

We are indebted to Mr. A. L. Loomis of Tuxedo Park, N. Y., for helpful advice concerning the photographic device described in the Experimental Section.

### Summary

It has been shown that salol, benzophenone and benzene crystallize spontaneously by a heterogeneous mechanism even in the absence of overheatable nuclei. The tendency to form overheatable nuclei and the spontaneous tendency to crystallize, appear to be entirely unrelated, since the former may be destroyed by heating without affecting the latter. A tentative mechanism is suggested whereby one type of absorptive force might result in both forms of activity. The study has been related to previous investigations on the subject.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

## Phase Equilibrium Relationships in the Binary System, Sodium Oxide-Boric Oxide, with Some Measurements of the Optical Properties of the Glasses

BY G. W. MOREY AND H. E. MERWIN

The literature contains a number of observations on some of the compounds in the system,  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ , which will be referred to in connection with those compounds, but there has been no systematic study of the system as a whole, except that by Ponomareff,<sup>1</sup> the results of which are as near correct as would be expected from his experimental method.

Most of the information relating to the phase equilibrium relations in the system was obtained by the usual quenching method. In this method a small sample of the material, usually in the form either of a homogeneous glass, or the product obtained by crystallizing such a glass, is held at constant temperature long enough for equilibrium to be attained, then cooled quickly enough to freeze that equilibrium. The quenched charge is then examined with the petrographic microscope. If it originally contained crystals and has become all glass, the temperature of heat treatment was above the liquidus; if both crystals and glass, below the liquidus. The crystals may be positively identified by their optical properties, and thus assurance given as to the crystalline phase present. The quenching method is preferred by experienced workers whenever it can be applied, but in some cases crystallization takes place so rapidly that the melt cannot be quenched. In such cases recourse must be had to the method of

heating curves, and it was necessary to study the metaborate in this manner. The heating-curve method can give good results with sodium diborate, when the necessary care is exercised, as was shown by Day and Allen;<sup>2</sup> and it has been applied by the present authors to sodium tetraborate with satisfactory results. With intermediate mixtures, however, the heating-curve method is of doubtful assistance.

### Preparation and Analysis of Materials

The raw materials used were sodium carbonate, borax ( $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ). The sodium carbonate was from a specially purified stock which contained less than 0.009%  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . The borax and boric acid were from several sources, but were purified by recrystallization before using. The mixtures were made by adding sodium carbonate or boric oxide to fused  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ , with careful mixing, and the composition was usually known from the synthesis having been carried on under controlled conditions.

The composition of some of the mixtures was established by analysis, using a novel method. It was found that when a mixture of  $\text{Na}_2\text{O} + \text{B}_2\text{O}_3$  containing an excess of boric oxide over the ratio of 1:1 was evaporated on the steam-bath with hydrofluoric acid, it was changed quantitatively to sodium borofluoride,  $\text{NaBF}_4$ . The properties of this compound will be discussed by us in another place. For our present purpose, it is sufficient to say that it can be dried to constant weight at  $110^\circ$ , and that numerous checks made by converting it to sodium sulfate established its constancy of composition. It melts, with some decomposition, at  $373^\circ$ . The original weight can be restored by adding a little boric acid and again evaporating with hydrofluoric acid. For example, a sample of borax, prepared by recrystallization of a commercial preparation and dehydra-

(1) J. F. Ponomareff, *Z. anorg. allgem. Chem.*, **89**, 383 (1924); *J. Soc. Glass Techn.*, **11**, 39 (1927). The second reference apparently represents no new experimental work, contains several errors, *e. g.*, p. 43, where the compound  $\text{Na}_2\text{O} \cdot 7\text{B}_2\text{O}_3$  is claimed, probably a misprint for  $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ , and without justification claims the crystallization of  $\text{B}_2\text{O}_3$ , reproducing in support a picture of a crystal given in the earlier paper as  $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ .

(2) "The Isomorphism and Thermal Properties of the Feldspars," by Arthur L. Day and E. T. Allen, Carnegie Institution of Washington, Publ. No. 31, 1905, p. 29.

