

THE TERNARY SYSTEM LIME-BORIC OXIDE-SILICA

By

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## TABLE OF CONTENTS

	Page
I. Introduction .....	1
II. The Components and Binary Systems.....	2
III. Theory.....	4
IV. General Procedure.....	6
1. Preparation and Analysis of Mixtures.	6
2. Apparatus.....	8
3. Methods.....	10
V. The Stability Fields.....	12
VI. The Two Liquid Area.....	35
VII. Characteristics of the Fusion Surfaces.	39
VIII. Crystallization Curves.....	45
IX. Applications.....	52
X. Summary.....	55

## THE TERNARY SYSTEM LIME-BORIC OXIDE-SILICA

### I. Introduction

The close similarity of boric oxide and silica, and especially their property of limited miscibility in the liquid state with oxides of certain of the alkaline earths and other divalent elements, renders a study of the system  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  of unusual theoretical interest. From the practical viewpoint this system is equally worthy of investigation for the high silica-boric oxide portion has a bearing upon the constitution of borosilicate glasses, enamels, and ceramic glazes, while the high lime portion shows the effect of boric oxide upon the calcium silicates occurring in portland cement. The investigation of this last point furnished the initial motive for the study which, it was thought, might indicate the possibility of producing a well burned clinker at a relatively low temperature by the use of boric oxide as a flux. This paper represents the completion of a program first outlined in 1930 and reported on at intervals subsequently (1).

The only previous studies in the ternary system are those of Morey and of Morey and Ingerson (2) who attempted unsuccessfully to synthesize danburite,  $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$ , the only naturally occurring calcium borosilicate. It was found that a mixture of lime, boric oxide, and silica having this composition melted to two immiscible liquids. The mineral itself melted with decomposition producing two liquids.

## II. The Components and Binary Systems

Before beginning a study of the ternary system it is desirable to have as complete information as possible upon the components and upon the three binary systems which they form. Previous investigations have supplied most of the necessary data. Only the melting temperatures of the compounds will be given here and for their optical properties the original papers must be consulted.

The melting point of lime was determined by Kanolt (3) as  $2572^\circ$  and by Schumacher (4) as  $2576^\circ$ . Taylor and Cole (5) in 1934 reported having prepared pure crystalline boric oxide and gave its melting point as  $294^\circ$ . Silica in the system  $\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$  occurs as tridymite and cristobalite and, as the latter, melts at  $1713^\circ$  (6).

The binary system lime-silica has been investigated by Day, Shepherd, and Wright (7), Rankin and Wright (8), Ferguson and Merwin (9), and Greig (6). Four compounds exist in this system: monocalcium silicate, m.p. 1544°; tricalcium disilicate, which decomposes into dicalcium silicate and liquid at 1475°; dicalcium silicate, m.p. 2130°; and tricalcium silicate, which decomposes at 1900° into dicalcium silicate and lime, and does not appear at the liquidus in the binary system. Monocalcium silicate appears in two crystalline modifications, an alpha or high temperature form, and a beta or low temperature form. Dicalcium silicate exists in three crystalline modifications, alpha, beta, and gamma, which are, respectively, the high, intermediate, and low temperature forms. In the binary system, compositions containing between 0.6 and 27.5 percent lime melt with the formation of two immiscible liquids.

The compounds in the binary system lime-boric oxide, investigated by Carlson (10), are calcium diborate, m.p. 986°; monocalcium borate, m.p. 1054°; dicalcium borate, m.p. 1304° (11); and tricalcium borate, m.p. 1479°. Compositions containing between 0.2 and 23 percent lime melt with the formation of two immiscible liquids.

Only limited information on the system boric oxide-silica is available and the course of the liquidus is unknown. Greig (6) has demonstrated the probability that the liquids formed by these oxides are miscible in all proportions.

Cousen and Turner (12) found that the glasses of the system  $B_2O_3-SiO_2$  gave density, refractive index, and thermal expansion curves which did not deviate much from straight lines.

### III. Theory

In a ternary system a maximum of five phases may co-exist and the concentration and temperature at which this condition occurs is known as a quintuple point. Two solids, liquid, and vapor may coexist over a range of temperatures and lines representing such equilibria are known as boundary curves. The boundary curves enclose concentrations within which one solid phase may be in equilibrium with liquid and vapor at various temperatures and such areas are known as fields of primary crystallization.

The commonest representation of ternary systems is that in which the compositions are represented by points within an equilateral triangle, the sides of which represent the three binary systems formed by the components. Boundary curves start from binary eutectics or quadruple points on the sides of the triangle and proceed to the interior ending in quintuple points where three boundaries meet. When the temperatures along all three boundaries fall as they approach the point of intersection, the point is called a eutectic. Temperatures in the fields and along boundaries are indicated

by isotherms drawn at suitable temperature intervals. These isotherms show the contours which the fields would have in a solid model where temperature is plotted vertical to the composition triangle as a base.

When a ternary composition is completely melted and allowed to cool the following changes will occur (assuming the absence of solid solutions): At a definite temperature the compound, within whose field of stability the ternary composition lies, will begin to crystallize from the melt. The composition of the liquid will alter along a straight line connecting the ternary composition and the composition of the primary phase until a boundary curve is intersected. Here a second crystal phase will begin to separate along with the first and the crystallization path follows the boundary until a eutectic is reached where the third solid phase crystallizes and the liquid disappears. On heating these phenomena occur in reverse order.

The appearance of liquid immiscibility in a ternary system introduces further possibilities. The presence of two liquids reduces the maximum possible number of solid phases by one. Hence no ternary eutectics can exist in an immiscibility region and fields entering such an area must persist until liquid miscibility is again encountered. Moreover, boundaries between fields in the immiscibility area must be straight lines of constant temperature as the two liquids which they connect and the two solids are all of definite composition. The course of crystallization in this region is quite different

from that in the one liquid area and will be discussed later.

Liquid immiscibility of the type found in the system  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  has not previously been encountered in ternary oxide systems but analogies are to be found in certain organic systems such as the system water-phenol-aniline studied by Schreinemakers (13).

#### IV. General Procedure

##### 1. Preparation and Analysis of Mixtures

The study of the ternary system required first of all the preparation of an appropriate number of lime, boric oxide, silica mixtures having known compositions. For starting materials calcium carbonate, boric acid, and silica gel were used. The calcium carbonate was of reagent quality for alkali determinations. Analysis showed it to contain 56.06%  $\text{CaO}$  (theoretical for  $\text{CaCO}_3 = 56.08\% \text{CaO}$ ). The boric acid was analyzed for impurities by the chemistry division of the National Bureau of Standards as follows: Fe, less than 0.001%;  $\text{SO}_3$ , less than 0.01%; Cl, less than 0.001%. 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 showed it to contain 0.04% non-volatile material based on the weight of the ignited silica.

Boric acid volatilizes appreciably on heating and boric

oxide, though not volatile even at red heat, 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 burning. All burns here and subsequently were made in covered platinum dishes or crucibles. The products were then 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 reburned, ground, and analyzed as before. This was repeated until homogeneous, finely ground products having very nearly the theoretical compositions were obtained. Two or three burns were generally sufficient. Stock quantities of the four calcium silicates were prepared in a similar manner starting with calcium carbonate and silica gel.

Most of the ternary compositions were prepared along conjugation lines connecting the compositions of the calcium silicates and calcium borates in the triangular diagram. In making up such series the binary preparations were weighed out into dry bottles in appropriate proportions and with allowance made for their ignition losses. The mixtures were then shaken thoroughly, ground in an agate mortar, and burned over a Fisher blast burner enclosed in a refractory shield.

The products were then reground and the burning repeated once or twice, depending upon whether the preparations were fused or well sintered or only slightly sintered. Analyses of representative mixtures prepared in this way showed satisfactory agreement between actual and calculated compositions. Mixtures not on conjugation lines were prepared by mixing appropriate quantities of calcium carbonate, silica gel, and calcium borate, burning, 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 oxide 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.

In the compositions analyzed, determinations were made of ignition loss, silica, and lime, and boric oxide obtained by difference. Half gram samples were decomposed by 1:1 HCl, evaporated almost to dryness, and the moist residue evaporated three times with 10 cc. 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.

#### a. Apparatus

The behavior of the ternary preparations on heating or

on crystallization from their melts was studied by means of a vertical tube resistance furnace. This consisted of an alundum tube 14" long,  $\frac{3}{4}$ " inside diameter, and 1" outside diameter, wound for  $7\frac{1}{2}$ " of its length with 80% platinum-20% rhodium wire in turns spaced  $\frac{1}{8}$ " apart. The winding was covered with alundum cement and the tube surrounded by an alundum cylinder 12" long, and of  $1\frac{1}{2}$ " inside diameter and  $\frac{3}{4}$ " wall. The inner tube was held in place by alundum cement closing the ends of the outer cylinder and leaving a  $\frac{3}{8}$ " air gap between the tubes. The whole was surrounded by 4" of magnesia powder contained in a copper cylinder of 10" outside diameter, 12" high, and having  $\frac{3}{16}$ " walls. Automatic temperature control of the furnace to within  $\pm 1^\circ$  over the periods of time required was secured by the circuits described by Adams (14), wherein the furnace is made one arm of a Wheatstone bridge.

Temperature measurements were made by means of platinum-platinum rhodium thermocouples, the emf's being measured by a Leeds and Northrup precision potentiometer and galvanometer. The single thermocouples were calibrated periodically against the melting points of potassium sulfate,  $1069^\circ$ ; monocalcium borate,  $1154^\circ$ ; diopside,  $1391.5^\circ$ ; and monocalcium silicate,  $1544^\circ$ . The differential thermocouple used in heating curves was calibrated against potassium sulfate,  $1069^\circ$ ; dicalcium borate,  $1304^\circ$ ; and monocalcium silicate,  $1544^\circ$ .

### 3. Methods

For investigation of the ternary mixtures the quenching method (15) was principally used. In this method a small charge of the mixture (about 0.1 gram) is wrapped in platinum foil, and suspended in the furnace in such a way as to be almost touching the thermocouple junction. The furnace is maintained at constant temperature until the sample is at equilibrium. The charge is then quenched by dropping it into water or mercury. Any liquid present at the furnace temperature is thus frozen to a glass and any crystalline material remains unchanged and can be identified under the petrographic microscope. If more than one crystalline phase is found to be present determinations are made at higher temperatures until a temperature is fixed, with the desired accuracy, above which the charge is all glass and below which it consists of glass and a single crystalline phase (the primary phase). By this means temperatures on the melting surfaces are fixed. The furnace was periodically checked for location of its hot zone at which the temperature varied less than  $2^{\circ}$  over 2 cms. of the tube's length in the range of temperatures used. As the quench envelopes were approximately 0.5 cm. in length the charge was not exposed to any appreciable temperature gradient.

