THE MELTING OF DANBURITE:[*] A STUDY OF LIQUID IMMISCIBILITY IN THE SYSTEM, CaO–B_2O_3–SiO_2

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In an orienting study of the quaternary system, Na_2O–CaO–B_2O_3–SiO_2, Morey[1] found that the mineral danburite, $CaO \cdot B_2O_3 \cdot 2SiO_2$, melts with formation of two liquid layers. Since in each of the two limiting binary systems, CaO–SiO_2,[2] and CaO–B_2O_3,[3] there is a range of composition within which two layers are formed, it was inferred that a band of immiscibility extends across the ternary system, CaO–B_2O_3–SiO_2. Our study has confirmed that inference, and brought out other facts which make this system one of unusual interest.

1. THE IMMISCIBLE LIQUIDS

In the binary system, CaO–SiO_2, Greig[2] found that the limits of immiscibility are from 27.5 to 0.6% CaO. The composition of the lighter layer was estimated from the refractive index of the glass, which was 1.460+ for the liquid which separated at 1700°. Carlson[4] found the immiscibility in the system, CaO–B_2O_3, to extend from 23 to 0.2 per cent CaO. In the binary system, B_2O_3–SiO_2, there is no indication of immiscibility. Homogeneous glasses can be obtained over the entire range of composition by mixing, repeated grinding and subsequent fusion, but mixtures high in SiO_2 are difficult to obtain as homogeneous glasses because of the volatility of boric oxide at the high temperatures required.[5] The glasses have refractive indices[6] and densities[7] lower than correspond to an additive relationship between the two components.[8]

When CaO is added to the binary system, B_2O_3–SiO_2, it immediately results in the formation of a second liquid phase. CaO is almost insoluble

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[*] Presented at the New York Meeting of the Mineralogical Society, Dec. 26, 1935. Abstract, *Am. Mineral.*, vol. **21**, p. 194, 1936.

[1] Morey, G. W., *Jour. Am. Ceram. Soc.*, vol. **15**, p. 457, 1932.

[2] Greig, J. W., *Am. Jour. Sci.*, vol. **13**, p. 1, 1927.

[3] Guertler, W., *Zeit. anorg. Chem.*, vol. **40**, p. 337, 1904.

[4] Carlson, E. T., *Bur. Standards J. Research*, vol. **9**, p. 825, 1932.

[5] The glass in this system richest in SiO_2 that has been described is that containing 89.2% (Greig, *op. cit.*, p. 139).

[6] Morey, G. W., and Merwin, H. E., unpublished results.

[7] Cousen, A., and Turner, W. E. S., *Jour. Soc. Glass Tech.*, vol. **12**, p. 169, 1926.

[8] The refractive index of SiO_2 glass is 1.458 (Sosman, *The Properties of Silica*). The index of B_2O_3 is dependent on heat treatment to an unusual degree, and it may range from 1.450 to above 1.460. Wulff P. and Majumdar S. K. (*Zeit. physik. Chem.*, **B31**, p. 319, 1936) consider that the best value of the refractive index of thoroughly dehydrated and annealed B_2O_3 glass is 1.4584; but the problem has not yet received definitive study.

in the layer richer in boric oxide and silica, which is the layer of lower density and refractive index. The amount of CaO dissolved is not sufficient to raise the index to 1.46.

