Phase Equilibrium Relations in the System, Na_2SiO_3–Li_2SiO_3

By F. C. Kracek

The experimental investigation reported upon in this article is a continuation of the work of this Laboratory on phase equilibrium relations in silicate systems involving one or more alkalies. The system described is a binary section within the ternary system, Na_2O–Li_2O–SiO_2, which is now under investigation, in preparation for a study of the mineralogically more interesting relationships of the sodium and lithium aluminosilicates.

The two metasilicates, Na_2SiO_3 and Li_2SiO_3, cocrystallize in two series of solid solutions with intermediate compound formation, one series extending from Na_2SiO_3 to $NaLiSiO_3$, while the other, a limited series, is at the Li_2SiO_3 end of the system, with Na partially replacing Li in crystalline Li_2SiO_3.

The freezing point relations in this and several other binary systems of silicates were investigated by Wallace[1] in Tammann's laboratory, by the method of cooling curves, supported by microscopic examination. It is now well realized that the results of cooling curve thermal analysis must be interpreted with care, even with rapidly crystallizing substances; with silicates, the arrest temperatures are always found to be too low in comparison with the equilibrium values as determined by quenching.[2] The reason for this lies in the reluctance with which most silicates crystallize. Although, in the system under discussion, the crystallization is comparatively rapid, the temperatures as determined by cooling curves are below the equilibrium values by as much as 72° for mixtures at the Na_2SiO_3 end of the system.

Wallace concluded from his data that mixtures of the two components crystallize together in a complete series of solid solutions with a minimum on the freezing curve between 40 and 50% Li_2SiO_3, and noted that, under the microscope, the crystalline phase changed at about 20 to 30% Li_2SiO_3 from Na_2SiO_3-like to Li_2SiO_3-like aspect. As no measurements of the refractive indices are presented, these observations have only qualitative value at the present time.

Experimental Details

The mixtures of sodium and lithium metasilicates employed in this work were synthesized by fusing together pure silica, sodium and lithium carbonates in the required proportions. The fusions were made in platinum crucibles. The reagents used were: (1) purified quartz, first converted to cristobalite by heating in a gas furnace at about 1500° to enhance its reactivity in the fusions. It left a residue of 0.03% after evaporation with hydrogen fluoride and sulfuric acid. (2) Reagent grade $Na_2CO_3 \cdot H_2O$, converted to sodium carbonate by drying at about 250° in an atmosphere containing carbon dioxide. Analysis by E. G. Zies gave 0.001% of $Fe_2O_3 + Al_2O_3$, 0.001% of CaO, and negligible amounts of other impurities. (3) Reagent grade lithium carbonate, stated to contain 0.003% $Fe_2O_3 + Al_2O_3$ and only a trace of Na.

A standardized method of fusing the mixtures was employed for the reason that, unless special precautions are taken, the lithium carbonate present, on melting in air, corrodes platinum with the formation of a greenish to black deposit which tends to crawl over the surface of the crucible. Experiments show that the attack is not caused by the lithium carbonate itself, as fusions of this carbonate in a carbon dioxide atmosphere have no appreciable action on platinum. Another reason for exercising special care in making the fusions is that mixtures of sodium carbonate and lithium carbonate begin to melt as low as 510°,[3] and when silica is present, vigorous bubbling and mechanical losses may occur at very low temperatures.

The procedure adopted is to heat the mixtures in covered crucibles over a small Méker burner to incipient fusion until a large part of the carbon dioxide in the charge is driven off. The temperature is then raised slowly to complete the fusion. The carbon dioxide from the burner provides a sufficiently inert atmosphere to prevent the corrosion of the crucibles. In order to expel the carbon dioxide completely, the charges must be heated finally in a carbon dioxide-free atmosphere, such as that of an electric furnace; access of oxygen to the charges at this stage is no longer harmful because the alkali is now well incorporated in the melt. Precaution must, however, be taken to avoid excessive volatilization of the alkali. Instead of heating to a high temperature, and allowing the carbon dioxide to escape by diffusion and bubbling, the desired result may be accomplished more safely by crystallizing the melt, which causes the carbon dioxide to be forced out during the last stages of the crystallization. For this purpose the crucibles are alternated between two electric furnaces, one kept at a temperature high enough to produce complete melting, the other at a temperature sufficiently lower to allow the melt to crystallize. About five successive crystallizations and remeltings suffice to expel the carbon dioxide completely from the mixtures in this system.

