

# Thermodynamics of the Ternary System $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3$

## I. A Calorimetric Study of the Liquid Mixtures

$\text{B}_2\text{O}_3 + (\text{NaBO}_2)_2$ ,  $(\text{NaPO}_3)_2 + \text{Na}_4\text{P}_2\text{O}_7$ ,  $(\text{NaPO}_3)_2 + \text{B}_2\text{O}_3$  and  $\text{Na}_4\text{P}_2\text{O}_7 + (\text{NaBO}_2)_2$

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The enthalpies of mixing of the liquid mixtures of  $(\text{NaBO}_2)_2 + \text{B}_2\text{O}_3$ ,  $\text{Na}_4\text{P}_2\text{O}_7 + (\text{NaPO}_3)_2$ ,  $(\text{NaPO}_3)_2 + \text{B}_2\text{O}_3$  and  $\text{Na}_4\text{P}_2\text{O}_7 + (\text{NaBO}_2)_2$  have been measured by liquid + liquid calorimetry. The results are discussed in terms of tentative structural models of the melts, and in terms of  $\text{O}^{2-}$  ion transfers from phosphorus groups to boron groups in  $(\text{NaPO}_3)_2 + \text{B}_2\text{O}_3$  and from boron groups to phosphorus groups in  $\text{Na}_4\text{P}_2\text{O}_7 + (\text{NaBO}_2)_2$ .

In recent years there has been an increasing interest in the properties of oxide melts, both from the point of view of glass science and of geology. We have for some time been interested in applying high temperature reaction calorimetry for more detailed studies of such melts. In this connection we have recently completed a study of the quasi-binary system  $\text{NaBO}_2-\text{SiO}_2$  carried out at 1394 K [1]. The present investigation, which covers four cuts in the ternary liquid system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ , represents a further exploration in the same area. Among the mixtures considered in the present work only the liquid system  $\text{B}_2\text{O}_3-(\text{NaBO}_2)_2$  has been investigated previously by calorimetry. However, a large part of the ternary phase diagram  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$  recently was studied by Mikhailovich [2]. We shall refer to this diagram in the discussion of specific quasi-binary cuts below. The binary system  $\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$  shows a compound,  $\text{BPO}_4$ , which has a large primary crystallization field in the ternary system. In this compound boron and phosphorus are both four-coordinated by oxygen, forming a cristobalite-like structure [3].

## Experimental

The calorimetric measurements were carried out in a Calvet-type twin microcalorimeter. The ex-

perimental set up was similar to that used in our recent work on mixtures of  $\text{NaBO}_2$  and  $\text{SiO}_2$  [1]. The crucible, dipper and plunger were made from a 90% gold – 10% palladium alloy, and the silica liner was protected by a silica tube. The experiments were performed under a nitrogen atmosphere at a temperature of  $975 \pm 2^\circ\text{C}$  for  $(\text{NaBO}_2)_2 + \text{B}_2\text{O}_3$  and at  $999 \pm 2^\circ\text{C}$  for the other systems.

All the experiments were of the liquid + liquid type, with both components maintained and brought to reaction at calorimeter temperature. The measurements were carried out in two ways. A few compositions in each system were measured by mixing of the pure components, yielding the integral enthalpies of mixing directly. To these mixtures one of the two components was added in consecutive experiments, and the heat effects measured for each addition. The integral enthalpies of mixing were then calculated by summing all the observed heat effects, correcting for the changes in the total amount of the mixtures. Either way, the compositions which were measured are indicated in Tables 1–4.

The calorimeter was calibrated by dropping pieces of 2 mm platinum wire from room temperature into the calorimeter at the operating temperature. The heat effects were calculated using enthalpy data for platinum recommended by Kelley [4]. The reproducibility of the calibrations was about  $\pm 1\%$ .

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Table 1. Enthalpies of mixing in the liquid system  $(\text{NaBO}_2)_2-\text{B}_2\text{O}_3$  at 1248 K (\* the enthalpies were measured by mixing the pure components (see text)).

$N_{(\text{NaBO}_2)_2}$	$\Delta H_{\text{mix}}$ J/mol	$\Delta H_{\text{mix}}/N_1 N_2$ kJ/mol
0.9410 *	-5159	-92.9
0.8425	-13 092	-98.7
0.7147	-22 468	-110.2
0.6090	-30 145	-126.6
0.5117	-35 873	-143.6
0.4558	-38 324	-154.5
0.3916	-40 362	-169.4
0.3474	-40 387	-178.1
0.2917	-38 898	-188.3
0.2460	-36 555	-197.1
0.2098	-32 748	-197.5
0.0169 *	-2766	-166.5
0.0844	-12 811	-165.8
0.1541	-23 045	-176.8

Table 2. Enthalpies of mixing in the liquid system  $\text{Na}_4\text{P}_2\text{O}_7-(\text{NaPO}_3)_2$  at 1272 K (\* the enthalpies were measured by mixing the pure components (see text)).

