THE SYSTEM: CaO–B$_2$O$_3$

By Elmer T. Carlson

ABSTRACT

The phase equilibrium diagram for the system CaO-B$_2$O$_3$ has been partially worked out by means of heating curves. Completion of the diagram was impossible because the melting point of B$_2$O$_3$ could not be determined, while that of CaO was beyond the range of the apparatus. The following compounds were identified and their optical properties determined with the petrographic microscope: CaO·2B$_2$O$_3$, melting at 986°±5° C.; CaO·B$_2$O$_3$, melting at 1,154°±5° C.; 2CaO·B$_2$O$_3$, melting at 1,298°±5° C.; and 3CaO·B$_2$O$_3$, melting at 1,479°±5° C. Mixtures containing less than 23 per cent CaO were found to separate, on fusion, into two liquid layers, one of which contained 23 per cent CaO, while the other was nearly pure B$_2$O$_3$. This immiscibility region extended above 1,500° C.

CONTENTS

I. INTRODUCTION

The study of this system was undertaken as a preliminary to a study of part of the ternary system, CaO-B$_2$O$_3$-SiO$_2$, the purpose of the latter being to determine the effect of the addition of small amounts of B$_2$O$_3$ to the calcium silicates found in Portland cement. It is hoped, however, that the results of the investigation of the binary system, CaO-B$_2$O$_3$, may also prove of interest in connection with the production of glazes and other ceramic materials.

Very little work has been done on the anhydrous calcium borates in recent years, and much of the earlier data is conflicting or inconclusive. The first comprehensive study of the system CaO-B$_2$O$_3$ was made by W. Guertler,[1] who constructed the liquidus diagram through the use of cooling curves. He found maxima at 1,030°,[2] 1,095°, and 1,225°, corresponding to the compounds CaO·2B$_2$O$_3$, CaO·B$_2$O$_3$, and 2CaO·B$_2$O$_3$, respectively. Due to the limitations of his apparatus, he was unable to go much beyond the last of these, although he argued from analogy with the system BaO-B$_2$O$_3$ that the compound 3CaO·B$_2$O$_3$ should exist. Due to the excessive super-

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[1] Guertler, On the Melting Points of Mixtures of the Alkaline Earths with Boric Anhydride, Z. anorg. Chem., vol. 40, pp. 337-354, 1904.
[2] All temperatures given in °C. unless otherwise stated.

cooling which occurs in this system, the accuracy of his results is somewhat doubtful.

The four borates mentioned have since been prepared by R. Griveau,[3] who also studied their heats of formation. He gives the values 1,025°, 1,100°, and 1,215° as the approximate melting points of the compounds $CaO \cdot 2 B_2O_3$, $CaO \cdot B_2O_3$, and $2CaO \cdot B_2O_3$, respectively. Roberts[4] reported a melting point of 1,304° for $2CaO \cdot B_2O_3$. Optical properties for the metaborate, $CaO \cdot B_2O_3$, are given by A. N. Winchell.[5]

Burgess and Holt[6] reported that CaO is insoluble in B_2O_3 in small quantities, but if present in larger amounts the mixture fuses to a clear glass. Guertler[7] found that a fused mixture of B_2O_3 and a small amount of CaO separated into two liquid layers which were immiscible even at 1,400°.

The melting point of pure CaO was placed at 2,572° by Kanolt,[8] and at 2,849° K. (2,576° C.) by Schumacher.[9] The melting point of boric oxide is unknown, as this compound has never been obtained in crystalline form.

Because of the absence of optical data for most of the calcium borates, as well as the conflicting nature of the melting-point data, it seemed desirable to make a study of the system CaO-B_2O_3, tracing the liquidus as far as possible and determining the optical properties of the various phases appearing in the system.

The general plan followed was to prepare mixtures of CaO and B_2O_3 in varying proportions and to determine their melting points by means of heating curves. The phases existing in equilibrium with the melt at the liquidus were identified by petrographic examination of samples quenched from various temperatures near the liquidus.

