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The Density and Molar Volume of a Binary Liquid, B_2O_3-H_2O

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The density of the binary B_2O_3-H_2O liquid system with concentrations of from 4.9 to 83.0 mol% B_2O_3 has been measured, and the mean volume expansivity has been calculated. The molar volume and the expansivity of this system has then been compared with those of other binary borates. The experimental results suggest a change in the boron-to-oxygen coordination number between the $3B_2O_3 \cdot H_2O$ and $B_2O_3 \cdot H_2O$ compositions. The thermal expansivity of this system shows a different trend from those of alkali borate melts.

On the structure of B_2O_3 in glass and liquid states many investigations[1] have been made. While the presently-available data are insufficient for any structural conclusions to be drawn particularly for the molten state, it can be said that the oxide is formed from a random network structure constructed of planar BO_3 triangular units in the two states except for the high-temperature range, *e.g.*, the temperature range far above the liquidus. The network link is gradually disrupted by the addition of alkali oxides, alkaline earth oxides[1] and other basic oxides.[2,3] These are, therefore, called "network modifiers." The thermodynamic and kinetic properties of the binary oxidic melts change continuously with their composition. In addition to this trend, binary metal borate melts show a so-called boron anomaly, which has been interpreted in terms of the structural change from BO_3 triangular to BO_4 tetrahedral units in the network.[4-6] This change in coordination number also takes place on binary alkali germanates.[7]

As to the binary B_2O_3-H_2O system, so far the experimental investigations have been restricted to a dilute aqueous solution of boric acid, on the one hand, and to a boron trioxide melt with trace of water, on the other hand. On the basis of the experimental evidence on the latter, such as the B–OH absorption band and the dependence of the solubility of water on its partial pressure, it seems that the dissolution can be expressed by the following equation:[8]

$$\rangle B\text{–}O\text{–}B\langle + H_2O = 2\rangle B\text{–}O\text{–}H \qquad (1)$$

Thus, the water molecule modifies the network as do alkali metal oxides. The solubility decreases with the alkali content in the melt. In other works, water behaves as a base weaker than the alkali oxides. On the other hand, boric acid dissociates at three steps in a dilute aqueous solution, the dissociation being, respectively, promoted and inhibited by the presence of a basic and a strong acid substance.

The purpose of the present study is to make a structural examination of this binary system over the whole composition range by studying the molar-volume trend especially. The electrical conductivity of this system is now being studied.

Experimental

Materials and Reagent. Specimens with the desired compositions were prepared by mixing proper amounts of two reagents from among boric acid, metaboric acid, and boron trioxide of a guaranteed reagent grade, and distilled water. It was useful to start from combinations of H_3BO_3 and B_2O_3, and of HBO_2 and B_2O_3 corresponding to the desired composition except in the range of water content higher than 75 mol% (boric acid). The mixture was heated in a sealed Pyrex glass tube in order to make a uniform solution. The melts' compositions were determined from the quantities of chemicals employed over the H_2O and H_3BO_3 range. Otherwise, the quenched samples were analyzed by volumetric titration with NaOH in the presence of manitol.

Apparatus and Procedure. In order to cover the melt of the whole composition, the temperature had to be raised to a point where the vapor pressure was

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1) See for review, J. D. MacKenzie, "Modern Aspects of the Vitreous State," Vol. 1, Butterworths, London (1960).

2) H. Kodama, Y. Kimura, T. Yokokawa and K. Niwa, This Bulletin, **42**, 681 (1969).

3) T. Maekawa, T. Yokokawa and K. Niwa, *ibid.*, **42**, 677 (1969).

4) L. Shartsis, W. Capps and S. Spinner, *J. Amer. Ceram. Soc.*, **36**, 319 (1953).

5) L. Shartsis and H. F. Shermer, *ibid.*, **37**, 544 (1954).

6) J. Krogh-Moe, *Phys. Chem. Glass*, **3**, 1 (1962).