(1) R. C. Wallace, Z. anorg. Chem., **63**, 1 (1909).

(2) E. S. Shepherd, G. A. Rankin and F. E. Wright, Am. J. Sci., **28**, 293 (1909).

(3) W. Eitel and W. Skaliks, Z. anorg. allgem. Chem., **183**, 263 (1929).

TABLE I

EQUILIBRIUM DATA[a] FOR THE SYSTEM Na_2SiO_3–Li_2SiO_3

Composition in weight, per cent.		Refr. index of quenched glass ± 0.003	Temperature, degrees, °C. ± 0.5°						Ref. no.
			Liquidus		Solidus		Peritectic		
Na_2SiO_3	Li_2SiO_3		g + c	g	c	c + g	Below	Above	
Primary Phase: Solid Solution, Na_2SiO_3 to $NaLiSiO_3$									
100.0	0.0	1.517	1089		1089				574
90.0	10.0	1.527	1022	1024	975	983			664
85.0	15.0	1.528	987	988	919	927			783
			987h						
80.0	20.0	1.529	954	955	882	892			665
76.5	23.5	1.529	930	931	863	868			782
			925h						
73.1	26.9	1.530	905	907	851	854			725
70.0	30.0	1.532	885	886	848	849			666
67.5	32.5	1.534	869	870	848	849			741
66.0	34.0	1.534	861	862	847	848			745
64.0	36.0	1.536	851	853	845	..			736
64.0	36.0	1.537	851	852	845	846			779
62.0	38.0	1.536	846	847	845	846			744
61.2	38.8	1.538	846	847	845	..			781
60.7	39.3	1.539	..	..	845	..	846	848	
Primary Phase: Li_2SiO_3 Limited Solid Solution									
60.7	39.3	1.539	848	848	845	..	847	848	778
60.0	40.0	1.538	852	855	845	846	847	848	667
59.0	41.0	...	860	862	846	847	847	..	777
57.57	42.43	1.539	872	873	847	..	847	..	737
57.57	42.43	1.539	872	874	846	..	..	848	742
57.57	42.43	1.540	872	873	847	..	847	848	776
57.0	43.0	1.540	877	878	..	..	847	848	780
50.0	50.0	1.542	931	935	..	..	846	848	668
40.0	60.0	1.545	998	1004	..	..	846	848	669
			1005h						
30.0	70.0	...	1072h		..	..	847	..	670
20.0	80.0	...	1125h		..	..	..	848	671
15.0	85.0	...	1147h		860	880			793
10.0	90.0	...	1169h		970	990			672
5.0	95.0	...	1185h		1077	1092			792
0.0	100.0	1.557	1201		1201				602

[a] All preparations were pre-crystallized for quenching. Under the headings "Liquidus" and "Solidus" the letter "c" denotes crystals alone, and "g" glass alone, in the quenched samples. "c + g" or "g + c" denotes the presence of both glass and crystals; "h" denotes determinations by heating curve thermal analysis.

Slight losses of alkali by volatilization occur in spite of the precautions, particularly from mixtures of more than 70% lithium metasilicate. These losses, which may be as much as 0.1% of the total weight of the charge, appear to be mainly due to lithium oxide. To compensate for them a small excess of lithium carbonate is weighed out in preparing the mixtures, in accordance with a previously determined estimate. This method of compensating for the losses was found to be preferable to the alternative one of adding a small amount of the desired constituent after the mixture had been prepared, as it avoids a number of additional reheatings.