For the majority of compositions in the high lime portion of the system the quenching method was not applicable as crystallization occurred during quenching. The melting behavior of such mixtures was determined by means of heating

curves. For containers small platinum half thimbles holding 1-2 grams of sample were used. One of the half thimbles was filled with alundum as a reference medium; the other contained the mixture to be studied; and in each of the two materials one junction of a differential thermocouple was imbedded. The thimbles were suspended together in the furnace with their flat sides adjacent and the temperature of the furnace raised at a uniform rate of  $5^{\circ}$  per minute. The temperature of the charge was read by the usual potentiometer arrangement and the differential temperature between charge and alundum indicated by a galvanometer attached directly to the thermocouple leads from the two thimble sections. Readings of temperature and differential were made every minute. The temperature of melting was taken as the temperature of the charge when the differential reading was a maximum and the thermocouple calibration made on this basis. A normal heating curve ordinarily shows three heat effects; the one at lowest temperature corresponding to the first appearance of liquid; the second, to the melting of one of the two remaining crystalline phases; and the third to the melting of the primary phase.

Microscopic examinations were made by the immersion method and generally a rough determination of the indices of the crystals and of one or two other easily observable characteristics sufficed to identify the phases present.

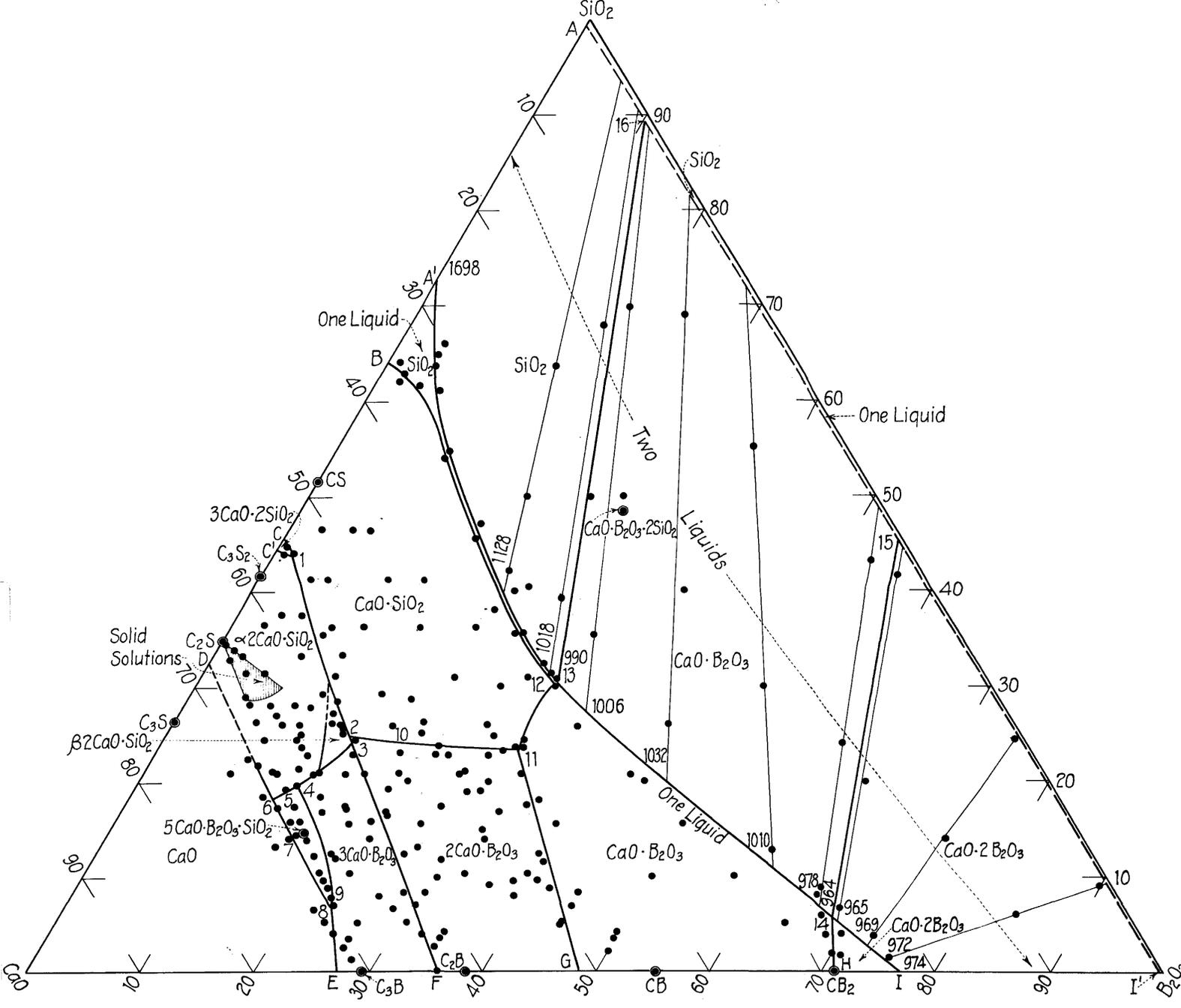
## V. The Stability Fields

The components and all the binary compounds except tricalcium silicate were found to possess fields of stability in the triangular concentration diagram. In addition the existence of one new ternary compound,  $5\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ , was established. The other expected ternary compound, the mineral danburite,  $\text{CaO}\cdot\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$ , was not obtained as a crystalline phase. Its composition was found to lie in the immiscible liquid portion of the mono-calcium borate field.

A convenient system of abbreviation has been developed for formulas of compounds occurring in oxide systems of this type and will be used in the following. The formulas of the compounds and corresponding abbreviations are:  $\text{CaO}\cdot\text{SiO}_2$ , CS;  $3\text{CaO}\cdot 2\text{SiO}_2$ ,  $\text{C}_3\text{S}_2$ ;  $2\text{CaO}\cdot\text{SiO}_2$ ,  $\text{C}_2\text{S}$ ;  $3\text{CaO}\cdot\text{SiO}_2$ ,  $\text{C}_3\text{S}$ ;  $3\text{CaO}\cdot\text{B}_2\text{O}_3$ ,  $\text{C}_3\text{B}$ ;  $2\text{CaO}\cdot\text{B}_2\text{O}_3$ ,  $\text{C}_2\text{B}$ ;  $\text{CaO}\cdot\text{B}_2\text{O}_3$ , CB;  $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ ,  $\text{CB}_2$ ;  $5\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ ,  $\text{C}_5\text{BS}$ ;  $\text{CaO}\cdot\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$ ,  $\text{CBS}_2$ .

The diagram of the ternary system is shown in figure 1 and the more important binary and pseudo-binary systems in figure 2. The fields of the various compounds will now be considered and the data establishing the limits of each field.

The field of monocalcium silicate (B-12-11-10-2-1-C,  
fig. 1):



This figure is a ternary phase diagram for the  $\text{CaO}-\text{SiO}_2-\text{B}_2\text{O}_3$  system. The vertices of the triangle represent the pure components:  $\text{SiO}_2$  (top),  $\text{CaO}$  (bottom left), and  $\text{B}_2\text{O}_3$  (bottom right). The diagram illustrates the phase relationships, including liquidus lines, solid solution regions, and invariant points.

Key features and labels include:

- Vertices:**  $\text{SiO}_2$  (A),  $\text{CaO}$ ,  $\text{B}_2\text{O}_3$  (I).
- Axes:**  $\text{SiO}_2$  (0-100),  $\text{CaO}$  (0-100),  $\text{B}_2\text{O}_3$  (0-100).
- Phase Regions:**
  - One Liquid
  - Two Liquids
  - Solid Solutions
  - $\text{CaO} \cdot \text{SiO}_2$
  - $\text{CaO} \cdot \text{B}_2\text{O}_3$
  - $\text{CaO} \cdot 2\text{B}_2\text{O}_3$
  - $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$
  - $3\text{CaO} \cdot \text{B}_2\text{O}_3$
  - $2\text{CaO} \cdot \text{B}_2\text{O}_3$
  - $5\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$
  - $3\text{CaO} \cdot 2\text{SiO}_2$
  - $\text{C}_3\text{S}_2$
  - $\text{C}_2\text{S}$
  - $\text{C}_3\text{S}$
  - $\text{C}_2\text{B}$
  - $\text{C}_3\text{B}$
  - $\text{CB}$
  - $\text{CB}_2$
  - $\text{I}'$
- Invariant Points (Temperature in °C):**
  - 1698
  - 1128
  - 1018
  - 990
  - 1006
  - 1032
  - 1010
  - 978
  - 964
  - 965
  - 969
  - 972
  - 974
- Other Labels:** A, B, C, D, E, F, G, H, I, A', B', C', D', E', F', G', H', I'.

The compositions determining this area are listed in table 1.

