ionic potential is defined as z_i/r_i. According to the model, one expects that the smaller the ionic potential, the more negative is the enthalpy of mixing; since $r_{Ba} > r_{Ca}$ one anticipates the barium borate mixture to be more stable relative to the component oxides.

Second, the enthalpy curves plotted in figure 2 display a rather strong deviation from the symmetrical, parabolic relationship predicted by the first-approximation solution theories, and the variation of the interaction parameter given in figure 4 shows pronounced energetic asymmetry, i.e. the λ values in the B_2O_3-rich region are considerably different from those in the AO-rich region.

Third, below about $x = 0.8$, the compositional dependence of λ exhibits remarkable deviations from linearity. Note that both the energetic asymmetry and the deviation from linearity apparently increase with decreasing ionic potential of the metal cation.

The last two features indicate that profound structural changes occur in the borate melts as a function of composition [1]. It is the purpose of the following discussion to elucidate, as far as possible, the relationship between the thermochemical and structural properties of the borate melts.

Starting point of the discussion is the observation that both enthalpy-of-mixing curves in figure 2 are composed of three different sections, which stand out one against another. On the B_2O_3-rich side of the diagram, the curvature of the enthalpy-of-mixing curve is positive; this range of positive curvature extends from $x = 0.8$ to 1 in the BaO$-B_2O_3$ system and from $x = 0.75$ to 1 in the CaO$-B_2O_3$ system. In the region below these compositions, where the curvature is negative, one may distinguish two further sections which can, over a certain range, be approximated by straight lines dotted in figure 2. On extrapolation, these lines intersect at $x \approx 0.65$ in the BaO$-B_2O_3$ system, and at $x \approx 0.52$ in the CaO$-B_2O_3$ system. Each dissection of the integral enthalpy-of-mixing curves in figure 2 clearly has its correlate on the partial enthalpy-of-mixing curves in figures 3a and b. At that composition where in figure 2 the curvature changes from negative to positive (BaO$-B_2O_3$: $x = 0.80$; CaO$-B_2O_3$: $x = 0.75$), extrema are found in figures 3a and b; and at approximately that composition where in figure 2 the (dotted) straight lines cross, points of inflection occur in figures 3a and b (BaO$-B_2O_3$: $x \approx 0.67$; CaO$-B_2O_3$: $x \approx 0.53$).



Figures 3a and b. Partial molar enthalpy of mixing $\Delta\bar{H}_i$ a) of BaO(c.) and B_2O_3(l.) in the liquid mixture BaO$-B_2O_3$ at 1551 K, b) of CaO(c.) and B_2O_3(l.) in the liquid mixture CaO$-B_2O_3$ at 1725 K as a function of composition x.

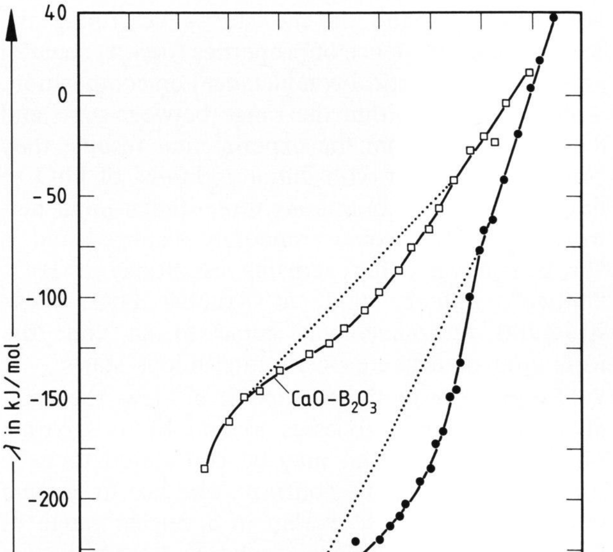


Figure 4. Interaction parameter $\lambda \equiv \Delta_m H/(x\,(1-x))$ of liquid mixtures of B_2O_3 with BaO at 1551 K and of B_2O_3 with CaO at 1725 K as a function of composition x; reference states: BaO(c.), CaO(c.), and B_2O_3(l.).