The compositions of the mixtures are known from the initial and final weights during the synthesis. They were in all cases within 0.10% of the desired values. Any departure toward ternary compositions could have been detected under the microscope by the presence of more than traces of residual glass in quenches from temperatures which are below the lowest point on the solidus in the binary system, but above the eutectics in the ternary system.

The liquidus and solidus relations were determined mainly by quenching in mercury. It was found, however, that in compositions of more than 60% lithium metasilicate, the equilibrium at the liquidus cannot be satisfactorily quenched, because of rapid crystallization of lithium metasilicate. The quenching determinations in this region were supplemented by heating curves, where use was made of a special technique which was described in an earlier paper,[4] and in which a thimble crucible with a centrally reëntrant sheath for a differential thermocouple provides an accurately centralized location of the junction in the melting charge.

The temperatures were measured by calibrated Pt vs. 90 Pt–10 Rh thermocouples connected to a shielded potenti-

(4) F. C. Kracek, N. L. Bowen and G. W. Morey, J. Phys. Chem., 41, 1183 (1937).

ometer system. The conversion of the thermocouple readings to degrees was made with the aid of standard tables.[5] The furnaces used in the quenching work were thermostatically controlled with a precision of ±0.3 to 0.5° at the various required temperatures. In short runs (up to three hours) the precision was somewhat closer, but in long runs it approached the value given.

Equilibrium in the various charges was reached in approximately one hour, but two hours were usually allowed in the study of the liquidus relations. For the solidus the runs lasted a day or more in testing certain questions that arose during the course of the work.

Experimental Results

The essential thermal measurements are presented in Table I, as determined by quenching, and, for a few of the preparations, by heating-curve thermal analysis. The latter determinations are distinguished by the letter "h." The quenching results are presented by listing the two nearest temperatures determined above and below the transformation point in question for each composition, rather than by giving a detailed abstract of the experimental record.

The Phase Equilibrium Diagram

Figures 1 and 2 represent the phase equilibrium relations in the system (at atmospheric pressure). Instead of a complete series of solid solutions with a minimum on the liquidus, as outlined by Wallace,[1] there is an incongruently melting intermediate compound, NaLiSiO₃, and two series of solid solutions. One of these series extends from Na₂SiO₃ to NaLiSiO₃; the other is a Li₂SiO₃-rich solid solution, the composition limits of which lie between 83 ± 3 and 100% Li₂SiO₃.

The compound, NaLiSiO₃ (42.43% Li₂SiO₃), at its incongruent melting point of 847 ± 1°, decomposes into a melt, containing 39.3 ± 0.2% of Li₂SiO₃, and the above-mentioned Li₂SiO₃-rich solid solution. The extent of the peritectic line giving the compositions of these phases is determined by the measurements on the liquidus, on the one hand, and by a search with the microscope, on the other hand, for the presence of two kinds of crystals in quenches from below the peritectic, in

compositions near the Li₂SiO₃ end of the system. At 85% Li₂SiO₃, only Li₂SiO₃-like crystals were found; at 80%, in addition to these, there was present a small quantity of NaLiSiO₃. The position of the solidus curve for the Li₂SiO₃-rich solid solutions, as determined by quenching, must be regarded as only approximate, because of the difficulty of quenching the interstitial glass.