Table 1  
Compositions in the Monocalcium Silicate Field

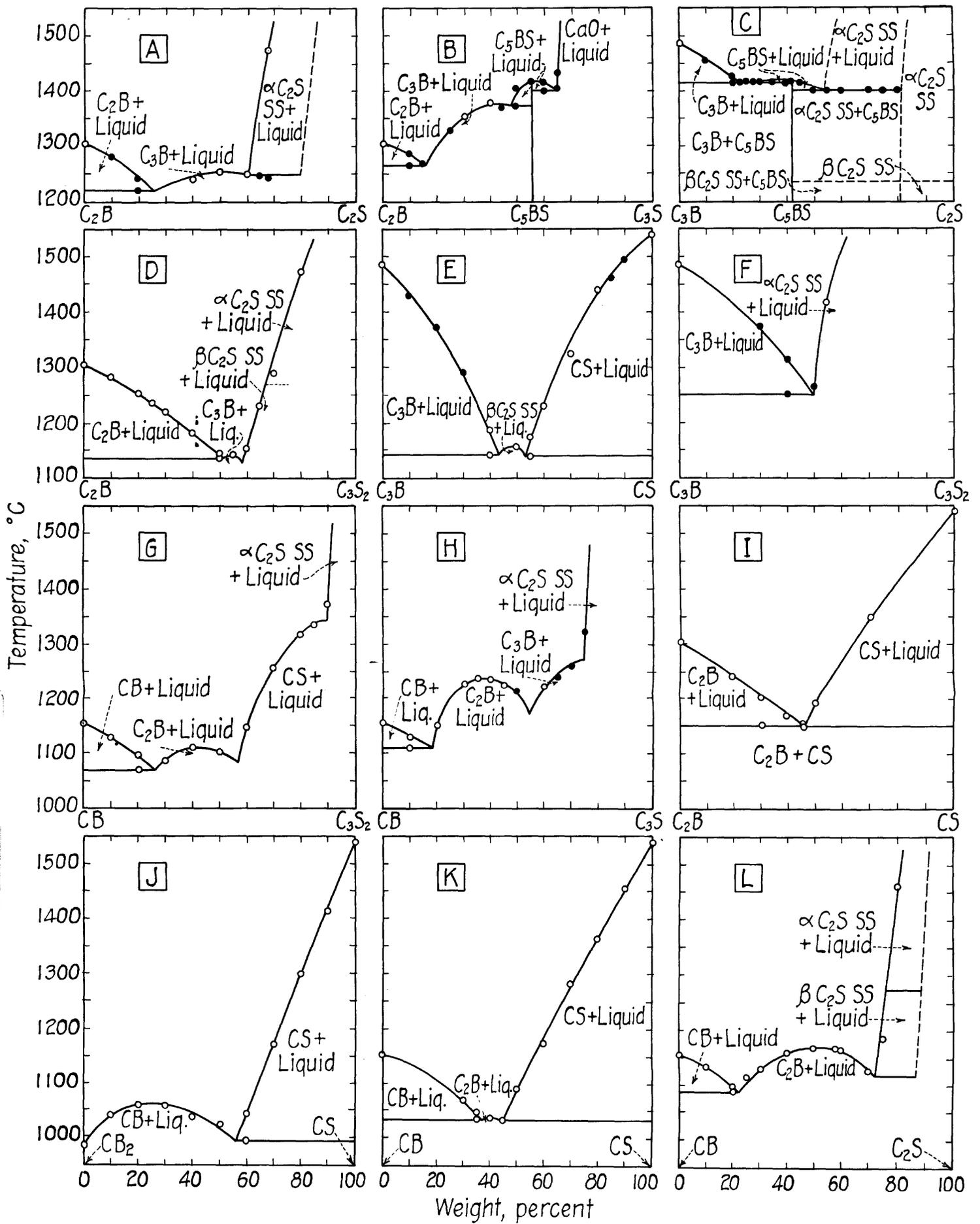
No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
1	46.3	7.1	46.5	1/4	1418	All glass
				1/4	1415	CS + glass
2	44.4	14.3	41.3	2	1305	All glass
				1/4	1301	Trace CS + glass
3	42.4	21.4	36.2	4	1177	All glass
				4	1170	CS + glass
4	40.4	28.6	31.0	17	1043	All glass
				17	1041	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	1/4	1460	All glass
				1/4	1454	CS + glass
6	47.6	11.1	41.3	1/4	1372	All glass
				1/4	1365	Trace CS + glass
7	47.2	16.6	36.2	1/4	1285	All glass
				1/4	1283	CS + glass
8	46.8	22.2	31.0	1/4	1178	All glass
				1/4	1173	CS + glass
9	46.4	27.7	25.9	1/4	1095	All glass
				1/4	1090	CS + glass
10	46.4	28.8	24.8	1/4	1046	All glass
				1/4	1039	CS + glass
11	52.3	11.5	36.2	1/4	1353	All glass
				1/4	1348	CS + glass
12	55.0	19.2	25.8	1/4	1198	All glass
				1/4	1193	Trace CS + glass
13	50.5	2.9	46.6	h.c.	1494	Liquidus
				h.c.	1119	Eutectic (2)
14	51.7	4.4	41.4	h.c.	1459	Liquidus
				h.c.	1118	Eutectic (2)
15	52.8	5.8	41.4	1/4	1440	All glass
				1/4	1437	CS + glass
16	55.0	8.8	36.2	1/4	1326	All glass
				1/4	1323	CS + glass
17	57.3	11.7	31.0	1/4	1233	All glass
				1/4	1230	CS + glass
18	58.4	13.2	28.4	1/4	1179	All glass
				1/4	1175	CS + glass
				1/4	1144	CS + glass
				1/4	1136	CS + C <sub>2</sub> S + glass

Table 1 (Contd.)

No.	Composition,		% SiO <sub>2</sub>	Time in hours	Temp. °C.	Phases present
	CaO	B <sub>2</sub> O <sub>3</sub>				
19	56.3	8.3	35.4	1/4	1336	All glass
					1334	CS + glass
20	55.6	11.1	33.3	1/4	1318	All glass
					1316	CS + glass
21	54.2	16.6	29.2	1/4	1258	All glass
					1256	CS + glass
22	52.8	22.2	25.0	1/4	1148	All glass
					1145	CS + glass
23	46.3	28.7	25.0	1/4	1058	All glass
					1055	CS + glass
24	43.2	26.8	30.0	1/4	1087	All glass
					1079	Trace CS + glass
25	36.0	2.0	62.0	1/4	1413	All glass
					1406	CS + glass
26	36.0	10.0	54.0	1/4	1278	All glass
					1271	CS + SiO <sub>2</sub> + glass
27	37.6	16.8	45.6	17	1191	All glass
					1183	CS + glass
28	39.7	22.2	38.1	17	1112	All glass
					1108	CS + glass
29	39.2	25.2	35.6	17	1067	All glass
					1062	CS + glass
30	54.4	1.5	44.1	1/4	1450	All glass
					1448	CS + glass
31	52.0	19.4	28.6	1/4	1435	CS + C <sub>2</sub> S + glass
					1207	All glass
32	52.0	21.8	26.2	1/4	1204	CS + glass
					1164	All glass
33	45.2	31.2	23.6	17	1162	CS + glass
					1028	All glass
				17	1020	CS + glass

Composition in the Tricalcium Disilicate Field

34	54.5	0.6	44.9	1/4	1459	All glass
					1455	C <sub>3</sub> S <sub>2</sub> + glass
					1452	C <sub>3</sub> S <sub>2</sub> + CS + glass



In column 5 is given the length of heat treatment of each charge in the furnace before quenching. The last column shows the results of microscopic examinations upon the quenched samples. These data serve to fix the liquidus temperature within sufficiently narrow limits, and, for some compositions (such as No. 4), the temperatures of boundaries and quintuple points or eutectics.

In this and subsequent tables melting data obtained by heating curves will be designated under the "Time in hours" column by the letters "h.c.". Under the column headed "Phases present" the data given in such cases represent the interpretation placed upon breaks in heating curves. Thus for composition 13, table 1, the first break in the heating curve occurred at  $1119^{\circ}$  and the last at  $1494^{\circ}$ . The former was ascribed to the melting of dicalcium borate at the ternary eutectic (point 2, fig. 1), and the latter to melting of the primary phase, monocalcium silicate. No break corresponding to the boundary temperature was obtained in this heating curve. Failure of expected breaks to appear was of rather frequent occurrence and was probably due, in most cases, to smallness of the energy changes involved.

For quench determinations compositions in the monocalcium silicate field crystallized readily with the exception of those in the vicinity of the monocalcium borate boundary and the lower part of the silica boundary (B-12). Quench charges of these compositions are held overnight to insure attainment of

equilibrium.

Composition 4, table 1, determines the temperature of a point on the boundary (11-12); composition 18, on the boundary (1-2); and composition 26, on the boundary (B-12). The temperature of the ternary eutectic: monocalcium silicate, monocalcium borate, silica (point 2), is determined by quenches on composition 4.

No appreciable variation in the indices of  $\alpha\text{-CaO}\cdot\text{SiO}_2$  from the values given by Rankin and Wright (8) was observed. The possible existence of solid solutions with the calcium borates and their effect upon the alpha-beta inversion of monocalcium silicate has not been investigated and therefore no attempt is made in figure 1 to indicate a boundary between the fields of alpha and beta monocalcium silicate. It is believed, however, that solid solution of the borates with monocalcium silicate is much less than that of the borates with dicalcium silicate.

The limits of the very small area occupied by the field of tricalcium disilicate (C-1-C<sup>1</sup>, fig. 1) are indicated by compositions 30 and 34 of table 1 and 69 of table 2. Composition 34 locates the temperature of a point on boundary (C-1).

The field of dicalcium silicate (C'-1-2-3-4-5-6-D, fig.1):  
Dicalcium silicate forms solid solutions with the calcium borates and the partial limits of these solutions are indicated

by the shaded area in figure 1. The compositions prepared in the dicalcium silicate field are given in table 2.

Table 2  
Compositions in the Dicalcium Silicate Field

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
35	57.0	5.5	37.5	$\frac{1}{4}$	1382	All glass
				$\frac{1}{2}$	1373	Trace C <sub>2</sub> S + glass
				$\frac{3}{4}$	1345	C <sub>2</sub> S + CS + glass
				h.c.	1343	Boundary (1,2)
36	58.7	3.8	37.5	h.c.	1125	Eutectic (2)
				h.c.	1382	Boundary (1,2)
37	59.0	7.7	33.3	$\frac{1}{4}$	1491	All glass
38	59.3	11.5	29.2	$\frac{1}{4}$	1473	C <sub>2</sub> S + glass
				1	1319	All glass
39	59.5	13.4	27.1	$\frac{1}{4}$	1311	C <sub>2</sub> S + glass
				$\frac{1}{2}$	1234	All glass
40	59.7	15.3	25.0	$\frac{1}{4}$	1226	C <sub>2</sub> S + glass
				$\frac{1}{2}$	1157	All glass
41	62.4	9.5	28.1	$\frac{1}{4}$	1151	C <sub>2</sub> S + glass
				h.c.	1271	alpha-beta C <sub>2</sub> S
42	63.0	11.0	26.0	h.c.	1165	Boundary (3,4)
				h.c.	1120	Eutectic (2)
				h.c.	1251	alpha-beta C <sub>2</sub> S
				h.c.	1122	Eutectic (2)
43	63.3	11.7	25.0	h.c.	1241	alpha-beta C <sub>2</sub> S
				h.c.	1127	Quintuple point (3)
44	64.0	13.5	22.5	$\frac{1}{4}$	1421	All glass
				$\frac{1}{2}$	1413	C <sub>2</sub> S + glass
				h.c.	1245	Boundary (3,4)
				h.c.	1133	Quintuple point (3)
45	64.5	14.7	20.8	h.c.	1122	Eutectic (2)
				h.c.	1266	Liquidus
				h.c.	1125	Quintuple point (3)
46	64.9	0.6	34.5	h.c.	1390	alpha-beta C <sub>2</sub> S
47	64.5	1.7	33.8	h.c.	1343	alpha-beta C <sub>2</sub> S
48	64.1	2.8	33.1	h.c.	1322	alpha-beta C <sub>2</sub> S
49	63.1	5.5	31.4	h.c.	1289	alpha-beta C <sub>2</sub> S
50	62.1	8.3	29.6	h.c.	1280	alpha-beta C <sub>2</sub> S
51	61.0	11.1	27.9	$\frac{1}{4}$	1465	All glass
				$\frac{1}{2}$	1461	C <sub>2</sub> S + glass
				h.c.	1272	alpha-beta C <sub>2</sub> S
				h.c.	1117	Eutectic (2)

Table 2 (contd.)