The amount of CaO dissolved by the lighter layer in the ternary system is indicated by the following experiments. When 0.5% CaO was added to a homogeneous glass containing 60% B_2O_3, 40% SiO_2, the cooled glass appeared solidly white. With 0.25%, the glass appeared clear and homogeneous at 1400°, but became cloudy on cooling, at a temperature probably above 1000°. A mixture containing 0.1% CaO remained clear and transparent. It is concluded that the lighter liquid at 1000° contains less than 0.25% CaO, and as the temperature is raised the CaO-content is slightly increased.
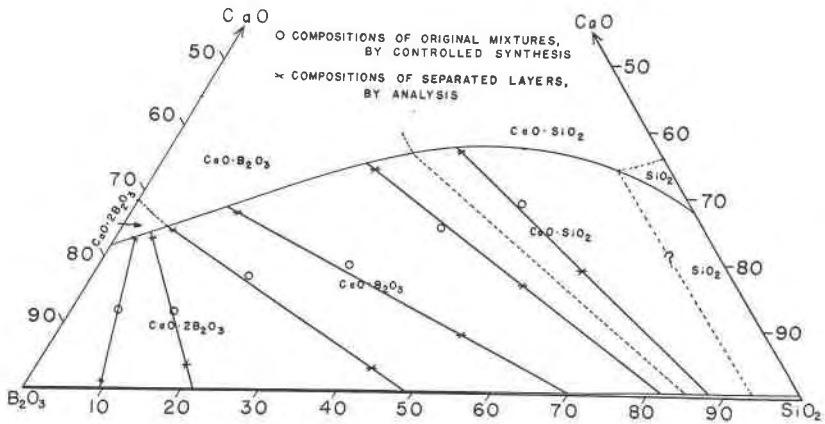

FIG. 1. The compositions of the mixtures used in determining the tie-lines, and of the two layers obtained for analysis. Each of the liquids contains some of the other phase, but the separation is much better in the CaO-rich layer.

The heavy liquid in the binary system, CaO–SiO_2, contains 27.5% CaO. As B_2O_3 is added this increases to a maximum of 38% CaO at a ratio of B_2O_3 to SiO_2 of 40% B_2O_3 to 60% SiO_2. The curve representing the composition of the heavier layer accordingly is concave toward the side B_2O_3–SiO_2, as shown in Fig. 1. For this reason it is possible to mix homogeneous glasses in the two limiting binary systems, CaO–SiO_2 and CaO–B_2O_3 containing less than 38% CaO and obtain two immiscible liquids.

On raising the temperature the CaO-content of the heavier liquid phase diminishes slightly, although the change is more evident than is the change in composition of the lighter layer. With increasing temperature the compositions of the two liquids tend to approach each other, and at a sufficiently high temperature it is possible that the two layers

would disappear in the middle of the diagram, giving rise to two critical solutions and two separated regions of immiscibility.

The compositions which separate into two liquid layers are easy to determine by making up mixtures of varying composition and observing if they give clear glasses or contain globules of a second layer of differing refractive index. The determination of the coexisting liquids themselves, that is, of the direction of the tie-lines, is not so easy. It is necessary to prepare mixtures within the region of immiscibility, to make them as homogeneous as possible by repeated heating and grinding, and to allow the two layers to separate at a temperature a little above that of coexistence with a solid phase. The separation into two layers is not always satisfactory. Mixtures containing more B_2O_3 than SiO_2 are fluid enough to give a poor to fairly clean separation of the two layers, but mixtures rich in silica are so viscous that a clean separation is not possible. The difficulty is evident from the fact that the upper layer at the melting of danburite, 1000°, contains almost 85% silica. The several tie-lines determined are shown in Fig. 1 and the compositions in Table 1.

TABLE 1

THE COMPOSITIONS OF THE MIXTURES USED IN DETERMINING THE TIE-LINES, AND OF THE
TWO LAYERS OBTAINED FOR ANALYSIS. EACH OF THE LIQUIDS CONTAINS
SOME OF THE OTHER PHASE, BUT THE SEPARATION IS MUCH
BETTER IN THE CaO-RICH LAYER

	SiO_2	CaO	B_2O_3
Original[1]	6.0	12.0	82.0
Upper	9.5	1.2	89.3[2]
Lower	2.4	23.0	74.6
Original	13.0	12.0	75.0
Upper	18.8	4.0	77.2
Lower	4.4	23.2	72.4
Original	19.7	17.7	62.6
Upper	42.5	3.9	53.6
Lower	6.1	24.2	69.7
Original	31.8	19.4	48.8
Upper	51.0	9.0	40.0
Lower	13.2	27.0	59.8
Original	40.7	25.3	34.0
Upper	55.5	16.8	27.8
Lower	27.7	34.1	38.2
Original	49.0	29.3	21.7
Upper	62.0	19.1	17.9
Lower	37.0	37.1	25.9

[1] All original compositions by controlled syntheses.

