ment of these projections by familiar methods of successive approximations lead to the complete determination of the structure (Figs. 1 and 2). The parameter data of Table III account satisfactorily for the intensities of X-ray reflections (Table II) and lead to generally reasonable interatomic distances (Table IV).

The structure (Fig. 2) is an aggregate of K^+ ions, $Mo(CN)_8^{-4}$ ions, and water molecules. The configuration of the $Mo(CN)_8$ group (Fig. 3) seems to be stereochemically very reasonable. The $Mo(CN)_8$ polyhedron is a duodecahedron with eight vertices and triangular faces. Although required by the space group to possess only a plane of symmetry, the complex ion in the crystal approximates to the symmetry of the point group D_2^d–$\bar{4}2m$.

ITHACA, N. Y. RECEIVED JULY 20, 1939

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Phase Equilibrium Relations in the System, Na_2SiO_3–Li_2SiO_3–SiO_2*

BY F. C. KRACEK

The work described in this paper concerns itself with the general equilibrium relations at one atmosphere pressure in the system Na_2SiO_3–Li_2SiO_3–SiO_2, and comprises the experimental determination of the temperatures at which the various crystalline phases are in equilibrium with one another, and with melts of the appropriate composition. The crystallization relations are comparatively simple, being only slightly complicated by the occurrence of solid solutions arising from a partial mutual replacement of sodium and lithium in the silicate compounds. Only one ternary compound is present in the system. This is $NaLiSiO_3$, formed by replacement of Li for Na in Na_2SiO_3; it is the Li-rich limit of the solid solution series $(Na_2,NaLi)SiO_3$. The other silicates in the system, Li_2SiO_3, $Na_2Si_2O_5$, and $Li_2Si_2O_5$, all form solid solutions of only limited extent.

Experimental Methods

The methods of study were in all respects similar to those already made familiar through the publications of this Laboratory on phase equilibrium relations. The liquidus and other significant temperatures were determined by quenching combined with microscopic examination,[1] except in compositions high in lithium metasilicate which crystallize too rapidly for the quenching technique to be effective. In such cases the temperatures were established by heating curve thermal analysis for the liquidus, and by both heating and cooling curve methods in studying transition phenomena.[2]

Homogeneous glasses of the various compositions in the system were prepared from purified silica, used in the form of cristobalite derived from powdered quartz heated at 1500°, and from reagent grade lithium carbonate and sodium carbonate. Analyses proved the reagents all to be of high purity.[3] The preparations were made up quantitatively from the thoroughly dried reagents, special care being taken to avoid losses, either mechanical, or by volatilization. Losses by volatilization were negligible except in the lithium metasilicate region of the system, where they approached 0.1% of the weight of the preparation. They were almost entirely of lithium, and could be compensated for by small additions of lithium carbonate to the original mixture. The fusions were made in platinum crucibles. To avoid attack on the crucibles by the corrosive melts of the easily fusible carbonate mixtures, it is necessary to exclude oxygen during the initial stages of the heating, until the reaction of the melt with the silica has absorbed most of the free alkali present. This was done by heating the mixtures in covered crucibles over carefully controlled Méker burners (the more convenient initial sintering of the mixtures by heating in electric furnaces always resulted in bad attack on the crucibles), the temperature being kept at the point of incipient fusion until most of the carbon dioxide was driven off. The final heatings were

* Presented before the Division of Physical and Inorganic Chemistry at the 98th meeting of the American Chemical Society, Boston, Mass., September, 1939.

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

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

(3) See F. C. Kracek, THIS JOURNAL, **61**, 2157 (1939), for analyses of reagents and further experimental details.

