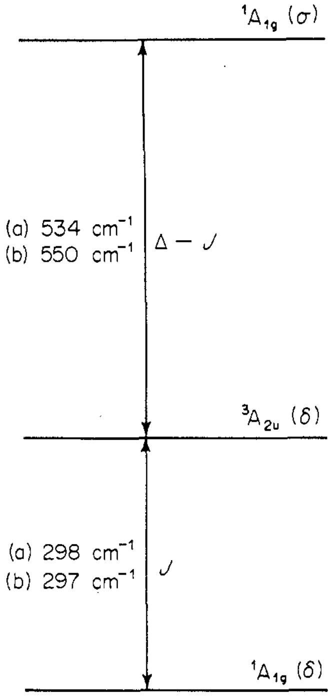

Figure 4.—Thermally populated states of cupric acetate monohydrate: (a) least-squares fit of susceptibility; (b) solving equations in χ and $\partial\chi/\partial T$.

mental values of g and J (Table IIa), values calculated from eq 1 using experimental values of g and the best-fit values of J (Table IIb), values calculated from eq 1 using experimental values of J and best-fit values of g (Table IIc), and finally values calculated from eq 3 by least-squares procedures. Method IIb was originally used by Bleaney and Bowers[5] and method IIc by Figgis and Martin.[6] The value of 2.193 used for g in early work[5] has been revised to 2.167 as a result of more accurate esr measurements,[12] and the commonly used value of $N\alpha$ for two Cu(II) ions was revised[22] from 0.000120 to 0.000150 on the basis of the electronic spectrum. For each calculation, the closeness of fit is indicated by an average deviation. The most successful calculation based on eq 1 is the case where only J was allowed to vary freely in the fitting procedure. The effect of varying J on the calculated susceptibility is much more profound than that of varying g, so that when both are allowed to vary freely for a series of cupric acetate homologs the values obtained for g vary more widely than the J values.[4] As neither g nor $N\alpha$ are expected to vary greatly for binuclear Cu(II) complexes,[22] we would suggest that the practice of treating these as free parameters should be discontinued. When an experimental value is not available for g, its value might well be constrained within the limits $g = 2.17 \pm 0.02$. Likewise $N\alpha$ may usually be estimated from the electronic spectrum.[22]

We emphasize that, as a result of the large electron repulsion energies (which may normally be neglected when discussing the magnetic properties of Cu(II) systems), the metal–metal bonding energies contribute very little to the overall stability of the dimeric complex. This view correlates with the relative positions of the metal atoms with respect to the coordinated oxygen atoms in dimeric copper and molybdenum acetates.[28,29]

Acknowledgments.—We are indebted to Dr. L. Dubicki for helpful comments and to the Science Research Council for support.

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[28] D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).
[29] F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Thermochemistry of Liquid Borates. II. Partial Enthalpies of Solution of Boric Oxide in Its Liquid Mixtures with Lithium, Sodium, and Potassium Oxides

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The partial enthalpies of solution of B_2O_3 in its liquid mixtures with Li_2O, Na_2O, and K_2O have been measured at 940° (Li_2O–B_2O_3, $0.4 < N_{B_2O_3} < 1.0$) and at 985° (Na_2O–B_2O_3, $0.5 < N_{B_2O_3} < 1.0$; K_2O–B_2O_3, $0.7 < N_{B_2O_3} < 1.0$). In all these systems the partial enthalpy of B_2O_3 is slightly positive in the high B_2O_3 range ($N_{B_2O_3} > 0.85$–0.90) but becomes negative at lower B_2O_3 contents, the exothermic character increasing in the sequence Li_2O–B_2O_3 < Na_2O–B_2O_3 < K_2O–B_2O_3. The results are discussed in terms of recent observations of subliquidus immiscibility in alkali borate glasses and of attempts to derive structural information on the nature of borate species in the melts from phase diagram data.

Introduction

During the past several years we have developed calorimetric methods which allow detailed and precise thermochemical studies of ionic melts at temperatures up to about 1000°. Recently these methods were applied for a thermochemical investigation of the liquid system PbO–B_2O_3 at 800°.[1] At this temperature the viscosity of B_2O_3 is still quite high. Therefore, we were unable to study the concentration range between 65 and 100% B_2O_3.