The existence of distinct regions on the enthalpy-of-mixing curves is obviously connected with the structure of the borate melts. Thus, each section of a curve is assumed to be related to a certain type of structure predominant in the composition range of this section, and each end point of a section is supposed to be linked to the existence of a certain type of structural group (polyborate complex) in the liquid. In the following, these findings are to be substantiated with the aid of the results given in the literature on the structure of borate melts or glasses.

First valuable information may be obtained from the work of Bockris et al. [13 to 15] who have investigated by indirect methods (e.g. measurement of density and transport properties) the structural changes occurring in liquid (network-forming) B_2O_3 on first additions of a basic (network-modifying) oxide. In the liquid system $PbO-B_2O_3$, Bockris and Mellors [13] found on the curves describing the functional dependence of properties (density, heat of activation of electrical conductance) on composition, a sharp change within the range between zero and 8 mol% PbO. From the experimental results, they concluded: a) that with initial additions of PbO to liquid B_2O_3, the continuous three-dimensional network of B_2O_3 becomes randomly distorted and is "broken down", but remains essentially a B_2O_3 "lattice", and b) that, at 8 mol% PbO, these structural rearrangements come to an end; the formation of discrete polyborate anions starts.

From a thermodynamic point of view, the strict allocation of the processes a) and b) to separate ranges of composition may be considered to be a simplification. On the contrary, one has to assume that these processes overlap in a certain range of composition; but the occurrence of essentially two processes ("structure breaking", production of discrete anionic entities) as observed in the high B_2O_3 range of the liquid $PbO-B_2O_3$ system appears to be characteristic of all fused oxide systems composed of non-metal oxides with largely continuous network structures, on the one hand, and network-modifying metal oxides, on the other hand [14 and 15]. Hence, these processes may also be expected to proceed, in a qualitatively similar way, in the $BaO-B_2O_3$ and $CaO-B_2O_3$ systems. Thus, the general features of the enthalpy-of-mixing curves in the high B_2O_3 range (figure 2) may tentatively be explained as reflecting the concurrent presence of the aforementioned processes: process a), predominant at very high B_2O_3 contents, is expected to be endothermic, and process b), prevailing with decreasing B_2O_3 contents, is considered to be exothermic. In the following, an attempt is made to obtain further information on these processes from results given in the literature.

There are strong indications [16 to 25] that pure liquid and vitreous B_2O_3 is made up from six-membered boroxol rings (figure 5a) and randomly connected planar BO_3 triangles; the bonding is predominantly covalent. At comparatively low temperatures, the boroxol ring appears to be the most prevalent structural group. With temperature increase this group dissociates increasingly into "free" BO_3 triangles which are assumed to organize into a random network.

