U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP941

Part of Journal of Research of the National Bureau of Standards, Volume 17, November 1936

THE SYSTEM LIME—BORIC OXIDE—SILICA

By E. P. Flint* and Lansing S. Wells

ABSTRACT

The equilibrium diagram for the system $CaO–B_2O_3–SiO_2$, constructed from data on 200 ternary compositions, is presented. The portion of the diagram immediately adjacent to the binary system $B_2O_3–SiO_2$ is incomplete. A unique feature of the system is the appearance of an area of liquid immiscibility extending across the diagram from the lime-silica side to the lime-boric oxide side and crossing the fields of silica, monocalcium borate, and calcium diborate. A newly established ternary compound, $5CaO.B_2O_3.SiO_2$, melts congruently at 1,419° C. Tricalcium silicate does not appear at the liquidus in the ternary system. Dicalcium silicate forms partial solid solutions with calcium borates whereby the α–β inversion temperature is lowered by a maximum of 190° C.

CONTENTS

I. INTRODUCTION

The existence of liquid immiscibility in binary systems of boric oxide with oxides of certain of the alkaline earths and other divalent elements was early established in phase equilibrium investigations [1].[1] It was not recognized until much later that liquid immiscibility

---

* A part of this paper was presented by E. P. Flint to the Graduate School of the University of Maryland, represented by Dr. M. M. Haring, in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June 1936.

[1] Figures in brackets here and elsewhere throughout the text refer to references at the end of this paper.

of a similar type occurs in the corresponding binary systems of silica [2]. The system $CaO–B_2O_3–SiO_2$ is the first ternary system investigated to include both B_2O_3 and SiO_2 as components, and also furnishes the first example of a type of liquid immiscibility in ternary oxide systems wherein the immiscibility region crosses more than one field of primary crystallization.

The system $CaO–B_2O_3–SiO_2$ is a fundamental one in ceramics, for the high silica–boric oxide portion may serve as a starting point for investigations of borosilicate glasses, enamels, and ceramic glazes. The initial motive for the present study was furnished by observations of the effect of small quantities of boric oxide on calcium silicates occurring in portland cement, which apparently indicated the possibility of producing a "well-burned" clinker at a relatively low temperature. This paper represents the completion of a program first outlined in 1930 and reported on at intervals subsequently [3].

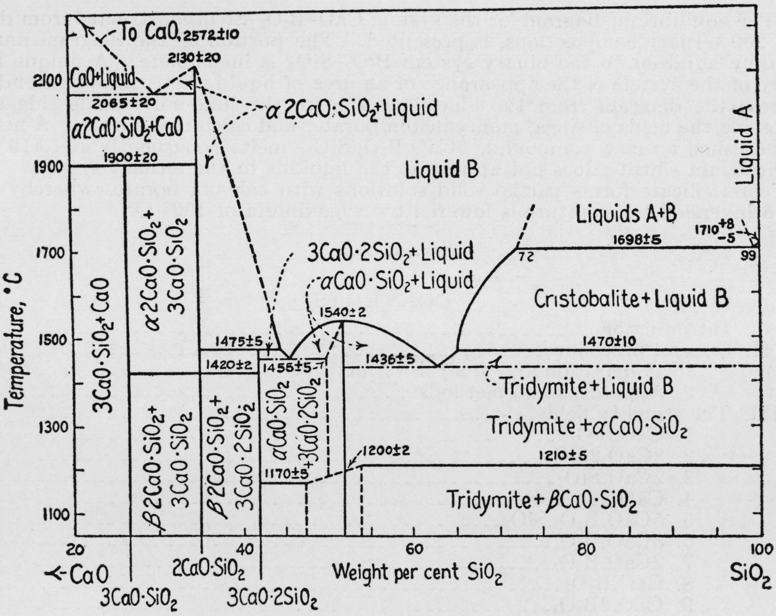

FIGURE 1.—*The binary system* CaO–SiO.

(See literature references [2, 7, 8, 9])

(Reproduced from that given by F. P. Hall and H. Insley, J. Am. Ceram. Soc. **16** p. 492, fig. 37 (1933))

Previous investigations have supplied most of the necessary data on the components and the three binary systems which they form.

The melting point of lime was determined by Kanolt [4] as 2,572° C and by Schumacher [5] as 2,576° C. Taylor and Cole [6] in 1934 reported having prepared crystalline boric oxide and gave its melting point as 294° C. Silica, as cristobalite, melts at 1,713° C [2].

The binary system lime–silica (fig. 1) has been investigated by Day, Shepherd, and Wright [7]; Rankin and Wright [8]; Ferguson and Merwin [9]; and Greig [2].

Phase equilibria in the system lime–boric oxide (fig. 2) were established by Carlson [10].

Only limited information on the system B_2O_3–SiO_2 is available and the course of the liquidus is unknown. Greig [2], and Cousen and Turner [11] have demonstrated the probability that the liquids formed by these oxides are miscible in all proportions. The latter authors found that the thermal expansion and density-composition curves of boric oxide—silica glasses gave no indication of the formation of compounds and concluded that the oxides form only simple solutions.

Morey, and Morey and Ingerson [12] have reported briefly on the melting of danburite, $CaO.B_2O_3.2SiO_2$, the only known naturally occurring calcium borosilicate. This mineral was found to melt with the formation of two ternary liquid layers. Some general characteristics of the immiscibility region of the system CaO–B_2O_3–SiO_2, within which the composition of danburite lies, have also been pointed out by these investigators.

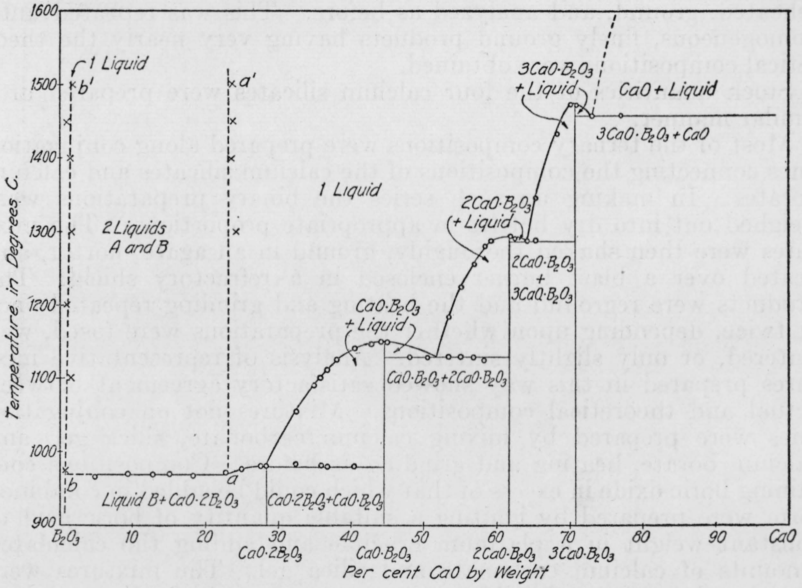

FIGURE 2.—*The binary system* CaO–B_2O_3.

(Reproduced from fig. 2 of reference [0])

II. GENERAL PROCEDURE

1. PREPARATION AND ANALYSIS OF MIXTURES

Calcium carbonate, boric acid, and silica gel were used as starting materials.

The calcium carbonate was of reagent quality for alkali determinations. Analyses showed 56.06 percent of CaO (theoretical for $CaCO_3 = 56.08$ percent of CaO). Impurities in the boric acid were reported by the Chemistry Division of the National Bureau of Standards as follows: $Fe < 0.001$ percent; $SO_3 < 0.01$ percent; $Cl < 0.001$ percent. The silica gel was a commercial granular product which was purified by boiling with concentrated nitric acid and subsequently thoroughly washed and dried. Treatment with hydrofluoric and sulfuric acids gave 0.04 percent of nonvolatile material based on the weight of the ignited silica.

Boric acid volatilizes appreciably on heating and boric oxide, though much less volatile, is extremely hygroscopic and difficult to handle. It was, therefore, considered advantageous in preparing the ternary compositions to add boric oxide already combined with lime. For this purpose the four calcium borates were prepared by mixing boric acid in excess with calcium carbonate and fusing or sintering. All heat treatments were made in covered platinum containers. The products were ground in an agate mortar, their ignition losses and lime contents determined, and the latter brought to the theoretical values by the addition of calcium carbonate. They were then reheated, ground, and analyzed as before. This was repeated until homogeneous, finely ground products having very nearly the theoretical compositions were obtained.

Stock quantities of the four calcium silicates were prepared in a similar manner.

Most of the ternary compositions were prepared along conjugation lines connecting the compositions of the calcium silicates and calcium borates. In making up such series the binary preparations were weighed out into dry bottles in appropriate proportions. The mixtures were then shaken thoroughly, ground in an agate mortar, and heated over a blast burner enclosed in a refractory shield. The products were reground and the heating and grinding repeated once or twice, depending upon whether the preparations were fused, well sintered, or only slightly sintered. Analysis of representative mixtures prepared in this way showed satisfactory agreement between actual and theoretical compositions. Mixtures not on conjugation lines were prepared by mixing calcium carbonate, silica gel, and calcium borate, heating and grinding as before. Compositions containing boric oxide in excess of that which could be added in combined form were prepared by igniting a suitable quantity of boric acid to constant weight in a platinum crucible and adding the calculated amounts of calcium carbonate and silica gel. The mixtures were then fused, ground, refused, and reground twice, and finally analyzed.

Analytical determinations were made of ignition loss, silica, and lime; boric oxide was obtained by difference. Half-gram samples were decomposed by 1:1 hydrochloric acid, evaporated almost to dryness and the moist residue evaporated three times with 10-ml portions of methyl alcohol to remove the boric acid. Silica was then determined by double dehydration in the usual way and lime precipitated as calcium oxalate, which was ignited to the oxide and weighed.