II. EXPERIMENTAL WORK

1. PREPARATION OF MIXTURES

Calcium carbonate ($CaCO_3$) and boric acid (H_3BO_3) were used in the preparation of the mixtures. The percentage composition of the calcium carbonate was as follows: Ignition loss, 43.65; SiO_2, 0.07; R_2O_3, 0.04; MgO, 0.04; CaO (by difference), 56.20. The boric acid was analyzed only for impurities (analysis by chemistry division of this bureau), which were reported as follows: Fe, < 0.001 per cent; SO_3, < 0.01 per cent; Cl, < 0.001 per cent. This material was recrystallized in order to render it finer, as it was difficult to pulverize the flakes by grinding.

For each mixture the calculated amount of calcium carbonate was first calcined and then thoroughly mixed with the required quantity of boric acid and heated over a burner (Meker type). The materials combined readily to form a mixture sufficiently homogeneous for the

[3] Griveau, Heats of Formation of the Anhydrous Calcium Borates, Compt. rend., vol. 166, pp. 993–995 1918.

[4] Roberts, Some New Standard Melting Points at High Temperatures, Phys. Rev., vol. 23, pp. 386–395, 1924.

[5] A. N. Winchell, The Optic and Microscopi Characters of Artificial Minerals. Univ. of Wisconsin Studies in Science, 1924.

[6] Burgess and Holt, The Behavior of Metallic Oxides Toward Fused Boric Anhydride, Proc. Chem. Soc., vol. 19, pp. 221–222, 1903.

[7] Guertler, On the Limits of Miscibility of Boric Anhydride and Borates in the Fused State, Z. anorg. Chem., vol. 40, pp. 225–53, 1904.

[8] Kanolt, Melting Points of Some Refractory Oxides, B. S. Bull., vol. 10, pp. 295–313, 1914.

[9] Schumacher, Melting Points of Barium, Strontium, and Calcium Oxides, J. Am. Chem. Soc., vol. 48, pp. 396–405, 1926.

purpose for which it was intended. The product varied in appearance from a glass to a soft clinker, depending on the compostion. In some instances a test for free lime was made by the ammonium acetate titration method,[10] but no free lime was found except in one mixture containing CaO in excess of $3CaO \cdot B_2O_3$.

2. ANALYSIS OF MIXTURES

Due to the loss of boric acid by volatilization during the preparation of the mixtures, it was necessary to analyze the product in each case.

CaO was determined by titration with half-normal hydrochloric acid, using methyl red as indicator. The acid also served as a solvent for the sample, as the calcium borates are only slightly soluble in water. The B_2O_3 was then determined on the same sample by adding mannite and titrating with half-normal sodium hydroxide to the end point indicated by phenolphthalein.

In general, it was found that mixtures containing an excess of either uncombined lime or boric oxide were hygroscopic, while the others showed low ignition losses. The moisture present was of no significance, since it was expelled when the samples were heated in the furnace. Consequently the percentages of CaO and B_2O_3 were in all cases adjusted so as to total 100 per cent on a nonvolatile basis.

Although free boric oxide is somewhat volatile at high temperatures, it was found by analysis that no appreciable loss of B_2O_3 occurred when the mixtures, prepared as described above, were subsequently used in obtaining heating curves.

3. EXPERIMENTAL PROCEDURE

The melting points of the various mixtures were determined by means of heating curves. For this purpose a platinum-wound, vertical-tube furnace, equipped with automatic temperature control,[11] was used. Temperatures were measured by means of platinum:platinum-rhodium thermocouples.

In obtaining a heating curve the sample was placed in one compartment of a small platinum thimble which was divided vertically by a platinum septum welded in place. The other half of the thimble was filled with artificial corundum as a reference medium. The two hot junctions of a differential thermocouple were imbedded in the two materials and the thimble suspended in the furnace. The temperature was raised at a rate of 5° per minute, and readings of the actual and differential temperatures were taken every minute, or, when necessary, every half minute.

Due to pronounced supercooling, no satisfactory cooling curves could be obtained.

In order to determine the solid phase present at the liquidus, a small sample of each mixture was wrapped in platinum foil, suspended in the furnace, and held at a constant temperature near the melting point for 15 minutes to allow it to come to equilibrium. It was then quenched by dropping it into water or mercury, and the phases present identified with the aid of the microscope. This process was then repeated at a temperature 2° or 3° higher or lower until a point was found, above which the primary solid phase did not appear.

