[Contribution from the Geophysical Laboratory, Carnegie Institution of Washington]

THE CRISTOBALITE LIQUIDUS IN THE ALKALI OXIDE–SILICA SYSTEMS AND THE HEAT OF FUSION OF CRISTOBALITE

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It is desirable to know the exact course of the cristobalite liquidus curves for alkali silicate mixtures rich in silica, for two principal reasons. The first, and the more important practical reason, is that these curves might be expected to furnish a basis for the calculation of the heat of fusion of cristobalite, a quantity which has not yet been measured directly in the calorimeter. The second reason is of a theoretical nature and arises from a generalization based on the periodic table. Liquid immiscibility occurs in certain silicate mixtures rich in silica, as shown by Greig;[1] on recalculation, his results for the alkaline earth silicate mixtures in mole per cent. indicate a decreasing extent of immiscibility from MgO to SrO, that is, in the order of increasing basicity of the alkaline earth oxides. Barium silicate mixtures show no immiscibility, but present on the other hand a characteristic type of reverse S cristobalite melting curve. Owing to the great basicity of the alkali oxides, little or no immiscibility is to be expected in alkali silicate preparations, and, if found, it should be expected to decrease rapidly in the order of increasing atomic weights of the alkalies.

The papers hitherto published from this Laboratory dealing with alkali silicate systems[2] indicate that no liquid immiscibility occurs in sodium or potassium silicate mixtures at the cristobalite liquidus. The present paper deals with an extension of the study to all the alkali silicate systems in this region of temperatures. The results show that no liquid immiscibility exists in these systems, but that the two alkalies of lowest atomic weight, lithium and sodium, give rise to the reverse S type of melting point curve, which still persists slightly in the case of potassium; rubidium and cesium on the other hand give nearly ideal curves,[3] coincident when the composition is expressed in mole per cent. of the component oxides. The coincidence of the curves for rubidium and cesium lends itself to the interpretation that their slope is very nearly ideal at 100% silica, and they are accordingly employed in the calculation of the heat of fusion of cristobalite.

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[1] J. W. Greig, *Am. J. Sci.*, **13**, 1 (1927).

[2] (a) Morey and Fenner, This Journal, **39**, 1173 (1917); (b) Morey and Bowen, "The Binary System Sodium Metasilicate–Silica," *J. Phys. Chem.*, **28**, 1167 (1924); (c) Kracek, Bowen and Morey, "The System K_2SiO_3–SiO_2," *ibid.*, **33**, 1857 (1929).

See also (d) Jaeger and van Klooster, "On the Compounds of Lithium Oxide and Silica," *Proc. Acad. Sci. Amsterdam*, **16**, 857 (1914).

[3] J. H. Hildebrand, *Proc. Nat. Acad.*, **13**, 267 (1927).

Experimental Part

1. **Materials.**—The preparations employed were made from the Laboratory stock of quartz, which was converted into cristobalite before adding the alkali. Decomposition with hydrofluoric and sulfuric acids gave a residue of 4.5 mg. on a 10-g. sample. Lithium, sodium, potassium and rubidium were in the form of carbonates. Each gave the theoretical factor on conversion to nitrate and sulfate, within close limits. Cesium was available in the form of the hydroxide,[4] which was converted to the nitrate for ease in weighing. To obviate excessive loss of cesium by volatilization, pure ammonium carbonate was mixed in excess with the nitrate and silica and carefully sintered at about 250 to 300° preliminary to fusion.

2. **Preparation of Mixtures.**—The required amounts of cristobalite and the alkali salt were weighed out, thoroughly mixed and sintered to drive off carbon dioxide (or carbon dioxide and nitrogen pentoxide in the case of cesium) over a Méker burner. The sintered mass was crushed and ground several times, with sintering intervening between crushings, to insure a uniform distribution of alkali in the mixtures. There was no appreciable loss of alkali under these conditions. The mixtures were sufficiently homogeneous. The composition was checked by evaporation with hydrofluoric acid, followed usually by fuming with sulfuric acid with the addition of ammonium carbonate.