2. APPARATUS AND METHODS

The behavior of the ternary preparations on heating or on crystallization from their melts was studied by means of a vertical tube resistance furnace [13] wound with 80-percent platinum—20-percent rhodium wire. Temperatures were measured by platinum—platinum-rhodium thermocouples in conjunction with a precision potentiometer and galvanometer. The single thermocouples used were calibrated frequently against the melting points of potassium sulphate, 1,069.1° C; monocalcium borate, 1,154° C; diopside, 1,391.5° C; and monocalcium silicate, 1,544° C. The differential thermocouple used in heating curves was calibrated against potassium sulphate, 1,069.1° C; dicalcium borate, 1,304° C; and monocalcium silicate, 1,544° C.

The quenching method [14] was used principally for investigation of the ternary mixtures. Phases present in quenched samples were identified with the petrographic microscope. However, for the majority of compositions in the high-lime portion of the diagram this method was not applicable, as crystallization occurred during quenching. The melting behavior of such mixtures was determined by means of heating curves.

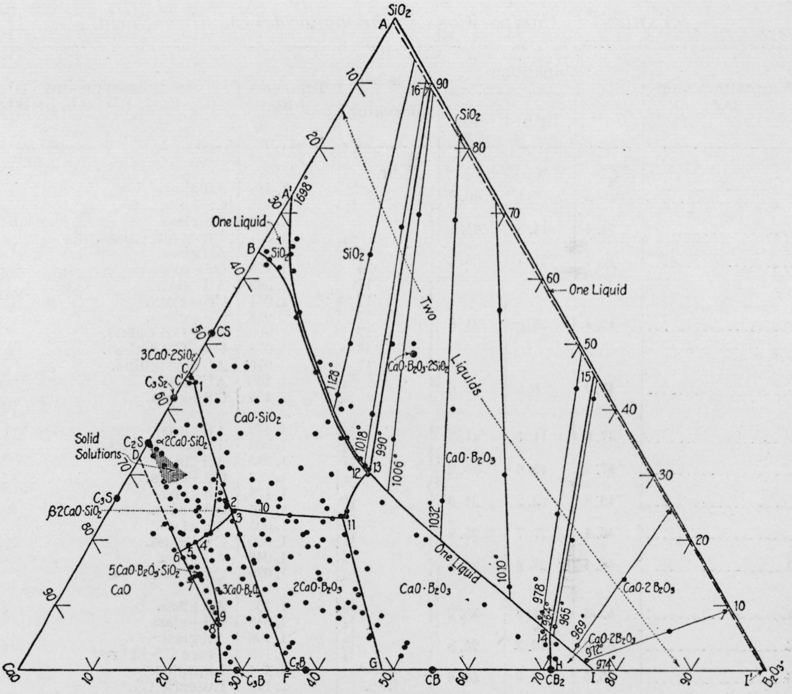

FIGURE 3.—*Triangular concentration diagram of the system* $CaO–B_2O_3–SiO_2$ *giving the compositions investigated and the limits of the stability fields in weight percent.*

III. THE STABILITY FIELDS

1. $CaO.SiO_2$

The compositions determining the area within which monocalcium silicate occurs as a primary phase (B–12–11–10–2–1–C, fig. 3) are listed in table 1. Column 5 gives the length of heat treatment of each charge in the furnace before quenching. The last column shows the results of microscopic examinations on the quenched samples. Formulas of binary and ternary compounds given in this and other tables are abbreviated by designating each component oxide by its first letter, C for CaO; B for B_2O_3; and S for SiO_2. The data in table 1 serve to fix the liquidus temperatures within sufficiently narrow limits and, for some compositions such as no. 4, the temperatures of boundaries and of quintuple points or eutectics.

Crystallization from melts in the monocalcium silicate field occurred readily except in the case of a few compositions located near the monocalcium borate boundary and the lower part of the silica boundary. Charges of these compositions were held overnight to insure attainment of equilibrium.

No marked variation in the indices of α–CaO.SiO$_2$ from the values of the pure compound was observed. The possible existence of solid solutions with calcium borates and their effect on the alpha-beta inversion of monocalcium silicate have not been investigated and therefore no attempt is made in figure 3 to indicate a boundary between the fields of alpha- and beta-monocalcium silicate.

TABLE 1.—*Compositions in the monocalcium silicate field*

Composition number	Composition			Time held before quenching	Temperature	Phases present (C=CaO, B=B_2O_3, S=SiO_2)
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
1	46.3	7.1	46.6	¼	1,418	All glass.
				¼	1,415	CS+glass.
2	44.4	14.3	41.3	2	1,305	All glass.
				¾	1,301	Trace CS+glass.
3	42.4	21.4	36.2	4	1,177	All glass.
				4	1,170	CS+glass.
4	40.4	28.6	31.0	17	1,043	All glass.
				17	1,041	CS+glass.
				17	998	CS+glass.
				17	993	CS+CB+glass.
				17	978	CS+CB+glass.
				17	976	All crystalline.
5	47.9	5.5	46.6	¼	1,460	All glass.
				¼	1,454	CS+glass.
6	47.6	11.1	41.3	¼	1,372	All glass.
				¼	1,365	Trace CS+glass.
7	47.2	16.6	36.2	¼	1,285	All glass.
				¼	1,283	CS+glass.
8	46.8	22.2	31.0	¼	1,178	All glass.
				¼	1,173	CS+glass.
9	46.4	27.7	25.9	¼	1,095	All glass.
				¼	1,090	CS+glass.
10	46.4	28.8	24.8	¼	1,046	All glass.
				¼	1,039	CS+glass.
11	52.3	11.5	36.2	¼	1,353	All glass.
				¼	1,348	CS+glass.
12	55.0	19.2	25.8	¼	1,198	All glass.
				¼	1,193	Trace CS+glass.
13	50.5	2.9	46.6	h. c.[a]	1,494	Liquidus.
				h. c.	1,119	Eutectic (2).[b]
14	51.7	4.4	41.4	h. c.	1,459	Liquidus.
				h. c.	1,118	Eutectic (2).
15	52.8	5.8	41.4	¼	1,440	All glass.
				¼	1,437	CS+glass.
16	55.0	8.8	36.2	¼	1,326	All glass.
				¼	1,323	CS+glass.
17	57.3	11.7	31.0	¼	1,233	All glass.
				¼	1,230	CS+glass.
18	58.4	13.2	28.4	¼	1,179	All glass.
				¼	1,175	CS+glass.
				¼	1,144	CS+glass.
				¼	1,136	CS+C_2S+glass.
19	56.3	8.3	35.4	¼	1,336	All glass.
				¼	1,334	CS+glass.
20	55.6	11.1	33.3	¼	1,318	All glass.
				¼	1,316	CS+glass.

[a] "h. c." indicates data obtained by heating curves. Under the column headed "phases present" the data given in such cases represent interpretations placed on breaks in heating curves.

[b] Numbers in parentheses in all the tables refer to points or boundaries in figure 3.

TABLE 1.—*Compositions in the monocalcium silicate field*—Continued

Composition number	Composition			Time held before quenching	Temperature	Phases present ($C=CaO$, $B=B_2O_3$, $S=SiO_2$)
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
21	54.2	16.6	29.2	¼	1,258	All glass.
				¼	1,256	CS+glass.
22	52.8	22.2	25.0	¼	1,148	All glass.
				¼	1,145	CS+glass.
23	46.3	28.7	25.0	¾	1,058	All glass.
				1	1,055	CS+glass.
24	43.2	26.8	30.0	½	1,087	All glass.
				1	1,079	Trace CS+glass.
25	36.0	2.0	62.0	¼	1,413	All glass.
				¼	1,406	CS+glass.
26	36.0	10.0	54.0	¾	1,278	All glass.
				½	1,271	CS+SiO_2+glass.
27	37.6	16.8	45.6	17	1,191	All glass.
				½	1,183	CS+glass.
28	39.7	22.2	38.1	17	1,112	All glass.
				17	1,108	CS+glass.
29	39.2	25.2	35.6	17	1,067	All glass.
				17	1,062	CS+glass.
30	54.4	1.5	44.1	¼	1,450	All glass.
				¼	1,448	CS+glass.
				½	1,435	CS+trace C_2S+glass.
31	52.0	19.4	28.6	¼	1,207	All glass.
				¼	1,204	CS+glass.
32	52.0	21.8	26.2	¼	1,164	All glass.
				¼	1,162	CS+glass.
33	45.2	31.2	23.6	17	1,028	All glass.
				17	1,020	CS+glass.

Figure 4I shows the binary system $CaO.SiO_2$–$2CaO.B_2O_3$, and figures 4J and 4K, the pseudobinary systems $CaO.SiO_2$–$CaO._2B_2O_3$ and $CaO.SiO_2$–$CaO.B_2O_3$, respectively.

2. $3CaO.2SiO_2$

Tricalcium disilicate crystallizes as a primary phase within a very restricted area (C–1–C′, fig. 3), being obtained only from melts which contain less than 2 percent of B_2O_3. Quenches on composition no. 34 in this field (54.5 percent of CaO, 0.6 percent of B_2O_3, 44.9 percent of SiO_2) gave a liquidus temperature of 1,457° C and a C_3S_2–CS boundary temperature of 1,453° C.

3. $2CaO.SiO_2$

Dicalcium silicate forms solid solutions with the calcium borates and the partial limits of these solutions are indicated by the shaded area in figure 3. The compositions prepared in the dicalcium silicate field (C′–1–2–3–4–5–6–D, fig. 3) are given in table 2.