[2] B_2O_3 determined by difference in analyses of the upper and lower layers.

2. Coexistence with Crystalline Phases

When mixtures of the three components within the composition area of immiscibility are heated at sufficiently high temperatures, they separate into two liquid phases, and a vapor phase, consisting essentially of B_2O_3. This region is consequently divariant. When the temperature is lowered crystalline phases make their appearance; and the divariant region of immiscibility is bounded by several divariant regions representing equilibrium between solid, liquid and vapor. The line of contact between these regions represents equilibrium between four phases, and is consequently univariant. The compositions studied in outlining these fields, and the results of their study, are indicated in Fig. 2. The compositions of the mixtures and the details of their experimental study are given in Table 2.

Table 2

The Compositions of the Mixtures Used in Studying the Phase Equilibrium Relationships in and Adjacent to the Region of Immiscibility, and the Details of the Experimental Study

SiO_2	CaO	B_2O_3	Time	Temp.	Phases
2.0	23.7	74.3	30′	976.2	Glass
			45′	975.9	Glass
			30′	974.7	Glass+$CaO \cdot 2B_2O_3$
			45′	973.7	Glass+$CaO \cdot 2B_2O_3$
			45′	971.5	Glass+$CaO \cdot 2B_2O_3$
4.9	23.8	70.3	45′	972.3	Glass
			45′	971	Glass
			45′	969	Glass+$CaO \cdot 2B_2O_3$
			45′	968	Glass+$CaO \cdot 2B_2O_3$+$CaO \cdot B_2O_3$
6.9	24.8	68.3	30′	973	Glass
			1 hr.	972	Glass+$CaO \cdot B_2O_3$
			30′	968	Glass+$CaO \cdot B_2O_3$
10.2	30.6	59.4	10′	1029	Glass
			10′	1025	Glass
			10′	1023	Glass+$CaO \cdot B_2O_3$
			10′	1022	Glass+$CaO \cdot B_2O_2$
17.9	31.8	50.3	45′	1037	Glass
			45′	1034	Glass
			20′	1030	Glass+$CaO \cdot B_2O_3$

TABLE 2—(*Continued*)

THE COMPOSITIONS OF THE MIXTURES USED IN STUDYING THE PHASE EQUILIBRIUM
RELATIONSHIPS IN AND ADJACENT TO THE REGION OF IMMISCIBILITY,
AND THE DETAILS OF THE EXPERIMENTAL STUDY

SiO_2	CaO	B_2O_3	Time	Temp.	Phases
10.1	40.3	49.6	10'	1122	Glass
			10'	1101	Glass
			10'	1097	Glass$+$CaO$\cdot$B$_2$O$_3$
			10'	1095	Glass$+$CaO$\cdot$B$_2$O$_3$
			10'	1093	Glass$+$CaO$\cdot$B$_2$O$_3$
20.2	40.4	39.4	10'	1052	Glass
			15'	1051	Glass
			30'	1049	Glass$+$CaO$\cdot$B$_2$O$_3$
			30'	1047	Glass$+$CaO$\cdot$B$_2$O$_3$
			10'	1046	Glass$+$CaO$\cdot$B$_2$O$_3$
25	35	40	30'	1029	Glass
			1 hr.	1026	Glass
			1 hr.	1024	Glass$+$CaO$\cdot$B$_2$O$_3$
			30'	1022	Glass$+$CaO$\cdot$B$_2$O$_3$
24.9	39.8	35.3	45'	1034	Glass
			30'	1027	Glass
			30'	1020	Glass$+$CaO$\cdot$B$_2$O$_3$
			2 hr.	1019	Glass$+$CaO$\cdot$B$_2$O$_3$
			2 hr.	1017	Glass$+$CaO$\cdot$B$_2$O$_3$
29	36	35	30'	1017	Glass
			30'	1011	Glass
			30'	1009	Glass$+$CaO$\cdot$B$_2$O$_3$
			2 hr.	1007	Glass$+$CaO$\cdot$B$_2$O$_3$
30.3	40.4	29.3	10'	1007	Glass
			10'	994	Glass
			10'	992	Glass$+$CaO$\cdot$SiO$_2$
			10'	990	Glass$+$CaO$\cdot$SiO$_2$
			10'	985	Glass$+$CaO$\cdot$SiO$_2$
32.2	37.2	31.4	30'	982	2 glasses
			45'	980	2 glasses
			30'	979	2 glasses$+$CaO$\cdot$SiO$_2$$+CaO\cdot$B$_2O_3$
			30'	978.6	2 glasses$+$CaO$\cdot$SiO$_2$$+CaO\cdot$B$_2O_3$
			30'	978	2 glasses$+$CaO$\cdot$SiO$_2$$+CaO\cdot$B$_2O_3$