3. **Melting Point Determinations.**—These were made by the now familiar quenching method of Shepherd and Rankin,[5] in conjunction with microscopic examination, using a cascade furnace wound with platinum–rhodium wire on the inner tube, and iridium-free furnace platinum wire on the outer tube. The furnace was controlled by the Wheatstone bridge type of regulator[6] with satisfactory constancy of the high temperatures required.

The temperatures were read by means of a Pt *vs.* 90 Pt–10 Rh thermocouple, using a Feussner type Wolff potentiometer and a highly sensitive galvanometer. The thermocouple was checked frequently at the melting point of palladium, and showed very little deterioration with use, probably because of the absence of iridium in the materials of the furnace. Day, Sosman and Allen's[7] value (1549.5°) for the melting point of palladium and Adams'[8] tables were used in the conversion of e. m. f. into degrees Centigrade.

4. **The experimental results** obtained are collected in Table I, giving the composition in weight and mole per cent. of silica calculated on the basis of the component oxides, and the results of critical quenches on each preparation. The preparations were held at constant temperature for about twenty minutes, long enough to insure equilibrium in each case, at the prevailing high temperatures.

Discussion

1.—The results are shown graphically in Fig. 1, plotting the reciprocal of the absolute temperature against the logarithm of the mole per cent. of silica, assuming 1713° for the melting point of cristobalite.[9] This type of plot was selected for theoretical reasons in order to facilitate the calculation of the heat of fusion of cristobalite, considered in the next section. Scales

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[4] Kindly furnished by my colleague, G. W. Morey.

[5] Shepherd and Rankin, *Am. J. Sci.*, **28**, 293 (1909).

[6] H. S. Roberts, *J. Wash. Acad. Sci.*, **11**, 401 (1921).

[7] Day, Sosman and Allen, "High Temperature Thermometry," Carnegie Inst. of Washington, Publ. 157.

[8] L. H. Adams, THIS JOURNAL, **36**, 65 (1914); "International Critical Tables," Vol. I, **1926**, p. 58.

[9] Ferguson and Merwin, *Am. J. Sci.*, **46**, 417 (1918); J. W. Greig, Ref. 1, p. 1436.

of temperature and mole per cent. of silica have been added for ready visualization of the various systems.

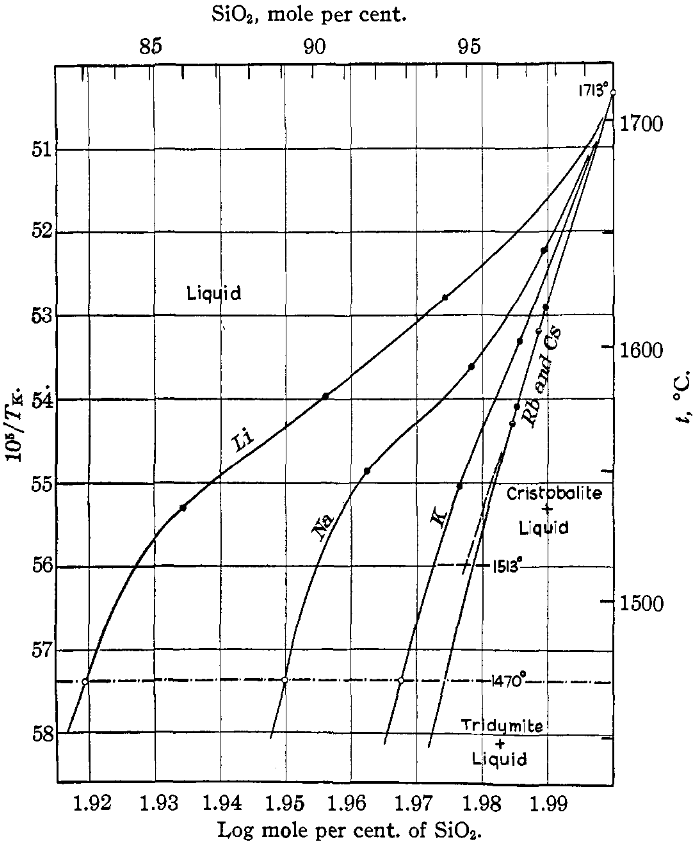

Fig. 1.—Cristobalite melting point curves for alkali silicate mixtures, plotting $1/T$ *vs.* log mole per cent. of SiO_2, with direct temperature and mole per cent. scales appended. Note the progressive change in the contour of the curves, and the coincidence of the curves for Rb and Cs.