In the present communication we report an extension

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[1] J. L. Holm and O. J. Kleppa, *Inorg. Chem.*, **6**, 645 (1967).

of this work to the solutions of Li_2O, Na_2O, and K_2O in B_2O_3. Due to the attack of the basic melts on the platinum containers, we were unable to study melts high in the alkali oxides. Our work covers the range 40–100% B_2O_3 in the system Li_2O–B_2O_3, 50–100% B_2O_3 in Na_2O–B_2O_3, and 70–100% B_2O_3 in K_2O–B_2O_3.

Experimental Section

The chemicals used for preparing the alkali borate melts were boric acid (Baker Analyzed reagent), lithium metaborate (Lithcoa, $LiBO_2 \cdot 2H_2O$), lithium tetraborate (Lithcoa, $Li_2O \cdot 2B_2O_3$), lithium peroxide (Lithcoa, Li_2O_2, 95%), sodium metaborate (Fisher, $Na_2B_2O_4 \cdot 8H_2O$, purified), and potassium metaborate (K & K Laboratories, Inc., 95–99%). Semiquantitative spectrographic analyses showed no metallic impurities beyond 0.05% by weight in any of the salts. After the salts had been melted, analysis for the alkali metal content showed that the various borates used had the following alkali oxide to boric oxide ratios: $Li_2O:B_2O_3 = 1.00$; $Li_2O:B_2O_3 = 0.499$; $Na_2O:B_2O_3 = 1.00$; $K_2O:B_2O_3 = 1.20$. The potassium metaborate also contained carbonate impurities. Since the potassium to boron ratio in the potassium metaborate differed considerably from the theoretical value 1.00, all the borate glasses prepared from this salt were analyzed for potassium. The lithium peroxide was analyzed for lithium. On the basis of the lithium content, this salt was found to contain 97.5% Li_2O_2 by weight, the probable impurities being Li_2O and Li_2CO_3. Anhydrous B_2O_3 glass was prepared from boric acid by heating the boric acid in air in a platinum dish at 1250° for 20–30 hr. This treatment gives a B_2O_3 glass with a water content of ~0.2 mol %.[2] The B_2O_3 melt was quenched on a silver plate, crushed to small lumps of about 0.1–0.2 g, and stored in a closed container. The total time the glass was exposed to the air in the laboratory before use was of the order of 10 min or less.

The calorimetric experiments were performed at two different temperatures. The Li_2O–B_2O_3 mixtures were investigated at 940°, and the Na_2O–B_2O_3 and K_2O–B_2O_3 mixtures at 985°. The calorimeter was a single-unit microcalorimeter which was constructed for temperatures up to 1100°. Apart from its single (rather than twin) construction, this apparatus is similar to the one used by Hersh and Kleppa[3] at temperatures up to about 800°. In the absence of a twin construction the furnace surrounding the calorimeter is equipped with a very stable Leeds and Northrup proportional temperature controller. The calorimeter assembly also is heavily lagged with respect to the furnace so as to avoid as far as possible short-term drifts resulting from slight variations in the controlled temperature.

The temperature-sensing device of this calorimeter consists of a 54 + 54 junction Pt—Pt–13% Rh thermopile, the output of which is amplified by means of a Leeds and Northrup 9835-B dc amplifier and recorded on a Leeds and Northrup type H-Azar recorder.

The oxide melt in an amount of about 20 g was contained in a platinum crucible of 17-mm diameter and 60-mm height. The boron oxide to be dissolved in the melt was kept in a very shallow platinum cup of about 10-mm diameter. This cup was suspended, by means of three platinum wires, from a fused-silica tube which could be manipulated from outside the furnace system. The solution reaction was initiated by lowering the platinum cup into the melt. Stirring was accomplished by means of a platinum-covered silica plunger. The liquid B_2O_3 was displaced and brought to reaction by inserting the plunger into the platinum cup. Dry nitrogen gas at a flow rate of about 10 cm^3/min was flushed through the silica envelope during all calorimetric experiments.