Compositions 41, 42, 46, 47, 48, 49, 50, 51, 52, 54, 55, 56, 57, 60, 61, 62, and 63 show the effect of solid solution on the alpha-beta inversion of dicalcium silicate, which normally occurs at 1,420° C, as is shown in figure 5. Lowering of this temperature by a maximum of 190° C was observed. If this lowering is assumed to be due entirely to solid solution of the calcium borates, no further change in the inversion temperature should occur when a saturated solid solution is formed. Furthermore, heating curves on compositions containing less than the saturation amount of solid solution should exhibit no eutectic or boundary breaks. This was found to be the case for mixtures containing less than approximately 15 percent of added monocalcium borate, 20 percent of added dicalcium borate, and 35 percent of added pentacalcium borosilicate, and solid solution is therefore placed at these limits. It is of interest that these percentages represent approximately the same mole fractions of the respective compounds in the solid solutions: a mole fraction of 0.19 for monocalcium borate and dicalcium borate, and of 0.18 for pentacalcium borosilicate. Lowering of the inversion temperature to about 1,270° C occurs in the monocalcium borate solid solutions, and to about 1,230° C in solid solutions of the other two compounds. The extent of the solid solution area from the C_2S–C_5BS and C_2S–CB

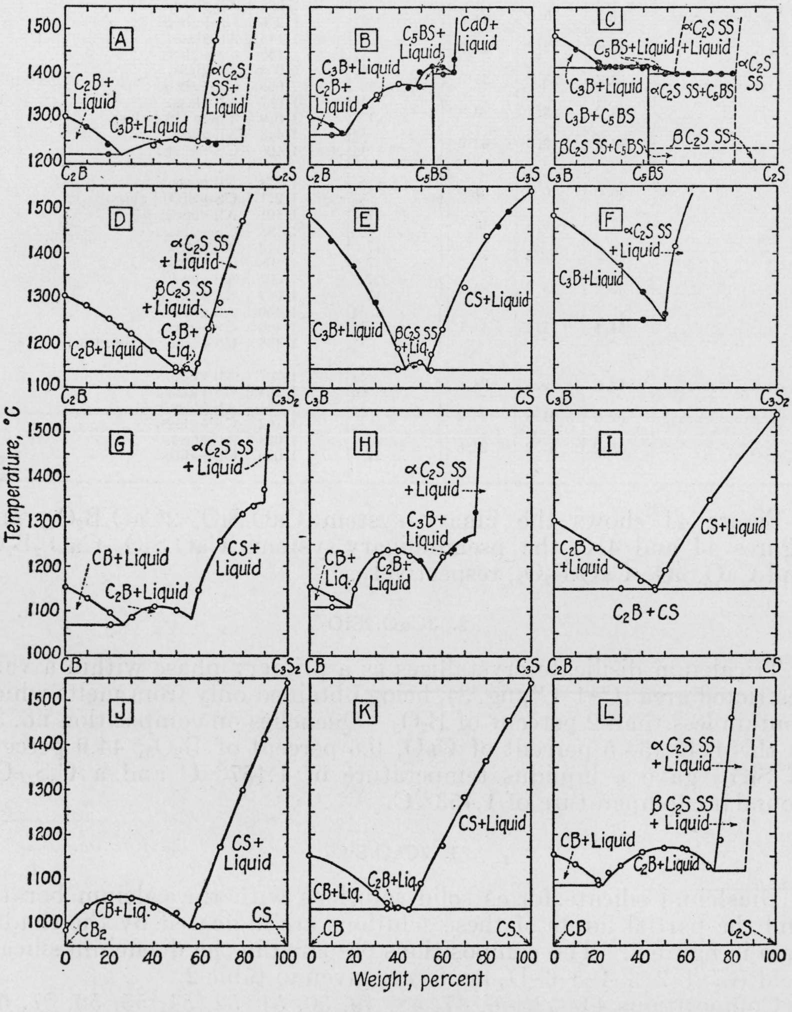

FIGURE 4.—*Binary and pseudobinary systems investigated in the system* CaO–B_2O_3–SiO_2.

(*SS*=solid solution.)

conjugation lines toward the CaO–SiO_2 side line has not been determined.

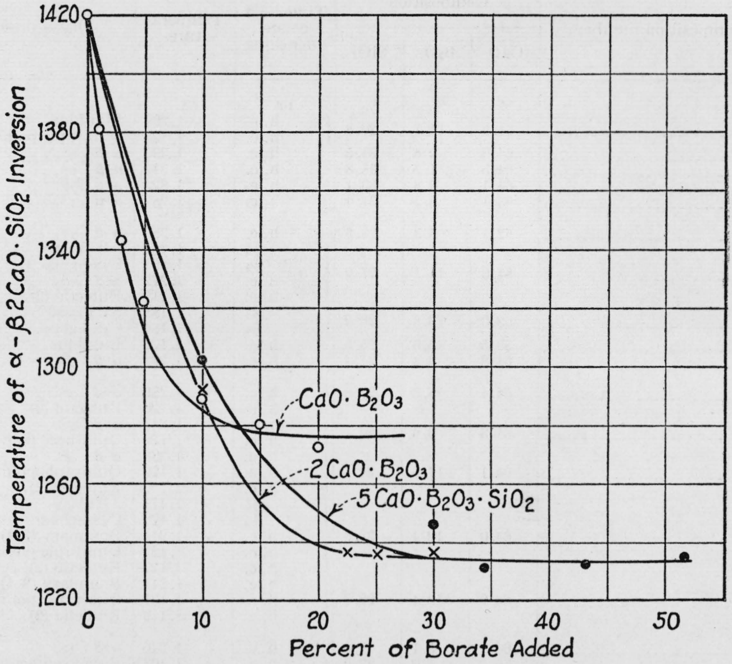

FIGURE 5.—*Effect of solid solution on the α–β inversion of dicalcium silicate.*

TABLE 2.—*Compositions in the dicalcium silicate field*

Composition number	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
35	57.0	5.5	37.5	¼	1,382	All glass.
				¼	1,373	Trace C_2S+glass.
				¼	1,345	C_2S+CS+glass.
				h. c.	1,343	Boundary (1–2).
				h. c.	1,125	Eutectic (2).
36	58.7	3.8	37.5	h. c.	1,382	Boundary (1–2).
37	59.0	7.7	33.3	¼	1,491	All glass.
				¼	1,473	C_2S+glass.
				h. c.	1,293	Boundary (1–2).
38	59.3	11.5	29.2	1	1,319	All glass.
				¼	1,311	C_2S+glass.
				h. c.	1,185	Boundary (1–2).
39	59.5	13.4	27.1	¼	1,234	All glass.
				¼	1,226	C_2S+glass.
40	59.7	15.3	25.0	¼	1,157	All glass.
				¼	1,151	C_2S+glass.
41	62.4	9.5	28.1	h. c.	1,271	α–β C_2S.
				h. c.	1,165	Boundary (3–4).
				h. c.	1,120	Eutectic (2).
42	63.0	11.0	26.0	h. c.	1,251	α–β C_2S.
				h. c.	1,122	Eutectic (2).
43	63.3	11.7	25.0	h. c.	1,241	α–β C_2S.
				h. c.	1,127	Quintuple point (3).
44	64.0	13.5	22.5	¼	1,421	All glass.
				¼	1,413	C_2S+glass.
				h. c.	1,245	Boundary (3–4).
				h. c.	1,133	Quintuple point (3).
				h. c.	1,122	Eutectic (2).

TABLE 2.—*Compositions in the dicalcium silicate field*—Continued

Composition number	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
45	64.5	14.7	20.8	h. c.	1,266	Liquidus.
				h. c.	1,125	Quintuple point (3).
46	64.9	0.6	34.5	h. c.	1,390	α–β C_2S.
47	64.5	1.7	33.8	h. c.	1,343	α–β C_2S.
48	64.1	2.8	33.1	h. c.	1,322	α–β C_2S.
49	63.1	5.5	31.4	h. c.	1,289	α–β C_2S.
50	62.1	8.3	29.6	h. c.	1,280	α–β C_2S.
51	61.0	11.1	27.9	¼	1,465	All glass.
				¼	1,461	C_2S+glass.
				h. c.	1,272	α–β C_2S.
				h. c.	1,117	Eutectic (2).
52	60.0	13.8	26.2	¼	1,188	All glass.
				¼	1,184	C_2S+glass.
53	59.5	15.0	25.5	h. c.	1,122	Liquidus.
54	64.8	3.8	31.4	h. c.	1,292	α–β C_2S.
55	64.4	8.6	27.0	h. c.	1,236	α–β C_2S.
				h. c.	1,120	Eutectic (2).
56	64.3	9.6	26.1	h. c.	1,235	α–β C_2S.
				h. c.	1,126	Quintuple point (3).
57	64.1	11.5	24.4	h. c.	1,236	α–β C_2S.
				h. c.	1,129	Quintuple point (3).
				h. c.	1,120	Eutectic (2).
58	64.0	12.4	23.6	¼	1,477	All glass.
				½	1,472	C_2S+glass.
				h. c.	1,244	Boundary (3–4).
				h. c.	1,127	Quintuple point (3).
				h. c.	1,121	Eutectic (2).
59	63.9	13.4	22.7	h. c.	1,247	Boundary (3–4).
				h. c.	1,131	Quintuple point (3).
				h. c.	1,119	Eutectic (2).
60	66.1	5.1	28.8	h. c.	1,246	α–β C_2S.
61	66.2	5.9	27.9	h. c.	1,403	Binary eutectic (5).
				h. c.	1,231	α–β C_2S.
62	66.5	7.3	26.2	h. c.	1,400	Binary eutectic (5).
				h. c.	1,232	α–β C_2S.
63	66.8	8.8	24.4	h. c.	1,403	Binary eutectic (5).
				h. c.	1,234	α–β C_2S.
64	67.4	11.7	20.9	h. c.	1,400	Binary eutectic (5).
				h. c.	1,262	Quintuple point (4).
65	67.6	13.2	21.4	h. c.	1,399	Binary eutectic (5).
				h. c.	1,266	Quintuple point (4).
66	68.6	9.7	21.7	h. c.	1,400	Eutectic (6).
67	66.4	13.9	19.7	h. c.	1,323	Liquidus.
				h. c.	1,258	Boundary (3–4).
68	59.5	14.6	25.9	¼	1,159	All glass.
				¼	1,155	C_2S+glass.
69	55.3	0.7	44.0	¼	1,459	All glass.
				¼	1,455	Trace C_2S+glass.

Pseudo-binary systems of $2CaO.SiO_2$ with $2CaO.B_2O_3$ and $CaO.B_2O_3$ are shown in figures 4A and 4L, respectively; and the true binary system formed by $2CaO.SiO_2$ and $5CaO.B_2O_3.SiO_2$ is given in figure 4C.