Table 2—(*Continued*)

The Compositions of the Mixtures Used in Studying the Phase Equilibrium
Relationships in and Adjacent to the Region of Immiscibility,
and the Details of the Experimental Study

SiO₂	CaO	B₂O₃	Time	Temp.	Phases
34.5	37.5	28.0	30′	1018	2 glasses
			1 hr.	1012	2 glasses
			30′	1011	2 glasses+$CaO \cdot SiO_2$
			30′	1007	2 glasses+$CaO \cdot SiO_2$
			20′	997	2 glasses+$CaO \cdot SiO_2$
40.2	37.1	22.7	14 hr.	1131	2 glasses
			1 hr.	1115	2 glasses
			1 hr.	1107	2 glasses+$CaO \cdot SiO_2$
			1 hr.	1097	2 glasses+$CaO \cdot SiO_2$
			1 hr.	1079	2 glasses+$CaO \cdot SiO_2$
39.0	38.6	23.4	25′	1104	Glass
			3 hr.	1088	Glass
			25′	1087	Glass+$CaO \cdot SiO_2$
			30′	1076	Glass+$CaO \cdot SiO_2$
			30′	1065	Glass+$CaO \cdot SiO_2$
39.2	39.2	21.6	30′	1156	Glass
			1 hr.	1147	Glass+$CaO \cdot SiO_2$
			1 hr.	1144	Glass+$CaO \cdot SiO_2$
			2 hr.	1133	Glass+$CaO \cdot SiO_2$
49.8	39.8	10.4	10′	1331	Glass
			30′	1312	Glass
			45′	1308	Glass+$CaO \cdot SiO_2$
			10′	1306	Glass+$CaO \cdot SiO_2$
			45′	1281	Glass+$CaO \cdot SiO_2$
49.5	36.2	14.3	1 hr.	1256	2 glasses+trace $CaO \cdot SiO_2$
			1 hr.	1248	2 glasses+$CaO \cdot SiO_2$
			1 hr.	1206	2 glasses+$CaO \cdot SiO_2$
55	35	10	1 hr.	1298	2 glasses
			30′	1294	2 glasses+$CaO \cdot SiO_2$
			2 hr.	1291	2 glasses+$CaO \cdot SiO_2$
			45′	1288	2 glasses+$CaO \cdot SiO_2$
			1 hr.	1283	2 glasses+$CaO \cdot SiO_2$
59.3	34.6	6.1	30′	1397	Glass
			30′	1377	Glass
			30′	1370	Glass
			30′	1367	Glass+$CaO \cdot SiO_2$
			1 hr.	1358	Glass+$CaO \cdot SiO_2$

TABLE 2—(*Continued*)