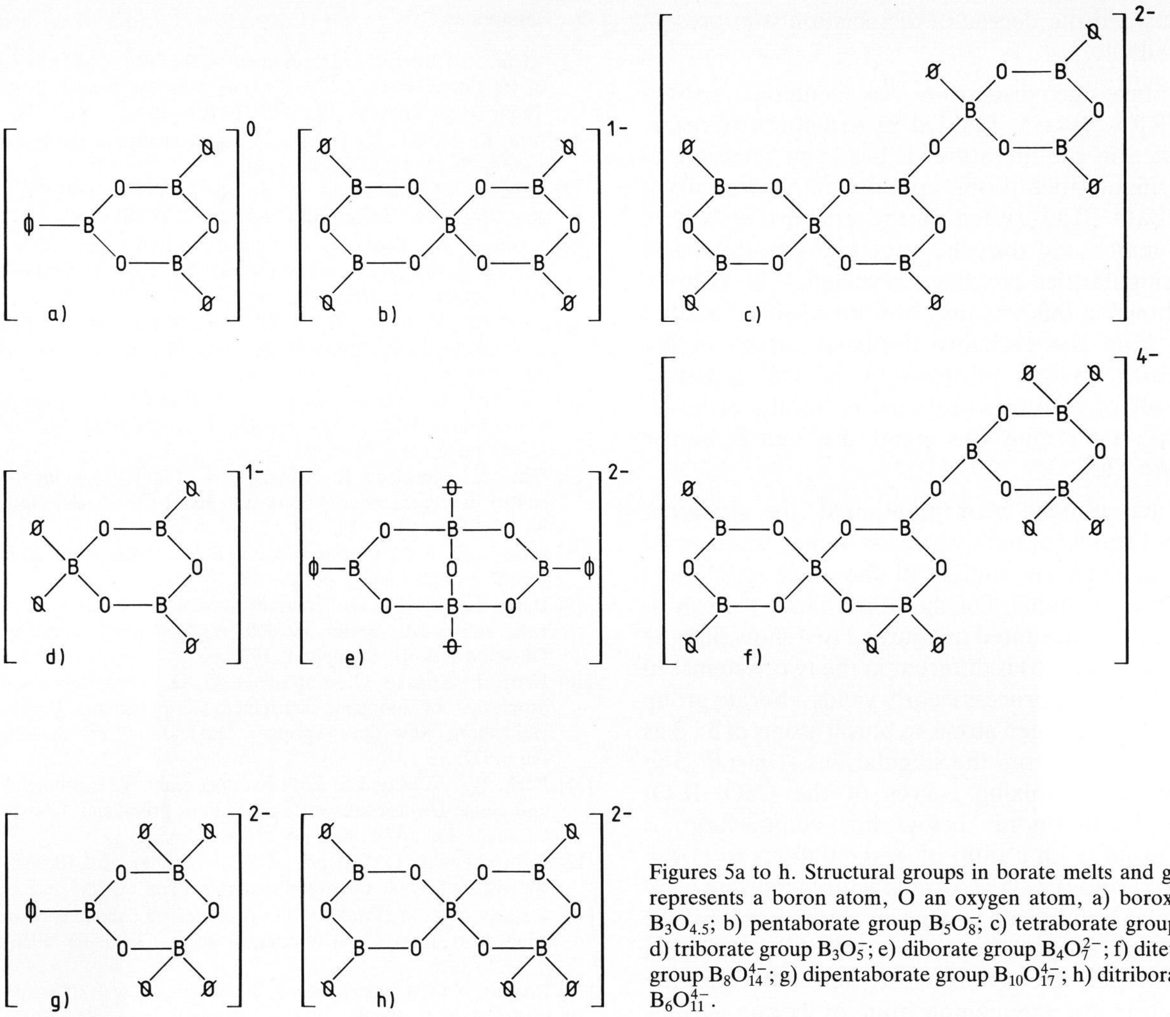
On the addition of BaO to an excess of liquid B_2O_3, boroxol groups are broken up and trigonal BO_3 units are converted into tetrahedral BO_4 units [20 and 26]; for each oxygen added to B_2O_3 as BaO, 2.12 ± 0.2 BO_4 tetrahedra are formed [26]. During the progress of these reactions and under the influence of the electrical charges introduced into the B_2O_3 network by the addition of BaO, rearrangements in the network must occur. Changes of B−O bond length appear on the whole to be insignificant because these processes presumably require a comparatively large expenditure of energy; but bending of bridging B−O−B bonds, i.e. deformation of average bond angle, is expected, as has already been proposed for silica-rich oxide melts [27]. From this discussion there is reason to believe that process a) is composed of (at least) three reactions: destruction of boroxol groups, formation of BO_4 units and deformation of average bond angle, and guided by the results given in figure 2, it may be presumed that the overall enthalpy effect of these reactions is endothermic. Note that, from the temperature dependence of the intensity of characteristic Raman peaks, the value of the enthalpy of dissociation of the boroxol group into "free" BO_3 triangles,

$$B_3O_{9/2} \longrightarrow 3\,BO_{3/2}\,,\ \Delta_d H$$

has been estimated to be $\Delta_d H = 49.4$ kJ [18] or 26.8 kJ [23] per mol boroxol units.

On entering into the discussion on the nature of process b) it should first be pointed out that the existence of well-defined and stable anionic groups in borate melts and glasses has been a subject of many theoretical and experimental studies [16, 20 and 28 to 31]. With respect to barium borate glasses, this point has in particular been investigated by X-ray diffraction [32 and 33], Raman spectroscopy [20], and nuclear magnetic resonance [26]. The results of these investigations strongly indicate that the tetraborate group $B_8O_{13}^{2-}$ (figure 5c) − i.e. a couple consisting of one pentaborate and one triborate group (figures 5b and d) − is an important structure element in B_2O_3-rich barium borate glasses.