Dicalcium silicate, crystallized from melts, had the appearance of rounded grains usually imbedded in glass, making an exact determination of the indices difficult. A marked lowering of the indices was observed, however. Thus composition 18, table 1 (58.4 percent of CaO, 13.2 percent of B_2O_3, 28.4 percent of SiO_2), which lies just inside the monocalcium silicate field, when held below the temperature of secondary crystallization, gave spherules of C_2S having an average index only slightly above the 1.65 index of the glass in which they were imbedded (normal indices of β–$2CaO.SiO_2$: $\alpha=1.717$; $\gamma=1.735$).

The field of β–$2CaO.SiO_2$ has been located in figure 3 in accordance with the lowest temperatures found for the alpha-beta inversion.

4. CaO

The compositions prepared in the lime field (D–6–7–8–E–CaO, fig. 3) and melting data obtained by heating curves are given in table 3. Quenches were also made on these compositions to establish the primary phase.

TABLE 3.—*Compositions in the lime field*

Composition number	Composition			Temperature [a]	Phases present
	CaO	B_2O_3	SiO_2		
	%	%	%	°C	
70	69.3	8.3	22.4	1,398	Eutectic (6).
71	71.3	7.7	21.0	1,399	Do.
72	69.1	11.5	18.4	1,398	Do.
73	69.5	13.4	17.1	1,435 1,406	Liquidus. Boundary (6–7–8).
74	71.3	23.4	5.3	1,412	Boundary (8–E).
75	71.5	21.9	6.6	1,410	Do.
76	70.0	16.1	13.9	1,413	Binary eutectic (7).
77	71.5	15.3	13.2	1,412	Do.

[a] Obtained from heating curves.

5. $5CaO.B_2O_3.SiO_2$

Pentacalcium borosilicate is the only ternary compound found to possess a field (4–5–6–7–8–9, fig. 3) in the ternary diagram. It may be considered as formed by the combination of dicalcium silicate with tricalcium borate, mole for mole; or by the combination of tricalcium silicate with dicalcium borate, mole for mole. Tricalcium silicate does not occur as a primary phase in this sytem, the ternary compound occupying the region where it might be expected to appear.

The compound, $5CaO.B_2O_3.SiO_2$, melts congruently at 1,419° C. The optical properties [15] are: biaxial negative with moderate optic axial angle; $\alpha=1.666 \pm 0.003$, $\beta=1.682 \pm 0.003$, $\gamma=1.690 \pm 0.003$. Polysynthetic twinning is extremely common. The optic axial angle appears to be variable, probably because of twinning. The compound appears in irregular or rounded grains without definite crystal outline.

Pentacalcium borosilicate forms true binary systems with dicalcium silicate, tricalcium borate (fig. 4C), and lime. In accordance with the theorem of Alkemade [16] the maximum temperature on the boundary 4–5–6 (fig. 3) was found to occur at the binary eutectic (point 5); the maximum on boundary 6–7–8 at the binary eutectic (point 7); and the maximum on boundary 4–9–8 at the binary eutectic (point 9).

Complete crystallization of most charges in this field occurred on quenching; hence melting data were obtained exclusively by heating curves. The results are listed in table 4.

Possible solid solution of $2CaO.SiO_2$ in $5CaO.B_2O_3.SiO_2$ was not indicated.

TABLE 4.—*Compositions in the pentacalcium borosilicate field*

Composition number	Composition			Temperature [a]	Phases present
	CaO	B_2O_3	SiO_2		
	%	%	%	°C	
78	67.9	14.7	17.4	1,400	Binary eutectic (5).
79	68.2	16.1	15.7	1,415	Liquidus.
80	68.4	17.0	14.6	1,419	Do.
81	68.5	17.6	13.9	1,414	Do.
82	68.8	19.0	12.2	1,417	Do.
83	69.0	20.5	10.5	1,415	Do.
				1,262	Quintuple point (4).
84	69.2	21.2	9.6	1,415	Binary eutectic (5).
85	69.3	22.0	8.7	1,417	Liquidus.
86	68.9	15.3	15.8	1,417	Do.
				1,401	Boundary (5-7-8).
87	67.7	19.1	13.2	1,406	Liquidus.
				1,373	Boundary (8-9-4).
88	69.2	16.5	14.3	1,414	Liquidus.

[a] Obtained from heating curves.

6. $3CaO.B_2O_3$

Heating curves on a tricalcium borate preparation having very nearly the theoretical composition (by analysis: 70.74 percent of CaO, 29.26 percent of B_2O_3; theoretical: 70.73 percent of CaO; 29.27 percent of B_2O_3) gave its melting temperature as 1,488° C, a value 9° higher than that reported by Carlson [10] for this compound.

In this field (E–8–9–4–3–F, fig. 3) most of the melting data were secured by heating curves, owing to difficulties caused by quench crystallization. The data are given in table 5.

TABLE 5.—*Compositions in the tricalcium borate field*

Composition number	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
89	68.5	26.3	5.2	h. c.	1,429	Liquidus.
				h. c.	1,120	Quintuple point (3).
90	66.3	23.4	16.3	h. c.	1,370	Liquidus.
				h. c.	1,124	Quintuple point (3).
91	64.0	20.5	15.5	h. c.	1,291	Liquidus.
				h. c.	1,129	Quintuple point (3).
92	61.7	17.6	20.7	¼	1,191	All glass.
				¼	1,185	C_3B+glass.
				½	1,147	C_3B+glass.
				½	1,140	C_3B+C_2S+glass.
93	59.9	17.2	22.9	¼	1,150	All glass.
				¼	1,143	Trace C_3B+glass.
94	67.0	20.5	12.5	h. c.	1,375	Liquidus.
				h. c.	1,123	Quintuple point (3).
95	65.8	17.5	16.7	h. c.	1,316	Liquidus.
				h. c.	1,253	Boundary (3-4).
				h. c.	1,123	Quintuple point (3).
96	63.8	15.3	20.9	¾	1,252	All glass.
				¾	1,248	C_3B+C_2S+glass.
				h. c.	1,125	Quintuple point (3).
				h. c.	1,118	Eutectic (2).
97	63.4	19.2	17.4	¼	1,257	All glass.
				¼	1,252	C_3B+glass.
98	63.1	23.0	13.9	¼	1,243	All glass.
				½	1,239	C_3B+glass.

TABLE 5.—*Compositions in the tricalcium borate field*—Continued

Composition number	Composition CaO	Composition B_2O_3	Composition SiO_2	Time held before quenching	Temperature	Phases present
	%	%	%	hr	°C	
99	70.2	26.3	3.5	h. c.	1,456	Liquidus.
100	69.6	23.4	7.0	h. c.	1,428	Do.
				h. c.	1,416	Binary eutectic (9).
101	69.5	22.7	7.8	h. c.	1,416	Liquidus.
102	65.0	16.6	18.4	h. c.	1,261	Do.
				h. c.	1,122	Quintuple point (3).
103	63.5	19.4	17.1	h. c.	1,239	Liquidus.
				h. c.	1,122	Quintuple point (3).
104	62.0	22.2	15.8	¼	1,226	All glass.
				¼	1,219	C_3B+glass.
105	67.1	21.1	11.8	h. c.	1,371	Liquidus.
				h. c.	1,123	Quintuple point (3).
106	66.5	23.0	10.5	¾	1,384	All glass.
				2	1,374	C_3B+glass.
				h. c.	1,126	Quintuple point (3).
107	65.3	26.8	7.9	¼	1,354	All glass.
				¼	1,351	C_3B+glass.
				h. c.	1,170	Boundary (F-3).
108	64.7	28.7	6.6	h. c.	1,330	Liquidus.
109	64.1	30.6	5.3	h. c.	1,245	Boundary (F-3).
110	70.9	27.8	1.3	h. c.	1,476	Liquidus.
				h. c.	1,404	Eutectic (8).
111	71.0	26.4	2.6	h. c.	1,456	Liquidus.
				h. c.	1,404	Eutectic (8).
112	71.1	24.9	4.0	h. c.	1,441	Liquidus.

7. $2CaO.B_2O_3$

Dicalcium borate forms a true binary system with monocalcium silicate (fig. 4I) and accordingly boundary 2–11 (fig. 3) shows a maximum temperature at point 10, as determined by a heating curve on composition 124, and quenches on composition 125, table 6.

TABLE 6.—*Compositions in the dicalcium borate field*

Composition number.	Composition CaO	Composition B_2O_3	Composition SiO_2	Time held before quenching	Temperature	Phases present
	%	%	%	hr	°C	
113	62.9	34.5	2.6	h. c.	1,287	Liquidus.
				h. c.	1,266	Boundary (F-3).
114	63.5	32.6	3.9	h. c.	1,270	Liquidus.
115	62.0	34.5	3.5	h. c.	1,281	Liquidus.
116	62.4	30.6	7.0	h. c.	1,240	Liquidus.
				2	1,221	C_2B+trace C_3B+glass.
117	71.3	34.5	4.2	½	1,287	All glass.
				½	1,280	C_2B+glass.
118	61.0	30.7	8.3	¼	1,256	All glass.
				¼	1,248	C_2B+glass.
119	60.9	28.7	10.4	¼	1,239	All glass.
				¼	1,235	C_2B+glass.
120	60.7	26.8	12.5	¼	1,225	All glass.
				¼	1,221	Trace C_2B+glass.
121	60.3	23.0	16.7	¼	1,184	All glass.
				¼	1,180	C_2B+glass.
122	60.0	19.2	20.8	¼	1,151	All glass.
				¼	1,142	Trace C_2B+glass.
				¼	1,136	C_2B+C_3B+glass.
123	59.1	31.0	9.9	h. c.	1,243	Liquidus.
124	57.7	26.8	15.5	h. c.	1,203	Liquidus.
				h. c.	1,153	Binary eutectic (10).
125	55.7	21.3	23.0	¼	1,155	All glass.
				¼	1,153	C_2B+glass.
				¼	1,150	C_2B+CS+glass.