TABLE I

ENTHALPIES OF SOLUTION OF LIQUID B_2O_3 IN ALKALI BORATE MELTS (KCAL/MOL)

Li_2O–B_2O_3, 940°		Na_2O–B_2O_3, 985°		K_2O–B_2O_3, 985°	
$N_{B_2O_3}$	$\Delta H_{B_2O_3}/\Delta n_{B_2O_3}$	$N_{B_2O_3}$	$\Delta H_{B_2O_3}/\Delta n_{B_2O_3}$	$N_{B_2O_3}$	$\Delta H_{B_2O_3}/\Delta n_{B_2O_3}$
0.951	0.10	0.951	0.09	0.951	0.25
0.950	0.09	0.950	0.18	0.952	0.19
0.903	0.20	0.903	0.28	0.901	−0.03
0.902	0.16	0.901	0.19	0.836	−1.9
0.853	0.01	0.853	−0.25	0.778	−8.2
0.851	0.04	0.851	−0.35	0.778	−7.0
0.803	−1.5	0.805	−3.4	0.721	−15.3
0.801	−1.7	0.803	−3.6	0.721	−14.5
0.760	−2.7	0.801	−4.3	0.682	−20.8
0.703	−6.0	0.755	−6.9		
0.701	−5.8	0.753	−7.6		
0.674	−7.1	0.751	−8.1		
0.671	−7.5	0.705	−11.3		
0.669	−7.7	0.703	−10.9		
0.609	−10.0	0.701	−12.4		
0.607	−10.5	0.655	−14.2		
0.603	−10.8	0.653	−14.4		
0.576	−11.7	0.651	−13.6		
0.556	−11.8	0.603	−15.7		
0.553	−12.0	0.601	−16.6		
0.551	−12.0	0.555	−17.9		
0.528	−13.9	0.551	−18.0		
0.526	−13.8	0.504	−19.1		
0.504	−14.2	0.501	−19.3		
0.502	−14.6				
0.501	−14.2				
0.458	−15.3				
0.455	−14.8				
0.453	−14.8				
0.406	−14.9				
0.404	−14.9				
0.402	−14.7				

From one to four experiments were performed for each filling of the platinum crucible. In each experiment 1–5 mmol of liquid B_2O_3 was added to the melt. Through each addition the mole fraction of boron oxide in the melt never changed by more than 0.005. Corrections were made for the heat effect associated with each set of stirrings. This heat effect is endothermic in character and is largely due to a small mass displacement along the vertical temperature gradient of the calorimeter. This gradient was about 0.1°/in. over about 7 in. The stirring correction represented from 1 to 50% of the total heat of reaction, depending on the magnitude of the heat effect.

The calibration of the calorimeter was carried out by dropping, from room temperature into the apparatus at working temperature, small pieces of pure 2-mm Pt wire, which weighed a total of about 0.5 g. The evaluation of the resulting endothermic heat effect was based on Kelley's equation for the heat content of platinum.[4] No difference was found between calibrating into the platinum-covered plunger and calibrating directly into the alkali borate melt. During its fall into the calorimeter, the platinum wire picked up some heat. The magnitude of this effect was determined in separate experiments, by carrying out calibrations with platinum wires of different diameters. Extrapolation to zero surface area showed that for 2-mm wires, the pickup of heat represents 3% of the heat content at 900° and 4% at 1000°. These values were interpolated to give the corrections for 940 and 985°, respectively.

Results and Discussion

Partial Enthalpies of Solution of B_2O_3 in Alkali Borates.—In Table I we give a summary of the actual experimental results obtained in the course of the present work. The experimental quantities recorded in Table I are $\Delta H_{B_2O_3}/\Delta n_{B_2O_3}$. Since the changes in the

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[2] J. Boow, *Phys. Chem. Glasses*, **8**, 45 (1967).

[3] L. S. Hersh and O. J. Kleppa, *J. Chem. Phys.*, **42**, 1309 (1965).

[4] K. K. Kelley, Bureau of Mines Bulletin No. 584, U. S. Government Printing Office, Washington, D. C., 1960.