TABLE I<sup>a</sup>  
THE CHANGE OF BETA-SODIUM DIBORATE TO ALPHA-SODIUM DIBORATE

Run	Temp., °C.	Time	Results; remarks	Run	Temp., °C.	Time	Results; remarks
	Original material	beta-sodium diborate			Original material	a mixture of alpha- and beta-sodium diborate	
1	720	40 m	Changed to alpha				
2	660	20 m	Changed to alpha				
3	640	20 m	Changed to alpha, but still cloudy				
4	600	20 m	Cloudy; partly changed to alpha				
7	580	30 m	Traces of beta remain				
6	590	30 m	Much beta remains				
5	575	30 m	Mostly beta; trace of alpha	8	575	36 hr	All alpha
12	525	6 da	All changed to alpha	9	525	16 hr	All alpha
				10	510	48 hr	Practically all alpha
16	500	7 da	Unaltered beta; no alpha	16	500	7 da	Trace of beta remains, but has different look. Indices seem to be lowered somewhat
14	475	9 da	Unaltered beta; no alpha	11	475	16 hr	Beta is partly changed to alpha
				15	450	3 da	All grains of beta seem to have remained beta, but many of them have a different appearance from the original beta. Transformation may have begun.
13	360	5 da	Remains beta				

<sup>a</sup> We are indebted to our colleague, Dr. Earl Ingerson, for carrying out these experiments.

tion, gave 30.77% Na<sub>2</sub>O by the method of evaporation with hydrofluoric acid, to be compared with the theoretical value of 30.78%. A mixture made up by controlled synthesis, with a composition calculated to be 27.91% Na<sub>2</sub>O, gave 27.88% by the method using hydrofluoric acid. Another mixture gave 29.80% Na<sub>2</sub>O when decomposed by hydrofluoric acid and sulfuric acid, when the Na<sub>2</sub>O was weighed as Na<sub>2</sub>SO<sub>4</sub>, and 29.82% when the Na<sub>2</sub>O was weighed as NaBF<sub>4</sub>.

Temperature measurements were made with platinum *vs.* platinum + 10% rhodium thermocouples, with the cold junction in ice. Electromotive forces were measured on a White potentiometer. The thermocouples were calibrated at the following points: zinc,<sup>3</sup> melting point 419.4°; NaCl,<sup>4</sup> melting point, 800.4°; gold,<sup>5</sup> melting point, 1062.6°, and used with a deviation curve, as described by Adams.<sup>3</sup>

### Properties of the Compounds

The hygroscopicity, and the existence of more than one form, of some of the compounds has caused confusion as to the identity of the material on which some of the physical properties recorded in the literature have been determined. Because of this uncertainty we have made no comments on the discrepancy between the optical properties observed by us and by others. For the same reason we have not attempted to verify the x-ray patterns given by Cole, Scholes and Amberg,<sup>5</sup> or by Menzel.<sup>6</sup>

(3) L. H. Adams, *THIS JOURNAL*, **36**, 65 (1914).

(4) H. S. Roberts, *Phys. Rev.*, **23**, 336 (1924).

(5) S. S. Cole, S. R. Scholes and C. R. Amberg, *J. Am. Ceram. Soc.*, **18**, 58 (1935).

(6) H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935).

1. **Sodium Orthoborate, 2Na<sub>2</sub>O·B<sub>2</sub>O<sub>3</sub>.**—This is the only new compound found in the present study. It is easily obtained by fusing borax with sodium hydroxide or sodium carbonate in the theoretical proportions. It is remarkable for its low melting point, 625°, and the fact that in small quantities it can be obtained as glass. The system Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> is thus in marked contrast to the system Na<sub>2</sub>O-SiO<sub>2</sub>,<sup>7</sup> in which the (incongruent) melting point of the ortho-compound is higher than that of the meta-compound, and the tendency toward crystallization increases regularly with content of Na<sub>2</sub>O. Sodium orthoborate is very hygroscopic, and attacks the index liquid. It is biaxial, positive:  $\gamma = 1.550$ ,  $\beta = 1.520$ ,  $\alpha = 1.500$ .