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
52	60.0	13.8	26.2	¼	1188	All glass
				¼	1184	C <sub>2</sub> S + glass
53	59.5	15.0	25.5	h.c.	1122	Liquidus
54	64.8	3.8	31.4	h.c.	1292	alpha-beta C <sub>2</sub> S
55	64.4	8.6	27.0	h.c.	1236	alpha-beta C <sub>2</sub> S
				h.c.	1120	Eutectic (2)
				h.c.	1235	alpha-beta C <sub>2</sub> S
56	64.3	9.6	26.1	h.c.	1126	Quintuple point (3)
				h.c.	1236	alpha-beta C <sub>2</sub> S
57	64.1	11.5	24.4	h.c.	1129	Quintuple point (3)
				h.c.	1120	Eutectic (2)
				h.c.	1477	All glass
58	64.0	12.4	23.6	¼	1472	C <sub>2</sub> S + glass
				¾	1244	Boundary (3,4)
				h.c.	1127	Quintuple point (3)
				h.c.	1121	Eutectic (2)
				h.c.	1247	Boundary (3,4)
59	63.9	13.4	22.7	h.c.	1131	Quintuple point (3)
				h.c.	1119	Eutectic (2)
				h.c.	1246	alpha-beta C <sub>2</sub> S
60	66.1	5.1	28.8	h.c.	1403	Binary eutectic (5)
61	66.2	5.9	27.9	h.c.	1231	alpha-beta C <sub>2</sub> S
				h.c.	1200	Binary eutectic (5)
62	66.5	7.3	26.2	h.c.	1232	alpha-beta C <sub>2</sub> S
				h.c.	1403	Binary eutectic (5)
63	66.8	8.8	24.4	h.c.	1234	alpha-beta C <sub>2</sub> S
				h.c.	1400	Binary eutectic (5)
64	67.4	11.7	20.9	h.c.	1262	Quintuple point (4)
				h.c.	1399	Binary eutectic (5)
65	67.6	13.2	21.4	h.c.	1266	Quintuple point (4)
				h.c.	1400	Eutectic (6)
66	68.6	9.7	21.7	h.c.	1323	Liquidus
				h.c.	1258	Boundary (3,4)
67	66.4	13.9	19.7	h.c.	1159	All glass
				h.c.	1155	C <sub>2</sub> S + glass
68	59.5	14.6	25.9	¼	1459	All glass
				¼	1455	Trace C <sub>2</sub> S + glass
				¼	1445	C <sub>2</sub> S + C <sub>3</sub> S <sub>2</sub> + glass
				¼	1436	C <sub>2</sub> S + C <sub>3</sub> S <sub>2</sub> + small
				¼		amt. CS + glass
69	55.3	0.7	44.0	¼		

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 upon the alpha-beta inversion of dicalcium silicate which normally occurs at  $1420^{\circ}$ . Lowering of this temperature by a maximum of  $190^{\circ}$  was observed. If this lowering is assumed to be due entirely to solid solution of the calcium borates, then when a saturated solid solution is formed no further change in the inversion temperature should occur. Curves of inversion temperature against percent of borate added show this to be the case. 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 14 percent monocalcium borate, 18 percent dicalcium borate, and 32 percent pentacalcium borosilicate, and the amount of solid solution is therefore placed at these limits. Lowering of the inversion temperature to about  $1270^{\circ}$  occurs in the monocalcium borate solid solutions and to about  $1230^{\circ}$  in solid solutions of the other two compounds. The extent of the solid solution area from the  $C_2S-C_5BS$  and  $C_2S-CB$  conjugation lines toward the  $CaO-SiO_2$  side line has not been determined.

Dicalcium silicate, crystallized from melts, had the appearance of droplets, invariably imbedded in glass, making an exact determination of indices impossible. A marked lowering of the indices was observed, however. Composition 18, table 1 (58.4%  $CaO$ , 13.2%  $B_2O_3$ , 28.4%  $SiO_2$ ) which lies just inside the

monocalcium silicate field, when held below the boundary temperature, gave spherules of  $C_2S$  having indices only slightly above the 1.65 index of the glass in which they were imbedded (normal indices of beta- $2CaO.SiO_2$ : alpha = 1.717; gamma = 1.735).

The field of beta- $2CaO.SiO_2$  has been drawn in figure 1 in accordance with the lowest temperatures found for the alpha-beta inversion.

Compositions 35 and 36 establish the temperatures of two points on the boundary (1-2) and compositions 41, 44, 58, 59, and 67, of three points on the boundary (3-4). Breaks corresponding to the eutectic: dicalcium silicate, monocalcium silicate, dicalcium borate (point 2), occurred in heating curves on compositions 41, 42, 44, 55, 57, 58, and 59; and breaks corresponding to the quintuple point: dicalcium silicate, dicalcium borate, and tricalcium borate (point 3), for compositions 43, 44, 45, 56, 57, 58, and 59. Compositions 64 and 65 give the temperature of the quintuple point: dicalcium silicate, pentacalcium borosilicate, tricalcium borate (point 4). These two compositions were prepared from dicalcium silicate and tricalcium borate and the appearance of this break showed that combination of these two compounds to form the binary system dicalcium silicate-pentacalcium borosilicate was not complete. Composition 66 gives the temperature of the eutectic: dicalcium silicate, lime, pentacalcium borosilicate (point 6). The temperature of the binary eutectic between dicalcium

silicate and pentacalcium borosilicate (point 5) is given by Nos. 61, 62, 63, 64, and 65.

The field of lime (D-6-7-8-E-CaO, fig. 1): The compositions prepared in this field and melting data obtained by heating curves are given in table 3.

Table 3  
Compositions in the CaO Field

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
70	69.3	8.3	22.4	h.c.	1398	Eutectic (6)
71	71.3	7.7	21.0	h.c.	1399	Eutectic (6)
72	69.1	11.5	18.4	h.c.	1398	Eutectic (6)
73	69.5	13.4	17.1	h.c.	1435	Liquidus
				h.c.	1406	Boundary (6,7,8)
74	71.3	23.4	5.3	h.c.	1412	Boundary (8,E)
75	71.5	21.9	6.6	h.c.	1410	Boundary (8,E)
76	70.0	16.1	13.9	h.c.	1413	Binary eutectic(7)
77	71.5	15.3	13.2	h.c.	1412	Binary eutectic(7)

Nos. 70, 71, and 72 indicate the temperature of the ternary eutectic: dicalcium silicate, lime, pentacalcium borosilicate (point 6); No. 73 fixes a temperature on boundary (6-7-8); Nos. 74 and 75, a temperature on boundary (8-E); and Nos. 76 and 77, the temperature of the binary eutectic between lime and pentacalcium borosilicate. Only one liquidus temperature was determined; that of composition 73. Quenches were made on most of the compositions to check interpretations given heating curves

but were not used to establish melting data because of the fact that practically complete crystallization occurred during quenching.

The field of pentacalcium borosilicate (4-5-6-7-8-9,fig.1):

This is the only ternary compound found to possess a field of stability in the ternary diagram. It may be considered as formed by the combination of dicalcium silicate with tricalcium borate, mol for mol; or by the combination of tricalcium silicate<sup>v</sup> with dicalcium borate, mol for mol. Tricalcium silicate does not occur as a primary phase in this system, the ternary compound occupying the region where it might be expected to appear.

The ternary compound,  $5\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ , melts congruently at  $1419^\circ$ . The optical properties (16) 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 due to twinning. The compound crystallizes in irregular or rounded grains without definite crystal outline.

Pentacalcium borosilicate forms true binary systems with dicalcium silicate, lime, and tricalcium borate. In accordance with the theorem of Alkemade (17), the maximum temperature on the boundary (4-5-6) was found to occur at the binary eutectic (point 5); the maximum temperature on boundary (6-7-8) at the binary eutectic point 7); and the maximum temperature 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.

Table 4  
Compositions in the Pentacalcium Borosilicate Field

No.	Composition, %			Time in hours	Temp. °C.	Phases present
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>			
78	67.9	14.7	17.4	h.c.	1400	Binary eutectic (5)
79	68.2	16.1	15.7	h.c.	1415	Liquidus
80	68.4	17.0	14.6	h.c.	1419	Liquidus
81	68.5	17.6	13.9	h.c.	1414	Liquidus
82	68.8	19.0	12.2	h.c.	1417	Liquidus
83	69.0	20.5	10.5	h.c.	1415	Liquidus
				h.c.	1262	Quintuple point (4)
84	69.2	21.2	9.6	h.c.	1415	Liquidus
85	69.3	22.0	8.7	h.c.	1417	Liquidus
86	69.9	15.3	15.8	h.c.	1417	Liquidus
				h.c.	1401	Boundary (5,7,8)
87	67.7	19.1	13.2	h.c.	1406	Liquidus
				h.c.	1373	Boundary (8,9,4)
88	69.2	16.5	14.3	h.c.	1414	Liquidus

Composition 73, in the binary system C<sub>2</sub>S-C<sub>5</sub>BS, showed melting at the temperature of the quintuple point: dicalcium silicate, tricalcium borate, pentacalcium borosilicate (point 4), owing to incomplete combination of the tricalcium borate to give the ternary compound. Composition 78 indicates the temperature of the binary eutectic between C<sub>2</sub>S and C<sub>5</sub>BS (point 5). No. 86 locates a temperature on boundary (6-7-8) and No. 87, on boundary (8-9-4).

Possible solid solution of  $C_2S$  in  $C_5BS$  was not investigated. The field of tricalcium borate (E-8-9-4-3-F): Heating curves upon a tricalcium borate preparation having very nearly the theoretical composition (by analysis: 70.74%  $CaO$ , 29.26%  $B_2O_3$ ; theoretical: 70.73%  $CaO$ , 29.27%  $B_2O_3$ ) gave its melting temperature as  $1488^\circ$ , a value  $9^\circ$  higher than that reported for this compound by Carlson (10).

In this field most of the melting data was secured by means of heating curves owing to difficulties caused by quench crystallization. The data are presented in table 5.