TABLE I

RESULTS OF MELTING POINT DETERMINATIONS

No. of prepn.	Percentage of SiO_2 wt.	mole	Temp., °C.	Time, min.	Microscopic examination
	A. Li_2O–SiO_2 mixtures.				(Li_2O = 29.88, SiO_2 = 60.06)
621	92.48	85.95	1529	20	Cristobalite + glass
			1535	20	Glass + very rare cristobalite
			Liquidus 1535°		
622	94.96	90.36	1566	20	Cristobalite + glass
			1581	20	Very rare cristobalite + glass
			1583	20	Glass
			Liquidus 1581°		

Table I (*Concluded*)

No. of prepn.	Percentage of SiO_2 wt.	mole	Temp., °C.	Time, min.	Microscopic examination
623	97.01	94.17	1607	20	Cristobalite + glass
			1621	20	Rare cristobalite + glass
			1624	20	Glass
			Liquidus 1622°		
B. Na_2O–SiO_2 mixtures. (Na_2O = 61.99, SiO_2 = 60.06)					
566	91.46	91.79	1541	20	Cristobalite + glass
			1550	20	Rare cristobalite + glass
			1554	20	Glass
			Liquidus 1551°		
567	95.00	95.13	1592	20	Rare cristobalite + glass
			1595	20	Glass
			Liquidus 1593°		
568	97.50	97.57	1639	20	Cristobalite + glass
			1643	20	Rare cristobalite + glass
			1646	20	Glass
			Liquidus 1644°		
C. K_2O–SiO_2 mixtures. (K_2O = 94.19, SiO_2 = 60.06)					
286	92.01	94.76	1541	20	Cristobalite + glass
			1544	20	Rare cristobalite + glass
			1547	20	Glass
			Liquidus 1544°		
287	95.00	96.75	1599	20	Cristobalite + glass
			1602	20	Rare cristobalite + glass
			1607	20	Glass
			Liquidus 1603°		
D. Rb_2O–SiO_2 mixtures. (Rb_2O = 186.88, SiO_2 = 60.06)					
506	89.86	96.50	1559	20	Cristobalite + glass
			1567	20	Rare cristobalite + glass
			1571	20	Glass
			Liquidus 1569°		
507	92.35	97.41	1604	20	Rare cristobalite + glass
			1609	20	Glass
			Liquidus 1607°		
E. Cs_2O–SiO_2 mixtures. (Cs_2O = 281.6, SiO_2 = 60.06)					
151	86.03	96.65	1560	20	Cristobalite + glass
			1574	20	Rare cristobalite + glass
			1578	20	Glass
			Liquidus 1575°		
152	89.90	97.66	1613	20	Cristobalite + glass
			1615	20	Cristobalite + glass
			1618	20	Glass
			Liquidus 1617°		

It is seen that Li_2O–SiO_2 and Na_2O–SiO_2 mixtures present pronounced reverse S melting point curves of cristobalite. With K_2O–SiO_2 mixtures the curvature is greatly reduced, and the curve becomes normal with Rb_2O–SiO_2 and Cs_2O–SiO_2.