The eutectic between sodium orthoborate and sodium metaborate is close to the composition of the orthoborate, but its exact composition was not determined. The liquids in this composition region contain about 1% carbon dioxide, but in spite of this the orthoborate melted fairly sharply, with the first sign of sintering not more than 5° below the melting point. Mixtures intermediate between the ortho- and metaborates yield thin liquids which crystallize readily, and the presence of a small amount of metaborate makes it impossible to cool the melt to yield a glass. No liquidus

(7) F. C. Kracek, *J. Phys. Chem.*, **34**, 1583 (1930).

determinations were made in this region, which is not indicated in Fig. 1.

**2. Sodium Metaborate,  $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ .**—A melting point for this composition was approximately determined by Burgess and Holt<sup>8</sup> as 930°. Van Klooster<sup>9</sup> found for the compound 966°, a value confirmed by Cole, Scholes and Amberg<sup>5</sup> ( $965 \pm 2^\circ$ ), and by us (966°). It crystallizes too readily to be obtained as glass. It is uniaxial, negative,  $\omega = 1.568$ ,  $\epsilon = 1.457$ . It is very hygroscopic, and it slowly attacked the immersion liquid used for refractive index determination.

**3. Sodium Diborate,  $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ ,  $\alpha$ -Form.**—This is the well-known "dehydrated borax," whose melting point was determined to be 742° by Day and Allen.<sup>2</sup> Other investigators have reported lower melting points. Ponomareff<sup>1</sup> found 732°, Cole, Taylor and Scholes,<sup>5</sup>  $735 \pm 5^\circ$ , Menzel,<sup>6</sup> 738°. Burgess and Holt<sup>8</sup> found roughly 791°, but considered that this was not a true compound, but a eutectic mixture. This higher melting point is difficult to explain, but the lower ones are accounted for by the ease with which the compound takes up water from moist air. This is illustrated by the following observations, made to determine the suitability of the compound for the standardization of thermocouples.

A sample of borax was purified by recrystallization, dehydrated carefully, melted and crystallized, and the melting point of this product determined by the quenching method. It was found to melt sharply; at 741° it was not sintered, at 742° there was a very little sintering, while at 742.7° it was completely melted. The melting point is inferred to be 742.5°. The sample was then left in a screw-topped vial over the summer, when it showed a melting point of 736°. On remelting a part of the stock and recrystallizing, a melting point of 741.2° was obtained. A study of the rate of drying of some of the stock exposed over the summer showed a loss, from 10 g., at 115°, of 26 mg. in three hours, followed by 1.3 mg. in eighteen hours; subsequent heating at 300° gave an initial loss of 32.5 mg., in twenty-four hours, but on further heating the sample gained 2.1 mg. in weight. This was during a period of very humid weather, and it was found that during such weather not only would the crystalline material take up water at 300°, but the melt itself would take up water. For

(8) C. H. Burgess and A. Holt, *Proc. Roy. Soc. (London)*, **74**, 285 (1904).

(9) H. S. Van Klooster, *Z. anorg. Chem.*, **69**, 135 (1911).

example, a 10-g. crystalline sample, dried at 700° (at which temperature the whole of the water was lost), on melting increased in weight 5.6 mg. The melt had been cooled quickly, so that it remained glassy; on heating to just below the melting point until it crystallized, a matter of about two hours, the crucible had returned to within 0.3 mg. of the previous weight. Quenching experiments gave a liquidus only slightly lower than the original material. There was some formation of glass at 736°, indicating a small range of melting. It is evident that during humid weather crystalline anhydrous sodium diborate will take up enough water to lower its melting point appreciably; that some water is taken up even at 300°; that the water can be entirely driven off from the crystalline compound at 700°; and that the just molten glass can take up some water. It is not a favorable material for the standardization of thermocouples.

Another sample of 4 g. on heating at 700° showed, in eighteen hours, a loss of 2.4 mg.; further twelve hours, no change in weight; twenty-two hours, loss of 0.5 mg. It is evident that the rate of evaporation from molten borax near its melting point is small. At 1200° in twenty-two hours the same sample lost 0.7215 g.; further heating for twenty hours showed a loss of 0.5235 g. The total loss was 1.2479 g., and analysis showed the composition to be 25.30%  $\text{Na}_2\text{O}$ . The original pure diborate contained 30.81%  $\text{Na}_2\text{O}$ , hence this indicates that more sodium oxide than boric oxide had evaporated, and calculation shows the average composition of the vapor to be 43%  $\text{Na}_2\text{O}$ . Experience has shown that while boric oxide passes into the vapor phase readily in the presence of water, anhydrous boric oxide, which can be obtained from the hydrous crystals only by prolonged heating at temperatures above 1200°, is not especially volatile even at 1200°.