THE COMPOSITIONS OF THE MIXTURES USED IN STUDYING THE PHASE EQUILIBRIUM
RELATIONSHIPS IN AND ADJACENT TO THE REGION OF IMMISCIBILITY,
AND THE DETAILS OF THE EXPERIMENTAL STUDY

SiO_2	CaO	B_2O_3	Time	Temp.	Phases
61.3	33.8	4.9	1 hr.	1427	2 glasses
			40′	1409	2 glasses+SiO_2 (?)
			1 hr.	1387	2 glasses+SiO_2
			1 hr.	1368	2 glasses+SiO_2+$CaO \cdot SiO_2$

The compounds whose fields are adjacent to the region of immiscibility are: $CaO \cdot 2B_2O_3$, $CaO \cdot B_2O_3$, $CaO \cdot SiO_2$ and silica, in the forms of cristobalite and tridymite, respectively, above and below 1470°. The positions of the invariant points at which pairs of these compounds can
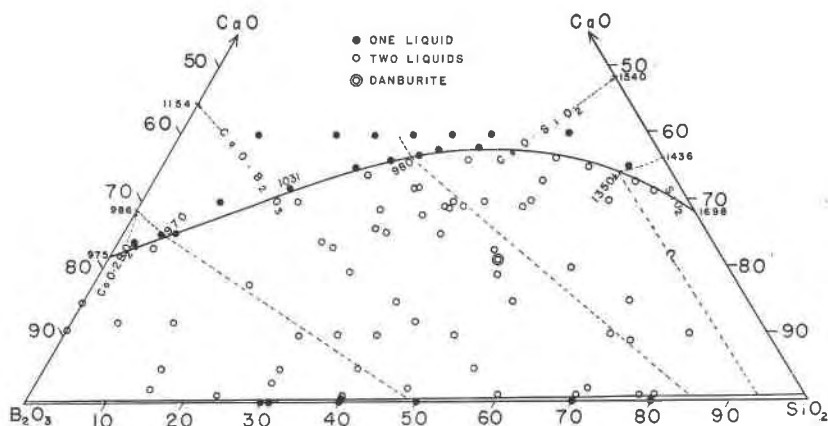
FIG. 2. The boundaries of the region of immiscibility and the adjacent fields, and the compositions of the mixtures used in their study.

coexist in equilibrium with two liquids are indicated in Fig. 2. These invariant points are quintuple points, and from each proceed five univariant equilibria. The sequence of *P-T* curves around the quintuple points may be deduced and correlated with the *T-X* diagram from general theory,[9] but in this case may be deduced from simpler considerations.

From the quintuple point $V+L_1+L_2+CaO \cdot 2B_2O_3+CaO \cdot B_2O_3$, five univariant equilibria may be obtained by the disappearance of each

[9] Morey, G. W., and Williamson, E. D., *Jour. Am. Chem. Soc.*, vol. **40**, p. 59, 1918.
Morey, G. W., *Jour. Franklin Inst.*, vol. **194**, p. 425, 1922.

one of the coexisting phases in turn. That obtained by the disappearance of the vapor phase, the curve showing the effect of pressure on the temperature and composition of the variable phases at the quintuple point, will not be considered. The equilibria obtained at this and the other quintuple points by the disappearance of the heavy liquid will be considered in detail later.