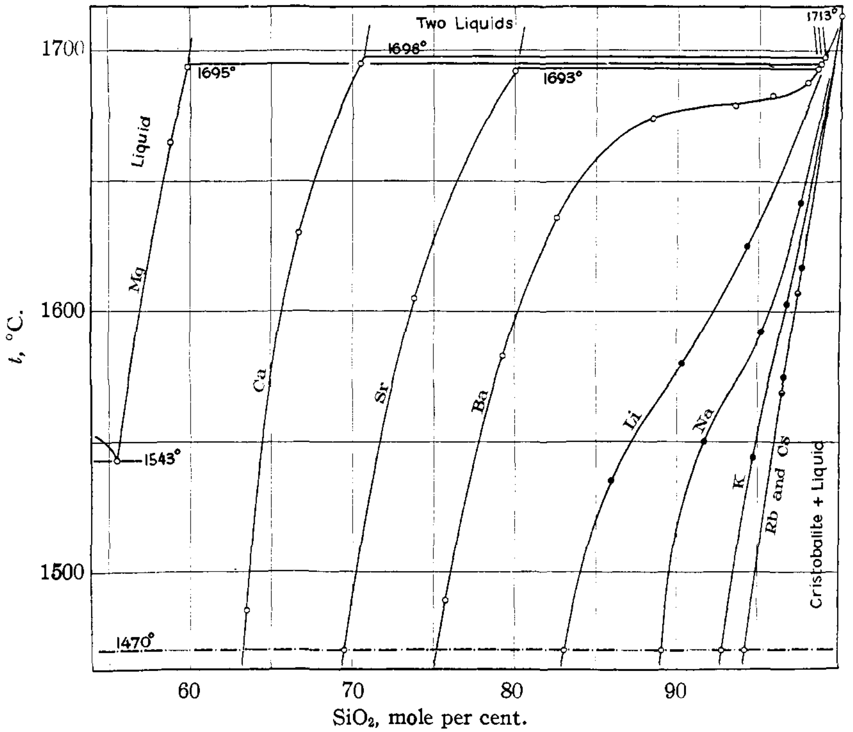

Fig. 2.—Diagram to illustrate the periodicity of the cristobalite melting point curves for the alkaline earth and alkali silicate mixtures. Full circles denote results of this investigation. Open circles taken from work published by this Laboratory. The curve for Ra would be found between Ba and Li, if Ra mixtures could be studied.

To bring out clearly the periodic progression in the change of type of melting point curves of cristobalite, the data for the alkaline earths and alkalies have been collected in Fig. 2. The experimental data[10] for the alkaline earths have been recalculated to mole per cent. on the basis of the component oxides. The black circles represent values obtained in the present investigation. The periodic relationship is obvious from the figure and need not be further enlarged upon.

2. **Heat of Fusion of Cristobalite.**—The available information on this subject has been critically considered by Sosman,[11] who comes to the con-

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[10] J. W. Greig, Ref. 1; Bowen and Andersen, *Am. J. Sci.*, **37**, 487 (1914); P. Eskola, *ibid.*, **4**, 331 (1922).

[11] R. B. Sosman, "The Properties of Silica," The Chemical Catalog Co., Inc., New York, **1927**, pp. 310–359.

clusion that the heat of fusion of cristobalite is of the order of 20 cal./g. This quantity is not easily amenable to direct measurement, and Sosman's estimate has been derived from Wietzel's[12] work on the differences between the heat of solution of cristobalite and of fused silica in hydrofluoric acid. Washburn[13] and Sosman[14] employed the eutectic in the system Al_2O_3–SiO_2. Washburn's value was based on an approximate location of the eutectic and is obviously too high. Sosman employed Bowen and Greig's[15] figures for the eutectic and obtained a value (25.9 cal./g.) somewhat smaller than that calculated in this paper. If a point on the cristobalite liquidus (3.01 mole per cent. of Al_2O_3, 1615°) is used for the calculation, the result is 38.7 cal./g.

Inspection of Fig. 1 shows that the cristobalite liquidus $1/T$ *vs.* log mole per cent. of silica curve is very nearly straight for at least 100° below the melting point of cristobalite in the Rb_2O–SiO_2 and Cs_2O–SiO_2 systems. This straight line was produced to 1513°, where the melting point lowering, ΔT, is 200°. The corresponding value of log mole per cent. of SiO_2 = 1.9774. Applying the Schröder–Le Chatelier[16] formula for ideal solubility in the form

$$L_f = \frac{4.578\ T\ T_0}{\Delta T} \log \frac{X_0}{X}$$

where L_f is heat of fusion, T_0 is absolute melting point of cristobalite, 1986°K., T is $1513 + 273 = 1786$°K. and $\log X_0/X = 2 - 1.9774 = 0.0226$, the value 1835 cal./mole or 30.5 cal./g. is obtained.