The above discussion has referred to the form of crystalline sodium diborate ordinarily obtained, which should be called  $\alpha$ -sodium diborate. The granular crystals have two or more good cleavages, and are biaxial, positive,  $\alpha = 1.471$ ,  $\beta = 1.493$ ,  $\gamma = 1.528$ .

Another form of crystalline sodium diborate is sometimes obtained when a borax glass is crystallized. We have obtained it in pure form only once, and it has occasionally been observed mixed with the  $\alpha$ -form. That it is probably monotropic

is shown by the experiments of Table I. Above 600° it changes to the  $\alpha$ -form in twenty minutes. At lower temperatures the change is slower, but is accelerated by the presence of the  $\alpha$ -form. At low temperatures the change is very slow, or does not take place within a few days, but in no case was the transformation from the  $\alpha$ -form to the  $\beta$ -form observed.

TABLE II

EXPERIMENTAL RESULTS IN THE SYSTEM Na <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub>			
Weight fraction Na <sub>2</sub> O	Weight fraction B <sub>2</sub> O <sub>3</sub>	Liquidus temp., °C.	Solid phases
0.4721	(0.5279) <sup>a</sup>	966 <sup>b</sup>	Na <sub>2</sub> O·B <sub>2</sub> O <sub>3</sub>
.3664	(.6336)	839	Na <sub>2</sub> O·B <sub>2</sub> O <sub>3</sub>
.325	.675	744	Na <sub>2</sub> O·B <sub>2</sub> O <sub>3</sub>
.3077	(.6923)	742	Na <sub>2</sub> O·2B <sub>2</sub> O <sub>3</sub>
.3001	(.6999)	739	Na <sub>2</sub> O·2B <sub>2</sub> O <sub>3</sub>
.2982	(.7018)	737	Na <sub>2</sub> O·2B <sub>2</sub> O <sub>3</sub>
.2788	(.7212)	723	Na <sub>2</sub> O·2B <sub>2</sub> O <sub>3</sub>
.2746	(.7254)	725	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub>
		719	Na <sub>2</sub> O·2B <sub>2</sub> O <sub>3</sub> + Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub> . No glass
.2688	(.7312)	736	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub>
.2507	(.7493)	759	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub>
.2476	(.7524)	761	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub>
.2360	(.7640)	766	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub> + Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub> + liquid
		769	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.2308	.7692	766	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub> + Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub> + liquid
		776	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.2274	(.7726)	766	Na <sub>2</sub> O·3B <sub>2</sub> O <sub>3</sub> + Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub> + liquid
		777	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.2168	.7832	792	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.2009	.7991	803	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.1862	.8138	814	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.1820	.8180	815	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.1778	.8222	814	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.155	.845	800	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.1175	(.8825)	753	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.0701	(.9299)	661 ± 3	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.0524	(.9476)	620 ± 3	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.0299	.9701	585 ± 5	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>
.01	.99	560 ± 10	Na <sub>2</sub> O·4B <sub>2</sub> O <sub>3</sub>

<sup>a</sup> The weight fraction B<sub>2</sub>O<sub>3</sub> in parentheses indicates that the Na<sub>2</sub>O was determined by analysis, B<sub>2</sub>O<sub>3</sub> by difference. The other compositions represent controlled syntheses.

<sup>b</sup> Determined by heating-curve method.

A careful search for an enantiotropic inversion was made from below 500° to the melting point, using a differential thermocouple and a neutral body. No indication of an inversion was obtained.

Beta-sodium diborate forms granular crystals,  $\alpha = 1.50$ ,  $\beta = 1.52-3$ ,  $\gamma = 1.555$ .