Above the peritectic, the liquidus for the Li₂SiO₃-rich solid solutions rises smoothly to the melting point of Li₂SiO₃ at 1201 ± 1°.[6]

Between Na₂SiO₃ and the end of the peritectic line the liquidus and solidus relations are as illustrated in Figs. 1 and 2, the crystalline phase being
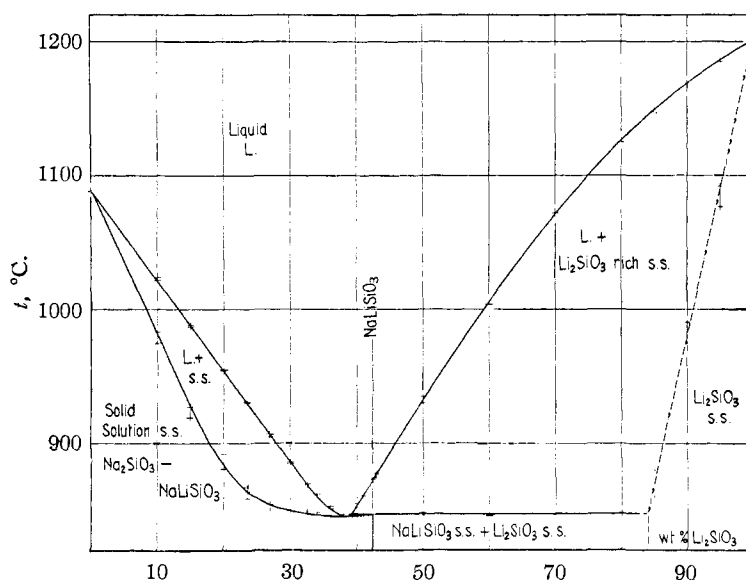

Fig. 1.—Equilibrium diagram for the system, Na₂SiO₃–Li₂SiO₃. Liquidus determinations, 60.0 to 100.0% Li₂SiO₃ by heating curve thermal analysis. All other determinations by quenching.

a continuous series of solid solutions whose composition varies from Na₂SiO₃ to NaLiSiO₃. Beginning at the melting point of Na₂SiO₃, 1089 ± 1°,[7] the liquidus and the solidus curves first drop, and follow their courses separately to meet again at the minimum point, 38.5 ± 0.2% Li₂SiO₃, 845 ± 1°. From the minimum point the liquidus curve rises to the end of the peritectic line, 39.3% Li₂SiO₃, 847 ± 1°. The solidus also rises to the peritectic, but meets it at the composition of the compound, NaLiSiO₃. The solid solution series becomes saturated at this composition, or, at the

(5) L. H. Adams, "International Critical Tables," Vol. 1, 1926, p. 57.

(6) F. M. Jaeger, J. Wash. Acad. Sci., 1, 49 (1911); A. L. Day. R. B. Sosman and E. T. Allen, "High Temperature Gas Thermometry," Carnegie Inst. Wash. Pub., 157, 101 (1911).

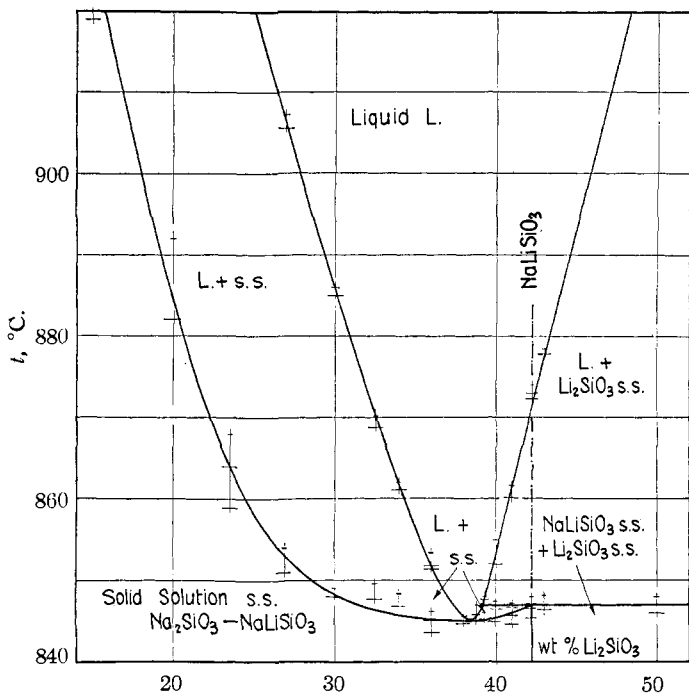(7) F. M. Jaeger, ref. 6; F. C. Kracek, J. Phys. Chem., 34, 1583 (1930).