The equilibrium obtained by the disappearance of the lighter liquid, $V+L_2+CaO \cdot 2B_2O_3+CaO \cdot B_2O_3$, terminates at the binary eutectic between these two solid phases, and the temperature must rise to the side of the diagram. Similarly, that obtained by the disappearance of $CaO \cdot B_2O_3$, the temperature of the equilibrium $V+L_1+L_2+CaO \cdot 2B_2O_3$, must rise from the quintuple point to the side of the diagram. Also, temperatures must rise along the curve $V+L_1+L_2+CaO \cdot B_2O_3$, because the maximum temperature along this curve will be at the point at which the three phases $CaO \cdot B_2O_3$, L_1 and L_2 lie on a straight line. This is at about 33% SiO_2. On further change in composition, temperature will fall, until the curve ends at the quintuple point $V+L_1+L_2+CaO \cdot B_2O_3+CaO \cdot SiO_2$. The other curves which proceed from this point are: $V+L_2+CaO \cdot B_2O_3+CaO \cdot SiO_2$, along which temperatures will rise toward the line joining the two compounds; and $V+L_1+L_2+CaO \cdot SiO_2$, along which the temperature will rise to its end at the quintuple point $V+L_1+L_2+CaO \cdot SiO_2+SiO_2$. Each of the curves representing equilibria in which a solid phase is present, the curves $V+L_2+CaO \cdot SiO_2+SiO_2$ and $V+L_1+L_2+SiO_2$, go to higher temperatures as they approach their ends on the side of the component triangle.

3. The Invariant Points of the Type $V+L_1+S_1+S_2+S_3$
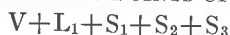
In the preceding discussion of the invariant points of the type $V+L_1+L_2+S_1+S_2$, the univariant equilibria of the type $V+L_1+S_1+S_2$ have been omitted. These are obtained by the disappearance of the heavier liquid, and their prolongation must lie within the region between the side $B_2O_3-SiO_2$ and the curve giving the composition of the lighter liquid, as indicated diagrammatically in Fig. 3. It has been shown that this liquid contains only a small quantity of CaO, less than one-fourth of one per cent at about 50 per cent SiO_2, hence the field is exceedingly narrow. Nevertheless, within this narrow strip several important phase changes must take place.

Along each of the curves representing the univariant equilibria derived by the disappearance of the heavier liquid from the several invariant points, the temperature falls until the curve terminates at an invariant point of the type $V+L_1+S_1+S_2+S_3$. These curves bound

fields within the area between the region of immiscibility and the side of the triangle, and there must be fields corresponding to each of the compounds adjacent to the curve giving the composition of the heavy liquid. These, in order of increasing SiO_2 content of the liquid, are: $CaO \cdot 2B_2O_3$, $CaO \cdot B_2O_3$, $CaO \cdot SiO_2$, and SiO_2.

The field of SiO_2 occupies a unique position. All the other crystalline phases in contact with the region of immiscibility are richer in CaO than the liquids in equilibrium with them. In the binary system, $CaO–B_2O_3$, the solid phase in equilibrium with the two liquids is $CaO \cdot 2B_2O_3$, the field of which must extend across the region of immiscibility, then fall to the (unknown) boundary of the field of crystalline B_2O_3, and the field of crystalline boric oxide cannot come into contact with the region of immiscibility. But in the binary system, $CaO–SiO_2$, the two liquid layers

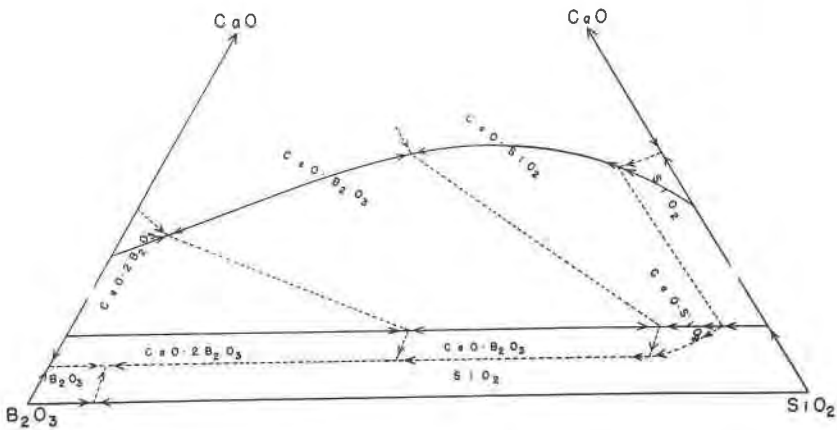FIG. 3. Diagrammatic representation of the phase equilibrium relationships in the ternary system, $CaO–B_2O_3–SiO_2$, adjacent to the region of immiscibility.