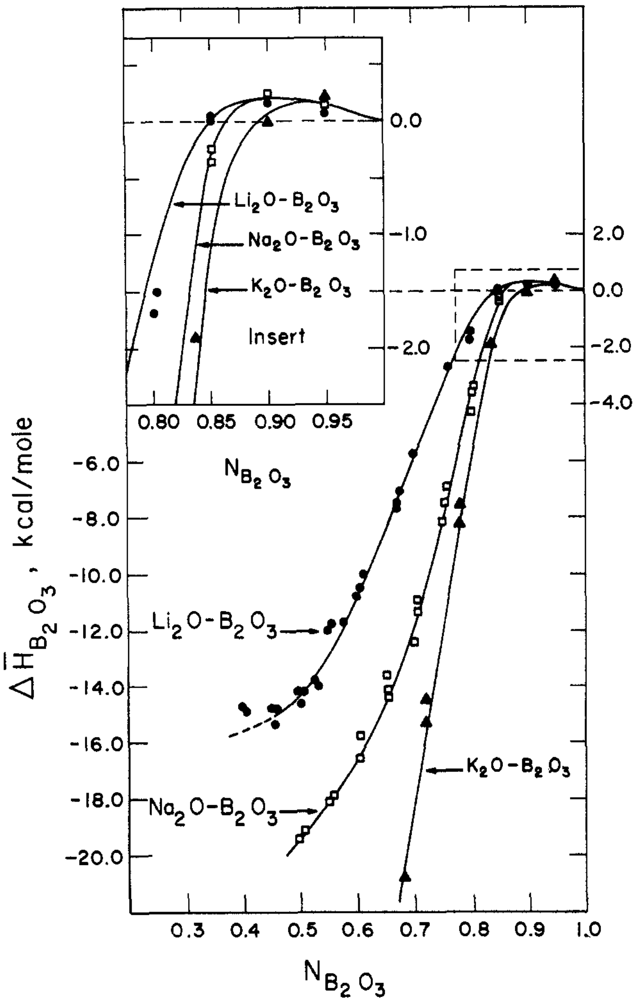

Figure 1.—Relative partial enthalpies of B_2O_3 in the lithium, sodium, and potassium borate melts at 940, 985, and 985°, respectively.

composition of the melt which result from the additions of boron oxide are quite small (see above), this ratio may be considered to approximate the relative partial molar enthalpy of boron oxide, $\Delta\bar{H}_{B_2O_3}$. In two previous publications[1,5] experimental justification has been given for this.

As already noted above the potassium metaborate from which the potassium borate melts were prepared contained carbonate impurities. A basic melt will tend to dissolve the carbonate impurity. When $B_2O_3(l)$ is added to a carbonate-containing melt, the reaction

$$CO_3^{2-} \text{ (in melt)} + B_2O_3(l) = CO_2(g) + \text{borate (in melt)}$$

may occur and contribute to the total heat effect developed during the experiment. Under these conditions the experimentally observed enthalpies may deviate from the true partial enthalpies of boron oxide. Hence, the reported enthalpy data for the potassium borate system may be associated with systematic errors. They are presented here principally for the purpose of illustrating the general trend in the data toward more exothermic behavior from $Li_2O-B_2O_3$, through $Na_2O-B_2O_3$, to $K_2O-B_2O_3$.

A similar reaction may occur due to the presence of small amounts of water in the B_2O_3 glass used in the calorimetric experiments. However, Holm and Kleppa[1] did not observe any significant difference between their experimental partial enthalpies of B_2O_3 in lead-borate melts and the same quantities calculated by a Gibbs–Duhem integration of the corresponding lead oxide data. It is believed that the small amounts of water present in the B_2O_3 glasses will be of little or no importance within the limits of error achieved in the present work.

Figure 1 gives a graphical representation of the dependence of $\Delta\bar{H}_{B_2O_3}$ on composition for the three borate systems studied. Note in particular the positive relative partial enthalpies of boron oxide in the B_2O_3-rich melts. These positive values are related to the tendency of the alkali borates to develop immiscibility at subliquidus temperatures.[6] This problem will be discussed further below.

In their earlier work on the system $PbO-B_2O_3$ Holm and Kleppa[1] noted a relatively sharp dependence of the partial enthalpies on composition in two rather narrow concentration regions, $N_{B_2O_3} = 0.16–0.20$ and $N_{B_2O_3} = 0.55–0.60$. They suggested that this behavior might be related to acid–base reactions of the type

$$O^{2-} + B_2O_3 = \text{borate-1 anion} \qquad (1)$$

$$\text{borate-1 anion} + B_2O_3 = \text{borate-2 anion} \qquad (2)$$

The location of the two relatively sharp changes in partial enthalpy was attributed to the essential "completion" of these two acid–base steps at the two compositions in question.