A third form of sodium diborate,  $\gamma$ -, was obtained under conditions which cannot be speci-

fied precisely. A stock of the crystalline material was prepared as usual by recrystallizing commercial borax, dehydrating, melting and crystallizing. This was to be used in making some other mixtures; and because the weather at the time was humid it was kept in a covered beaker on a hot plate, at about 300°. Some of this material was left for two and a half years, after which it was found to have the following optical properties: positive, with large axial angle,  $\alpha = 1.526$ ,  $\beta = 1.544$ ,  $\gamma = 1.576$ . It has one fair cleavage.

Analysis gave 30.84% Na<sub>2</sub>O, which indicates that the composition had not changed. On heating at 700° for fifteen minutes the material was unaltered; but in four hours it contained both the  $\alpha$ -form and unaltered material. Heated for fifteen minutes at 725° it was entirely changed to the ordinary form. In both cases in which alteration was observed there were indications that fusion had preceded recrystallization. Since the material remained largely in discrete grains, the fusion was probably local with immediate crystallization.

In one experiment sodium metaborate crystallized from a melt of the composition of sodium diborate.<sup>10</sup> There was, of course, much glass, but no other crystals. An attempt to determine the metastable liquidus of sodium metaborate at this composition failed, because of formation of sodium diborate.

4. **Sodium Triborate**, Na<sub>2</sub>O·3B<sub>2</sub>O<sub>3</sub>.—Ponomareff gave 694° for the melting point of this compound, while Cole, Taylor and Scholes found 720 ± 5°. We have found that it has an incongruent melting point at 766°, decomposing at that temperature into crystals of sodium tetraborate and a liquid containing 76% B<sub>2</sub>O<sub>3</sub>. It is biaxial, negative,  $\alpha = 1.453$ ,  $\beta = 1.525$ ,  $\gamma = 1.551$ .

5. **Sodium Tetraborate**, Na<sub>2</sub>O·4B<sub>2</sub>O<sub>3</sub>.—This compound was first obtained by Le Chatelier.<sup>11</sup> Burgess and Holt gave for it a melting point of 858°, and Cole, Taylor and Scholes gave 810 ± 5°; our determination is 816 ± 0.5°. The form which separates from the melt at high temperatures is biaxial, positive,  $\alpha = 1.499$ ,  $\beta = 1.525$ ,  $\gamma = 1.582$ . This same compound was usually obtained on crystallizing all mixtures containing

(10) H. Menzel, *Z. anorg. allgem. Chem.*, **224**, 1 (1935), claimed to have obtained two new allotropic forms of sodium diborate, which melted at 710 and 663°, respectively. One of these may have been the above  $\beta$ -sodium diborate, the other, sodium metaborate, but the information as to their properties is so meager that identification is not possible.

(11) H. Le Chatelier, *Bull. soc. chim.*, **21**, 34 (1899).

up to 99%  $B_2O_3$ ; but in some cases a second form was obtained, which crystallized in thin blades,  $\alpha = 1.52$ ,  $\beta = 1.54$ ,  $\gamma = 1.56$ . It was at first thought that this might be a higher borate, but when a mixture containing 98%  $B_2O_3$  was held for ten months at a little below  $300^\circ$ , boric oxide evaporated, leaving crystals which had these properties, together with a little glass. Analysis gave 14%  $Na_2O$ , 86%  $B_2O_3$ , near the composition of the tetraborate. On heating for two hours at