7) E. F. Riebling, *J. Chem. Phys.*, **39**, 3022 (1963).

8) H. Franz, *J. Amer. Ceram. Soc.*, **49**, 473 (1966).

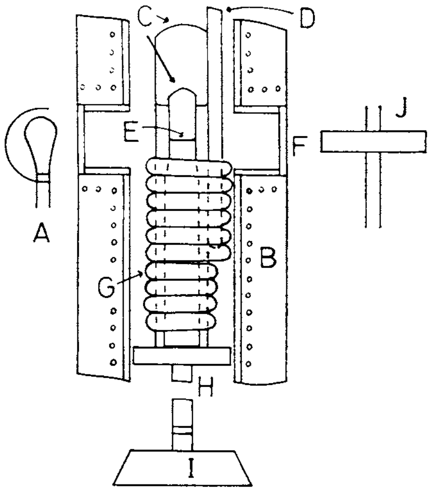

Fig. 1. Apparatus for measurement of density.
A: light source, B: electrical furnace, C: glass tube, D: thermocouple sheath, E: liquid level, F: glass window, G: cupper wire, H: alumina tube, I: lift, J: cathetometer

as high as seven atm.[9] A diagramatic sketch of the apparatus for measuring the density is given in Fig. 1. The Pyrex glass tube shown in Fig. 2 was employed as a densimeter. Figure 1 shows how it was wound with a copper wire and set at the center of an electric resistance furnace, through the windows of which the liquid level could be observed. The densimeter tube was moved up and down at the rate of 2.11 mm/min by means of a lifting device equipped with a synchronus motor. The time needed to drive the motor to reach a given liquid level gave the height. The relation between the height of the liquid column and its volume was calibrated with distilled water at room temperature.

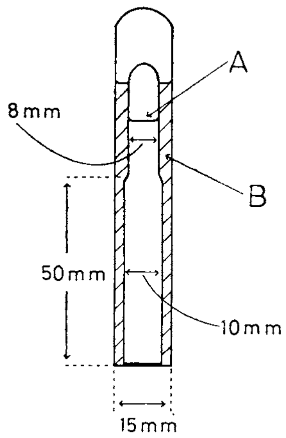

Fig. 2. Specimen cell.
A: liquid level of sample after melting.
B: octhyl alcohol or air

As is shown in Fig. 2, the densimeter was sealed in a second Pyrex tube in order to moderate the stress due to differences in pressure. Sometimes a third enclosure was employed. The measurements were carried out in the temperature range from the liquidus points to 50—150°C above them. The temperature was controlled within ±1°C. The accuracy of the measured density was found to be 99.5% by the use of distilled water at 153°C.

Results

The data on the density isotherms for the B_2O_3-H_2O system are presented in Fig. 3. They were obtained by the intra- or by the extrapolation of the density temperature relations. The densities

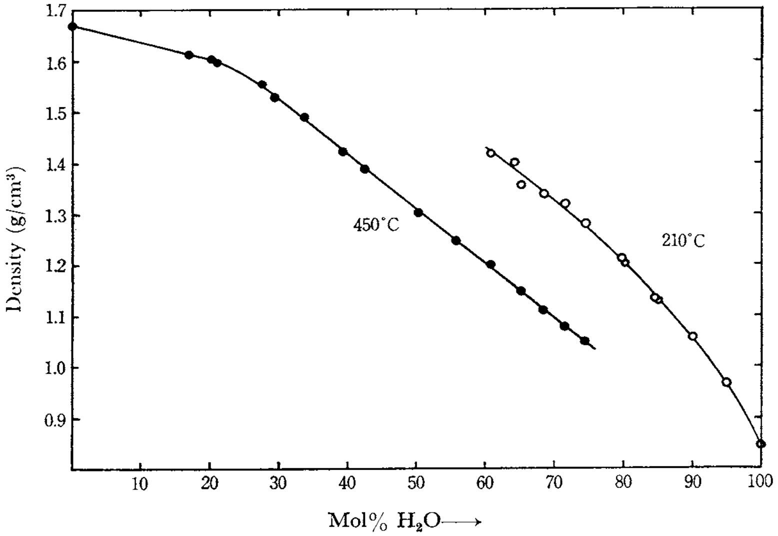

Fig. 3. Density as a function of composition at 210°C and 450°C.