This calculation is made on the basis of the moles of the component oxides present in the mixtures, as has already been stated, rather than on the assumption of the existence of definite compounds in the melts. It is not improbable that compound formation does take place to some extent in these melts, even at the temperatures of the cristobalite liquidus, but since silicates are essentially additive compounds whose dissociation increases with rising temperatures, and since even the metasilicates of the alkalies are considerably dissociated at their melting points,[17] it seems reasonable to suppose that no important amount of any alkali silicate is present at the temperatures and compositions in question. This assumption gains some weight on consideration that silica behaves as a non-polar liquid (dielectric constant at 25° = 3.2 to 3.9) at high temperatures, in its tendency to form two liquid layers with many highly polar oxides in solution.

Many physical constants of silica have apparently anomalous values, and in this respect the heat of fusion of cristobalite forms no exception. The

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[12] R. Wietzel, *Z. anorg. allgem. Chem.*, **116**, 71 (1921).

[13] E. W. Washburn, *J. Am. Ceram. Soc.*, **2**, 1007 (1919).

[14] R. B. Sosman, Ref. 11, p. 358.

[15] Bowen and Greig, *J. Am. Ceram. Soc.*, **7**, 238 (1924).

[16] I. Schröder, *Z. physik. Chem.*, **11**, 449 (1893); H. Le Chatelier, *Compt. rend.*, **118**, 638 (1894).

[17] Morey and Bowen, *J. Phys. Chem.*, **28**, 1167 (1924).

ratio of the molar heat of fusion to the absolute melting point, L_f/T_0 for cristobalite, 1835/1986 = 0.924 is exceptionally small, and falls below that of the normal (non-polar) substances carbon tetrachloride (2.49) and methane (2.58).

3. Concluding Remarks.—The errors in the determinations given in this paper are estimated to be within 0.10% interval in composition and a 5° interval in temperatures based on the scale used in this Laboratory. This precision is possible, and can be exceeded, principally through the use of the static method of quenching[5] and its attendant technique, which makes it possible to attain equilibrium in the sample at each point, and hence does not depend upon heat effects or the velocity of formation or solution of crystals, characteristic of dynamic methods of melting point determination. It would be idle to claim that high precision is always attained in quenching work, nor is it always aimed at. In many cases crystals grow or dissolve very slowly, or the melt may be so viscous that diffusion of the dissolved material into the melt takes place extremely slowly; in other cases moderate precision suffices to establish the course of a curve within close enough limits. In the present instance comparison may be made with the results of Morey and Bowen[2b] for the system Na_2SiO_3–SiO_2 and of Kracek, Bowen and Morey[2c] for the system K_2SiO_3–SiO_2. In each of these systems one point had been established on the cristobalite liquidus, namely, at 4.07 wt. per cent. of Na_2O, 1596°, and at 4.5 wt. per cent. of K_2O, 1638°. The point in the Na_2O system lies practically upon the newly determined curve, while that in the K_2O system lies above the curve, which is found to pass through 1627° at the given composition. The agreement is considered adequate in view of the fact that only moderate accuracy was attempted in locating the latter point.

It is hoped that the results given in this paper will help in gaining a wedge with which to attempt to open the question of the chemical behavior and nature of silica. It seems assured that vitreous silica behaves as a fairly normal, non-polar liquid of comparatively low ionizing power at high temperatures, judging from the results obtained; data on the conductivity of vitreous silica itself are, however, of such conflicting nature that no conclusions can be drawn from them respecting vitreous solutions.

Summary

The melting point curves of cristobalite in silica-rich mixtures of Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O with SiO_2 have been determined and the characteristics of these curves have been discussed.

The heat of fusion of cristobalite has been calculated as 30.5 cal./g. from the melting point lowering of cristobalite by Rb_2O and Cs_2O.

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