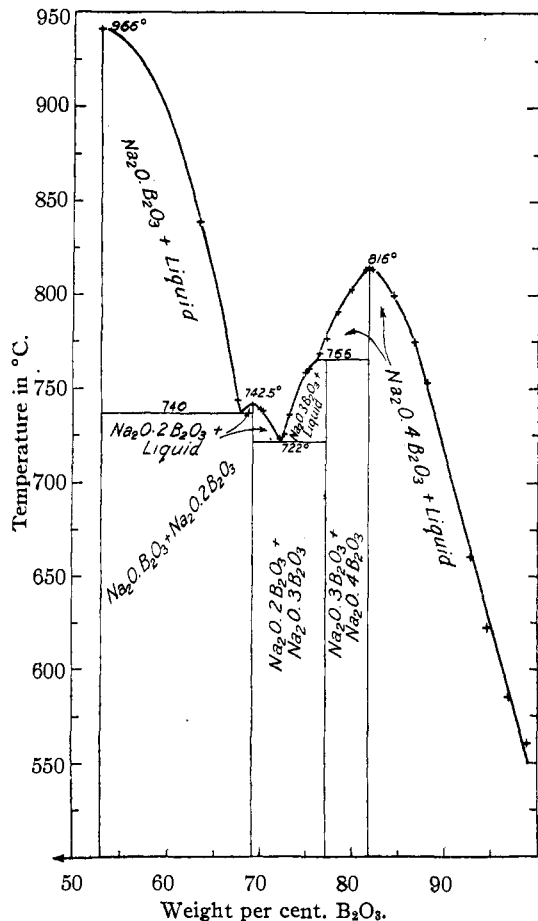


Fig. 1.—Phase equilibrium relations in the binary system,  $Na_2O-B_2O_3$ .

$630^\circ$  the crystals were unaltered, but the glass was more evident; at  $685^\circ$  the crystals were about one-half altered to the high-temperature form of the tetraborate; while in thirty minutes at  $770^\circ$  it was more than three-quarters glass, and the crystals were all the high form of the tetraborate. The most probable conclusion is that these two crystals are an allotropic form of the tetraborate. Thus the form appearing at low temperatures is either monotropic, or it is enantiotropic, with a slow rate of inversion.

A careful search for an enantiotropic inversion was made from below  $500^\circ$  to the melting point, using a differential thermocouple and a neutral body. No indication of an inversion was obtained.

### The Phase Equilibrium Diagram

The phase equilibrium relations between the various crystalline compounds and liquids are shown in Fig. 1, and the experimental results on which that figure is based are assembled in Table II.

The lowest melting compound is the orthoborate, and the eutectic between it and metaborate is close to the composition of the orthoborate. The liquid in this part of the diagram contains about 1% of carbon dioxide, but in spite of this the orthoborate melted fairly sharply, with the first sign of sintering not more than  $5^\circ$  below the melting point, so that its melting point is fairly accurate. Mixtures intermediate between ortho- and metaborate yield thin liquids which crystallize readily, and the presence of but a small amount of metaborate makes it impossible to cool the melt to form a glass.

The metaborate,  $Na_2O \cdot B_2O_3$ , has the highest melting point of any of the compounds, and it crystallizes so readily that it is not possible to obtain it as glass. The eutectic between it and sodium diborate is at  $740^\circ$  68 weight per cent.  $B_2O_3$ . The melting point then rises to that of sodium diborate,  $742.5^\circ$ ; then falls to the eutectic between diborate and triborate, at  $722^\circ$ , 72.3%  $B_2O_3$ . Sodium triborate melts incongruently at  $766^\circ$ , giving crystals of sodium tetraborate,  $Na_2O \cdot 4B_2O_3$ , and a liquid containing 76%  $B_2O_3$ . From this incongruent melting point the liquidus rises to the melting point of the tetraborate, at  $816^\circ$ . This compound remains the primary phase up to 99%  $B_2O_3$ , but below  $700^\circ$  a second sort of crystals, probably of the same composition, sometimes appears. In all the mixtures whose liquidus temperatures were determined, however, the crystalline phase which was present was the high-temperature form.

The phase equilibrium diagram shows the melting point curve of sodium tetraborate extending to within about 1% of the  $B_2O_3$  side. Whether or not the lower part of this curve is metastable cannot be stated because boric oxide has not been crystallized from these melts. If the above curve is not metastable and the melting point of boric

oxide and the eutectic between  $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  lies at a temperature considerably lower than  $500^\circ$ , then the melting point curve must be nearly vertical at the eutectic. This is to be expected from thermodynamic considerations. As the liquid phase approaches one of the components in composition, while the crystalline phase contains a finite amount of the other component, the slope of the  $T$ - $X$  curve must approach infinity.