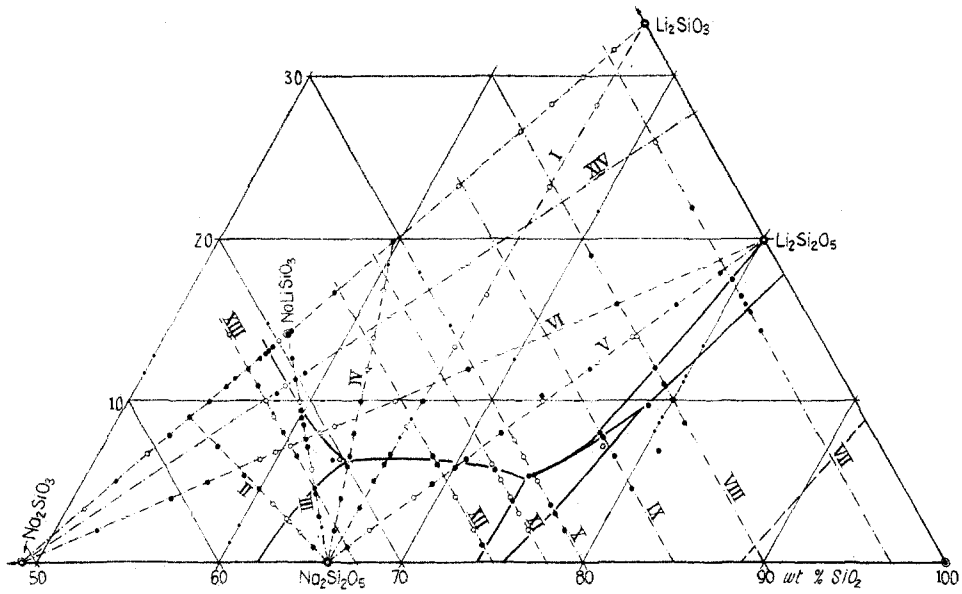

Fig. 1.—Ternary diagram of the system, Na_2SiO_3–Li_2SiO_3–SiO_2, showing the equilibrium fields at the liquidus, and location of the experimental points. Black dots represent compositions for which refractive indices of glasses are included in Table I.

made in electric furnaces in the usual manner, keeping the temperature as low as possible, consistent with complete displacement of the carbon dioxide. The more alkali-rich glasses were crystallized several times during the process, to drive off the carbon dioxide at lower temperatures, and thus to avoid losses by volatilization. The safe maximum temperatures, at which losses are negligible, are roughly, 1100° in the metasilicate, and 1300° in the disilicate regions of the system.

The temperatures were measured by means of platinum against platinum–10% rhodium thermoelements, using a shielded Feussner potentiometer system. The readings of the calibrated thermoelements were converted into temperatures on the Day and Sosman gas thermometer scale with the help of standard tables.[4]

The temperatures of the quenching furnaces were controlled automatically with a precision of ±0.3 to ±0.5°. The time of the individual runs, several of which are needed for each determination by the quenching method, varied from one hour to several days, depending upon the speed with which equilibrium is reached in the different regions of the system. This is most rapid for the metasilicates, and slowest for quartz at the Na_2O–SiO_2 side-line. The rate of dissolution of quartz increases rapidly with even small additions of lithium and, within the system, the reactivities of quartz and tridymite are sufficiently high to permit their mutual conversion (quartz $\rightleftarrows$ tridymite) near the inversion temperature in about twenty-four hours. This has made it possible to redetermine the inversion temperature with somewhat less uncertainty than before.

In presenting the experimental results below, certain minor revisions of previously published data are made. Such revisions are primarily based on very frequent recalibrations of the thermoelements, combined with a general improvement both in apparatus and technique (see ref. 2). Particular attention was given to the attainment of equilibrium in the charges. This is especially important in the cases of the more sluggish reactions, such as the mutual conversion of quartz and tridymite, and the various eutectic meltings, where certain phases tend to persist above the reaction temperatures for considerable periods of time. The measured limits of uncertainty of each determination are given by means of a ± bracket, or by quoting the measured temperature limits, as the case may be.

Experimental Results

The distribution of the compositions studied in the ternary system is represented in Fig. 1, which also shows the boundary curves between the fields. The experimental points are located mainly along certain sections across the ternary

(4) L. H. Adams, "International Critical Tables," Vol. I, 1925, p. 57.

system, chosen so as to present a net of points which would allow for easy interpolation in deriving the liquidus surfaces for the various primary phases. These sections are numbered in the figure by Roman numerals to correspond with the numbering of the sections in Table I. This table contains the experimentally determined temperatures for the various phase reactions. The temperatures given are the nearest determined temperatures, above, and below, the transformation point in question—in other words, the phase reaction temperature lies between the values given. Most of the measurements represent determinations of the liquidus temperatures; at appropriate places in the table, however, temperatures for other phase reactions,