$N_{\text{Na}_4\text{P}_2\text{O}_7}$	$\Delta H_{\text{mix}}$ J/mol	$\Delta H_{\text{mix}}/N_1 N_2$ kJ/mol
0.0266 *	-823	-31.8
0.0984	-2884	-32.5
0.1907	-5023	-32.5
0.2772	-6004	-30.0
0.3572	-6737	-29.3
0.4290	-7217	-29.5
0.8168 *	-5446	-36.4
0.7276	-7016	-35.4
0.6482	-7583	-33.3
0.5788	-7686	-31.5
0.5068	-7578	-30.3
0.4443	-7227	-29.3
0.9962 *	-145	-38.4
0.9308	-2298	-35.7
0.8710	-3934	-35.0

Anhydrous  $(\text{NaBO}_2)_2$  was prepared from  $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Fisher Scientific Co., purified) by heating for 24 h at 460 °C, then crushed and heated for another 10 h at 750 °C.

Anhydrous  $\text{B}_2\text{O}_3$  was prepared from  $\text{H}_3\text{BO}_3$  (Baker Analyzed (min 99.5%)). The  $\text{H}_3\text{BO}_3$  was heated in a platinum crucible over a gas burner until bubbling subsided, and then kept for 24 h at 1250 °C. The melt was then quenched on a silver plate, and kept in a dessicator.

$(\text{NaPO}_3)_2$  (Baker and Adamson, reagent) was dried under vacuum at 160 °C for 48 h, then heated for 24 h at 1000 °C, cooled and crushed.

Table 3. Enthalpies of mixing in the liquid system  $(\text{NaPO}_3)_2-\text{B}_2\text{O}_3$  at 1272 K (\* the enthalpies were measured by mixing the pure components (see text)).

$N_{(\text{NaPO}_3)_2}$	$\Delta H_{\text{mix}}$ J/mol	$\Delta H_{\text{mix}}/N_1 N_2$ kJ/mol
0.9337 *	-4828	-78.0
0.8164 *	-12 184	-81.3
0.7483 *	-15 652	-83.1
0.6046	-19 095	-79.9
0.4815	-18 782	-75.2
0.5254 *	-19 346	-77.6
0.4203	-18 142	-74.5
0.3281	-16 602	-75.3
0.2670	-13 803	-70.5
0.3956 *	-17 983	-75.2
0.2318	-11 451	-64.3
0.1339	-5878	-50.7
0.3104	-14 267	-66.7
0.1362 *	-6012	-51.1
0.0124 *	32	2.6
0.0540	-1314	-25.7

Table 4. Enthalpies of mixing in the liquid system  $\text{Na}_4\text{P}_2\text{O}_7-(\text{NaBO}_2)_2$  at 1272 K (\* the enthalpies were measured by mixing the pure components (see text)).

$N_{\text{Na}_4\text{P}_2\text{O}_7}$	$\Delta H_{\text{mix}}$ J/mol	$\Delta H_{\text{mix}}/N_1 N_2$ kJ/mol
0.0495 *	-113	-2.4
0.1045	-724	-7.7
0.1507 *	-1410	-11.0
0.1840	-2361	-15.7
0.3195	-4792	-22.0
0.4279	-6225	-25.4
0.5173	-6964	-27.9
0.5817	-7385	-30.4
0.6333	-7415	-31.9
0.9618 *	-1859	-50.6
0.8981	-4282	-46.8
0.8327	-5797	-41.6
0.7673	-6613	-37.0
0.7036	-6830	-32.8
0.6438	-6983	-30.5

$\text{Na}_4\text{P}_2\text{O}_7$  was made from  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  (Baker Analyzed reagent, 99%) by dehydration. The salt was heated for 24 h at 350 °C, then crushed and heated again for 48 h at 950 °C.

## Results

The molar integral enthalpies of mixing for the four systems studied are given in Tables 1–4. In Figs. 1–4 the results are presented graphically as functions of composition. In these figures are also shown the partial enthalpies of mixing of the two

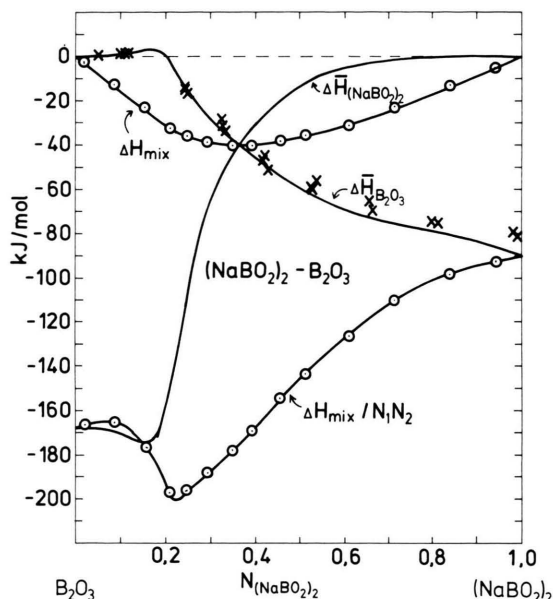


Fig. 1. Molar enthalpies of mixing in the liquid system  $(\text{NaBO}_2)_2-\text{B}_2\text{O}_3$ .  $\times$  — measured data from Østvold and Kleppa (7).