TABLE 6.—*Compositions in the dicalcium borate field*—Continued

Composition number.	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
126	52.4	32.6	15.0	¼	1,180	All glass.
				¼	1,172	C_2B+glass.
127	49.4	30.6	20.0	¼	1,097	All glass.
				¼	1,095	C_2B+glass.
128	50.4	44.3	5.3	¼	1,153	All glass.
				¼	1,150	C_2B+glass.
129	53.3	38.8	7.9	¼	1,230	All glass.
				¼	1,224	C_2B+glass.
130	54.8	36.0	9.2	¼	1,240	All glass.
				¼	1,236	C_2B+glass.
131	56.3	33.2	10.5	3	1,241	All glass.
				4	1,233	C_2B+glass.
132	57.7	30.5	11.8	1¼	1,226	All glass.
				½	1,223	C_2B+glass.
133	59.1	27.7	13.2	h. c.	1,214	Liquidus.
134	49.8	41.5	8.7	¼	1,122	All glass.
				¼	1,115	Trace C_2B+glass.
135	50.8	38.8	10.4	¼	1,134	All glass.
				¼	1,131	Trace C_2B+glass.
136	52.8	33.2	14.0	¼	1,162	All glass.
				¼	1,158	C_2B+glass.
				h. c.	1,017	Quintuple Point (11).
137	54.9	27.7	17.4	¼	1,170	All glass.
				¼	1,168	C_2B+glass.
				h. c.	1,120	Boundary (2–11).
138	56.5	23.4	20.1	¼	1,177	All glass.
				¼	1,169	C_2B+glass.
139	56.9	22.2	20.9	¼	1,170	All glass.
				¼	1,163	C_2B+glass.
140	59.0	16.6	24.4	¼	1,128	All glass.
				¼	1,126	C_2B+glass.
				¼	1,119	C_2B+C_2S+glass.
141	48.7	38.8	12.5	¼	1,089	All glass.
				¼	1,085	Trace C_2B+glass.
142	50.1	33.2	16.7	¼	1,112	All glass.
				¼	1,111	C_2B+glass.
143	51.5	27.7	20.8	¼	1,104	All glass.
				¼	1,102	C_2B+glass.
144	46.1	33.2	20.7	¼	1,039	All glass.
				¼	1,037	C_2B+glass.
145	46.3	30.4	23.3	¼	1,035	All glass.
				¼	1,027	C_2B+CS+glass.
146	47.2	35.2	17.5	¼	1,037	All glass.
				¼	1,033	C_2B+glass.
				¼	1,030	C_2B+CB+glass.
147	50.8	28.1	21.0	¼	1,109	All glass.
				¼	1,107	C_2B+glass.
148	52.6	24.6	22.8	¼	1,128	All glass.
				¼	1,123	C_2B+glass.
149	50.7	44.3	5.0	¼	1,139	All glass.
				¼	1,132	C_2B+glass.
				¼	1,105	C_2B+CB+glass.
150	51.6	38.9	9.5	¼	1,164	All glass.
				¼	1,159	C_2B+glass.
151	50.2	40.1	9.7	h. c.	1,130	Liquidus.
152	48.6	39.7	11.7	¼	1,083	All glass.
				¼	1,080	C_2B+glass.
				¼	1,075	C_2B+CB+glass.
153	51.8	29.2	19.0	¼	1,134	All glass.
				¼	1,129	C_2B+glass.
154	50.5	30.5	19.0	¼	1,113	All glass.
				¼	1,108	C_2B+glass.
155	58.7	22.2	19.1	¼	1,172	All glass.
				¼	1,170	C_2B+glass.
156	48.0	29.3	22.7	¼	1,054	All glass.
				¼	1,052	C_2B+glass.
157	51.7	25.5	22.8	¼	1,127	All glass.
				¼	1,121	C_2B+glass.
				¼	1,107	C_2B+CS+glass.
158	51.9	24.3	23.8	¼	1,125	All glass.
				¼	1,124	Trace C_2B+glass.
				¼	1,117	C_2B+CB+glass.

8. $CaO.B_2O_3$

Monocalcium borate is obtained from melts as lath-shaped crystals occasionally showing hexagonal outline. Sluggish crystallization of some compositions containing the higher percentages of silica in this field necessitated holding the charges overnight. Data relative to the monocalcium borate field are given in table 7.

About one-third of the monocalcium borate field (G–11–12–13–14–H, fig. 3) lies in the one-liquid area, and about two-thirds (13–16–15–14, fig. 3) in the immiscibility region. The boundary of the field in the one-liquid area proceeding inward from the SiO_2–B_2O_3 side line was not determined.

The composition corresponding to that of the mineral danburite, $CaO.B_2O_3.2SiO_2$, is located within the immiscibility portion of the monocalcium borate field.

TABLE 7.—*Compositions in the monocalcium borate field*

Composition number	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
159	47.5	49.9	2.6	¼	1,131	All glass.
				¼	1,129	CB+glass.
				¼	1,110	CB+C_2B+glass.
160	46.7	49.8	3.5	¼	1,134	All glass.
				¼	1,132	CB+glass.
161	48.7	44.3	7.0	¼	1,099	All glass.
				¼	1,096	CB+glass.
				¼	1,087	CB+C_2B+glass.
162	46.0	49.8	4.2	¼	1,131	All glass.
				¼	1,128	CB+glass.
163	47.4	44.3	8.3	¼	1,099	All glass.
				¼	1,096	CB+glass.
				¼	1,070	CB+C_2B+glass.
164	45.7	38.8	15.5	¼	1,071	All glass.
				¼	1,067	CB+glass.
165	45.9	36.0	18.1	¼	1,046	All glass.
				¼	1,043	CB+glass.
				¼	1,035	CB+C_2B+glass.
166	40.1	49.9	10.0	17	1,111	All glass.
				17	1,104	CB+glass.
167	35.7	44.3	20.0	17	1,045	All glass.
				17	1,041	CB+glass.
168	30.6	64.2	5.2	17	1,041	All glass.
				17	1,036	CB+glass.
169	32.6	57.1	10.3	17	1,058	All glass.
				17	1,053	CB+glass.
				17	1,013	CB+2 glasses.
170	34.6	49.9	15.5	17	1,059	All glass.
				17	1,053	CB+glass.
				17	1,028	CB+2 glasses.
171	36.5	42.8	20.7	17	1,041	All glass.
				3½	1,033	CB+glass.
172	38.5	35.7	25.8	17	1,023	All glass.
				17	1,017	CB+glass.
173	38.4	31.6	30.0	17	991	All glass.
				17	984	CB+SiO_2+glass.
174	28.0	70.0	2.0	½	993	All glass.
				½	989	Trace CB+glass.
175	27.5	68.5	4.0	½	981	All glass.
				½	979	CB+glass.
176	26.9	67.1	6.0	¼	971	All glass.
				½	969	CB+glass.
177	44.4	32.0	23.6	17	1,018	All glass.
				17	1,017	CB+glass.
178	44.0	31.6	24.4	1½	1,027	All glass.
				1½	1,017	Trace CB+glass.
179	26.4	65.6	8.0	1½	976	Two glasses.
				1½	968	CB+glass.

9. $CaO.2B_2O_3$

Only a small portion of the calcium diborate field (H–14–I, fig. 3) lies within the one-liquid region; compositions in the area 14–15–I′–I melt with the formation of two liquids. The boundary of the field in the one-liquid area extending inward from the SiO_2–B_2O_3 side line was not determined.

The liquidus temperatures of two compositions, 180 (27.3 percent of CaO, 70.9 percent of B_2O_3, 1.8 percent of SiO_2) and 181 (26.2 percent of CaO, 69.9 percent of B_2O_3, 3.9 percent of SiO_2), in the area H–14–I, are 982° C and 967° C, respectively.

10. SiO_2

This field is distorted in a curious manner by the occurrence of liquid immiscibility. It consists of a portion (A′–B–12–13) in the one-liquid area, a large region (A′–13–16–A) in the two-liquid area, and probably a narrow strip in the one-liquid area along the SiO_2–B_2O_3 side of the triangle extending an undetermined distance toward the B_2O_3 vertex.

In the melts studied (table 8) silica appeared as tridymite imbedded in the high-index glass.

TABLE 8.—*Compositions in the silica field*

Composition number	Composition			Time held before quenching	Temperature	Phases present
	CaO	B_2O_3	SiO_2			
	%	%	%	hr	°C	
182	35.0	1.0	64.0	2	1,425	All glass.
				1	1,417	SiO_2+CS+glass.
183	35.2	2.0	62.8	2	1,411	All glass.
				1	1,405	Trace SiO_2+glass.
				1	1,400	SiO_2+CS+glass.
184	34.4	4.0	61.6	1	1,388	All glass.
				½	1,380	SiO_2+glass.
				½	1,373	SiO_2+CS+glass.
185	31.2	4.0	64.8	1	1,370	SiO_2+two glasses.
				½	1,364	SiO_2+CS+glass.
186	32.0	4.4	63.6	1	1,465	Two glasses.
				1	1,457	SiO_2+glass.
				1	1,365	SiO_2+glass.
				1	1,357	SiO_2+CS+glass.
187	32.8	6.0	61.2	1	1,392	Two glasses.
				1	1,385	SiO_2+glass.
				¼	1,332	SiO_2+glass.
				¼	1,327	SiO_2+CS+glass.
188	35.2	10.0	54.8	1	1,292	Two glasses.
				¾	1,287	SiO_2+glass.
				1	1,276	SiO_2+glass.
				1½	1,271	SiO_2+CS+glass.
189	36.3	15.5	47.2	½	1,223	Two glasses.
				1	1,218	SiO_2+glass.
				½	1,205	SiO_2+glass.
				1½	1,197	SiO_2+CS+glass.
190	37.0	23.0	40.0	4	1,113	Two glasses.
				4	1,108	SiO_2+glass.
191	35.6	24.0	40.4	17	1,071	Two glasses.
				17	1,063	SiO_2+glass.
192	38.4	26.0	35.6	17	1,057	Two glasses.
				17	1,048	SiO_2+glass.
193	38.2	29.4	32.4	17	1,038	Two glasses.
				17	1,031	SiO_2+glass.
				17	1,010	SiO_2+glass.
				17	1,006	SiO_2+CS+glass.
194	38.2	30.4	31.4	17	1,019	Two glasses.
				17	1,012	SiO_2+glass.
				17	1,003	SiO_2+glass.
				17	1,000	SiO_2+CS+glass.
195	37.8	31.4	30.8	17	995	Two glasses.
				17	991	SiO_2+glass.
				17	989	SiO_2+CB+glass.