TABLE I

RESULTS OF EQUILIBRIUM MEASUREMENTS IN THE SYSTEM, Na_2SiO_3–Li_2SiO_3–SiO_2

No.	Wt. % B	Na_2O	Li_2O	SiO_2	Measured limits Liquidus temp. °C. Below	Above	Cryst. phases	Refr. index quenched glass
			I. Binary Section: A = $Na_2Si_2O_5$; B = Li_2SiO_3					
31	10.0	30.61	3.31	66.08	790	792	$Na_2Si_2O_5$	1.513
32	15.0	28.94	4.98	66.08	743	746	$Na_2Si_2O_5$	1.517
33	18.0	27.92	5.98	66.10	719	720	$Na_2Si_2O_5$	1.521
					709	710	$Na_2Si_2O_5$ + Li_2SiO_3 binary eutectic	
34	20.0	27.23	6.64	66.12	721	727	Li_2SiO_3	1.521
35	25.0	25.53	8.30	66.17	794	795	Li_2SiO_3	...
36	30.0	23.80	9.95	66.25	850	852	Li_2SiO_3	1.527
37	40.0	20.38	13.23	66.39	941	942	Li_2SiO_3	...
38	50.0	17.00	16.50	66.50	1011	1015	Li_2SiO_3	...
39	70.0	10.2	23.2	66.6	1111 h[a]		Li_2SiO_3	...
40	85.0	5.1	28.2	66.7	1164 h[a]		Li_2SiO_3	...
			II. Ternary Section: A = $Na_2Si_2O_5$; B = (theor.) $Na_4Li_2Si_3O_9$					
41	10.0	34.35	0.89	64.76	845	846	$Na_2Si_2O_5$	1.509
42	20.0	34.65	1.79	63.56	814	816	$Na_2Si_2O_5$	...
43	28.0	34.90	2.50	62.60	789	790	$Na_2Si_2O_5$	...
					781	782	$Na_2Si_2O_5$ + $(Na_2,NaLi)SiO_3$	
44	30.0	34.94	2.60	62.46	788	790	$(Na_2,NaLi)SiO_3$	
45	40.0	35.25	3.58	61.17	814	818	$(Na_2,NaLi)SiO_3$	...
46	50.0	35.58	4.47	59.95	841	842	$(Na_2,NaLi)SiO_3$	1.521
47	60.0	35.89	5.36	58.75	860	862	$(Na_2,NaLi)SiO_3$	1.523
48	80.0	36.50	7.15	56.34	891	893	$(Na_2,NaLi)SiO_3$	1.527
(5)	100.0	37.11	8.94	53.95	906	907	$(Na_2,NaLi)SiO_3$	1.528
			III. Ternary Section: A = $Na_2Si_2O_5$; B = $NaLiSiO_3$					
51	20.0	33.08	2.82	64.10	796	800	$Na_2Si_2O_5$	1.514
52	30.0	32.60	4.23	63.17	748	755	$Na_2Si_2O_5$	1.517
53	32.0	32.49	4.51	63.00	742	743	$(Na_2,NaLi)SiO_3$	1.519
					696	698	Ternary eutectic E_1	
54	40.0	32.12	5.64	62.24	755	758	$(Na_2,NaLi)SiO_3$	...
55	50.0	31.64	7.05	61.31	769	772	$(Na_2,NaLi)SiO_3$	1.525
56	60.0	31.15	8.45	60.40	789	790	$(Na_2,NaLi)SiO_3$	1.528
57	63.0	31.02	8.88	60.10	796	797	$(Na_2,NaLi)SiO_3$	1.531
58	66.0	30.87	9.30	59.83	803	805	Li_2SiO_3	>1.530
59	70.0	30.68	9.87	59.45	812	813	Li_2SiO_3	...
60	80.0	30.20	11.28	58.52	838	841	Li_2SiO_3	>1.530
61	90	29.7	12.6	57.7	860	862	Li_2SiO_3	1.535
(16)	100.0	29.23	14.06	56.71	872	873	Li_2SiO_3	1.538
			IV. Ternary Section: A = $Na_2Si_2O_5$; B = (theor.) $Na_2Li_4Si_3O_9$					
71	10.0	32.69	1.98	65.33	823	825	$Na_2Si_2O_5$	1.511
72	20.0	31.32	3.95	64.73	770	772	$Na_2Si_2O_5$	1.516
73	30.0	29.95	5.93	64.12	708	709	$Na_2Si_2O_5$	1.521
74	33.0	29.59	6.53	63.88	711	712	Li_2SiO_3	1.523
					696	697	Ternary eutectic E_1	
75	40.0	28.64	7.91	63.45	774	778	Li_2SiO_3	1.525