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[9] F. C. Kracek, G. W. Morey and H. E. Merwin, *Amer. J. Sci.*, **35A**, 143 (1938).

TABLE 1. DENSITY OF B_2O_3-H_2O

450°C		210°C	
Mol% H_2O	Density (g/cm^3)	Mol% H_2O	Density (g/cm^3)
17.0	1.612	60.9	1.420
20.4	1.604	64.4	1.402
21.0	1.600	65.3	1.358
27.5	1.556	68.4	1.340
29.4	1.531	71.6	1.320
33.7	1.489	74.6	1.288
39.3	1.423	79.9	1.214
42.5	1.388	80.3	1.205
50.4	1.304	85.0	1.146
55.8	1.246	85.2	1.131
60.9	1.202	90.2	1.058
65.3	1.149	95.1	0.967
68.4	1.111		
71.6	1.079		
74.6	1.051		

at two temperatures are summarized in Table 1. For the density of liquid B_2O_3, numerous values have been reported.[10-13] Among them, the value of Napolitano *et al.* is quoted in Fig. 1. The density of water was quoted from "The Chemical Handbook."[14] The measurement could not be done with a B_2O_3 content of over 83.0 mol%, because of the considerable difficulty of obtaining a uniform solution due to the high viscosity. Although a small contamination from the glass tube was observed with melts of a high B_2O_3 content, the amounts of the impurity were less than 1.5 wt%, and so the effect on the density was neglected. The mean volume expansivities of the melts for the temperature range covered are shown in Fig. 4. The value for the liquid B_2O_3 was estimated for the 450—600°C temperature range from the data of Napolitano *et al.*

Discussion

Molar and Partial Molar Volume. The molar volume isotherms presented in Fig. 5 were calculated from Eq. (2).

$$MW = X_{B_2O_3}MW_{B_2O_3} + X_{H_2O}MW_{H_2O} \qquad (2)$$

where X is the mole fraction of each component and where MW is the molecular weight. The molar volume is defined by:

$$V_M = MW/\rho \qquad (3)$$

where ρ is the density (g/cm^3). The addition of H_2O to molten B_2O_3 decreased the molar volume of this mixture below the 41.7 cm^3/mol value for B_2O_3. Attention should be paid to the abrupt change in the rate of decrease in the vicinity of the $3B_2O_3 \cdot H_2O$ composition. This suggests some structural change near this composition. There are, generally

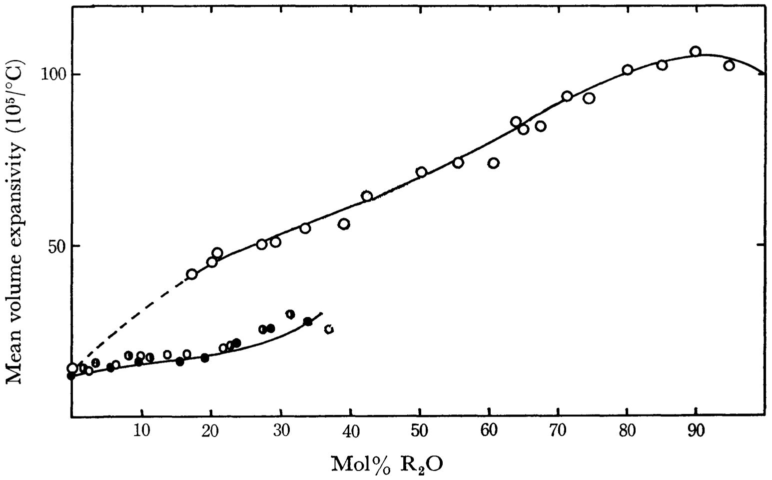

Fig. 4. Mean volume expansivity of $B_2O_3.H_2O$ and alkali borates. Values of the latter were quoted from Ref. 16.