In his discussion of possible anionic species present in sodium borate melts, Krogh-Moe[7] suggested that the following equilibrium exists between three borate species in the most acid region (0–33.3 mol % Na_2O) of the borate melt

$$3B_8O_{13}^{2-} \rightleftarrows 3B_4O_7^{2-} + 4B_3O_{4.5} \qquad (3)$$

On the assumption of a temperature-independent equilibrium constant and 10% dissociation of the tetraborate group at 20 mol % sodium oxide, Krogh-Moe calculated the melting point depressions of sodium tetraborate, $Na_2O \cdot 4B_2O_3$, by additions of B_2O_3 (and of Na_2O). He obtained the following equation for the relative partial entropy of the tetraborate

$$\Delta\bar{S}_{Na_2O \cdot 4B_2O_3} = -R \ln N_{Na_2O \cdot 4B_2O_3} - S^0_{Na_2O \cdot 4B_2O_3} - \frac{\alpha R}{3} \ln K \qquad (4)$$

Here $N_{Na_2O \cdot 4B_2O_3}$ is the mole fraction of the tetraborate anion $B_8O_{13}^{2-}$, α is the degree of dissociation, and K is the equilibrium constant for the equilibrium

$$3B_8O_{13}^{2-} = 3B_4O_7^{2-} + 4B_3O_{4.5}$$

$S^0_{Na_2O \cdot 4B_2O_3}$ is the entropy of pure liquid sodium tetraborate. By assuming $\alpha = 0.1$ at the tetraborate composition, and a temperature-independent equilibrium constant, α and $N_{Na_2O \cdot 4B_2O_3}$ can be obtained for different concentrations of boron oxide. Thus, the

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(5) T. Østvold and O. J. Kleppa, *Inorg. Chem.*, **8**, 78 (1969).

(6) R. R. Shaw and D. R. Uhlmann, *J. Am. Ceram. Soc.*, **51**, 377 (1968).

(7) J. Krogh-Moe, *Phys. Chem. Glasses*, **3**, 101 (1962).

relative partial entropy of tetraborate and the liquidus line can be calculated.

A part of the phase diagram for the system Na_2O–B_2O_3, which shows the melting point depression of sodium tetraborate by boron oxide, is shown in Figure 2. It will be seen that curve 1, which is based on the Krogh-Moe model calculation,[7] is in excellent agreement with the experimental[8] liquidus line. This calculation was based on the assumption that the partial enthalpy of the borate ($Na_2O\cdot4B_2O_3$) may be neglected over the considered range in composition. However, the new enthalpy data reported in the present work raise serious doubts about this assumption and accordingly about the significance of these calculations.

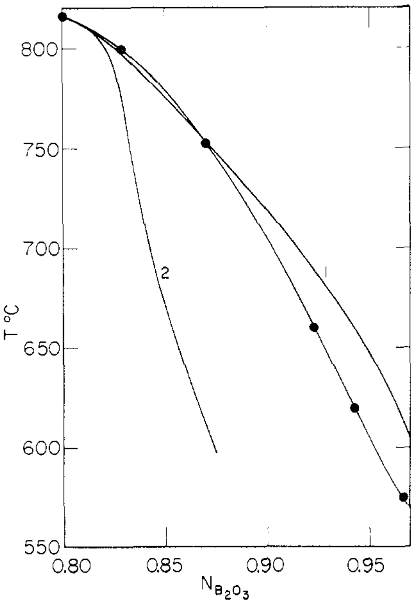

Figure 2.—Part of the phase diagram of the system Na_2O–B_2O_3 showing the melting point depression of $Na_2O\cdot4B_2O_3$ by B_2O_3. The experimental values according to Morey and Merwin[8] are shown as circles. Curves 1 and 2 give melting point depressions calculated on the basis of a structural model for the melt proposed by Krogh-Moe.[7] Krogh-Moe assumed a random distribution of the following structural elements: $B_8O_{13}^{2-}$, $B_4O_7^{2-}$, $B_3O_{4.5}$ (10% dissociation of the $B_8O_{13}^{2-}$ group at $N_{B_2O_3}$ = 0.80). For curve 1, $\Delta\bar{H}_{Na_2O\cdot4B_2O_3}$ was assumed to be zero. For curve 2, actual values of $\Delta\bar{H}_{Na_2O\cdot4B_2O_3}$ were used (see Figure 3).

This will be apparent from an inspection of Figure 3, in which we plot the relative partial enthalpies of the tetraborate melts for mole fractions of B_2O_3 larger than $N_{B_2O_3} = 0.80$ (*i.e.*, for $N_{\text{tetraborate}} \leq 1.00$). The plotted curves have been obtained by Gibbs–Duhem integrations of the partial enthalpy data for B_2O_3. In particular, we note that the relative partial enthalpy of sodium tetraborate assumes significant negative values already for relatively modest additions of B_2O_3. Hence, they clearly must be included in any meaningful calculation of the melting point depression of sodium tetraborate by additions of B_2O_3.