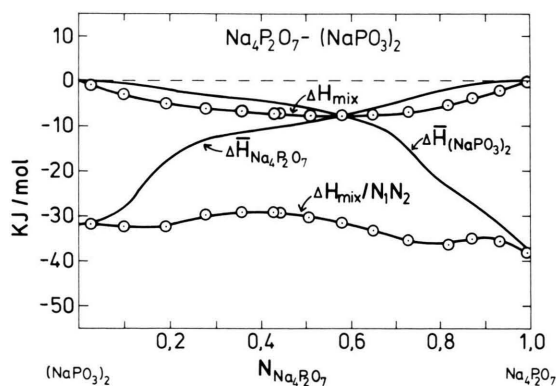


Fig. 2. Molar enthalpies of mixing in the liquid system  $\text{Na}_4\text{P}_2\text{O}_7-(\text{NaPO}_3)_2$ .

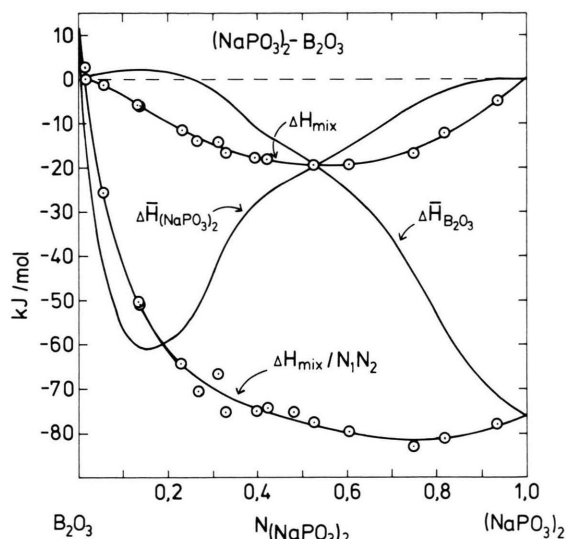


Fig. 3. Molar enthalpies of mixing in the liquid system  $(\text{NaPO}_3)_2-\text{B}_2\text{O}_3$ .

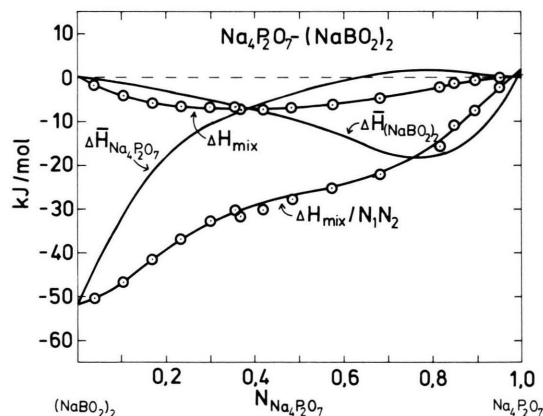
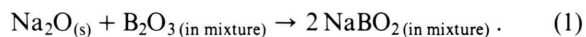


Fig. 4. Molar enthalpies of mixing in the liquid system  $\text{Na}_4\text{P}_2\text{O}_7-(\text{NaBO}_2)_2$ .

components as determined by drawing tangents to large scale plots of the integral enthalpies of mixing.

In Fig. 5 the partial enthalpies of  $\text{Na}_2\text{O}_{(s)}$  in the systems  $\text{B}_2\text{O}_3 + (\text{NaBO}_2)_2$  and  $(\text{NaPO}_3)_2 + \text{Na}_4\text{P}_2\text{O}_7$  are given. For  $\text{B}_2\text{O}_3 + (\text{NaBO}_2)_2$  these values were obtained by combining the partial enthalpies in  $(\text{NaBO}_2)_2 + \text{B}_2\text{O}_3$  with the enthalpies of formation of  $(\text{NaBO}_2)_{2(l)}$  ( $-2062.6 \text{ kJ/mol}$  (4)),  $\text{B}_2\text{O}_{3(l)}$  ( $-1230.1 \text{ kJ/mol}$  [5]) and  $\text{Na}_2\text{O}_{(s)}$  ( $-589.9 \text{ kJ/mol}$  [5]) at  $1000^\circ\text{C}$  according to the reaction



In the  $(\text{NaPO}_3)_2 + \text{Na}_4\text{P}_2\text{O}_7$  case the enthalpies of formation of the liquid phosphates at  $1000^\circ\text{C}$  were estimated from various sources of data to be  $-2752 \text{ kJ/mol}$  for  $(\text{NaPO}_3)_2$  [6] and  $-3640 \text{ kJ/mol}$  for  $\text{Na}_4\text{P}_2\text{O}_7$  [6]; otherwise the calculations were similar.