[10] Lerch and Bogue, Revised Procedure for the Determination of Uncombined Lime in Portland Cement, Ind. Eng. Chem., Anal. ed., vol. 2, pp. 296–298, 1930.
[11] Adams, J. Opt. Soc. Am., vol. 9, p. 599, 1924.

Unfortunately, mixtures containing more than about 45 per cent CaO were found to crystallize during quenching, thus limiting the use of this method.

4. INTERPRETATION OF HEATING CURVES

A few words regarding the interpretation of the heating curves may be helpful.

The curves fall into two general classes. In the first class are those which resemble the typical heating curve for a pure compound or a
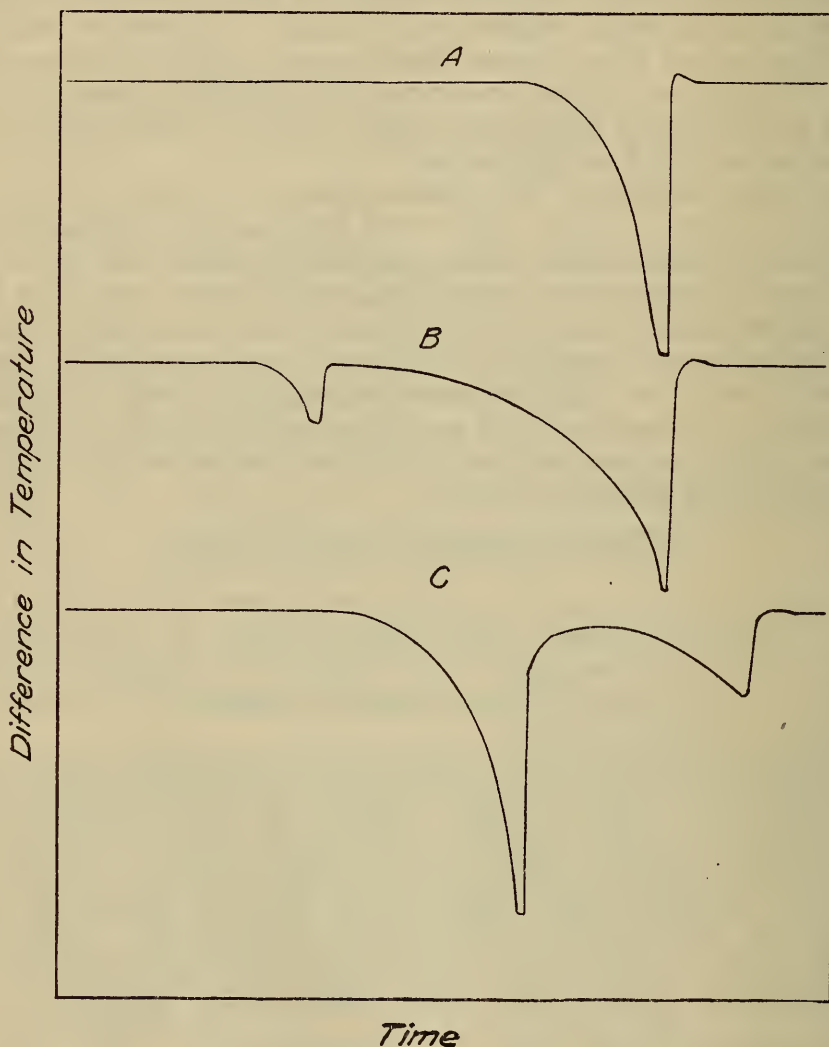

FIGURE 1.—*Types of differential heating curves*

eutectic mixture (curve *A*, fig. 1). Due to the temperature gradient in the sample, the outer edges fuse first, gradually reducing the amount of heat conducted to the thermocouple, which causes the curve of the differential temperature to dip downward. As the melting proceeds toward the center, the curve drops more and more sharply, reaching a minimum at the instant at which fusion is complete. Recovery is then very rapid, resulting in an almost vertical rise in the curve. The point at which the curve reaches the minimum was taken as the melting point of the sample. Heating curves for a pure reference material, potassium sulphate (m. p. = 1,069° [12]), confirmed this interpretation.