The exact concentration intervals between the two-liquid boundary and the silica-monocalcium silicate boundary have not been accurately determined, but probably are represented fairly closely by the region between the curves A′–13 and B–12 in figure 3.

IV. THE TWO-LIQUID AREA

The appearance of liquid immiscibility in a ternary system reduces the maximum possible number of solid phases within such an area by one. Hence, no ternary eutectics can occur in an immiscibility region, and fields entering it must persist until liquid miscibility is again encountered. Moreover, boundaries between fields must be straight lines of constant temperature in the immiscibility area. The course of crystallization in this region is quite different from that in the one-liquid area.

Liquid immiscibility of the type found in the system $CaO–B_2O_3–SiO_2$ probably occurs also in ternary systems of B_2O_3 and SiO_2 with MgO, SrO, ZnO, FeO, CoO, and NiO, as these last six oxides, like CaO, form binary systems with both B_2O_3 and SiO_2 in which liquid immiscibility occurs [1, 2]. Analogies are also to be found in certain organic systems such as the system water-phenol-aniline investigated by Schreinemakers [17].

Studies were made of the compositions of immiscible liquids formed by the melting of mixtures within the area A–A′–13–14–I–I′, figure 3. The results are listed in table 9.

TABLE 9.—*Tie-line compositions in the immiscibility area*

Composition number	Compositions									Time held before quenching	Temperature	Phases present
	Initial			High SiO_2 glass			Low SiO_2 glass					
	CaO	B_2O_3	SiO_2	CaO	B_2O_3	SiO_2	CaO	B_2O_3	SiO_2			
	%	%	%	%	%	%	%	%	%	hr	°C	
196	30.8	19.2	50.0	21.4	15.0	63.6	36.4	21.4	42.2	7	1,132	Two glasses.
										4	1,125	SiO_2 + glass.
197	25.2	24.8	50.0	15.1	17.1	67.8	33.3	27.4	39.3	17	1,021	Two glasses.
										17	1,014	SiO_2 + glass.
198	22.3	27.7	50.0	11.8	18.4	69.8	32.4	32.2	35.4	17	1,012	Two glasses.
										17	1,003	CB + glass.
199	22.0	38.0	40.0	7.4	23.8	68.8	30.6	43.5	25.9	17	1,035	Two glasses.
										17	1,029	CB + glass.
200	20.1	49.9	30.0	8.3	36.6	55.1	28.1	59.1	12.8	17	1,014	Two glasses.
										17	1,006	CB + glass.
201	16.0	60.0	24.0	3.9	52.8	43.3	25.6	65.5	8.9	17	980	Two glasses.
										17	977	CB + glass.
202	16.0	64.0	20.0	2.2	56.1	41.7	24.9	68.3	6.8	2½	967	Two glasses.
										3	965	Trace CB_2 + glass.
										2	964	CB_2 + CB + glass.
203	12.0	74.0	14.0	0.8	74.9	24.3	23.4	72.8	3.8	2	970	Two glasses.
										2	968	CB_2 + glass.
204	10.0	84.0	6.0	0.9	89.9	9.2	23.3	75.2	1.5	2	973	Two glasses.
										½	970	CB_2 + glass.

These compositions were prepared as described under section II, 1. They were fused three times, with intermediate grinding and mixing. After the third fusion the resulting glasses were broken into coarse fragments, and those of the high-silica glass separated from those of the low-silica glass. The two glasses were easily distinguishable and there was no difficulty in making this separation. Samples were then analyzed and quench determinations made on the low-silica glasses.

Complete separation of the two liquids was not obtained in any case, but it is evident that the initial composition of the mixture and the compositions of the two liquids resulting must lie on a straight line regardless of the degree of separation, unless the initial composition is changed during the fusions. The intersections of this line, which is a tie line, with the boundaries of the immiscibility area give the compositions of the conjugate liquids.

Two tie-line compositions were prepared in the silica field. On melting, the high-silica layer formed a very viscous liquid which remained at the center of the crucible and the low-silica liquid flowed to the sides. Separation was very incomplete as the analyses show. The high-silica liquid, because of its high viscosity, tended to retain a considerable amount of the low-silica liquid.

Much better separations were obtained in the monocalcium borate field where four tie-line compositions were prepared. The liquidus temperature of composition 199 (1,032°C) is the maximum temperature for the immiscibility portion of the monocalcium borate field.

The tie lines in the calcium diborate field have a fan-shaped distribution as figure 3 shows. The liquids in this field separated almost completely. Quenches on composition 202 fix the temperature of the quintuple line 14–15 separating the fields of calcium diborate and monocalcium borate. Quenches on a binary composition (12 percent of CaO, 88 percent of B_2O_3) gave 974° C for the temperature of the liquidus, a value 3° higher than that reported by Carlson [10].

In an attempt to establish the phase formed on secondary crystgllization at the calcium diborate boundary in the one-liquid area along the SiO_2–B_2O_3 side line, a charge of the high-silica glass from composition 203 was held for 11 days at 525° C. The charge was found still to consist of undevitrified glass.

A striking feature of the immiscibility area is the marked increase in concentration of lime in the less siliceous liquids (of compositions represented by the curve A′–13–14–I, fig. 3), proceeding toward the interior of the diagram from either the lime-silica system or the lime-boric oxide system. The maximum concentration of lime in the ternary liquids is about 38.5 percent, which is 11 percent higher than the lime content of the corresponding lime-silica liquid (A′, fig. 3) and 15 percent higher than that of the lime-rich layer in the lime-boric oxide system (I, fig. 3). A similar observation was made by Morey and Ingerson [12].

Whether any appreciable increase in the lime concentration of the more siliceous ternary liquids (represented by the line A–16–15–I′, fig. 3) occurs has not been determined, but the analyses on compositions 203, 204, and 205 indicate that the concentration change is probably small. Owing to lack of further information the compositions of the more siliceous liquids in the ternary diagram have been indicated by a dotted line connecting the compositions of the high-silica and high-boric oxide liquids in the respective binary systems.

The maximum divergence in composition of the two liquids occurs in the monocalcium borate field, as inspection of the length of tie lines in figure 3 will show.

V. CHARACTERISTICS OF THE FUSION SURFACES

Isotherms showing temperatures of complete melting have been inserted in figure 6. The positions of the isotherms were determined by points read off the diagrams of figure 4 at 50 and 100° C intervals and also by melting data for other compositions not on conjugation lines.

In general, it may be said that the portion of the diagram to the left of the two-liquid boundary A′–13–14–I is of the usual type encountered in ternary oxide systems. To the right of that boundary the liquidus presents unusual features.

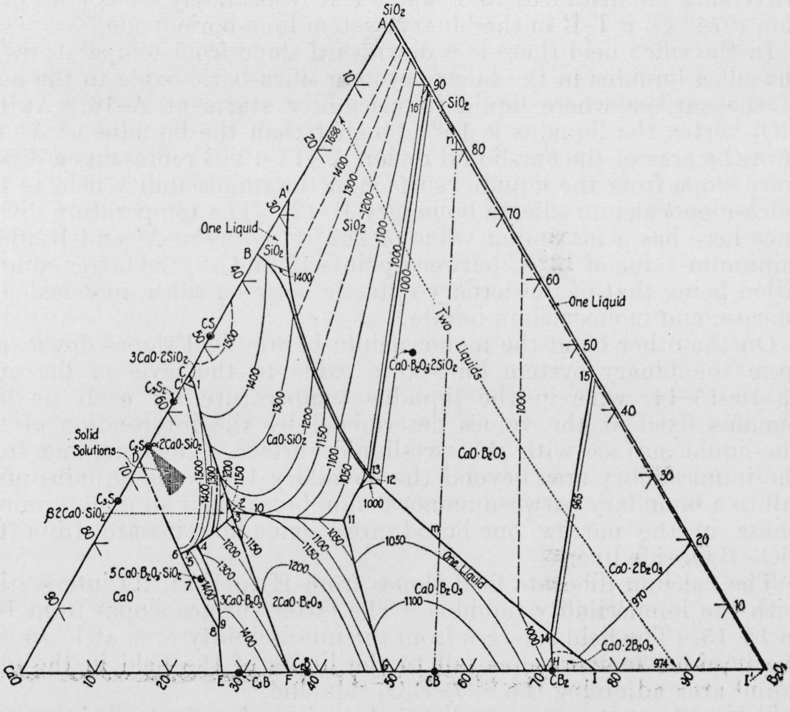

FIGURE 6.—*Triangular concentration diagram of the system* $CaO–B_2O_3–SiO_2$ *with isotherms showing temperatures of complete melting.*

In a solid model where temperature is plotted on a scale perpendicular to the concentration triangle as a base, the liquidus of the immiscibility region appears as a curved surface capable of being generated by a rotating, horizontal line of variable length [18]. In the silica field the line moves downhill, one end traversing the distance A–16 while the other end passes from A′ to 13. Successive positions of the line (from 1,698 to 990° C) are isotherms and tie lines, and its final position before leaving the field represents an invariant condition where two liquids of compositions given by points 13 and 16, two solids (silica and monocalcium borate), and vapor are in equilibrium.