## Discussion

**$(\text{NaBO}_2)_2 + \text{B}_2\text{O}_3$ :** The partial enthalpies of  $\text{B}_2\text{O}_3$  in this system were previously measured directly by

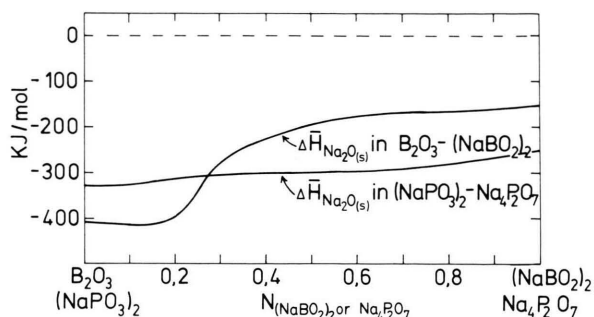


Fig. 5. Partial enthalpies of mixing  $\text{Na}_2\text{O}_{(s)}$  in the systems  $(\text{NaBO}_2)_2-\text{B}_2\text{O}_3$  and  $\text{Na}_4\text{P}_2\text{O}_7-(\text{NaPO}_3)_2$  (see text).

Østvold and Kleppa at  $985^\circ\text{C}$  [7]. Their results are included in Fig. 1, and show good agreement with the values derived from the present measurements. Itoh et al. [8] found from the temperature dependence of the emf of galvanic cells the partial enthalpies and entropies of  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  in this system at  $850^\circ\text{C}$ . Their values for  $\text{B}_2\text{O}_3$  are in very good agreement with the values of Østvold and Kleppa [7], and hence also with ours. However, their partial enthalpies of  $\text{Na}_2\text{O}$  deviate somewhat from our data, especially at very low concentrations of  $\text{Na}_2\text{O}$ . We believe that this may be due to the temperature difference between the two studies; we will return to this point below.

In order to interpret the calorimetric results a short overview of what is known about the structure of the considered melts is necessary. Recent investigations of  $\text{B}_2\text{O}_3$  glasses and liquids indicate that the boroxol ring, Fig. 6(a), is an important structural building bloc. Most investigations have been concerned with glasses [9, 10], but melts have also been studied by Raman [11] and X-ray methods [12]. It is found that in molten  $\text{B}_2\text{O}_3$  there is an increase with increasing temperature of randomly connected  $\text{BO}_3$ -groups compared to  $\text{BO}_3$ -groups incorporated into boroxol rings. From a study of the temperature dependence of the intensity of characteristic Raman lines Walrafen et al. [11] calculated the enthalpy of formation of a boroxol ring from three randomly connected  $\text{BO}_3$ -groups to be  $-26.8 \pm 1.7$  kJ/mol boroxol rings.

When a basic oxide (modifier oxide) is added to molten  $\text{B}_2\text{O}_3$  some of the boron atoms become four-coordinated. NMR-studies of borate glasses [13] have shown that the fraction of four-coordinated boron atoms appears to increase linearly up to  $N_{\text{Alk}_2\text{O}} \approx 0.28$  and has a maximum at  $N_{\text{Alk}_2\text{O}} = 0.33$ .

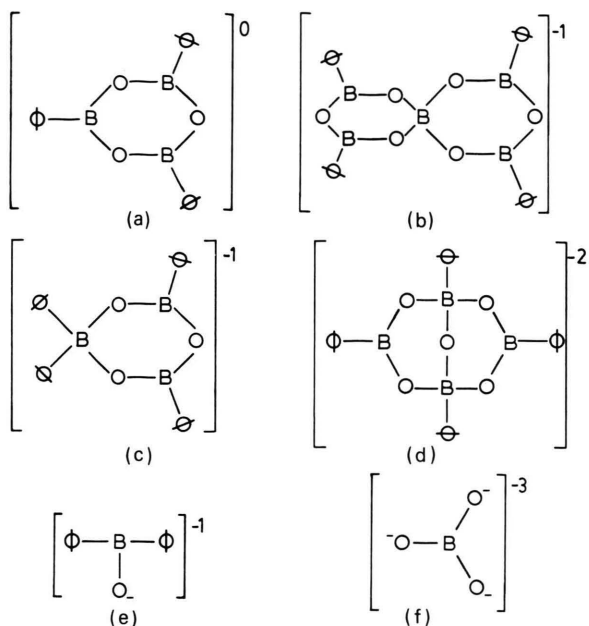


Fig. 6. Structural groups postulated to exist in the system  $\text{B}_2\text{O}_3-\text{Na}_2\text{O}$ .

- a) boroxol group, b) pentaborate group,  
c) triborate group, d) diborate group,  
e) metaborate group, f) orthoborate group.