Table 5

Compositions in the Tricalcium Borate Field

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	OC.	present
89	68.5	26.3	5.2	h.c.	1429	Liquidus
				h.c.	1120	Quintuple point (3)
90	66.3	23.4	16.3	h.c.	1370	Liquidus
				h.c.	1124	Quintuple point (3)
91	64.0	20.5	15.5	h.c.	1291	Liquidus
				h.c.	1129	Quintuple point (3)
92	61.7	17.6	20.7	h.c.	1191	All glass
				h.c.	1185	C <sub>3</sub> B + glass
				h.c.	1147	C <sub>3</sub> B + glass
				h.c.	1140	C <sub>3</sub> B + C <sub>2</sub> S + glass
93	59.9	17.2	22.9	h.c.	1150	All glass
				h.c.	1143	Trace C <sub>3</sub> B + glass
94	67.0	20.5	12.5	h.c.	1375	Liquidus
				h.c.	1123	Quintuple point (3)
95	65.8	17.5	16.7	h.c.	1316	Liquidus
				h.c.	1253	Boundary (3,4)
				h.c.	1123	Quintuple point (3)
96	63.8	15.3	20.9	h.c.	1252	All glass
				h.c.	1248	C <sub>3</sub> B + C <sub>2</sub> S + glass
				h.c.	1125	Quintuple point (3)
				h.c.	1118	Eutectic (2)
97	63.4	19.2	17.4	h.c.	1257	All glass
				h.c.	1252	C <sub>3</sub> B + glass
98	63.1	23.0	13.9	h.c.	1243	All glass
				h.c.	1239	C <sub>3</sub> B + glass
99	70.2	26.3	3.5	h.c.	1456	Liquidus
100	69.6	23.4	7.0	h.c.	1428	Liquidus
				h.c.	1416	Binary eutectic (9)
101	69.5	22.7	7.8	h.c.	1416	Liquidus
102	65.0	16.6	18.4	h.c.	1261	Liquidus
				h.c.	1122	quintuple point (3)
103	63.5	19.4	17.1	h.c.	1239	Liquidus
				h.c.	1122	quintuple point (3)
104	62.0	22.2	15.8	h.c.	1226	All glass
				h.c.	1219	C <sub>3</sub> B + glass
105	67.1	21.1	11.8	h.c.	1371	Liquidus
				h.c.	1123	quintuple point (3)
106	66.5	23.0	10.5	h.c.	1384	All glass
				h.c.	1374	C <sub>3</sub> B + glass
				h.c.	1126	Quintuple point (3)

Table 5 (contd.)

No.	Composition,		% SiO <sub>2</sub>	Time in hours	Temp. °C.	Phases present
	CaO	B <sub>2</sub> O <sub>3</sub>				
107	65.3	26.8	7.9	¼	1354	All glass
				¼	1351	C <sub>3</sub> B + glass
				h.c.	1170	Boundary (F,3)
108	64.7	28.7	6.6	h.c.	1330	Liquidus
109	64.1	30.6	5.3	h.c.	1245	Boundary (F,3)
110	70.9	27.8	1.3	h.c.	1476	Liquidus
				h.c.	1404	Eutectic (8)
111	71.0	26.4	2.6	h.c.	1456	Liquidus
				h.c.	1409	Boundary (E,8)
				h.c.	1404	Eutectic (8)
112	71.1	24.9	4.0	h.c.	1441	Liquidus
				h.c.	1410	Boundary (E,8)

Compositions 95 and 96 locate temperatures on boundary (3-4); Nos. 111 and 112, on boundary (E-8); and Nos. 92, 107 and 109, on boundary (F-3). The temperature of the quintuple point: dicalcium silicate, tricalcium borate, dicalcium borate, is given by heating curves on compositions 89, 90, 91, 94, 95, 102, 103, 105, and 106; and the temperature of the eutectic: dicalcium silicate, monocalcium silicate, dicalcium borate by No. 96. Compositions 110 and 111 give the temperature of the ternary eutectic: lime, pentacalcium borosilicate, tricalcium borate (point 8). Composition 100 indicates a value for the melting temperature of the binary eutectic: pentacalcium borosilicate, tricalcium borate (point 9).

The field of dicalcium borate (F-3-2-10-11-G, fig.1): Dicalcium borate forms a true binary system with monocalcium silicate and

accordingly boundary (2-11) shows a maximum temperature at point 10, as determined by a heating curve on composition 124, table 6; and quenches on composition 125.

Table 6

Compositions in the Dicalcium Borate Field

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
113	62.9	34.5	2.6	h.c.	1287	Liquidus
				h.c.	1266	Boundary (F,3)
114	63.5	32.6	3.9	h.c.	1270	Liquidus
115	62.0	34.5	3.5	h.c.	1281	Liquidus
116	62.4	30.6	7.0	h.c.	1240	Liquidus
				2	1221	C <sub>2</sub> B + trace C <sub>3</sub> B + glass
117	71.3	34.5	4.2	2	1287	All glass
				2	1280	C <sub>2</sub> B + glass
118	61.0	30.7	8.3	2	1256	All glass
				2	1248	C <sub>2</sub> B + glass
119	60.9	28.7	10.4	2	1239	All glass
				2	1235	C <sub>2</sub> B + glass
120	60.7	26.8	12.5	2	1225	All glass
				2	1221	Trace C <sub>2</sub> B + glass
121	60.3	23.0	16.7	2	1184	All glass
				2	1180	C <sub>2</sub> B + glass
122	60.0	19.2	20.8	2	1151	All glass
				2	1142	Trace C <sub>2</sub> B + glass
				2	1136	C <sub>2</sub> B + C <sub>3</sub> B + glass
123	59.1	31.0	9.9	h.c.	1243	Liquidus
124	57.7	26.8	15.5	h.c.	1203	Liquidus
				h.c.	1153	Binary eutectic (10)
125	55.7	21.3	23.0	2	1155	All glass
				2	1153	C <sub>2</sub> B + glass
				2	1150	C <sub>2</sub> B + CS + glass
126	52.4	32.6	15.0	2	1180	All glass
				2	1172	C <sub>2</sub> B + glass
127	49.4	30.6	20.0	2	1097	All glass
				2	1095	C <sub>2</sub> B + glass
128	50.4	44.3	5.3	2	1153	All glass
				2	1150	C <sub>2</sub> B + glass
129	53.3	38.8	7.9	2	1230	All glass
				2	1224	C <sub>2</sub> B + glass
130	54.8	36.0	9.2	2	1240	All glass
				2	1236	C <sub>2</sub> B + glass

Table 6 (Contd.)

No.	Composition, CaO B <sub>2</sub> O <sub>3</sub>		% SiO <sub>2</sub>	Time in hours	Temp. °C.	Phases present
131	56.3	33.2	10.5	3	1241	All glass
				4	1233	C <sub>2</sub> B + glass
132	57.7	30.5	11.8	1	1226	All glass
				2	1223	C <sub>2</sub> B + glass
133	59.1	27.7	13.2	h.c.	1214	Liquidus
134	49.8	41.5	8.7		1122	All glass
					1115	Trace C <sub>2</sub> B + glass
135	50.8	38.8	10.4		1134	All glass
					1131	Trace C <sub>2</sub> B + glass
136	52.8	33.2	14.0		1162	All glass
					1158	C <sub>2</sub> B + glass
				h.c.	1017	Quintuple point (11)
137	54.9	27.7	17.4		1170	All glass
					1168	C <sub>2</sub> B + glass
				h.c.	1120	Boundary (2,11)
138	56.5	23.4	20.1		1177	All glass
					1169	C <sub>2</sub> B + glass
139	56.9	22.2	20.9		1170	All glass
					1163	C <sub>2</sub> B + glass
140	59.0	16.6	24.4		1128	All glass
					1126	C <sub>2</sub> B + glass
					1119	C <sub>2</sub> B + C <sub>2</sub> S + glass
141	48.7	38.8	12.5		1089	All glass
					1085	Trace C <sub>2</sub> B + glass
142	50.1	33.2	16.7		1112	All glass
					1111	C <sub>2</sub> B + glass
143	51.5	27.7	20.8		1104	All glass
					1102	C <sub>2</sub> B + glass
144	46.1	33.2	20.7		1039	All glass
					1037	C <sub>2</sub> B + glass
145	46.3	30.4	23.3		1035	All glass
					1027	C <sub>2</sub> B + CS + glass
146	47.2	35.2	17.5		1037	All glass
					1033	C <sub>2</sub> B + glass
					1030	C <sub>2</sub> B + CB + glass
147	50.8	28.1	21.0		1109	All glass
					1107	C <sub>2</sub> B + glass
148	52.6	24.6	22.8		1128	All glass
					1123	C <sub>2</sub> B + glass
149	50.7	44.3	5.0		1139	All glass
					1132	C <sub>2</sub> B + glass
					1105	C <sub>2</sub> B + CB + glass
150	51.6	38.9	9.5		1164	All glass
					1159	C <sub>2</sub> B + glass

Table 6 (Contd.)

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
151	50.2	40.1	9.7	h.c.	1130	Liquidus
152	48.6	39.7	11.7	+	1083	All glass
				+	1080	C <sub>2</sub> B + glass
				+	1075	C <sub>2</sub> B + CB + glass
153	51.8	29.2	19.0	+	1134	All glass
				+	1129	C <sub>2</sub> B + glass
154	50.5	30.5	19.0	+	1113	All glass
				+	1108	C <sub>2</sub> B + glass
155	58.7	22.2	19.1	+	1172	All glass
				+	1170	C <sub>2</sub> B + glass
156	48.0	29.3	22.7	+	1054	All glass
				+	1052	C <sub>2</sub> B + glass
157	51.7	25.5	22.8	+	1127	All glass
				+	1121	C <sub>2</sub> B + glass
				+	1107	C <sub>2</sub> B + CS + glass
158	51.9	24.3	23.8	+	1125	All glass
				+	1124	Trace C <sub>2</sub> B + glass
				+	1117	C <sub>2</sub> B + CB + glass

Temperatures on boundary (F-3) are given by Nos. 113, 116, and 122; on boundary (2-11) by Nos. 137, 140, 145, and 157; and, on boundary (G-16) by Nos. 146, 149, and 152. The temperature of the quintuple point: dicalcium borate, monocalcium borate, monocalcium silicate, is given by a heating curve on No. 136.

Compositions in this field crystallized less rapidly than those of higher lime content and most of the melting data was secured by the quench method.

The field of monocalcium borate (G-11-12-13-16-15-14-H, fig. 1):

This compound is obtained from melts in lath shaped crystals occasionally showing hexagonal outline. In marked contrast

to the behavior of melts in the fields of  $C_2S$ ,  $CaO$ ,  $C_5BS$ ,  $C_3B$ , and part of the  $C_2B$  field, monocalcium borate crystallized very slowly and some of the charges, especially those containing the higher percentages of silica, had to be held overnight to insure crystallization.

The field of monocalcium borate occupies the largest area in the diagram and is of particular interest because more than two-thirds of this area lies within the region of liquid immiscibility. Within the immiscibility region of the field is included the composition corresponding to the mineral danburite,  $CaO.B_2O_3.2SiO_2$ .