Passing into the monocalcium borate field the line moves uphill assuming successively higher positions until it reaches mn, the maximum height on the surface in this region (1,032° C). In this position a plane passed through the line and perpendicular to the base will include the composition corresponding to monocalcium borate. From mn the line proceeds downhill, one end traversing the distance n–15 and the other the distance m–14. On reaching a minimum temperature (964° C) at 14–15 it represents an invariant condition wherein monocalcium borate, calcium diborate, and two liquids of compositions 14 and 15 are in equilibrium with vapor.

Entering the calcium diborate field, the line moves uphill, the ends traversing the distances 15–I′ and 14–I, respectively. Its final position (974° C) is I–I′ in the binary system lime-boric oxide.

In the silica field there is a downward slope from temperatures at the silica liquidus in the binary system silica-boric oxide to the level of the surface where liquid immiscibility starts at A–16. At the SiO_2 vertex the liquidus is 15° C higher than the liquidus at A. In turn the area of the one-liquid region A′–13–12–B represents a downward slope from the liquidus surface in the immiscibility field to the silica-monocalcium silicate boundary B–12. The temperature difference here has a maximum value of 262° C between A′ and B and a minimum value of 13° C between points 13 and 12, the latter composition being that of the ternary eutectic between silica, monocalcium silicate, and monocalcium borate.

On the other hand the monocalcium borate field slopes downward from the binary system lime-boric oxide to the level of the area 13–16–15–14, wherein the liquidus temperature for each tie line remains fixed at the values determined by the intersection of the one-liquid surface with the two-liquid surface. On emerging from the immiscibility area beyond the boundary 15–16 the liquidus must fall to a boundary between monocalcium borate and an undetermined phase in the narrow one-liquid area extending inward from the SiO_2–B_2O_3 side line.

The calcium diborate field slopes from H to I–14, it's intersection with the immiscibility liquidus. The latter surface slopes from I–I′ to 14–15. The field emerges from the immiscibility area at I′–15 and the liquidus temperatures fall to the limits of the field in the one-liquid area adjoining the SiO_2–B_2O_3 side line.

Figure 7 represents projections of the boundary curves of the solid model on planes vertical to the base. Boundaries between different fields are shown and also boundaries between the one- and two-liquid portions of fields (A′–13; 13–14; and 14–I). The numbers and letters by which the boundaries are designated correspond to those in figures 3 and 6.

It is seen in figure 7 that there are four boundary curves (4–6; 6–8; 8–4; and 2–11) separating fields of primary crystallization which exhibit a maximum temperature. The maxima in these curves correspond to the temperatures of eutectics in the respective binary systems. Boundaries A′–13; 13–14; and 14–I enable one to visualize partially the general contours of the surfaces in the immiscibility region.

The compositions and temperatures of eutectics and quintuple points and other significant data are contained in table 10.

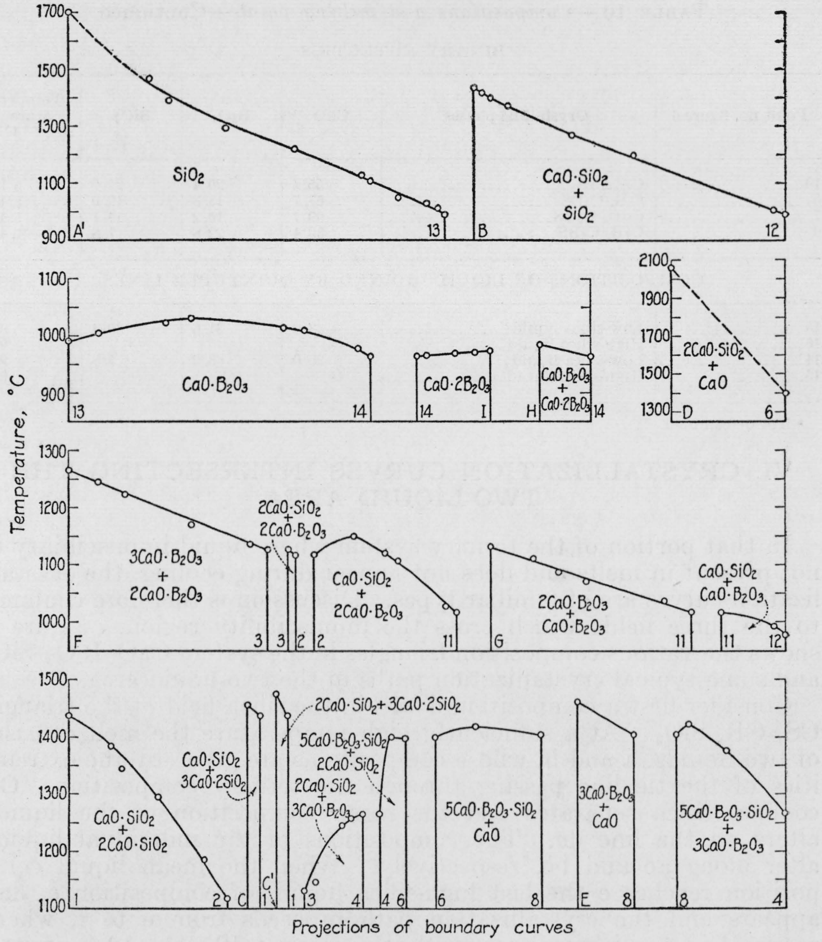

FIGURE 7.—*Temperature-concentration diagrams of boundary curves in the system* $CaO–B_2O_3–SiO_2$.

TABLE 10.—*Compositions and melting points*

TERNARY EUTECTICS

Point no. figure 6	Crystalline phases	CaO	B_2O_3	SiO_2	Temperature (± 5° C)
		%	%	%	°C
2	CS, C_2S, C_2B	59.2	16.0	24.8	1,118
6	C_2S, CaO, C_5BS	69.2	12.6	18.2	1,398
8	CaO, C_5BS, C_3B	70.0	23.2	6.8	1,404
12	CS, CB, SiO_2	38.3	31.5	30.2	977

QUINTUPLE POINTS, NOT EUTECTICS

Point no. figure 6	Crystalline phases	CaO	B_2O_3	SiO_2	Temperature (± 5° C)
1	CS, C_3S_2, C_2S	54.6	1.5	43.9	1,436
3	C_2S, C_3B, C_2B	59.4	16.6	24.0	1,128
4	C_2S, C_5BS, C_3B	66.2	14.1	19.7	1,266
11	CS, C_2B, CB	45.0	31.7	23.3	1,017

TABLE 10.—*Compositions and melting points*—Continued

BINARY EUTECTICS

Point no. figure 6	Crystalline phases	CaO	B_2O_3	SiO_2	Temperature (± 5° C)
10	CS, C_2B	55.4	20.4	24.2	1,150
5	C_2S, C_5BS	67.7	13.3	19.0	1,400
7	CaO, C_5BS	69.7	16.2	14.1	1,412
9	C_3B, C_5BS	69.4	22.8	7.8	1,415
COMPOSITIONS OF LIQUIDS JOINED BY QUINTUPLE LINES					
13	Low-silica liquid	38.0	31.6	30.4	990
16	High-silica liquid	([a])	([a])	([a])	990
14	Low-silica liquid	26.0	68.2	5.8	964
15	High-silica liquid	([a])	([a])	([a])	964

[a] Not determined.

VI. CRYSTALLIZATION CURVES INTERSECTING THE TWO-LIQUID AREA

In that portion of the ternary system where liquid immiscibility is not present in melts and does not appear during cooling, the crystallization curves are of familiar types. Discussion is therefore confined to the three fields which cross the immiscibility region. Figure 8 shows the various composition triangles in the system $CaO\text{–}B_2O_3\text{–}SiO_2$ and some typical crystallization paths in the two-liquid area.

Consider first a composition d within the silica field of the triangle CS, CB, SiO_2. At a sufficiently high temperature the melt consists of two liquids, a and b, whose compositions are given by the extremities of the tie line passing through the ternary composition. On cooling, silica separates and the mean composition of the liquids alters on the line de. The compositions of the individual liquids alter along ac and be, respectively. When the mean liquid composition reaches e the last high-silica liquid, of composition c, disappears and the crystallization path proceeds from e to f, where monocalcium silicate appears; thence along f–12. At 12 monocalcium borate crystallizes and liquid disappears.

Composition h, at a sufficiently high temperature, consists of two liquids, g and i. On cooling, with separation of silica, the mean composition of the liquids alters along hj. At j monocalcium borate crystallizes and the temperature remains constant while the mean composition of the liquids changes along j–13, accompanied by separation of monocalcium borate and silica in a constant ratio of a composition given by the intersection of the line 13–16 with the $CB\text{–}SiO_2$ conjugation line. When the mean liquid composition reaches point 13 the last high-silica liquid disappears and the crystallization curve follows the boundary 13–12 with falling temperature. At the ternary eutectic (point 12) monocalcium silicate crystallizes and liquid disappears.

Melt r in the composition triangle CB, CB_2, SiO_2 consists of two liquids, o and k. On cooling, monocalcium borate crystallizes and the mean liquid composition alters from r to p. At p silica appears, and from p to 16, liquids 13 and 16, silica and monocalcium borate are present. On disappearance of the low-silica liquid, the crystallization curve proceeds by an undetermined path to a quintuple point between CB, CB_2, and SiO_2 (assuming that no binary compounds are formed between B_2O_3 and SiO_2).

The line CB–m–n separates crystallization paths which diverge to its left and those which diverge to its right with falling temperature. This is because the temperature of mn is the maximum of the liquidus in the immiscibility portion of the monocalcium borate field.