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[12] See footnote 4, p. 826.

Mixtures lying between a eutectic and a compound give curves of the second type, represented by B (fig. 1). The first break represents the melting point of the eutectic; that is, the last portion of the mixture to solidify on cooling. Continued heating causes a gradual fusion (or solution) of the solid phase until it has completely disappeared. This is illustrated by the gradual drop in the curve, culminating as before in a sudden turn upward.

Curve C is of the same type as curve B, but in this case the composition is closer to that of the eutectic, causing the first break to be very pronounced, whereas the upper break, representing the true melting point, is relatively faint. For several of the mixtures whose compositions were close to those of the various eutectics the upper break was obscured entirely, making an absolute determination of the composition of the eutectic by this method impossible.

III. RESULTS

1. BINARY COMPOUNDS

Four binary compounds were found in the system: $CaO \cdot 2B_2O_3$, $CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, and $3CaO \cdot B_2O_3$.

Calcium diborate, or calcium tetraborate, $CaO \cdot 2B_2O_3$.—This compound occurred as the primary phase in all the mixtures containing up to about 28 per cent CaO. As ordinarily prepared it remained in the form of a glass; but by heating for a few minutes at a temperature slightly below the melting point, this could be devitrified readily. It appears as irregular grains, highly birefringent, uniaxial, negative; $\omega = 1.638$, $\epsilon = 1.568$. Whether or not it melts congruently could not be determined with certainty, as its composition apparently lies at the break in the liquidus. The melting point is $986° \pm 5°$.

Monocalcium borate or calcium metaborate, $CaO \cdot B_2O_3$.—This compound occurs as the primary phase in mixtures containing approximately 29 to 51 per cent CaO. It appears as long, flat plates, highly birefringent, biaxial, negative, with a large optic axial angle; $\alpha = 1.550$, $\beta = 1.660$, $\gamma = 1.680$. It melts congruently at $1,154° \pm 5°$.

Dicalcium borate or calcium pyroborate, $2CaO \cdot B_2O_3$.—This compound occurs as the primary phase in mixtures containing approximately 51 to 64 per cent CaO. It appears as irregular grains, highly birefringent, biaxial, negative, with small optic axial angle; $\alpha = 1.585$, $\beta = 1.662$, $\gamma = 1.667$. It melts at $1,298° \pm 5°$.

Tricalcium borate or calcium orthoborate, $3CaO \cdot B_2O_3$.—This compound occurs as the primary phase in mixtures containing from 64 to at least 71 per cent CaO, and probably somewhat higher. It appears as irregular grains, highly birefringent, uniaxial, negative; $\omega = 1.728$, $\epsilon = 1.630$. It melts at $1,479° \pm 5°$.

2. THE PHASE EQUILIBRIUM DIAGRAM

The phase equilibrium diagram is shown in Figure 2.

Mixtures containing less than 24 per cent CaO were found to separate into two immiscible liquids (which for convenience may be designated as A and B) on fusion. The heavier of the two liquids (A) on cooling formed a clear glass with a refractive index of about 1.56. It was nearly insoluble in water but soluble in hydrochloric acid. The other liquid (B) formed a cloudy glass, which was seen

under the microscope to be full of minute globules, presumably of the other glass. These appeared to separate during cooling, since in quenched samples both glasses were clear. The index of the lighter glass was about 1.45. It was soluble in water, thus affording a simple method of separating it from the other glass for analysis. The water-soluble glass was found to be practically pure B_2O_3, while the other contained about 23 per cent CaO.