At higher oxide contents the fraction of four-coordinated boron atoms decreases further with the formation of non-bridging oxygens; however, even at the metaborate composition ( $N_{\text{Alk}_2\text{O}} = 0.5$ ) the fraction of four-coordinated boron atoms still appears to be approximately 0.35. These observations have been interpreted to provide support for the model proposed by Krogh-Moe [14, 15] for borate glasses with  $N_{\text{Alk}_2\text{O}} < 0.33$ . He suggests that a borate melt or glass in this concentration range contains four structural units: Boroxol ( $\text{B}_3\text{O}_{4.5}$ ), pentaborate ( $\text{B}_5\text{O}_{11}$ ), triborate ( $\text{B}_3\text{O}_7$ ), and diborate ( $\text{B}_2\text{O}_5$ ), depending on the oxygen-to-boron ratio (see Fig. 6(a-d)). At  $N_{\text{Alk}_2\text{O}} = 0.33$ , he suggests that  $\text{B}_4\text{O}_7^{2-}$  should be the predominant group, and that the theoretical fraction of four-coordinated boron atoms in this group should be 0.5. However, the measured maximum is found to be about 0.45 in the sodium glass system (13), which indicates that the diborate structure probably is somewhat dissociated.

Abe [16] in 1952 postulated that diborate groups are unstable in borate glasses because two four-coordinated boron atoms are unable to link up with each other through a common oxygen bridge.

Recently this postulate again has come to the forefront of discussion as Araujo [17] has presented statistical mechanical models for borate glasses based on three-coordinated and four-coordinated borons, but with the restriction postulated by Abe. However, it has been argued by Bray et al. [18] that the indications in favor of the existence of diborate groups are strong, and they have presented an alternative model that allows for linked BO<sub>4</sub>-group. Even so, they also assume that BO<sub>4</sub>-groups linked to each other are associated with a higher energy than such groups linked only to BO<sub>3</sub>-groups.

The present measurements show that the partial enthalpy of (NaBO<sub>2</sub>)<sub>2</sub> in pure B<sub>2</sub>O<sub>3</sub> is roughly twice as large as that of B<sub>2</sub>O<sub>3</sub> in pure (NaBO<sub>2</sub>)<sub>2</sub> (–168 kJ/mol and –90 kJ/mol, respectively). While the minimum in  $\Delta H_{\text{mix}}$  occurs near  $N_{(\text{NaBO}_2)_2} \approx 0.33$ , the minimum in the enthalpy interaction parameter falls in the region 0.2 to 0.3; this is also the region where the only major changes in the partial enthalpies of (NaBO<sub>2</sub>)<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> occur and where Itoh et al. [8] find a minimum in the entropy of mixing.

On this background one is led to assume that the partial enthalpies of (NaBO<sub>2</sub>)<sub>2</sub> at high concentrations of B<sub>2</sub>O<sub>3</sub> and the partial enthalpies of B<sub>2</sub>O<sub>3</sub> at high concentrations of (NaBO<sub>2</sub>)<sub>2</sub> are linked to the formation of the same complex. This complex is expected to have a four-coordinated boron atom, and the relative amounts of metaborate-groups and BO<sub>3</sub>-groups is about 1:2. This composition corresponds to that of the triborate group B<sub>3</sub>O<sub>5</sub><sup>–</sup> (see Figure 6).

As was mentioned above, in pure molten B<sub>2</sub>O<sub>3</sub> a major part of the BO<sub>3</sub>-groups form boroxol-rings. When B<sub>2</sub>O<sub>3</sub> is dissolved in a large excess of (NaBO<sub>2</sub>)<sub>2</sub> all the BO<sub>3</sub>-tetrahedra are incorporated into B<sub>3</sub>O<sub>5</sub><sup>–</sup> groups. When B<sub>2</sub>O<sub>3</sub> is present in large excess, the B<sub>3</sub>O<sub>5</sub><sup>–</sup> groups formed from (NaBO<sub>2</sub>)<sub>2</sub> must be dissolved into the network of BO<sub>3</sub>-groups and boroxol rings. This will probably cause a larger fraction of the boroxol rings to break up, giving a positive contribution to the enthalpy of mixing of (NaBO<sub>2</sub>)<sub>2</sub> with B<sub>2</sub>O<sub>3</sub>; this explains the small positive partial enthalpies of B<sub>2</sub>O<sub>3</sub> at high concentrations of B<sub>2</sub>O<sub>3</sub>. This may possibly also explain the difference in the partial enthalpies of Na<sub>2</sub>O found in this study and found by Itoh et al. [8]. We mentioned already that their study was carried out at 850 °C. At this lower temperature the fraction of borate groups in boroxol

rings is expected to be larger than at the temperature of the present study. Hence the positive contribution to the enthalpy of mixing at high B<sub>2</sub>O<sub>3</sub> is expected to be larger; this is reflected in a stronger concentration dependence of the partial enthalpy of Na<sub>2</sub>O at high concentration of B<sub>2</sub>O<sub>3</sub> than found in the present investigation.

If our interpretation of the present measurements is correct, di-borate groups are not important in these melts, and Abe's rule is obeyed. The enthalpy of mixing at the stoichiometry of diborate (i.e.  $N_{(\text{NaBO}_2)_2} = 0.5$ ) is consistent with the formation of triborate groups as the only groups containing four-coordinated boron. Of course, this does not exclude the possibility that di-borate groups may be formed to some extent at lower temperatures, and may be important structural units in glasses. Even so, our results indicate that these groups are not very stable.

**Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + (NaPO<sub>3</sub>)<sub>2</sub>:** Meadowcroft and Richardson [19], on the basis of paper chromatography, studied the distribution of anionic chain lengths and proposed a structural model for the glasses in this system. They found that the glasses contain phosphate chains with chain lengths distributed around a mean given by the composition of the glass:

$$\bar{n} = 2/(R - 1), \quad (2)$$

where  $\bar{n}$  is the average number of phosphorus atoms in the chain, and

$$R = \frac{M}{P} = \frac{\text{number of metal equivalents}}{\text{number of phosphorus atoms}}.$$

Meadowcroft and Richardson [19] used a series of homologous equilibria to describe these findings:

$$2(\text{P}_n\text{O}_{3n+1})^{-n-2} = (\text{P}_{n+1}\text{O}_{3n+4})^{-n-3} + (\text{P}_{n-1}\text{O}_{3n-2})^{-n-1} \quad (3)$$

with equilibrium constants

$$K_n = \frac{[\text{P}_{n+1}][\text{P}_{n-1}]}{[\text{P}_n]^2}. \quad (4)$$

If the distribution of chain lengths were random, the equilibrium constants would all be unity. They found, however, for  $n < 4$   $K_n$  is less than 1, which makes the distribution narrower than for the ideal random case. By assuming the entropy of mixing of the chains of varying lengths to be ideal, the enthalpy of the equilibria [3] was calculated from the relation

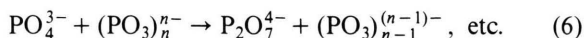
$$\ln K_n = -\Delta H/RT \quad (5)$$



setting  $T$  equal to the glass transition temperature. The enthalpy of the equilibria (3) for  $n = 2$  to 5 for the sodium system was found to be:

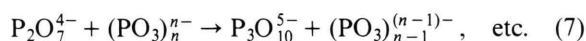
$$\begin{aligned} n = 2: \Delta H &> 41.8 \text{ kJ}, & n = 3: \Delta H &= 5.9 \text{ kJ}, \\ n = 4: \Delta H &= 1.8 \text{ kJ}, & n = 5: \Delta H &= 0.1 \text{ kJ}. \end{aligned}$$

Pure Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> corresponds to an average chain length  $\bar{n} = 2$ ;  $N_{\text{Na}_4\text{P}_2\text{O}_7} = 0.5$ ;  $\bar{n} = 4$ ;  $N_{\text{Na}_4\text{P}_2\text{O}_7} = 0.2$ ;  $\bar{n} = 10$ ;  $N_{\text{Na}_4\text{P}_2\text{O}_7} = 0.0$ ;  $\bar{n} = \infty$ . The partial enthalpies of solution of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in pure (NaPO<sub>3</sub>)<sub>2</sub> should then correspond to forcing all the equilibria (3) in pure Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> to the right. The enthalpy of the reaction



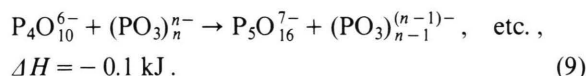
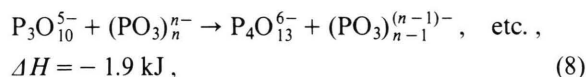
should be equal to the negative of the sum of the enthalpies of all the equilibria in (3) from  $n = 2$  to  $n = \infty$  ( $< -49.6$  kJ).

Next, the enthalpy of the reaction



should be equal to the negative of the sum of the enthalpies of the equilibria (3) from  $n = 3$  to  $n = \infty$  ( $-7.8$  kJ).

In a similar manner one has



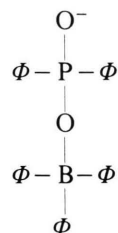
From Fig. 2 is seen that the observed partial enthalpy of solution of liquid Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in liquid (NaPO<sub>3</sub>)<sub>2</sub> is equal to  $-32$  kJ/mol. In order to explain this large negative enthalpy in terms of the values deduced by Meadowcroft and Richardson [19], one must assume a large dissociation of P<sub>2</sub>O<sub>7</sub><sup>4-</sup> in the molten state. In fact, quite a bit larger than calculated from the equilibrium constant derived from (5). As pointed out by Meadowcroft and Richardson there will be significant heat of mixing effects in addition to the distribution effect for solutions high in Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. The PO<sub>4</sub><sup>3-</sup>-ion should have a quite large negative enthalpy of solution when the other anions are mostly P<sub>2</sub>O<sub>7</sub><sup>4-</sup> and P<sub>3</sub>O<sub>10</sub><sup>5-</sup>. This might in part explain the large negative enthalpy of solution of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in (NaPO<sub>3</sub>)<sub>2</sub>.