Fig. 2.—Portion of the equilibrium diagram for the system, Na_2SiO_3–Li_2SiO_3, enlarged to demonstrate the phase relations in the neighborhood of the minimum on the liquidus.

most, only a few tenths of a per cent. beyond, since quenches of this composition from below the peritectic contained only the one kind of homogeneous crystals, while those of 43.0% Li_2SiO_3 contained, in addition, a definite quantity of the Li_2SiO_3-like crystals of the other series of solid solutions.

To establish the properties of the crystalline phase (or phases) in this region, we have examined, microscopically, quenched samples of the various compositions, first completely crystallized, and then brought to equilibrium by long annealing at temperatures both above and below the solidus.[8] Only one equilibrium crystalline phase could be found. Its refractive indices were found to vary continuously with the composition, as would be expected for a continuous series of solid solutions. This is illustrated in Fig. 3. The results of these optical measurements agree with the thermal data on the liquidus and solidus, and exclude from consideration the possibility of any type of eutectic relations in the system.

Optical Properties of the Various Phases

During the course of the work we have measured the refractive indices of the glasses and the

(8) I am indebted to my colleague H. E. Merwin for much valuable help on this question.

crystals in the quenched samples. The data for the glasses are listed in Table I. No measurements could be made on annealed glasses, since all the vitreous preparations within the system devitrify rapidly at annealing temperatures. The value for Na_2SiO_3 glass, 1.517, is interpolated from the data of Morey and Merwin.[9]

The refractive indices of the various phases are plotted against the composition in Fig. 3.

The optical properties of crystalline Na_2SiO_3 and Li_2SiO_3 are already known.[10]

The properties of $NaLiSiO_3$, end-member of the Na_2SiO_3–$NaLiSiO_3$ series of solid solutions, as measured by H. E. Merwin, are:

Orthorhombic prisms with two good lengthwise cleavages; elongation ∥ to γ; near endwise sections crystals show acute bisectrix or an optic axis, 2V very large. Refractive indices for Na light: γ 1.571, β 1.557, α 1.552, all within about 0.002.

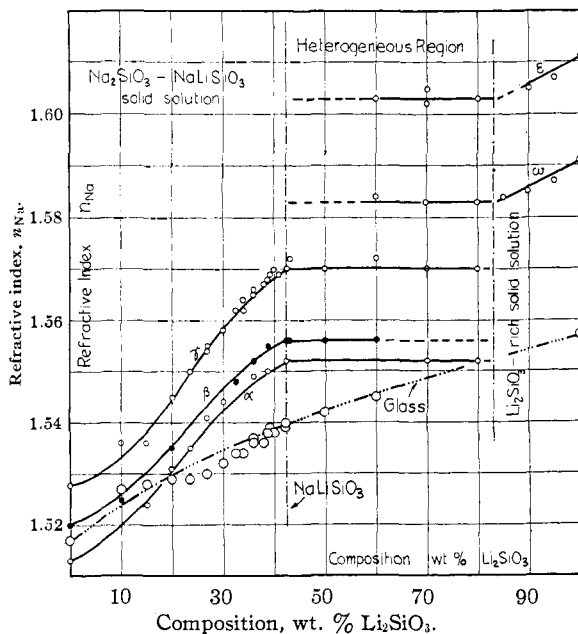In cleavage splinters, crystals of this compound bear a superficial resemblance

Fig. 3.—Representation of the refractive indices of the various phases in the system, Na_2SiO_3–Li_2SiO_3, as a function of the composition.

(9) G. W. Morey and H. E. Merwin, J. Optical Soc. Am., 22, 632 (1932).