On the basis of this result and on the assumption that the structural picture of borate melts is reflected by the properties of the corresponding glasses, it may be suggested that in the $BaO-B_2O_3$ system process b) comprises the formation of the $B_8O_{13}^{2-}$ group. Accordingly, the singularities at $x \approx 0.8$ on



Figures 5a to h. Structural groups in borate melts and glasses. B represents a boron atom, O an oxygen atom, a) boroxol group $B_3O_{4.5}$; b) pentaborate group $B_5O_8^-$; c) tetraborate group $B_8O_{13}^{2-}$; d) triborate group $B_3O_5^-$; e) diborate group $B_4O_7^{2-}$; f) ditetraborate group $B_8O_{14}^{4-}$; g) dipentaborate group $B_{10}O_{17}^{4-}$; h) ditriborate group $B_6O_{11}^{4-}$.

the enthalpy-of-mixing curves of the BaO–B$_2$O$_3$ system (figures 2, 3a and b) may be interpreted as marking the endpoint of this formation process. Thus, the data of the present study indicate, in agreement with the findings of previous work [20 and 32], the presence of a stable $B_8O_{13}^{2-}$ group in B$_2$O$_3$-rich barium borate melts.

From the results provided by X-ray diffraction [32] and Raman spectroscopy [20] it has been concluded that, below $x = 0.8$, the $B_8O_{13}^{2-}$ group is gradually converted into another structural arrangement. The nature of this arrangement could, however, not be revealed exactly, but there are indications that it is "characteristic of the diborate composition" [32]. This finding is corroborated by the results of the present study. From the location of the singularities at around $x \approx 0.66$ on the enthalpy-of-mixing curves related to the BaO–B$_2$O$_3$ system, it may be inferred that the new arrangement represents a borate group with a ratio of oxygen atoms to boron atoms of 7 : 4. Information concerning the structure of this group is indirectly provided by X-ray diffraction studies [32 and 33]. The results suggest that, near the diborate composition, the same borate groups occur in vitreous and crystalline barium borate [20], and the borate network of the latter ($BaO \cdot 2\,B_2O_3$) has been shown to consist of the ditetraborate group $B_8O_{14}^{4-}$ (figure 5f) [34], this group may be regarded as being composed of one ditriborate and one dipentaborate group joined together by a non-ring oxygen atom (figures 5g and h).

On the basis of, and in accordance with all the experimental results enumerated in section 3., it is suggested that the $B_8O_{14}^{4-}$ group constitutes the "new structural arrangement" which becomes prevalent below $x = 0.8$ and is predominant at the diborate composition in barium borate melts. There are no obvious indications for the existence of the diborate ($B_4O_7^{2-}$) group (figure 5e) in these melts in any large quantities, as was postulated in previous studies [20 and 32].

The existence of the relatively large $B_8O_{13}^{2-}$ and $B_8O_{14}^{4-}$ groups in barium borate melts is a surprising result of the preceding discussion. However, the thermal stability of these groups is certainly limited (similarly as it is in the case of the boroxol group, see earlier in this section), and one has to assume that increasing dissociation occurs with temperature. Information concerning the nature of the dissociation products and the degree of dissociation is at present not available.

So far, the discussion has centered on the $BaO-B_2O_3$ system. Guided by structural information given in the literature, it has been possible to relate singularities in the enthalpy-of-mixing curves of the $BaO-B_2O_3$ system to the structure of barium borate melts, and thus the structural significance of these singularities has been revealed. The correlations shown in this way may now inversely be used to derive from the enthalpy-of-mixing curves of the $CaO-B_2O_3$ system information on the structural behaviour of calcium borate melts; results of investigations concerning this point are scarce in the literature [20].