When the partial enthalpy of mixing of sodium tetraborate is included, the appropriate expression for the partial entropy, which in turn allows a calculation of the liquidus line (eq 4), is

$$\Delta\bar{S}_{Na_2O\cdot4B_2O_3} = \frac{\Delta\bar{H}_{Na_2O\cdot4B_2O_3}}{T} + \left[\Delta H_f - \frac{\Delta C_p}{2}(T_f - T)\frac{T_f}{T}\right]\left(\frac{1}{T} - \frac{1}{T_f}\right) \quad (5)$$

Here $\Delta\bar{S}_{Na_2O\cdot4B_2O_3}$ and $\Delta\bar{H}_{Na_2O\cdot4B_2O_3}$ are the partial molar entropy and enthalpy, respectively, of molten sodium tetraborate in the mixture relative to pure liquid sodium tetraborate at that temperature. ΔH_f is the enthalpy of fusion of sodium tetraborate at the melting point T_f. ΔC_p is the (assumed constant) difference in specific heat of crystallized sodium tetraborate and supercooled molten sodium tetraborate at the temperature T derived from heat capacity data. The values of ΔH_f (31.33 kcal/mol) and ΔC_p (48 cal/mol deg) were obtained from Smith and Rindone.[9]

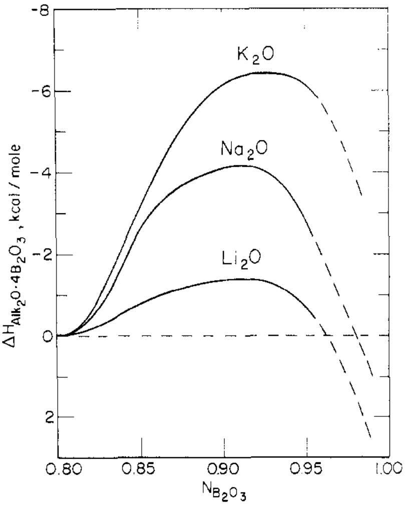

Figure 3.—Relative partial enthalpies of $Li_2O\cdot4B_2O_3$, $Na_2O\cdot4B_2O_3$, and $K_2O\cdot4B_2O_3$, respectively, in their borate melts calculated by Gibbs–Duhem integrations of the relative partial enthalpies of boron oxide in the same melts (Figure 1).

The results of our own calculation of the liquidus line, which takes into account the partial enthalpy of $Na_2O\cdot4B_2O_3$ in the melts, are given as curve 2 in Figure 2. The poor agreement with the experimental points seems to rule out the model based on eq 3 as an acceptable way of describing the considered sodium borate melts.

Other simple models proposed by Krogh-Moe based on random mixing of different borate anions in a three-dimensional framework or on random mixing of boron in fourfold and in threefold coordination similarly give poor agreement with the experimental liquidus line. Note, however, that since in all these calculations only configurational contributions to the entropy of mixing are considered, it is of course possible that the poor agreement may be due to our disregard of possible vibrational entropy changes associated with the mixing process.

Some 15 years ago Shartsis and Capps[10] determined

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[8] G. W. Morey and H. E. Merwin, *J. Am. Chem. Soc.*, **58**, 2248 (1936).

[9] G. S. Smith and G. Rindone, *J. Am. Ceram. Soc.*, **44**, 72 (1961).

[10] L. Shartsis and W. Capps, *ibid.*, **37**, 27 (1954).

the integral enthalpies of mixing of boron oxide–alkali oxide glasses from the enthalpies of solution of the glasses and of the components in the same solvent at room temperature. (However, the enthalpies of solution of the pure alkali oxides had to be calculated from heat of formation data.) We have calculated the relative partial enthalpies of boron oxide at 25° from the data of Shartsis and Capps. These are given as solid curves in Figure 4 for comparison with our own data (broken curves). Note in particular that the work of Shartsis and Capps gives no indication of the positive values of the relative partial enthalpies of B_2O_3 at high mole fractions of boron oxide.