are in equilibrium with crystalline silica, cristobalite, the field of which extends on both sides of the area giving the composition of the two liquid phases. From the invariant point $V+L_1+L_2+CaO \cdot SiO_2+SiO_2$ the univariant equilibrium $V+L_1+CaO \cdot SiO_2+SiO_2$ will continue with falling temperature to its end-point at the invariant point $V+L_1+CaO-$ $\cdot B_2O_3+CaO \cdot SiO_2+SiO_2$. Below and to the right of the curve representing this equilibrium is the field of crystalline silica. Since silica must remain solid phase in the binary system, $B_2O_3–SiO_2$, until the binary eutectic is reached, the silica field extends from the SiO_2-apex until it meets the field of crystalline B_2O_3. At each of the invariant points of the type $V+L_1+S_1+S_2+S_3$ crystalline silica, in the form first of cristobalite, then of tridymite, then of quartz, is one of the coexisting solid phases.

In the narrow strip of compositions between the region of immiscibility and the side of the triangle there must, then, be a field of silica which continues to the field of B_2O_3, and between the silica field adjacent to the side and the curve giving the composition of the lighter liquid, fields of $CaO \cdot SiO_2$, $CaO \cdot B_2O_3$, and $CaO \cdot 2B_2O_3$.

We know nothing about the phase equilibrium relations in the binary system, B_2O_3–SiO_2, but from the isotherms and tie-lines in the ternary system we can make some inferences. In general the content of CaO along the boundary of the silica field cannot differ much from one-tenth of one per cent, and the CaO-content of the lighter immiscible liquid is not very different from one-fourth of one per cent. It is not probable that these "impurities" can greatly affect the freezing points, and hence that the liquidus temperatures in the binary system, B_2O_3–SiO_2, can differ much from those of the univariant equilibria $V+L_1+L_2+S_1$. From the direction of the tie-lines it is evident that the liquidus temperature must fall rapidly on addition of B_2O_3 to SiO_2, because the tie-lines terminating at about 10% B_2O_3 correspond to about 1000°. The lighter liquid at the invariant point $V+L_1+L_2+CaO \cdot 2B_2O_3+CaO \cdot B_2O_3$ contains about 55% B_2O_3, and the temperature is 900°. It is therefore to be expected that the tridymite liquidus in the binary system will be flat over the range from 10 to 55% B_2O_3, but from that point its further course is pure guesswork. The adjoining field is that of $CaO \cdot 2B_2O_3$, and the temperatures along the boundary of the two fields, the univariant equilibrium $V+L+CaO \cdot 2B_2O_3+SiO_2$, fall to the ternary eutectic at which crystalline B_2O_3 appears. This temperature is not known, but it must be low; and it may be that in the binary system, B_2O_3–SiO_2, the liquidus temperature will fall slowly until the SiO_2 content is low, then with increasing slope until it becomes almost vertical. It is a thermodynamic necessity that as the content of SiO_2 approaches zero the slope of the melting point curve shall approach infinity.

4. The Melting of Danburite

The composition of danburite is in the region of immiscibility. The mineral remains unaffected by heating until 996°, when sintering begins. When left a long time—several days—at 1002°, the compound is entirely decomposed, with formation of two liquid layers. The crystalline compound is easily superheated, and is not entirely melted in an hour at 1000°.

The melting of danburite takes place at a temperature lower than corresponds to the univariant equilibrium $V+L_1+L_2+CaO \cdot B_2O_3$, and the heavy liquid should partially crystallize to calcium borate, with change in composition of both liquids. This series of reactions can be

realized in part by long-continued heating, but complete attainment of equilibrium would require protracted heat treatment.

We have not been able to re-form danburite by heat treatment below the melting temperature, even though the materials were repeatedly finely ground and re-heated. Its synthesis is possible by hydrothermal means, and the effect of the addition of water and other components to this system is being studied.