An attempt was made to determine the temperature above which the components would be completely miscible, but little evidence of a change in composition was found up to 1500°. For this experiment a small amount of one of the mixtures was placed in a platinum thimble and held at a definite temperature long enough to permit
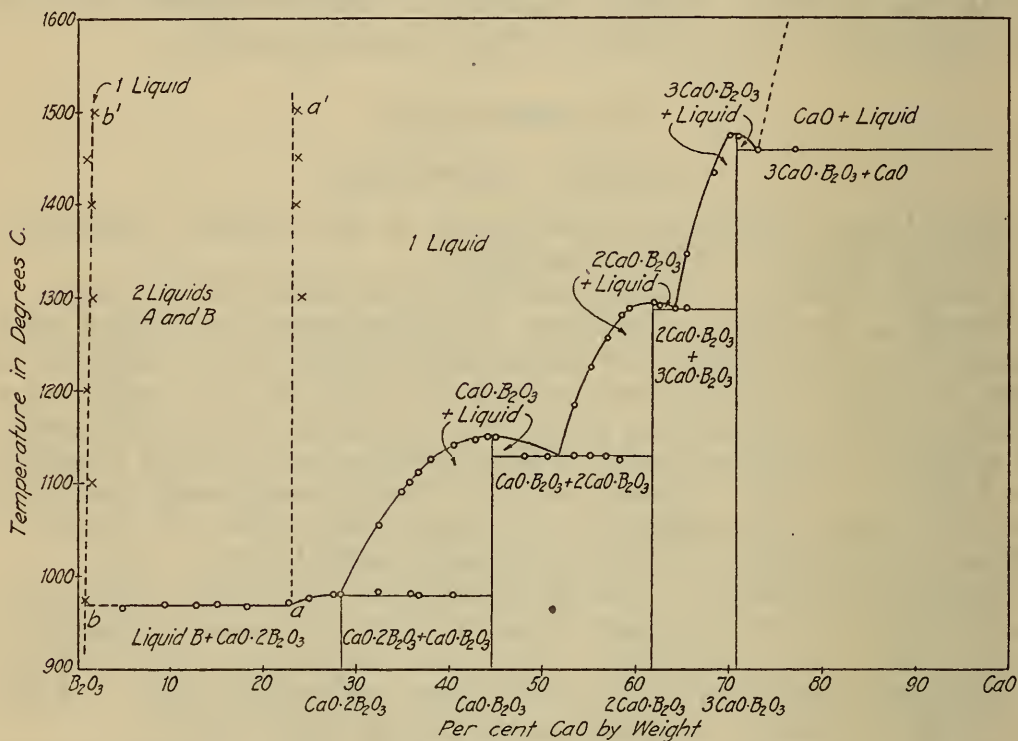

FIGURE 2.—*Phase equilibrium diagram for the system* $CaO-B_2O_3$

the liquids to separate into two layers. The charge was then cooled quickly, the two glasses separated by solution of the upper one in water, and the ratio of CaO to B_2O_3, determined in each. The results are given in Table 1.

TABLE 1.—*Composition of the immiscible liquids in the system* $CaO-B_2O_3$, *at various temperatures*

Temperature in °C.	Composition of glass A		Composition of glass B		Temperature in °C.	Composition of glass A		Composition of glass B	
	CaO	B_2O_3	CaO	B_2O_3		CaO	B_2O_3	CaO	B_2O_3
	Per cent	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*Per cent*
	23.0	77.0	0.6	99.4	1,200			.9	99.1
900–950	23.1	76.9	.6	99.4	1,300	24.2	75.8	1.5	98.5
	24.9	75.1	.2	99.8	1,400	23.5	76.5	1.4	98.6
975			.7	99.3	1,450	23.9	76.1	.9	99.1
1,100			1.5	98.5	1,500	23.7	76.3	1.7	98.3

It will be seen that the data are not entirely consistent, but this is not surprising considering the slowness of attainment of equilibrium, the possibility of particles of one glass remaining dispersed throughout the other, and the rather inexact method of separation. In considering the values for the composition of glass A it should be borne in mind that this glass represents the lower CaO limit of stable liquid mixtures in this system. Hence it seems reasonable to take the minimum value obtained, 23.0 per cent CaO and 77.0 per cent B_2O_3, as the most reliable figure for the composition of this glass.

The data seem to indicate a slight increase in the CaO content of glass B with increasing temperature, but this is not definitely proved. The low CaO values are more reliable because of the probability that glass B was contaminated with glass A. This supposition is supported by the observation that glass B was always cloudy, due to the suspension in it of minute droplets of the other phase.

It is probable that the compositions of these two liquids approach each other, and that there is some temperature above which only one liquid phase can exist. Data obtained at 1,600° showed a marked tendency in this direction, but they can not be considered reliable, as the problem is complicated by the high volatility of B_2O_3 at this temperature, as well as by the failure of the two glasses to separate completely.