The partial enthalpy of solution of (NaPO<sub>3</sub>)<sub>2</sub> in pure Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>,  $-39$  kJ/mol, likewise may reflect the

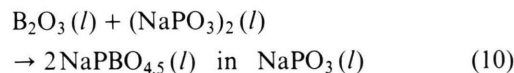
possibly large underestimate of the dissociation of the pyrophosphate ion according to the model of Meadowcroft and Richardson. The partial enthalpy of solution of (NaPO<sub>3</sub>)<sub>2</sub> seems to show a transition to more negative values in the composition range  $N_{\text{Na}_4\text{P}_2\text{O}_7} = 0.65$  to  $0.8$ , probably reflecting that the major anionic chain changes from P<sub>2</sub>O<sub>7</sub><sup>4-</sup> to P<sub>3</sub>O<sub>10</sub><sup>5-</sup> in the melt.

**(NaPO<sub>3</sub>)<sub>2</sub> + B<sub>2</sub>O<sub>3</sub>:** The (NaPO<sub>3</sub>)<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> cut in the ternary phase diagram is non-binary according to Mikhalkovich [2]. The cut crosses the primary crystallization field of at least one phase in addition to (NaPO<sub>3</sub>)<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. However, the composition of this phase is not accurately determined.

From Fig. 5 we infer that B<sub>2</sub>O<sub>3</sub> is a significantly stronger acid than (NaPO<sub>3</sub>)<sub>2</sub>. The partial enthalpy of Na<sub>2</sub>O in B<sub>2</sub>O<sub>3</sub> is  $-410$  kJ/mol, and the partial enthalpy of Na<sub>2</sub>O in (NaPO<sub>3</sub>)<sub>2</sub> is  $-330$  kJ/mol. The difference is  $-80$  kJ/mol, which is roughly the same as the partial enthalpy of B<sub>2</sub>O<sub>3</sub> in (NaPO<sub>3</sub>)<sub>2</sub>. We will therefore assume that the reaction of B<sub>2</sub>O<sub>3</sub> with the solvent when it is dissolved in (NaPO<sub>3</sub>)<sub>2</sub> leads to the transfer of about one O<sup>2-</sup> from (NaPO<sub>3</sub>)<sub>2</sub> to B<sub>2</sub>O<sub>3</sub>. Moreover, as was discussed above, it is reasonable to assume that this transfer of O<sup>2-</sup> leads to the formation of four-coordinated boron. As Abe's rule seems to be valid (see above), and four-coordinated borons therefore will not link up with each other, an entity such as



seems likely. From Fig. 3 we see that the enthalpy of the reaction



is about  $-76$  kJ/mol. At  $N_{(\text{NaPO}_3)_2} = 0.5$ , the measured value of the enthalpy of mixing is  $-19$  kJ/mol; this is consistent with a nearly random number of PBO<sub>4.5</sub>-groups. That these groups can link up to both metaphosphate groups and boronoxide tetrahedra is indicated by the near symmetry of the

partial enthalpies of both (NaPO<sub>3</sub>)<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> near  $N_{(\text{NaPO}_3)_2} = 0.5$ .

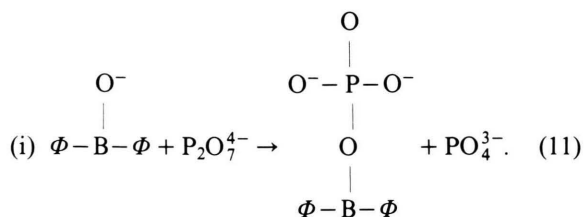
It still remains to find an explanation for the strong deviation from this apparent symmetry at quite high concentrations of B<sub>2</sub>O<sub>3</sub>. Pure molten B<sub>2</sub>O<sub>3</sub> is believed to be built up from boroxol-rings and BO<sub>3</sub> groups. When the PBO<sub>4,5</sub>-groups are dissolved into this structure it seems likely that some boroxol rings will break up for steric reasons.

The heat of formation of boroxol-rings from randomly connected BO<sub>3</sub> groups is about –27 kJ/mol boroxol rings (11). The deviation from symmetry in this system of about 86 kJ/mol might then be explained by the breakdown of about three rings per two PBO<sub>4,5</sub>-groups formed. This is not at all unreasonable considering that the complex attaches 5 boron-oxide groups in pure B<sub>2</sub>O<sub>3</sub>. Furthermore, if B<sub>2</sub>O<sub>3</sub> ideally consisted of only boroxol-rings, the addition of (NaPO<sub>3</sub>)<sub>2</sub> up to a mol-fraction of about 0.15 would have broken down all the boroxol-rings. From Fig. 3 it is seen that this approximately coincides with the minimum in the partial enthalpy of (NaPO<sub>3</sub>)<sub>2</sub>.

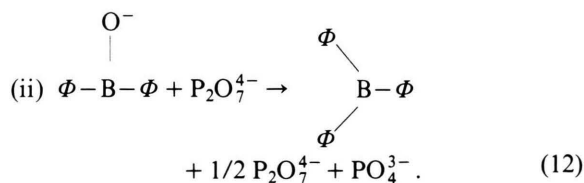
**Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + (NaBO<sub>2</sub>)<sub>2</sub>:** Figure 5 shows that Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is significantly more acid than (NaBO<sub>2</sub>)<sub>2</sub>. The partial enthalpy of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in (NaBO<sub>2</sub>)<sub>2</sub> is –52 kJ/mol, which is roughly one-half of the difference between the values for Na<sub>2</sub>O in Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and in (NaBO<sub>2</sub>)<sub>2</sub>. Using the same reasoning as above, it seems likely that approximately 1/2 O<sup>2–</sup> is transferred from (NaBO<sub>2</sub>)<sub>2</sub> to Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> for each Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> dissolved in (NaBO<sub>2</sub>)<sub>2</sub>.