All our attempts to crystallize boric oxide have failed. They include long heating of the anhydrous material at many temperatures. In one series of experiments, boric oxide glass was heated from a month to six weeks at a series of temperatures differing not more than  $10^\circ$ , and covering the range from  $700$  to  $200^\circ$ . In other experiments boric oxide glass was heated on a hot-plate, whose temperature ranged from  $260$  to  $285^\circ$ , for a year and a half. The material was in a covered crucible, and this in turn was in a covered glass dish. Under these conditions the glass took up some water during the humid summer months but no indication of crystallization was observed. It is elsewhere mentioned that under the same conditions a glass rich in boric oxide lost enough of this component to attain practically the composition of the crystalline tetraborate. It is probable that this loss in boric oxide was caused by the presence of moisture in the atmosphere. A glass containing 99%  $\text{B}_2\text{O}_3$  grew beautifully formed crystals of  $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$  in three months at  $525^\circ$ ; and, when heated for a year at a little below  $300^\circ$  in a sealed tube, crystals of the low-temperature form of  $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$  were formed. If these heatings had been below the melting point of boric oxide, certainly it might have been expected to crystallize, especially since the tetraborate did grow.

Other experiments include attempts to condense it from the vapor phase. In all work with anhydrous boric oxide emphasis must be placed on its extremely hygroscopic character. In making microscopical examination of the various products the material is usually crushed to a powder in an oil. In determining the properties of anhydrous boric oxide it is necessary to take the most extreme precautions to prevent the contamination by water, and that such contamination had not taken place should be proved. It was found that molecular distillation methods in which proper precautions were taken to exclude moisture gave only glassy boric oxide.

Other methods were tried. One was a pro-

longed pounding in a heated mortar, with exclusion of air, but this was a failure. Temperatures ranged from  $80$  to  $250^\circ$ , and at the highest temperature the glass was pounded into a cake, almost clear glass. Attempts were made to find "mineralizers" other than water. These included toluene, which was boiled for six weeks with the anhydrous glass, under a reflux condenser, provided with a guard tube, without result except for a slight film of boric acid. Other organic solvents were tried in bombs, usually at  $200^\circ$ , but no crystalline boric oxide could be found.

These experiments overlapped the temperature range in which Taylor and Cole believed they had crystallized boric oxide. The procedure described by them was tried several times, but crystalline boric oxide was not obtained. In our opinion, the crystallization of boric oxide is yet to be proved.

### Refractive Dispersions of Glasses

The only  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$  glasses for which refractive dispersions ( $C$ ,  $D$ ,  $F$ ) are recorded<sup>12</sup> are  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ . Three sets of these dispersions are fairly close to ones we have made. Errors of copying seem to appear in the other two, but values for  $n_D$  seem unaffected: for  $\text{B}_2\text{O}_3$  1.463 +, and for "borax glass" 1.515+. Corresponding densities are 1.850 + and 2.370. The density of boric oxide glass is greatly affected by annealing.<sup>13</sup>

TABLE III  
REFRACTIVE DISPERSIONS OF BORIC OXIDE AND BORATE GLASSES

	$\times 10^{-4}$		
	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$
4046 Hg	169+	173+	179
4340 (G')	137	140+	145
4358 Hg	135	138+	143
4861 (F)	93+	95+	98+
4916 Hg	89+	91+	94+
5461 Hg	58	59	61
5876 He	39+	40	41
5893 (D)	38+	39	40
6563 (C)	15	15	15
6678 He	11	11	11
7065 He	0	0	0
7682 (A')	-14+	...	...
$n_D$	1.458	1.501	1.516

$C$ ,  $D$ ,  $F$ ,  $G'$  are interpolated.

(12) P. P. Bedson and Carleton Williams, *Ber.*, **14B**, 2549 (1881).  
(13) Arnold Cousen and W. E. S. Turner [*J. Soc. Glass Tech.*, **12**, 169 (1928)] found for chilled droplets  $<1.81$ , which was raised to  $>1.84$  by annealing. Very recent work by P. Wulff and S. K. Majumdar [*Z. physik. Chem.*, **81B**, 319 (1936)] records a range of 1.778-1.838 for  $d$ , and 1.4502-1.4633 for  $n_D$ . Further study is required to show the effect of annealing and of small content of water on the specific refraction.