As has already been mentioned, the structural changes brought about by process a) may be assumed to be qualitatively similar in the $BaO-B_2O_3$ and $CaO-B_2O_3$ systems. On the other hand, the calorimetric data represented in figures 2 to 4 show that the nature of process b) is different in the two systems. In $CaO-B_2O_3$, this process clearly yields a borate group with a ratio of oxygen atoms to boron atoms of 5 : 3 as may be inferred from the singularities at $x \approx 0.75$ in the enthalpy-of-mixing curves of the $CaO-B_2O_3$ system. Furthermore, below this composition, a borate group with a ratio of oxygen atoms to boron atoms of around 2.05 is formed with increasing CaO content, as is indicated by the singularities at $x \approx 0.52$ to 0.53 on the corresponding enthalpy-of-mixing curves. While the calorimetric data thus provide information on the composition of borate groups prevailing in calcium borate melts, the data do not allow further conclusions to be drawn concerning the actual structure of these groups. One could assume that the borate anion indicated by the singularities at $x \approx 0.75$ is represented by the triborate group (figure 5d) and one might guess that the anion revealed by the singularities at $x \approx 0.52$ is characteristic of the metaborate composition. However, these assumptions are very speculative and obviously require further structural investigations by more direct spectroscopic methods. Also, in the $CaO-B_2O_3$ system, there is clearly no evidence for the diborate group (figure 5e).

In an investigation of borate glasses by Raman spectroscopy, a close structural relationship of alkaline earth borate glasses with a B_2O_3 content of 30 mol% has been noted [20]. In contrast to this, a structural dissimilarity of barium and calcium borate melts may be concluded from the results of the present study; in these melts, borate groups of different structures appear to exist (within the compositional range of investigation). Thus, it turns out that the structural differences which occur in the solid state of the $BaO-B_2O_3$ and $CaO-B_2O_3$ systems are reflected by structural dissimilarities in the liquid state of these systems.

5. References

[1] Klein, J.; Müller, F.: Measurement of the enthalpy of mixing of the liquid system $CaO-B_2O_3$ by drop calorimetry. High Temp. High Pressure **19** (1987) p. 201–209.

[2] Min, F.; Müller, F.; Fu, Z.: Thermodynamics of the liquid system Na_2O-SiO_2. To be publ.

[3] Levin, E. M.; McMurdie, H. F.: The system $BaO-B_2O_3$. J. Res. Natl. Bur. Stand. **42** (1949) no. 2, p. 131–138.

[4] Levin, E. M.; Cleek, G. W.: Shape of liquid immiscibility volume in the system barium oxide–boric oxide–silica. J. Am. Ceram. Soc. **41** (1958) no. 5, p. 175–179.

[5] Hageman, V. B. M.; Oonk, H. A. J.: The region of liquid immiscibility in the system B_2O_3-BaO. Phys. Chem. Glasses **20** (1979) no. 6, p. 126–129.

[6] Clemens, K.; Yoshiyagawa, M.; Tomozawa, M.: Liquid-liquid immiscibility in $BaO-B_2O_3$. J. Am. Ceram. Soc. **64** (1981) no. 6, p. C-91–C-92.

[7] Ohta, Y.; Morinaga, K.; Yanagase, T.: Liquid-liquid immiscibility in several binary borate systems. J. Ceram. Soc. Jpn. **90** (1982) no. 9, p. 511–516.

[8] Carlson, E. T.: The system: $CaO-B_2O_3$. J. Res. Natl. Bur. Stand. **9** (1932) no. 6, p. 825–832.

[9] Barin, I.; Knacke, O.: Thermochemical properties of inorganic substances. Berlin, Heidelberg, New York: Springer; Düsseldorf: Verl. Stahleisen, 1973.

[10] Barin, I.; Knacke, O.; Kubaschewski, O.: Thermochemical properties of inorganic substances. Supplement. Berlin, Heidelberg, New York: Springer; Düsseldorf: Verl. Stahleisen, 1977.

[11] Poch, W.: Vollständige Entwässerung einer B_2O_3-Schmelze und einige Eigenschaftswerte des daraus erhaltenen Glases. Glastech. Ber. **37** (1964) no. 12, p. 533–535.

[12] Kubaschewski, O.; Alcock, C. B.: Metallurgical thermochemistry. 5th ed. Oxford: Pergamon Press, 1978.

[13] Bockris, J. O'M.; Mellors, G. W.: Electric conductance in liquid lead silicates and borates. J. Phys. Chem. **60** (1956) p. 1321–1328.