Table 7

Compositions in the Monocalcium Borate Field

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
159	47.5	49.9	2.6	17	1131	All glass
				17	1129	CB + glass
160	46.7	49.8	3.5	17	1110	CB + C <sub>2</sub> B + glass
				17	1134	All glass
161	48.7	44.3	7.0	17	1132	CB + glass
				17	1099	All glass
				17	1096	CB + glass
162	46.0	49.8	4.2	17	1087	CB + C <sub>2</sub> B + glass
				17	1131	All glass
163	47.4	44.3	8.3	17	1128	CB + glass
				17	1099	All glass
				17	1096	CB + glass
164	45.7	38.8	15.5	17	1070	CB + C <sub>2</sub> B + glass
				17	1071	All glass
165	45.9	36.0	18.1	17	1067	CB + glass
				17	1046	All glass
				17	1043	CB + glass
166	40.1	49.9	10.0	17	1035	CB + C <sub>2</sub> B + glass
				17	1111	All glass
167	35.7	44.3	20.0	17	1104	CB + glass
				17	1045	All glass
168	30.6	64.2	5.2	17	1041	CB + glass
				17	1041	All glass
169	32.6	57.1	10.3	17	1036	CB + glass
				17	1058	All glass
170	34.6	49.9	15.5	17	1053	CB + glass
				17	1059	All glass
				17	1053	CB + glass
171	36.5	42.8	20.7	17	1028	CB + 2 glasses
				17	1041	All glass
172	38.5	35.7	25.8	3½	1033	CB + glass
				17	1023	All glass
173	38.4	31.6	30.0	17	1017	CB + glass
				17	991	All glass
174	28.0	70.0	2.0	17	984	CB + SiO <sub>2</sub> + glass
				17	993	All glass
175	27.5	68.5	4.0	17	989	Trace CB + glass
				17	981	All glass
176	26.9	67.1	6.0	17	979	CB + glass
				17	971	All glass
				17	969	CB + glass

Table 7 (contd.)

No.	Composition,		%	Time in	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	hours	°C.	present
177	44.4	32.0	23.6	17	1018	All glass
				17	1017	CB + glass
178	44.0	31.6	24.4	1 $\frac{1}{2}$	1027	All glass
				1 $\frac{1}{2}$	1017	Trace CB + glass
179	26.4	65.6	8.0	1 $\frac{1}{2}$	976	Two glasses
				1 $\frac{1}{2}$	968	CB + glass
Compositions in the Calcium Diborate Field						
180	27.3	70.9	1.8	17	986	All glass
				5	982	CB <sub>2</sub> + glass
181	26.2	69.9	3.9	17	975	All glass
				1	967	CB <sub>2</sub> + glass

Compositions 159, 161, 163, and 165 locate temperatures on boundary (G-11); and composition 173, a temperature on boundary (12-13). Composition 170 defines a temperature on the two liquid boundary (13-14).

The field of calcium diborate (H-14-15-I'-I, fig.1):

Only a small portion of this field, that comprising the triangle H-14-I, lies in the region of liquid miscibility; all other compositions in the area melt with the formation of two liquids. The melting temperatures of two compositions in the one liquid area are given in table 7.

The field of silica (SiO<sub>2</sub>-A-A'-B-12-13-16--, fig. 1): This field is distorted in a curious manner by the occurrence of liquid immiscibility. It consists of a portion B-12-13-A in the one liquid area; a large region A'-12-16-A in the two

liquid area; and a narrow strip in the one liquid area along the  $\text{SiO}_2\text{-B}_2\text{O}_3$  side of the triangle extending an undetermined distance toward the  $\text{B}_2\text{O}_3$  vertex.

In the melts studied silica appeared as tridymite in the form of needle-like crystals imbedded in glass. The data obtained are listed in table 8 where compositions 182, 183, 184, 185, 187, 188, 189, 190, 193, and 194 define temperatures on boundary (B-12). Composition 195 determines the temperature of the quintuple line (12-16) separating the fields of silica and monocalcium borate.

Table 8

Compositions in the Silica Field

No.	Composition,		% SiO <sub>2</sub>	Time in hours	Temp. °C.	Phases present
	CaO	B <sub>2</sub> O <sub>3</sub>				
182	35.0	1.0	64.0	2	1425	All glass
				1	1417	SiO <sub>2</sub> + CS + glass
183	35.2	2.0	62.8	2	1411	All glass
				1	1405	Trace SiO <sub>2</sub> + glass
				1	1400	SiO <sub>2</sub> + CS + glass
184	34.4	4.0	61.6	1	1388	All glass
				1	1380	SiO <sub>2</sub> + glass
				1	1373	SiO <sub>2</sub> + CS + glass
				1	1370	SiO <sub>2</sub> + two glasses
185	31.2	4.0	64.8	1	1364	SiO <sub>2</sub> + CS + glass
				1	1465	Two glasses
				1	1457	SiO <sub>2</sub> + glass
186	32.0	4.4	63.6	1	1365	SiO <sub>2</sub> + glass
				1	1357	SiO <sub>2</sub> + CS + glass
				1	1392	Two glasses
				1	1385	SiO <sub>2</sub> + glass
187	32.8	6.0	61.2	1	1332	SiO <sub>2</sub> + glass
				1	1327	SiO <sub>2</sub> + CS + glass
				1	1292	Two glasses
				1	1287	SiO <sub>2</sub> + glass
				1	1276	SiO <sub>2</sub> + glass
188	35.2	10.0	54.8	1	1271	SiO <sub>2</sub> + CS + glass
				1	1223	Two glasses
				1	1218	SiO <sub>2</sub> + glass
				1	1205	SiO <sub>2</sub> + glass
				1	1197	SiO <sub>2</sub> + CS + glass
189	36.3	15.5	47.2	4	1113	Two glasses
				4	1108	SiO <sub>2</sub> + glass
191	35.6	24.0	40.4	17	1071	Two glasses
				17	1063	SiO <sub>2</sub> + glass
192	38.4	26.0	35.6	17	1057	Two glasses
				17	1048	SiO <sub>2</sub> + glass
193	38.2	29.4	32.4	17	1038	Two glasses
				17	1031	Trace SiO <sub>2</sub> + glass
				17	1010	SiO <sub>2</sub> + glass
				17	1006	SiO <sub>2</sub> + CS + glass
				17	1019	Two glasses
194	38.2	30.4	31.4	17	1012	SiO <sub>2</sub> + glass
				17	1003	SiO <sub>2</sub> + glass
				17	1000	SiO <sub>2</sub> + CS + glass
				17	995	Two glasses
195	37.8	31.4	30.8	17	991	SiO <sub>2</sub> + glass
				17	989	SiO <sub>2</sub> + 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 lines A'-13 and B-12 in fig. 1. The temperature difference between these boundaries decreases from 262° in the lime-silica system to about 55° at composition 187, and finally to 13° between points 13 and 12.

#### VI. The Two Liquid Area

Studies were made of the compositions of immiscible liquids formed by the melting of mixtures within this area. The results are listed in table 9.

Table 9

## Tie Line Compositions

No.	Initial			Compositions, %			Low	SiO <sub>2</sub>	glass	Time	Temp.	Phases
	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	High	SiO <sub>2</sub>	glass						
196	30.8	19.2	50.0	21.4	15.0	63.6	36.4	21.4	42.2	7	1132	Two glasses
										4	1125	SiO <sub>2</sub> + glass
197	25.2	24.8	50.0	15.1	17.1	67.8	33.3	27.4	39.3	17	1021	Two glasses
										17	1014	SiO <sub>2</sub> + glass
198	22.3	27.7	50.0	11.8	18.4	69.8	32.4	32.2	35.4	17	1012	Two glasses
										17	1003	CB + glass
199	22.0	38.0	40.0	7.4	23.8	68.8	30.6	43.5	25.9	17	1035	Two glasses
										17	1029	CB + glass
200	20.1	49.9	30.0	8.3	36.6	55.1	28.1	59.1	12.8	17	1014	Two glasses
										17	1006	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	2 $\frac{1}{2}$	967	Two glasses
										3	965	Trace CB <sub>2</sub> +glass
										2	964	CB <sub>2</sub> + 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 <sub>2</sub> + glass
204	10.0	84.0	6.0	0.9	89.9	9.2	23.3	75.2	1.5	2	973	Two glasses
										2	970	CB <sub>2</sub> + glass
205	12.0	88.0	0.0							2	975	Two glasses
										2	974	CB <sub>2</sub> + 2 glasses

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 up 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 weighed out and analyzed. Quench determinations were made upon the powdered low silica glasses.

Complete unmixing 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 heat treatment. The intersections of this line, which is a tie line, with the boundaries of the immiscibility area give the compositions of the two liquids which may exist in equilibrium.

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. The resulting high silica glass was white and the low silica glass milky. Separation was very incomplete as the analysis showed. The high silica liquid, because of its high viscosity, tends 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 high silica glasses were opaque in all cases, while the low silica glasses of compositions 198 and 199 were milky and those of 200 and 201 clear. The temperature of composition 199 gives the maximum temperature of the liquidus in the immiscibility portion of the monocalcium borate field.

The tie lines in the calcium diborate field have a fan-shaped distribution, as fig. 1 shows. The liquids in this field separated almost completely. It was noticed that in these compositions the clear, less siliceous liquid collected at the center and bottom of the melt, with the more siliceous liquid at the sides and on top.

Quenches on composition 202 fixed the temperature of the quintuple line (14-15) separating the fields of calcium diborate and monocalcium borate. Quenches on the binary composition No. 205 gave  $974^{\circ}$  for the temperature of the liquidus, a value  $3^{\circ}$  higher than that reported by Carlson (10).

A striking feature of the immiscibility area is the marked increase in concentration of lime in the less siliceous liquids, proceeding 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 and 15 percent higher than that of the

lime rich layer of the lime-boric oxide system. Whether any appreciable increase in the lime concentration of the more siliceous ternary liquids occurs has not been determined but the analyses on compositions 203, 204, and 205 indicate that the concentration change is probably small. The compositions of the more siliceous liquids in the ternary diagram have therefore been indicated in fig. 1 by the dotted line AI' connecting the compositions of the high silica and high boric oxide liquids in the respective binary systems.