The measurements of Table III were made on prisms, from a few grams of glass cooled in air from fusion. The boric oxide prisms were protected from filming by oil and cover glasses.

### Summary

A study of the phase equilibrium relationships in the system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$  has shown the existence of the compounds: sodium orthoborate,  $2\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ , with a congruent melting point at  $625^\circ$ ; sodium metaborate,  $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ , with a congruent melting point at  $966^\circ$ ; sodium diborate,  $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ , with a congruent melting point at  $742^\circ$ ; sodium triborate,  $\text{Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ , with an incongruent melting point at  $766^\circ$ , 76 weight per cent.  $\text{B}_2\text{O}_3$ ; and sodium tetraborate,  $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ ,

with a congruent melting point at  $816^\circ$ . The orthoborate, which is a newly discovered compound, can be cooled to a glass, as can mixtures containing more boric oxide than the diborate. The metaborate and compositions near it crystallize too readily to be quenched to a glass. In addition to the forms stable at the liquidus, sodium diborate may occur in two, and the tetraborate in one, additional form which are probably monotropic. Attempts to prepare crystalline boric oxide were not successful, and doubt is expressed as to previous claims to its crystallization. Refractive dispersions were measured for boric oxide, sodium tetraborate and sodium diborate glasses.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

## Heat Content and Heat Capacity of Aqueous Sodium Chloride Solutions

BY T. F. YOUNG AND J. S. MACHIN

Computations of activity coefficients from cryoscopic and thermal data have been greatly limited by a lack of adequate measurements.<sup>1</sup> This investigation was undertaken primarily to supply the heats of dilution required for a reliable determination of relative activities of sodium chloride in aqueous solutions. Because electromotive force methods<sup>2,3</sup> have been employed extensively in thermodynamic investigations of that electrolyte, sodium chloride is especially suitable for a critical comparison of the cryoscopic and electrical methods of evaluating activity coefficients.

The calorimetric data presented are of further interest because they furnish information concerning the variation with composition of apparent and partial molal heat capacities, and consequently have an important bearing upon the validity of the Debye-Hückel theory.<sup>4</sup>

The advantages of the chord-area method for the precise evaluation of partial molal properties from heats of dilution have been discussed by Young and Vogel.<sup>5</sup> The procedure they employed depends upon the determination of the derivative,  $S$ , of the apparent molal heat content with respect to the square root of the molality,  $m$ . Each heat of dilution experiment furnishes one average value

of  $S$  which may be represented on a derivative plot by the ordinate of a horizontal line (called a "chord") extending between limits representing the initial and final values of  $\sqrt{m}$ , *i. e.*,  $\sqrt{m_1}$  and  $\sqrt{m_2}$ . A special procedure was suggested by Young and Vogel<sup>5</sup> (p. 3037) to facilitate the drawing of a derivative curve so as to balance appropriate areas accurately. That procedure depends upon the drawing of a preliminary  $S$  curve, and the evaluation (by successive approximations, if necessary) of  $S'$ , the first derivative, and  $S''$ , the second derivative of  $S$ . The final  $S$  curve is drawn in accordance with a series of points which have been plotted a distance,  $P_i - \bar{P}_i$ , above the center of each chord, computed from the equation

$$P_i - \bar{P}_i = -S'' (\Delta\sqrt{m})^2/24 \quad (1)$$

where  $P_i$  represents the ordinate of a point on the derivative curve above the center of the  $i$ th chord, and  $\bar{P}_i$  is the ordinate of the chord. For an application of this method it was desirable to produce chords so short that the uncertainties in values of  $P - \bar{P}$  would not be large in comparison with the probable errors in the experimentally determined values of  $\bar{P}$ . For experiments with concentrated solutions, a dilution vessel having a volume about 0.03 that of the final diluted solution was used; for experiments with relatively dilute solutions, a larger vessel having a volume about 0.085 that of the final diluted solution was employed.

(1) Young, *Chem. Rev.*, **13**, 103 (1933).

(2) Harned and Nims, *THIS JOURNAL*, **54**, 423 (1932).

(3) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(4) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(5) Young and Vogel, *THIS JOURNAL*, **54**, 3030 (1932).