(10) Na_2SiO_3: G. W. Morey and N. L. Bowen, J. Phys. Chem., 28, 1167 (1924). Li_2SiO_3: F. M. Jaeger, Proc. K. Akad. Wet. Amsterdam, 16, 857 (1914); measurements by H. E. Merwin, in F. C. Kracek, J. Phys. Chem., 34, 2647 (1930).

to Li_2SiO_3, in spite of their lower indices of refraction. This resemblance is due to (1) a similarity of the cleavage habit, (2) similarity in the orientation with respect to the indices of refraction, and (3) comparable magnitudes of the birefringence, that of $NaLiSiO_3$ being somewhat smaller. It explains, at least in part, why Wallace[1] found crystals resembling Li_2SiO_3 in compositions as low as 30% Li_2SiO_3. However, crystals of the Li_2SiO_3-rich solid solutions sometimes are formed from the melt in mixtures of Li_2SiO_3 content lower than 39.3%, the equilibrium termination of the liquidus for this phase at the peritectic (see Fig. 2). Such crystals are metastable, and are formed occasionally when a melt is cooled rapidly to a temperature below the metastable extension of this liquidus. In the completely crystallized preparation they remain as inclusions within crystals of the stable Na_2SiO_3–$NaLiSiO_3$ solid solution. On reheating they redissolve before the solidus temperature is reached, and the preparation recrystallizes to the stable solid solution phase.

Acknowledgment.—I am indebted to my colleague H. E. Merwin for measurements of the optical properties of the compound, $NaLiSiO_3$,

and for help in various other parts of this work.

Summary

The binary system, Na_2SiO_3–Li_2SiO_3, a binary section within the ternary system, Na_2O–Li_2O–SiO_2, contains an intermediate compound, $NaLiSiO_3$, which melts incongruently at 847 ± 1°. The liquidus consists of two branches. One of these begins at the melting point of Na_2SiO_3, 1089 ± 1°, falls to a minimum at 38.5 ± 0.2% Li_2SiO_3, 845 ± 1°, and then rises to its junction with the other branch at the peritectic point 39.3 ± 0.2% Li_2SiO_3, 847 ± 1°. The second branch of the liquidus rises from the peritectic point to the melting point of Li_2SiO_3, 1201 ± 1°. The primary phases in equilibrium with the liquid are two series of solid solutions. The first series extends from Na_2SiO_3 to $NaLiSiO_3$; the second series is a limited one, and ranges in composition from 83 ± 3 to 100% Li_2SiO_3. The optical properties of the various phases have been measured, and are reproduced graphically in a diagram giving the variation of the refractive indices with the composition.

"Effective Electron Density" and Chemical Behavior[1]

BY HEOU-FEO TSEOU

In a previous exposition a theory was proposed by us for the explanation of various types of organic reactions.[2] The purpose of the present paper is to show the concordance which it bears to the chemistry of other elements than carbon.

The essential idea of the theory was that as concerned with chemical properties an element may be imagined not to occupy a fixed position in the periodic table but it changes as the position of a part of the outer electrons is affected by certain adjoined atoms or groups of atoms; an inward shift causes a displacement of the element to the right side in the periodic series, while an outward shift displaces it toward the left side. The

change as stated should be most conspicuously reflected in a change of its effective atomic radius which corresponds to what we call a compact or open octet.[3] If this statement is universally true, then it would follow as a logical sequence that, in passing through a periodic series, a constant decrease in atomic radius will be observed as the atomic number of the elements increases. To testify to the validity of the statement the atomic dimensions of the first three short periods are collected in Table I.

A glance at the table will show immediately that these values arranged in the descending order fit in nicely with our postulate. Note should be taken that these are the dimensions of covalent linkages, which are what we have uniquely dealt with in organic reactions. These measurements

(3) The change of atomic radius of the carbon atom in different organic compounds as shown to be complying with the author's postulation rules is given in a table in the chapter "Evidence of Physical Measurements."