[14] Bockris, J. O'M.; Kitchener, J. D.: Viscous flow in silica and binary liquid silicates. Trans. Faraday Soc. **51** (1955) p. 1734–1748.

[15] Bockris, J. O'M.; Tomlinson, J. W.; White, J. L.: The structure of the liquid silicates: partial molar volumes and expansivities. Trans. Faraday Soc. **52** (1956) p. 299–310.

[16] Pye, L. D.; Fréchette, V. D.; Kreidl, N. J. (eds.): Borate glasses. New York: Plenum Press, 1978.

[17] Goubeau, J.; Keller, H.: Raman-Spektren und Struktur von Boroxol-Verbindungen. Z. Anorg. Allg. Chem. **272** (1953) no. 5–6, p. 303–312.

[18] Krogh-Moe, J.: The structure of vitreous and liquid boron oxide. J. Non-Cryst. Solids **1** (1968/69) p. 269–284.

[19] Mozzi, R. L.; Warren, B. E.: The structure of vitreous boron oxide. J. Appl. Crystallogr. **3** (1970) p. 251–257.

[20] Konijnendijk, W. L.; Stevels, J. M.: The structure of borate glasses studied by Raman scattering. J. Non-Cryst. Solids **18** (1975) p. 307–331.

[21] Golubkov, V. V.; Titov, A. P.; Vasilevskaya, T. N. et al.: The structure of vitreous B_2O_3. Sov. J. Glass Phys. Chem. **3** (1977) no. 4, p. 295–298.

[22] Zarzycki, J.: Diffraction analysis of vitreous and molten B_2O_3. In: Pye, L. D.; Fréchette, V. D.; Kreidl, N. J. (eds.): Borate glasses. New York: Plenum Press, 1978. p. 201–213.

[23] Walrafen, G. E.; Samanta, S. R.; Krishan, P. N.: Raman investigation of vitreous and molten boric oxide. J. Chem. Phys. **72** (1980) p. 113–120.

[24] Johnson, P. A. V.; Wright, A. C.; Sinclair, R. N.: A neutron diffraction investigation of the structure of vitreous boron trioxide. J. Non-Cryst. Solids **50** (1982) p. 281–311.

[25] Miyake, M.; Suzuki, T.; Morikawa, H. et al.: Structure analysis of molten B_2O_3. J. Chem. Soc., Faraday Trans. **80** (1984) p. 1925–1931.

[26] Greenblatt, S.; Bray, P. J.: Nuclear magnetic resonance investigation of the system $BaO-B_2O_3$. Phys. Chem. Glasses **8** (1967) no. 5, p. 190–193.
[27] Charles, R. J.: The origin of immiscibility in silicate solutions. Phys. Chem. Glasses **10** (1969) no. 5, p. 169–178.
[28] Krogh-Moe, J.: Structural interpretation of melting point depression in the sodium borate system. Phys. Chem. Glasses **3** (1962) no. 4, p. 101–110.
[29] Holm, J. L.; Kleppa, O. J.: Thermochemistry of the liquid system lead(II) oxide–boron oxide at 800 °. Inorg. Chem. **6** (1967) p. 645–648.
[30] Østvold, T.; Kleppa, O. J.: Thermochemistry of liquid borates. Pt. 2//Partial enthalpies of solution of boric oxide in its liquid mixtures with lithium, sodium, and potassium oxides. Inorg. Chem. **9** (1970) p. 1395–1400.
[31] Bray, P. J.: Structural models for borate glasses. J. Non-Cryst. Solids **75** (1985) p. 29–36.
[32] Krogh-Moe, J.: An X-ray study of barium borate glasses. Phys. Chem. Glasses **3** (1962) no. 6, p. 208–212.
[33] Block, S.; Piermarini, G. J.: Alkaline earth cation distribution in vitreous borates. Phys. Chem. Glasses **5** (1964) no. 5, p. 138–143.
[34] Block, S.; Perloff, A.: The crystal structure of barium tetraborate, $BaO \cdot 2\,B_2O_3$. Acta Cryst. **19** (1965) p. 297–300.

89R0192