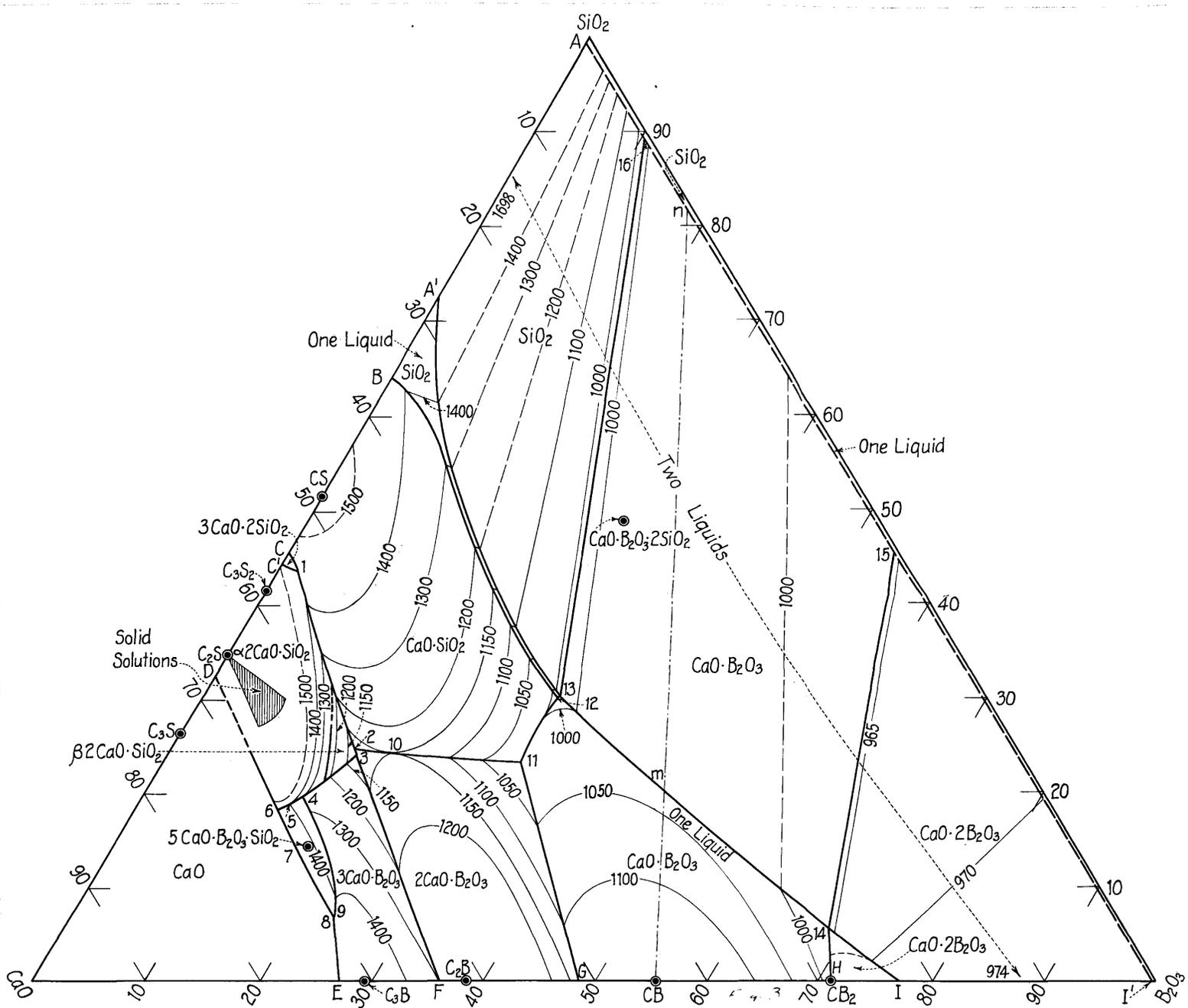
The maximum divergence in compositions of the two liquids occurs in the monocalcium borate field, as inspection of the length of tie lines in fig. 1 will show.

#### VII. Characteristics of the Fusion Surfaces

Figure 3 is a representation of the triangular diagram in which isotherms, showing temperatures of complete melting, have been inserted. The positions of the isotherms were determined by points read off the diagrams of fig. 2 at 50° and 100° intervals and also by 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.

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 which can be considered as generated by a straight line of variable length moving in such a manner as to be always parallel to the base and rotating as it goes (18). Successive positions of the line are isotherms and also tie lines. In the silica field the line moves downhill with falling temperatures, one end traversing the distance A-16 while the other end passes from A' to 13. The final position 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 rotating line moves uphill assuming positions of successively higher temperature until it reaches mn, the maximum height of the surface of this field in the immiscibility region. In this position a plane passed through the line and perpendicular to the base will include the composition corresponding to monocalcium borate. Proceeding from mn the line runs downhill assuming positions of successively lower temperature, one end traversing the distance m-15 and the other the distance n-14. On reaching a minimum temperature at 15-16 it represents an invariant condition such that 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 with increasing temperatures, the ends traversing the distances 14-I and 15-I', respectively. Its final position is I-I' in the binary system lime-boric oxide.

The area A-A'-13-16 thus consists of a curved surface representing a rapid decrease in temperature from 1698° at AA' to 990° at 13-16. The area 16-13-14-15 is a curved surface showing a gradual increase in temperatures from 990° at 13-16 to a maximum of 1032° at mn, and falling temperatures at 964° at 14-15. The area 15-14-I-I' is a curved surface showing a gradual increase in temperatures from 964° at 14-15 to 974° at I-I' in the binary system lime-boric oxide.

In the silica field there is a downhill slope from temperatures at the silica liquidus in the binary system lime-silica to the level of the surface where liquid immiscibility starts at A-16. At the SiO<sub>2</sub> vertex the liquidus temperature in the binary system is 15° higher than the liquidus at A and this temperature difference between the liquidus in the binary system and that in the immiscibility area diminishes from A to 16, becoming zero in the vicinity of point 16. In turn the area of the one liquid region B-12-13-A' 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° between

A' and B and a minimum value of  $13^{\circ}$  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 area surface with the two liquid area surface. On emerging from the immiscibility area beyond the boundary 15-16 the liquidus falls to a boundary between monocalcium borate and silica in the narrow one liquid region A-I'-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. In the vicinity of point 15 is a quintuple point between silica, monocalcium borate, and calcium diborate, assuming that the silica liquidus extends to higher percentages of boric oxide in the area A-I'-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> than that at point 15.

The calcium diborate field slopes from H to I-14, its intersection with the immiscibility area liquidus. The latter surface slopes from I-I' to 14-15. The field emerges from the immiscibility region at I'-15 and forms a boundary with that portion of the silica field assumed to extend below point 15, and with the narrow strip which forms the boric oxide field. The ternary eutectic between silica, boric oxide, and calcium diborate probably lies very near the binary eutectic between boric oxide and silica.

The boric oxide field and the adjacent section of the silica field are represented by an extremely narrow ledge on the  $B_2O_3-SiO_2$  of the solid model, far below the plateau representing the immiscibility liquidus. Thus the separation of the plateau from the boric oxide level at the vertex is about  $680^\circ$ .

In general the system is characterized by the extreme variation in temperatures which it displays, covering a range of almost  $2300^\circ$ .

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

Table 10

Significant Compositions and Temperatures  
in the System CaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

Ternary Eutectics

Phases present	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Temp. °C.
CaO.SiO <sub>2</sub> , 2CaO.SiO <sub>2</sub> , 2CaO.B <sub>2</sub> O <sub>3</sub>	59.2	16.0	24.8	1118
2CaO.SiO <sub>2</sub> , CaO, 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	69.2	12.6	18.2	1398
CaO, 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> , 3CaO.B <sub>2</sub> O <sub>3</sub>	70.0	23.2	6.8	1404
CaO.SiO <sub>2</sub> , CaO.B <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	38.4	31.4	30.2	977
CaO.2B <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , B <sub>2</sub> O <sub>3</sub>	Not determined			

Quintuple points

CaO.SiO <sub>2</sub> , 3CaO.2SiO <sub>2</sub> , 2CaO.SiO <sub>2</sub>	54.8	1.4	43.8	1436
2CaO.SiO <sub>2</sub> , 3CaO.B <sub>2</sub> O <sub>3</sub> , 2CaO.B <sub>2</sub> O <sub>3</sub>	59.4	16.6	24.0	1128
2CaO.SiO <sub>2</sub> , 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> , 3CaO. B <sub>2</sub> O <sub>3</sub>	63.4	14.0	19.6	1266
CaO.SiO <sub>2</sub> , 2CaO.B <sub>2</sub> O <sub>3</sub> , CaO.B <sub>2</sub> O <sub>3</sub>	44.9	31.7	23.4	1017
SiO <sub>2</sub> , CaO.B <sub>2</sub> O <sub>3</sub> , CaO.2B <sub>2</sub> O <sub>3</sub>	Not determined			

Binary Eutectics

Phases present	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Temp. °C.
CaO.B <sub>2</sub> O <sub>3</sub> , CaO.SiO <sub>2</sub>	55.3	20.2	24.5	1150
2CaO.SiO <sub>2</sub> , 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	67.7	13.4	18.9	1400
CaO, 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	69.7	16.2	14.1	1412
3CaO.B <sub>2</sub> O <sub>3</sub> , 5CaO.B <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	69.6	23.0	7.4	1415

Table 10 (contd.)

Compositions of Liquids Joined by Quintuple Lines

Liquid	CaO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
At point 13)	38.0	31.5	30.5
At point 16)	0.5	10.5	89.0
At point 14)	25.9	68.1	6.0
At point 15)	0.4	54.6	45.0

VIII. Crystallization Curves

On cooling a melt in a ternary system the first appearance of crystals occurs at the liquidus temperature for the given composition. These crystals consist of the primary phase within whose field the ternary mixture lies. As separation of the primary phase continues, the composition of the liquid alters on a straight line connecting the composition of the primary phase with that of the initial ternary mixture until a boundary curve is intercepted. At the boundary separation of a second crystalline phase begins and the liquid alters along the boundary until a eutectic is reached where a third phase separates and liquid disappears. Such a path represents the simplest type of ternary crystallization where no complications are introduced by such phenomena as

solid solution, incongruent melting, or liquid immiscibility.

When the crystallization curve lies entirely within the triangle formed by joining the compositions of the three solid phases produced by complete solidification of the melt the curve ends at a eutectic. When the curve lies partially outside such a triangle it ends at a quintuple point. This distinction will become clear in the specific instances to be considered.

Where a ternary composition lies exactly on a line joining two solid phases forming a binary system, the melt will go solid at the binary eutectic. Thus compositions on the conjugation lines  $C_5BS-C_2S$ ,  $C_5BS-CaO$ ,  $C_5BS-C_3B$ , and  $CS-C_2B$ , will solidify at points 5, 7, 9, and 10 respectively.

Compositions within the shaded area in the  $C_2S$  field will solidify completely to solid solutions of their own compositions. For simplicity the effect of solid solutions on crystallization curves in the remainder of the  $C_2S$  field will not be considered.