○ $R_2O=H_2O$
◐ K_2O } at 700—1000°C
● Na_2O } at 700—1000°C
○ Li_2O } at 700—1000°C

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[10] L. Shartsis, W. Capps and S. Spinner, *ibid.*, **36**, 35 (1953).

[11] J. D. MacKenzie, *J. Phys. Chem.*, **63**, 1875 (1959).

[12] Pei-Ching Li, A. C. Ghose and G. Jen Su, *J. Amer. Ceram. Soc.*, **45**, 89 (1962).

[13] A. Napolitano, P. B. Macedo and E. G. Hawking, *ibid.*, **48**, 613 (1965).

[14] Japan Chemical Association, "Chemical Handbood," Fundamental Volume II, Maruzen, Tokyo (1966).

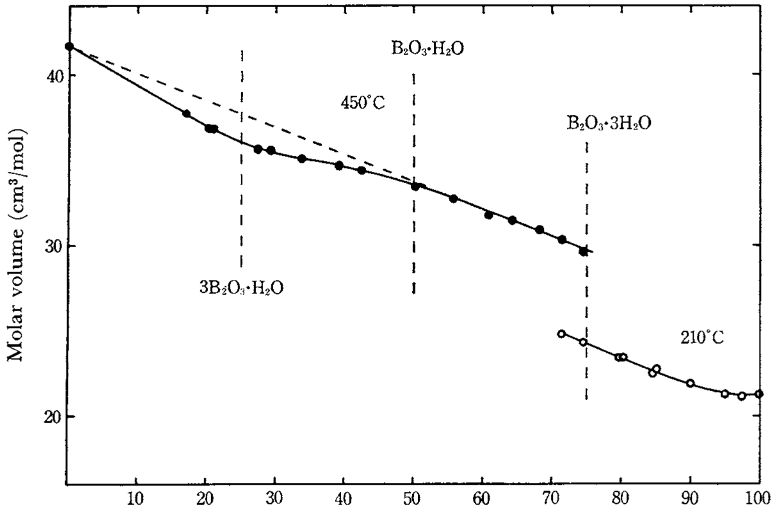


Fig. 5. Molar volume isotherms for B_2O_3-H_2O.

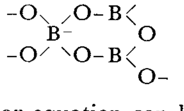
speaking, two types of molar volume decrease arising from the addition of another oxide to molten B_2O_3. One type is seen in the systems of borosilicate,[15] borogermanate[15] and aluminoborate,[16] in which the added oxide can be called a "network former." In these systems, the molar volume changes almost linearly with the addition of the second oxide. That is, the partial molar volume of B_2O_3 in the solution is nearly the same as that of B_2O_3. The coordination number probably remains unchanged. The other type is observed in the alkali,[10] alkaline earth borate,[5] and silver borate[17] systems, in which the decrease in the molar volume results in a convex curve downward. That is, the partial molar volume of B_2O_3 decreases rapidly below the volume of the pure B_2O_3. The latter type can be interpreted by the change in coordination from BO_3 to BO_4. In our system, the linear decrease in the molar volume over the $B_2O_3 \cdot H_2O$ range belongs to the former type in spite of the fact that H_2O has been regarded as a network modifier. Therefore, there is no change in coordination number over that range. Milberg and Meller[18] studied the structure of vitreous $B_2O_3 \cdot H_2O$, glass with a composition of B_2O_3, $B_2O_3 \cdot 0.42\ H_2O$-$B_2O_3 \cdot 0.5H_2O$ and $B_2O_3 \cdot 0.63H_2O$ by means of the X-ray scattering method. They indicated that the fundamental triangle coordination characteristic of vitreous B_2O_3 was maintained in the water-containing glasses, although the possibility that a small fraction of the boron atoms was coordinated by four oxygen atoms could not be completely excluded. Their results coincide well with the present result. With the increase in the water content to near the composition of $3B_2O_3 \cdot H_2O$, the partial molar volume of B_2O_3, which is read out from the intercept of the tangential line with the B_2O_3 axis, decreases abruptly to about 38 cm³/mol, then it returns gradually to the starting value. The decrease might be explained by the change in the coordination number, as in the case of binary metal borate. Silver[19] investigated the system over the B_2O_3 to $B_2O_3 \cdot 3H_2O$ range by the NMR method and confirmed that all the substances contained a planar BO_3 triangular unit. He also concluded that the BO_4 tetrahedral unit existed only in $B_2O_3 \cdot 0.6H_2O$ and $B_2O_3 \cdot 0.5H_2O$ glass samples and in monoclinic acid, not in B_2O_3 and $B_2O_3 \cdot 0.4H_2O$. Thus, there is a good correspondence between his results in glass and the present results in liquid. The partial molar volume of the $B_2O_3 \cdot 3H_2O$ composition returns exactly to that of pure B_2O_3.