Referring to the discussion of the system B<sub>2</sub>O<sub>3</sub> + (NaBO<sub>2</sub>)<sub>2</sub> above, we suggest that the partial enthalpy of Na<sub>2</sub>O in melts very high in (NaBO<sub>2</sub>)<sub>2</sub> is linked not to the formation of four-coordinated boron atoms, but to the formation from three-coordinated boron atoms with one non-bridging oxygen of three-coordinated boron atoms with only bridging oxygen atoms.

On this basis two possible reaction schemes are suggested:



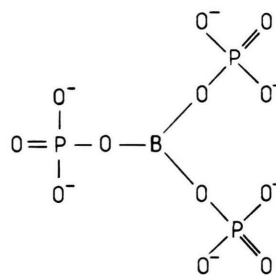
In this scheme sodium orthophosphate and a mixed complex, PBO<sub>5</sub><sup>2–</sup>, are formed.



In this scheme no mixed complex is formed, but the transfer of O<sup>2–</sup> results in the formation of uncharged, three-coordinated boron groups plus orthophosphate ions.

The phase diagram of Mikhalovich [2] shows that the Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + (NaBO<sub>2</sub>)<sub>2</sub> cut passes through the primary crystallization field of Na<sub>3</sub>PO<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, and (NaBO<sub>2</sub>)<sub>2</sub>. This has been confirmed in a separate study by Bergman and Mikhalkovich [20]. This observation may support any of the two reaction schemes suggested above. Even so, the absence of any ternary solid phase makes us inclined to favor reaction (12) compared to (11).

The rapid increase in the partial enthalpy of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> with increasing concentration of this salt in (NaBO<sub>2</sub>)<sub>2</sub> melts may be understood by taking into account that the increasing concentration of phosphate anions must be incorporated into the borate network, thus causing increasing strain. At very high concentrations of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> one would expect the borate network to be completely broken down, with the formation of complexes such as



In the reaction which generates this complex one O<sup>2–</sup> ion is transferred from borate to phosphate for each (NaBO<sub>2</sub>)<sub>2</sub> dissolved; this is also the case in reactions (11) and (12) above. From Fig. 4 it will be noted that the partial enthalpy of (NaBO<sub>2</sub>)<sub>2</sub> in pure Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is near zero, a value which must be compared with about –52 kJ/mol for Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in (NaBO<sub>2</sub>)<sub>2</sub> (i.e. about –104 kJ per mole of O<sup>2–</sup>). This difference may be understood when one takes

into account that in this quasibinary *all* the borate groups presumably transfer oxygen ions to phosphorus groups. From Fig. 5 we see that the enthalpy of adding  $\text{O}^{2-}(\text{Na}_2\text{O})$  to  $\text{Na}_4\text{P}_2\text{O}_7$  is about  $-250$  kJ/mol; on the other hand, subtracting  $\text{O}^{2-}$  from three-coordinated boron groups with one non-bridging oxygen involves an enthalpy change of about  $+150$  kJ/mol, and from four-coordinated boron groups about  $+410$  kJ/mol. If the fraction of four-coordinated boron atoms in  $(\text{NaBO}_2)_2$  is about  $0.35$  (see discussion of  $\text{B}_2\text{O}_3-(\text{NaBO}_2)_2$  above), the enthalpy of solution of  $(\text{NaBO}_2)_2$  in  $\text{Na}_4\text{P}_2\text{O}_7$  should be approximately

$$(0.35 \times 410 + 0.65 \times 150 - 250) \approx -9 \text{ kJ/mol.}$$

This crude estimate does not differ much from the observed partial enthalpy of  $(\text{NaBO}_2)_2$  which is close to zero.

**Concluding remarks:** The calorimetric results reported in this study have been interpreted to indicate that a basic building block in *acid mixtures of phosphates and borates* probably is a four-coordinated boron atoms connected to a phosphorus atom through an oxygen bridge. This group is part of a polymeric network.

In more *basic melts* the phosphate groups do not seem capable of linking up with four-coordinated boron atoms. This might be a result of the phosphate group with more non-bridging oxygen becoming too large. It is believed that the phosphate groups then link up with three-coordinated boron atoms.

The calorimetric data seem to indicate that four-coordinated boron atoms do not bridge significantly with each other at the temperature of the present study.

Work is in progress on more cuts in the ternary system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ . This should make it possible to further test the consistency and plausibility of the suggested interpretation.

#### Acknowledgements

We want to acknowledge constructive comments on this manuscript by Professor T. Yokokawa, Hokkaido University. The paper is based upon work supported by NSF under Grant CHE-8320560. The work also has benefitted from the Central Facilities of the University of Chicago-MRL.

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