The various types of crystallization occurring from melts within the possible composition triangles will now be considered.

The triangle formed by joining  $CaO$ ,  $C_5BS$ , and  $C_3B$ :  
Depending upon the location of the ternary composition the crystallization curve will intersect either boundary 7-8, E-8, or 8-9 and liquid will disappear at the ternary eutectic (point 8).

The triangle formed by joining CaO, C<sub>5</sub>BS, and C<sub>2</sub>S:

The crystallization curve may intersect either boundary D-6, 5-6, or 6-7, and liquid will disappear at the ternary eutectic (point 6).

The triangle formed by joining C<sub>2</sub>S, C<sub>3</sub>B, and C<sub>2</sub>B: If

the boundary 9-4 is intersected by the crystallization curve, C<sub>3</sub>B and C<sub>5</sub>BS will separate together until point 4 is reached. At point 4 C<sub>5</sub>BS redissolves completely and C<sub>2</sub>S then begins to crystallize. The liquid follows the curve 4-3 and disappears at quintuple point 3. If the boundary 5-4 is intersected C<sub>2</sub>S and C<sub>5</sub>BS will crystallize together. The latter compound redissolves completely at point 4, C<sub>3</sub>B appears and crystallization becomes complete when the liquid reaches point 3. If the boundary 4-3 is intersected the ternary compound does not appear at all and the liquid follows curve 4-3 to point 3.

The triangle formed by joining C<sub>2</sub>S, C<sub>2</sub>B, and CS: If

boundary 4-3 is intersected C<sub>3</sub>B and C<sub>2</sub>S will crystallize together; C<sub>3</sub>B dissolves completely at point 3; C<sub>2</sub>B and C<sub>2</sub>S crystallize together along 3-2; and with the appearance of CS at the ternary eutectic (point 2) complete solidification occurs. If the boundary F-3 is intersected C<sub>3</sub>B and C<sub>2</sub>B crystallize together up to point 3 where C<sub>3</sub>B redissolves. C<sub>2</sub>S and C<sub>2</sub>B then crystallize together along 3-2. If boundary C'-1 is intersected C<sub>2</sub>S and C<sub>3</sub>S<sub>2</sub> crystallize together to point 1 where C<sub>3</sub>S<sub>2</sub> redissolves completely after which the path follows boundary 1-2. Likewise if C-1 is intersected CS and C<sub>3</sub>C<sub>2</sub> crystallize together

and the latter redissolves at point 1, the liquid then proceeding along 1-2.

The triangle formed by joining CS, C<sub>2</sub>B, and CB: The crystallization curves follow either boundary segment 10-11 or 6-11 and liquid disappears at quintuple point 11.

The triangle formed by joining CS, CB, and SiO<sub>2</sub>: Those compositions whose crystallization paths can intersect the small segments of the CS, C<sub>2</sub>B, and CB, C<sub>2</sub>B boundaries included within this triangle will pass through quintuple point 11 and end at the ternary eutectic, point 12. All other compositions in this triangle whose crystallization curves do not intersect the two liquid boundary behave normally, ending at point 12 and will not be discussed further. Crystallization curves which intersect the two liquid boundary will now be considered.

(1) Any composition in the SiO<sub>2</sub> field within the two liquid area enclosed by the triangle. The melt will consist of two liquids whose compositions are given by the extremities of the tie line passing through the ternary composition. On cooling SiO<sub>2</sub> will separate and the mean composition of the liquids will alter on a line connecting SiO<sub>2</sub> and the ternary composition until the line 13-16 is intersected. The compositions of the individual liquids will alter along A-16 and A'-13, respectively, during this process, the proportion of low silica liquid to high silica liquid continually increasing. CB will then begin to crystallize and the temperature will remain

constant. The mean composition of the liquids alters along 13-16 until point 13 is reached, at which the high silica liquid disappears. Crystallization then proceeds along the line 13-12 with falling temperature. At the ternary eutectic (point 12) CS crystallizes and liquid disappears.

(2) The small one liquid area within the triangle near the  $\text{SiO}_2$  vertex. Separation of  $\text{SiO}_2$  will occur and the crystallization curve will intersect the two liquid boundary, after which the path will be as in (1).

(3) Compositions in the monocalcium borate field within the two liquid area of the composition triangle. The melt will consist of two liquids whose compositions are given by the extremities of the tie line passing through the ternary composition. On cooling CB will separate and the proportion of low silica liquid to high silica liquid will decrease, the former altering in composition along the curve m-13 and the latter along n-16. The mean composition of the liquids follows a line connecting CB and the initial ternary composition until boundary 13-16 is intersected. The temperature here remains constant and the proportion of low silica liquid to high silica liquid increases until at 13 the high silica liquid disappears. The crystallization path then proceeds from 13 to 12 where it ends.

(4) Compositions in the one liquid area of the monocalcium borate field and lying to the right of a line joining

CB and point 13. CB will separate and the two liquid area will be intersected, after which the changes will be as in (3).

The triangle formed by joining CB,  $CB_2$ , and  $SiO_2$ :

(1) In the silica field within the two liquid area. On separation of  $SiO_2$  the compositions of the two liquids alter along A-16 and A'-13, respectively. When the crystallization line representing the mean compositions of the two liquids intersects boundary 13-16, CB will separate, diminishing thereby the proportion of low silica liquid which disappears at 16. The liquid composition then follows the  $SiO_2$ -CB boundary (not shown) in the area A- $SiO_2$ - $B_2O_3$ -I' until  $CB_2$  crystallizes and the liquid disappears at a quintuple point between  $SiO_2$ , CB, and  $CB_2$  near point 15.

(2) In the  $SiO_2$  field within the one liquid area. After the boundary AI' is intersected the path is the same as in (1).

(3) In the CB field within the two liquid area and to the left of a line joining CB and point 16. The compositions of the two liquids alter along n-16 and m-13, respectively, and the crystallization curve intersects line 13-16. Subsequent changes occur as in (1).

(4) In the CB field within the two liquid area to the left of line mn and to the right of a line joining CB and point 16. When the crystallization curve intersects AI'

the low silica liquid disappears and, after reaching the CB-SiO<sub>2</sub> boundary in the one liquid area A-I'-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> the curve proceeds as in (1).

(5) In the CB field to the right of line mn and to the left of a line joining CB and point 15. The compositions of the two liquids alter along n-15 and m-14, respectively, until the line representing their mean compositions intersects AI' and the low silica liquid disappears. After reaching the CB-SiO<sub>2</sub> boundary in the area A-I'-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> crystallization proceeds as in (1). The path starting in the one liquid area would be the same as the foregoing after intersecting boundary 13-14.

(6) In the CB field to the left of mn and to the right of a line joining CB and point 15. The crystallization curves all intersect the boundary H-14-15 either before or after that boundary enters the immiscibility area. At point 15 the low silica liquid disappears and crystallization becomes complete at the CB, CB<sub>2</sub>, SiO<sub>2</sub> quintuple point.

The triangle formed by joining CB<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>:

(1) Compositions to the left of line H-14-16.

Crystallization is of the same type as that discussed in the preceding section except that CB must redissolve completely near point 15 and the liquid then proceeds along the SiO<sub>2</sub>, CB<sub>2</sub> boundary in the one liquid strip to a ternary eutectic between SiO<sub>2</sub>, CB<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub>.

(2) Compositions to the right of line H-14-16. If

these lie within the narrow triangle formed by joining the points 11, 14, and 15, the crystallization curves will pass through the quintuple point near 15 before proceeding to the ternary eutectic. Those which do not will intersect boundary 15-1' with disappearance of the low silica liquid and crystallization then proceeds to the eutectic.

(3) The crystallization paths within the fields occurring in the narrow one liquid region proceeding inward from the binary system  $B_2O_3-SiO_2$  are probably of the normal type.

### IX. 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 non-hydraulic. The beta-gamma inversion for the pure compound normally occurs at  $675^\circ$  with such rapidity that it is difficult to prepare the beta form in appreciable quantities even by quenching from temperatures of over  $1000^\circ$ . However, it was first noticed by Bates and Klein (19) that the presence of less than 1 percent of  $B_2O_3$  or  $Cr_2O_3$  entirely 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 (20) of

the National Bureau of Standards showed that progressive lowering of the alpha-beta inversion temperature of dicalcium silicate occurred upon 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 greatly lowered or perhaps inhibited completely by the existence of the solid solutions.

With reference to the possible use of boric oxide to lower clinkering temperatures of the portland cement raw mix, the non-appearance of tricalcium silicate in the system  $CaO-B_2O_3-SiO_2$  is of significance. The region where this compound might be expected is occupied by a ternary compound,  $5CaO.B_2O_3.SiO_2$ . This compound may be considered as formed by the combination of one mol of tricalcium silicate with one mol 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. Thus it appears that the compound does not possess appreciable hydraulic properties, although the question has not

yet been sufficiently investigated.

Furthermore, it was found by Carlson (19) that, although the addition of boric oxide to binary mixtures of CaO and SiO<sub>2</sub> or of CaO and Al<sub>2</sub>O<sub>3</sub> promoted combination of these constituents on burning, the addition of boric oxide to ternary mixtures of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> inhibited combination. That is, clinkers produced by burning CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> mixtures alone contained less uncombined lime than corresponding mixtures to which boric oxide had been added before burning. The percentage of uncombined lime in the clinkers was found to increase with increase in their boric oxide content. It is probable that there is a considerable broadening of the lime field in the quaternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>.

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-boric oxide and low lime portion of the system 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 region are being studied elsewhere (2).

## X. Summary

The foregoing investigation of the system  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  has disclosed a type of liquid immiscibility not previously encountered in 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 lie largely within the immiscibility area which extends in the triangular diagram from the immiscibility region in the  $\text{CaO-B}_2\text{O}_3$  system to that in the  $\text{CaO-SiO}_2$  system. The width of the area broadens very considerably in proceeding towards the interior of the triangular diagram.

The fusion surfaces in this system and types of crystallization which may occur are unusual and have been discussed.

One new compound, pentacalcium borosilicate,  $5\text{CaO.B}_2\text{O}_3.\text{SiO}_2$ , melting at  $1419^\circ$ , was found. Tricalcium silicate does not appear at the liquidus in the system. The region in which it might be expected to occur is occupied by the field of the ternary compound. The mineral danburite,  $\text{CaO.B}_2\text{O}_3.2\text{SiO}_2$ , was not obtained as a crystalline phase, its composition lying within the immiscible liquid portion of the

monocalcium borate field.

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

The possible effect of adding small quantities of boric oxide to the portland cement raw mix before burning is considered. The evidence indicates that such addition would not be advantageous.

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