The change in the coordination number may be expressed by the following process:

$$\rangle B\text{-}O\text{-}B\langle + Na_2O = 2\rangle B\text{-}O^- + 2Na^+ \qquad (4)$$

$$\rangle B\text{-}O^- + \text{-}B\langle = \rangle B\text{-}O\text{-}\overset{|}{\underset{|}{B}}{}^-\text{-} \qquad (5)$$

Krogh-Moe[20] observed an example in solid $Cs_2O \cdot 3B_2O_3$. That is,



Likewise, a similar equation can be written for the

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[15] E. F. Riebling, *J. Amer. Ceram. Soc.*, **47**, 478 (1964).

[16] E. F. Riebling, *ibid.*, **49**, 19 (1966).

[17] Y. Ono, T. Yokokawa and K. Niwa unpublished

[18] M. E. Milberg and F. Meller, *J. Chem. Phys.*, **31**, 126 (1959); F. Meller and M. E. Milberg, *J. Amer. Ceram. Soc.*, **43**, 353 (1960).

[19] A. H. Silver, *J. Chem. Phys.*, **32**, 959 (1960).

[20] J. Krogh-Moe, *Acta Crystallogr.*, **13**, 889 (1960).

B_2O_3-H_2O system;

$$\rangle B{-}O{-}B\langle + H_2O = 2\,\rangle B{-}O{-}H \tag{6}$$

$$\rangle B{-}O{-}H = \rangle B{-}O^- + H^+ \tag{7}$$

$$\rangle B{-}O^- + {-}B\langle = \rangle B{-}O{-}\underset{|}{\overset{|}{B}}{}^-{-} \tag{5}$$

or equivalently to the last two equations:

$$B{-}O{-}H + {-}B\langle = \rangle B{-}O{-}\underset{|}{\overset{|}{B}}{}^-{-} + H^+ \tag{8}$$

The above experimental results suggest that, while the (4) and (5) reactions proceed at the same time on the addition of Na_2O to B_2O_3, the (7) and (5) reactions preceed appreciably only after the H_2O content becomes higher than $3B_2O_3 \cdot H_2O$.

Thermal Expansivity. The volume expansivity (the mean values over the measured temperature) is shown in Fig. 4. The corresponding data on the binary alkali borates show a different trend. Any alkali oxide keeps a low expansivity at first as a result of BO_4 formation, and then it rises, probably because of the ionic nature of the melt. Water steadily increases the expansivity. The comparatively moderate increase in the range between $3B_2O_3 \cdot H_2O$ and $B_2O_3 \cdot H_2O$ confirms the notion that BO_4-unit formation occurs in this range.