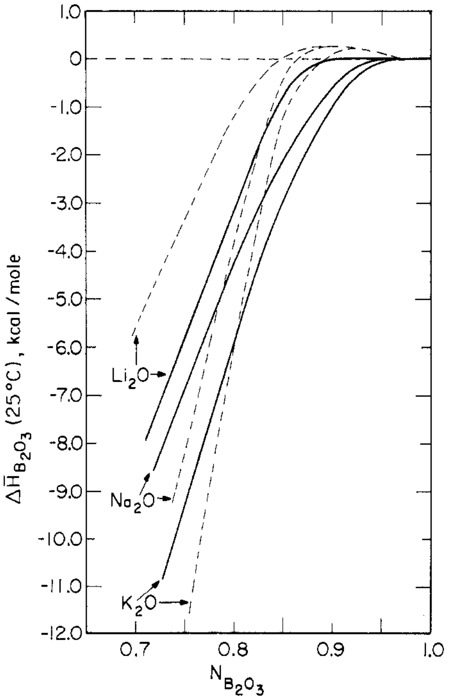

Figure 4.—Relative partial enthalpies of B_2O_3 in lithium, sodium, and potassium borates: solid lines, data for glasses at 25° calculated from the integral enthalpies of Shartsis and Capps;[10] broken lines, data from present work at 940–985°.

Shaw and Uhlmann[6] showed in a recent investigation that subliquidus immiscibility occurs in the B_2O_3-rich glasses in all binary alkali borate systems. This indicates that the partial enthalpies of B_2O_3 remain positive in the high B_2O_3 range even at lower temperatures. In view of the many uncertainties associated with the integral enthalpy data of Shartsis and Capps and the possible errors associated with deriving partial enthalpies from integral enthalpy values, we do not attach great significance to this discrepancy. Apart from this, there is semiquantitative agreement between our own new high-temperature results and the partial enthalpies derived from the room-temperature data of Shartsis and Capps. This suggests that the partial enthalpies of B_2O_3 in the alkali borate melts change little with temperature and is consistent with the modest temperature dependence of the enthalpy of mixing found in most simple fused-salt systems.

Partial Entropies of B_2O_3 in Alkali Borate Glasses for $N_{Alk_2O} < 0.15$.—The Raman spectrum of pure boron oxide glass suggests that the vitreous phase contains the boroxol group $B_3O_{4.5}$.[11] In this group three BO_3 triangles are combined into a six-membered ring with alternate boron and oxygen atoms. When alkali oxide is added to the boron oxide glass, fourfold coordination of boron occurs. According to Krogh-Moe[12] the fraction of boron atoms in fourfold coordination is

$$N_{BO_4} = \frac{N_{Alk_2O}}{1 - N_{Alk_2O}}$$

In a thermodynamic study of the system B_2O_3–Ag_2O, Willis and Hennessy[13] observed that the activity of silver oxide for dilute solutions of silver oxide in boron oxide melts is proportional to the concentration of silver oxide. This implies that the silver oxide is present in a structural entity of the type $Ag_2O \cdot nB_2O_3$ (rather than as $0.5Ag_2O \cdot nB_2O_3$), where "nB_2O_3" indicates that portion of B_2O_3 which has been affected by the Ag_2O.

Førland[14] pointed out that the freezing point depression in common anion systems, in cases where polymerization occurs, sometimes can be explained by assuming the existence of two kinds of anions, namely, bridging and nonbridging anions. In order to explain the freezing point depression caused by several metal oxides in silica Førland assumed a pairing of the nonbridging oxygens. In the same way the observations of Willis and Hennessy may be interpreted to indicate that the Ag^+ ions are structurally "paired" in silver oxide–boron oxide melts, when the boron oxide concentration is high.

Krogh-Moe[15] has discussed various structural models for borate melts, based on the structural entities outlined above, and has given the corresponding expressions for the partial entropy of B_2O_3 in B_2O_3-rich melts. In Figure 5 we have plotted our own relative partial enthalpies of B_2O_3 in sodium borate, along with corresponding relative partial Gibbs free energies (at 985°), obtained by combination of our own partial enthalpies with the entropies calculated from four different structural models considered by Krogh-Moe. Model (curve) 1: $\Delta\bar{G}_{B_2O_3}$ calculated from a random distribution of BO_3 triangles and BO_4 tetrahedra

$$\Delta\bar{G}_{B_2O_3} = \Delta\bar{H}_{B_2O_3}{}^{obsd} + 2RT \ln \frac{1 - 2N}{1 - N}$$

$$N = N_{Na_2O}$$

Model (curve) 2: $\Delta\bar{G}_{B_2O_3}$ calculated from a random mixing of bridging and nonbridging oxygen ions

$$\Delta\bar{G}_{B_2O_3} = \Delta\bar{H}_{B_2O_3}{}^{obsd} + 3RT \ln \frac{3 - 4N}{3 - 2N}$$

In these two models the metal ions are uniformly distributed. Model (curve) 3: $\Delta\bar{G}_{B_2O_3}$ calculated for

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(11) J. Goubeare and H. Keller, *Z. Anorg. Allgem. Chem.*, **272**, 303 (1953).