The region of liquid immiscibility up to 1,500° is represented approximately by the area between the dotted lines a a' and b b' in Figure 2. Any mixture in this area must exist as two liquid phases. On cooling, it will solidify to a mixture of two glasses; but if held for a few minutes at a temperature slightly below 970°, the compound $CaO \cdot 2B_2O_3$ starts to crystallize out from liquid A. As this will tend to increase the proportion of B_2O_3 remaining in A, it is evident that a small amount of liquid B must also separate out, and this will continue until the mixture consists entirely of the compound and liquid B, the latter solidifying to a glass on cooling. A heating curve of the partially crystallized mixture will show a break at about 971° corresponding to the melting of $CaO \cdot 2B_2O_3$ in the presence of B_2O_3 glass. The melting point for any mixture in this region is represented by the horizontal line in Figure 2, extending from 0.2 to 23 per cent CaO.

From a the liquidus rises gradually to 986°, the melting point of the diborate, $CaO \cdot 2B_2O_3$ (composition, CaO, 28.71 per cent; B_2O_3, 71.29 per cent). The curve near this point is nearly horizontal, and it could not be determined with certainty whether the compound melts congruently or not. A mixture consisting of 28.6 per cent CaO and 71.4 per cent B_2O_3 showed a trace of monocalcium borate as the primary phase. This would indicate that calcium diborate is unstable at the melting point. However, the composition of the mixture in question was so close to that of $CaO \cdot 2B_2O_3$ that if allowance is made for a slight error in chemical analysis the above conclusion is unwarranted.

From the melting point of $CaO \cdot 2B_2O_3$, the liquidus rises sharply, reaches a maximum of 1,154° at the composition $CaO \cdot B_2O_3$ (CaO, 44.61 per cent; B_2O_3, 55.39 per cent), and descends to 1,132°, the melting point of a eutectic containing approximately 51.5 per cent CaO and 48.5 per cent B_2O_3. As previously mentioned, the true melting points near the eutectic could not be determined from the heating curves. The two points to the left of the eutectic in the diagram,

therefore, represent the melting point of the eutectic itself, rather than those of the two mixtures.

The curve then rises to another maximum of 1,298°, corresponding to the melting point of $2CaO \cdot B_2O_3$ (CaO, 61.70 per cent; B_2O_3, 38.30 per cent), and drops to 1,291°, the melting point of a second eutectic containing approximately 64 per cent CaO. A maximum of 1,479° corresponds to the melting point of $3CaO \cdot B_2O_3$ (CaO, 70.73 per cent; B_2O_3, 29.27 per cent), which is followed by a drop in the curve to another eutectic melting at 1,460° and consisting of about 73 per cent CaO and 27 per cent B_2O_3. Heating curves on two mixtures still higher in lime indicated the melting of this eutectic, but showed no further breaks up to 1,600°, the maximum temperature attained. Petrographic examination of these samples after fusion showed that they consisted of two phases, $3CaO \cdot B_2O_3$ and CaO. Hence it is assumed that no compounds are formed containing more CaO than the orthoborate, $3CaO \cdot B_2O_3$, and that the liquidus rises continuously to the melting point of CaO at 2,572°.

IV. SUMMARY

The phase equilibrium diagram for the system $CaO \cdot B_2O_3$ has been partially worked out. A region of liquid immiscibility was found, extending from 0.2 to 23 per cent CaO, and from 971° to above 1,500° C. The optical properties of the four compounds in this system were determined. The melting points of these compounds are given in Table 2, together with the melting points determined by previous investigators.

TABLE 2.—*Melting points of the calcium borates*

Compound	Melting point, determined by—			
	Guertler (1904)	Griveau (1918)	Roberts (1924)	Carlson
	°C.	°C.	°C.	°C.
$CaO \cdot 2B_2O_3$	1,030	ca. 1,025		986±5
$CaO.2B_2O_3$	1,095	ca. 1,100		1,154±5
$2CaO \cdot B_2O_3$	1,225	ca. 1,215	1,304±5	1,298±5
$3CaO.B_2O_3$				1,479±5

WASHINGTON, October 10, 1932.