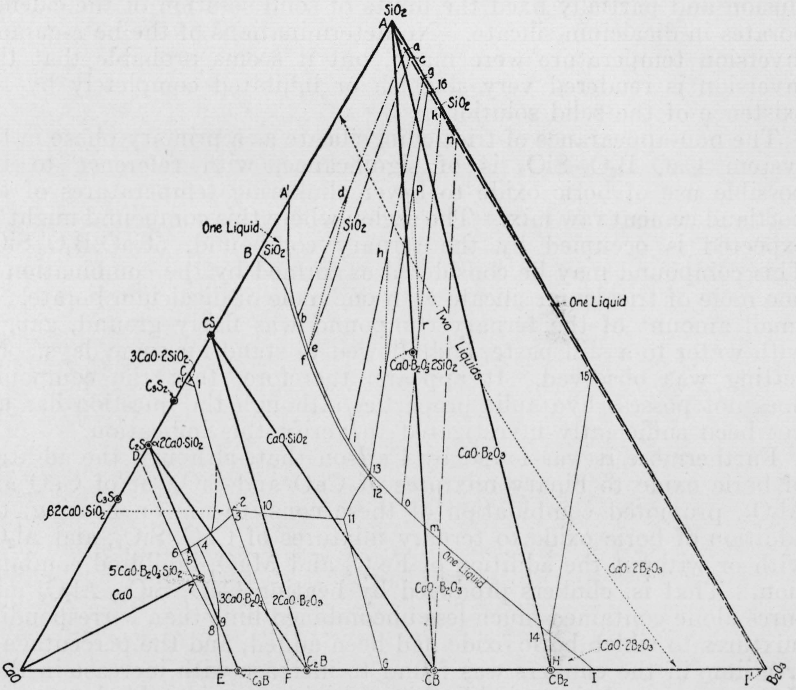

FIGURE 8.—*Composition triangles in the system* CaO–B_2O_3–SiO_2 *and some typical crystallization paths in the two-liquid area.*

Crystallization curves in the composition triangle CB_2, SiO_2, B_2O_3 are of types similar to those already discussed and will end at the ternary eutectic of these three compounds (again assuming the absence of binary compounds between B_2O_3 and SiO_2).

VII. APPLICATIONS

Dicalcium silicate occurs in portland cement in the unstable beta modification which possesses desirable hydraulic properties, whereas, in its low-temperature gamma modification, the compound is practically nonhydraulic. The beta-gamma inversion for the pure compound normally occurs at 675° C with such rapidity that it is difficult to prepare the beta form in appreciable quantities even on quenching from temperatures of over 1,000° C. However, it was first noticed by Bates and Klein [19] that the presence of less than 1 percent of B_2O_3 or Cr_2O_3 prevented the inversion and that the former oxide seemed to effect a marked lowering of the fusion temperature of the compound.

Further studies carried on by E. T. Carlson of this Bureau [20] showed that progressive lowering of the alpha-beta inversion temperature of dicalcium silicate occurred on the addition of 0.5 to 5 percent of B_2O_3 to the compound. Lowering of the indices of dicalcium silicate was also noted. It was concluded that these effects probably indicated solid solution of boric oxide in the silicate.

The results of the present investigation have verified this conclusion and partially fixed the limits of solid solution of the calcium borates in dicalcium silicate. No determinations of the beta-gamma inversion temperature were made, but it seems probable that this inversion is rendered very sluggish or inhibited completely by the existence of the solid solutions.

The non-appearance of tricalcium silicate as a primary phase in the system $CaO–B_2O_3–SiO_2$ is of significance, with reference to the possible use of boric oxide to lower clinkering temperatures of the portland cement raw mix. The region where this compound might be expected is occupied by the ternary compound, $5CaO.B_2O_3.SiO_2$. This compound may be considered as formed by the combination of one mole of tricalcium silicate with one mole of dicalcium borate. A small amount of the ternary compound was finely ground, gauged with water to a stiff paste, and allowed to stand for some days. No setting was observed. It appears, therefore, that the compound does not possess hydraulic properties although the question has not yet been sufficiently investigated to verify this indication.

Furthermore it was found by Carlson that, although the addition of boric oxide to binary mixtures of CaO and SiO_2, or of CaO and Al_2O_3, promoted combination of these constituents on heating, the addition of boric oxide to ternary mixtures of CaO, SiO_2, and Al_2O_3, with or without the addition of Fe_2O_3 and MgO, inhibited combination. That is, clinkers produced by heating CaO, SiO_2, Al_2O_3 mixtures alone contained much less uncombined lime than corresponding mixtures to which boric oxide had been added, and the percentage of free lime in the clinkers was found to increase with increase in their B_2O_3 content. It is probable that there is a considerable broadening of the lime field at various B_2O_3 levels in the quaternary system $CaO–Al_2O_3–SiO_2–B_2O_3$.

The above considerations indicate that the addition of appreciable quantities of boric oxide to the portland cement raw mix would not be desirable.

The high-silica low-lime portion of the diagram is of interest in connection with the constitution of borosilicate glasses. This aspect of the problem and the effect of addition of alkali oxide upon the liquid immiscibility are being studied elsewhere [12].

VIII. SUMMARY

The foregoing investigation of the system $CaO–B_2O_3–SiO_2$ has disclosed a type of liquid immiscibility not encountered in other ternary oxide systems. Whereas in previous instances immiscibility was confined to one field only, in this system compositions in any one of three fields may melt with the formation of two liquids. The fields of silica, monocalcium borate, and calcium diborate were found to be largely within the immiscibility area which extends in the triangular diagram from the immiscibility region in the lime–boric oxide system to that in the lime-silica system. The width of the area broadens very considerably in proceeding toward the interior of the triangular diagram.

Unusual features of the fusion surfaces in this system were discussed.

One new compound, pentacalcium borosilicate, $5CaO.B_2O_3.SiO_2$, melting at 1,419° C, was found. Tricalcium silicate does not appear at the liquidus in the system. The region in which it might be expected is occupied by the field of the ternary compound. The mineral danburite, $CaO.B_2O_3.2SiO_2$, was not obtained as a crystalline phase, its composition lying in the immiscible liquid portion of the monocalcium borate field.

Solid solution of monocalcium borate, dicalcium borate, and pentacalcium borosilicate occurs in dicalcium silicate, causing the alpha-beta inversion temperature of dicalcium silicate to be lowered by a maximum of about 190° C.

The evidence indicates that additions of small quantities of boric oxide to the portland cement raw mix before "burning" would not be advantageous.

The authors take pleasure in acknowledging their indebtedness to E. T. Carlson, who began this investigation, and from whose data on 35 compositions the binary system $2CaO.B_2O_3$–$CaO.SiO_2$ and part of the pseudo-binary systems $2CaO.B_2O_3$–$CaO.SiO_2$, $CaO.B_2O_3$–$2CaO.SiO_2$, are constructed.

IX. REFERENCES

[1] W. Guertler, *On the limits of miscibility of boric oxide and borates in melts,* Z. anorg. Chem. **40,** 225–53 (1904).

[2] J. W. Greig, *Immiscibility in silicate melts,* Am. J. Sci. [5], **13,** 1–44, 133–54 (1927).

[3] *Effect of boric acid on the clinkering of portland cement,* BS Tech. News Bul. 157, p. 46 (May 1930). *The system* CaC–B_2O_3, BS Tech. News Bul. 186, p. 94 (Oct. 1932). E. T. Carlson, *The system* CaO–B_2O_3, BS J. Research, **9,** 825–32 (1932). *The system* CaO–B_2O_3–SiO_2, BS Tech. News Bul. 209, p. 88 (Sept. 1934). *The system* CaO–B_2O_3–SiO_2, BS Tech. News Bul. 230, p. 49 (June 1936).

[4] C. W. Kanolt, *The melting points of some refractory oxides,* Bul. BS **10,** 295–313 (1914) S212.

[5] E. E. Schumacher, *The melting points of barium, strontium, and calcium oxides,* J. Am. Chem. Soc. **48,** 396–405 (1926).

[6] N. W. Taylor and S. S. Cole, *Crystalline boric oxide,* J. Am. Chem. Soc. **56,** 1648–49 (1934). S. S. Cole and N. W. Taylor, *The system* Na_2O–B_2O_3, I. *Preparation of crystalline* B_2O_3 *and some of its physical properties,* J. Am. Ceram. Soc. **14,** 55–58 (1935).

[7] A. L. Day, E. S. Shepherd, and F. E. Wright, *The lime-silica series of minerals,* Am. J. Sci. [4], **22,** 265–302 (1906).

[8] G. A. Rankin and F. E. Wright, *The ternary system* CaO–Al_2O_3–SiO_2, Am. J. Sci. [4], **39,** 1–79 (1915).

[9] J. B. Ferguson and H. E. Merwin, *The ternary system* CaO–MgO–SiO_2, Am. J. Sci. [4], **48,** 81–123 (1919).

[10] E. T. Carlson, *The system* CaO–B_2O_3, BS J. Research **9,** 825–832 (1932) RP 510.

[11] A. Cousen and W. E. S. Turner, *Studies of the glasses boric oxide-silica,* J. Soc. Glass Tech., Trans. **12,** 169–190 (1928).

[12] G. W. Morey, *The effect of boric oxide on the devitrification of the soda-lime-silica glasses. The quaternary system* Na_2O–CaO–B_2O_3–SiO_2, J. Am. Ceram. Soc. **15,** 457–475 (1932). G. W. Morey and Earl Ingerson, *The melting ofdanburite,* J. Mineralogical Soc. Am. **21,** 194 (1936).

[13] H. S. Roberts, *The Geophysical Laboratory furnace thermostat,* J. Opt. Soc. Am. Rev. Sci. Instr. **11,** 171–186 (1925).

[14] E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Binary systems of alumina with silica, lime, and magnesia,* Am. J. Sci. [4] **28,** 293 (1909).

[15] Determined by Dr. Herbert Insley of the National Bureau of Standards.

[16] W. D. Bancroft, The Phase Rule, p. 149; (published by J. Phys. Chem., 1897).

[17] F. A. H. Schreinemakers, *Equilibrium in the system water-phenol-aniline.* II, Z. phys. Chem. **30,** 460–480 (1899).

[18] Cf. J. W. Greig, *Immiscibility in silicate melts,* Am. J. Sci. [5] **13,** 32 (1927).

[19] P. H. Bates and A. A. Klein, *Properties of the calcium silicates and calcium aluminate occurring in normal portland cement,* Tech. Pap. BS8,, (1917) T78.

[20] E. T. Carlson, unpublished data.

WASHINGTON, July 15, 1936.