(12) J. Krogh-Moe, *Phys. Chem. Glasses*, **3**, 1 (1962).

(13) G. M. Willis and F. L. Hennessy, *J. Metals*, 1367 (1953).

(14) T. Førland in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co. Inc., New York, N. Y., 1964, p 150.

(15) J. Krogh-Moe, *Arkiv Kemi*, **14**, 553 (1959).

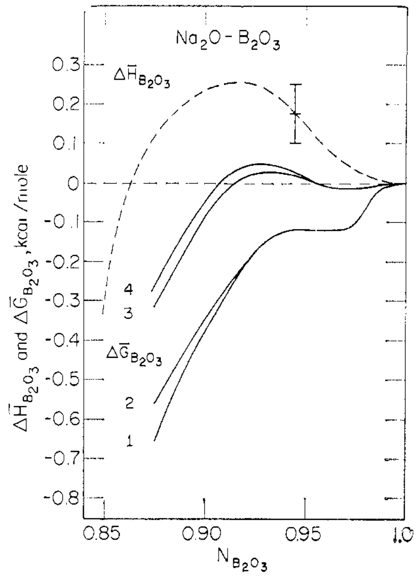

Figure 5.—Relative partial enthalpies and relative partial Gibbs free energies of boron oxide in the sodium borate melts at 985°. $\Delta\bar{H}_{B_2O_3}$ as a function of concentration is shown as the broken line. The vertical bar indicates the uncertainty in the experimental $\Delta\bar{H}_{B_2O_3}$. $\Delta\bar{G}_{B_2O_3}$ as a function of concentration is shown for four different models (1–4) for the sodium borate melts. The models are described in the text.

a mixture of BO_3 triangles (monomers) and pairs of BO_4 tetrahedra (dimers)

$$\Delta\bar{G}_{B_2O_3} = \Delta\bar{H}_{B_2O_3}{}^{obsd} + RT\left[\frac{N}{1-N} + 2\ln\frac{1-2N}{1-N}\right]$$

For mixtures of this type see ref 16. Model (curve) 4: $\Delta\bar{G}_{B_2O_3}$ calculated for a random mixture of bridging oxygens and nonbridging oxygen pairs

$$\Delta\bar{G}_{B_2O_3} = \Delta\bar{H}_{B_2O_3}{}^{obsd} + 3RT\ln\frac{3-4N}{3(1-N)}$$

Models 3 and 4 are based on an assumed pairing of the metal cations in the borate melt.

From Figure 5 it will be noted that all four models seem to predict demixing of the sodium borate melt at 985°. This is *not* consistent with the available experimental information. Thus we saw no evidence of demixing in our own calorimetric experiments at this temperature. Also, the consolute temperature for $Na_2O-B_2O_3$ glasses indicated by the work of Shaw and Uhlmann[6] is about 590°. On the other hand, it should be recognized that the values of $\Delta\bar{H}^{obsd}$, used in Figure 5, are associated with very considerable experimental uncertainty, and may possibly be in error by as much as ±0.1 kcal/mol. This is the largest difference between two measured experimental partial enthalpies at the same composition in the concentration range $N_{Na_2O} < 0.15$. There also may be vibrational entropy terms that should be taken into account. It is therefore difficult on the basis of Figure 5 to draw any definite conclusions concerning the validity of the considered models. However, the rather strong tendency toward demixing at 985° shown by the calculated curves for models 3 and 4 may possibly indicate that the Na^+ ions are not structurally "paired" in the sodium oxide–boron oxide melts. On the other hand, models 1 and 2 appear to be rather more acceptable, since the apparent tendency toward demixing at 985°, indicated by Figure 5, clearly is quite weak. It could easily be explained by assuming that the true relative partial enthalpy curve runs somewhat lower than the one given in Figure 5.

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(16) E. A. Guggenheim, "Mixtures," Oxford at the Clarendon Press, 1952, p 215.