TABLE I (*Continued*)

No.	Wt. % B	Na_2O	Li_2O	SiO_2	Measured limits Liquidus temp. °C. Below	Above	Cryst. phases	Refr. index quenched glass
76	50.0	27.28	9.89	62.83	844	847	Li_2SiO_3	1.529
77	60.0	25.94	11.87	62.19	889	893	Li_2SiO_3	...
78	70.0	24.59	13.85	61.56	927	933	Li_2SiO_3	...
79	85	22.5	16.8	60.7	977	981	Li_2SiO_3	...
(21)	100	20.5	19.8	59.7	1001[b]		Li_2SiO_3	
			V. Ternary Section: A = $Na_2Si_2O_5$; B = $Li_2Si_2O_5$					
81	5.0	32.29	0.99	66.71	845	846	$Na_2Si_2O_5$	1.507
82	10.0	30.64	1.99	67.37	816	818	$Na_2Si_2O_5$	1.509
83	20.0	27.23	3.98	68.79	758	762	$Na_2Si_2O_5$	...
84	24.0	25.87	4.78	69.35	735	736	$Na_2Si_2O_5$	1.513
85	29.2	24.11	5.81	70.08	701	702	$Na_2Si_2O_5$	1.515
					692	694	$Na_2Si_2O_5 + Li_2SiO_3$	
86	32.0	23.15	6.37	70.48	711	712	Li_2SiO_3	1.515
					692	695	$Na_2Si_2O_5 + Li_2SiO_3$	
87	40.0	20.43	7.97	71.61	780	782	Li_2SiO_3	1.518
88	50	17.19	9.94	72.87	849	851	Li_2SiO_3	...
89	60.0	13.62	11.95	74.43	908	912	Li_2SiO_3	1.526
90	70.0	10.20	13.93	75.87	954	956	Li_2SiO_3	...
91	80.0	6.81	15.92	77.28	986	989	Li_2SiO_3	1.530
92	90.0	3.41	17.90	78.69	1012	1014	Li_2SiO_3	1.532
...	100.0	...	19.92	80.08	1034[c]		Li_2SiO_3	...
			VI. Ternary Section: A = Na_2SiO_3; B = $Li_2Si_2O_5$					
101	10.0	45.70	1.99	52.31	1032	1037	$(Na_2,NaLi)SiO_3$	1.519
102	20.0	40.62	3.98	55.40	956	958	$(Na_2,NaLi)SiO_3$	1.523
103	25.0	38.10	4.98	56.92	906	908	$(Na_2,NaLi)SiO_3$	1.523
104	32.0	34.54	6.37	59.09	838	840	$(Na_2,NaLi)SiO_3$	...
105	34.0	33.52	6.77	59.70	819	821	$(Na_2,NaLi)SiO_3$	...
106	36.0	32.49	7.14	60.37	800	803	$(Na_2,NaLi)SiO_3$	...
107	38.0	31.48	7.57	60.95	777	783	$(Na_2,NaLi)SiO_3$	>1.525
108	40.0	30.45	7.92	61.62	762	764	Li_2SiO_3	...
109	42.0	29.45	8.34	62.21	780	783	Li_2SiO_3	...
110	50.0	25.36	9.91	64.73	848	850	Li_2SiO_3	...
111	60	20.26	11.88	67.86	911	913	Li_2SiO_3	1.528
112	80.0	10.14	15.90	73.96	996	998	Li_2SiO_3	1.532
			VII. Ternary Section at 3.0% Na_2O					
121	..	2.99	14.30	82.71	1088	1092	Tridymite	1.519
122	..	2.99	15.46	81.55	999	1001	Tridymite + $Li_2Si_2O_5$	...
					1012	1019	Tridymite	1.524
123	..	3.00	15.96	81.04	1002	1004	$Li_2Si_2O_5$	...
124	..	2.99	16.46	80.55	1004	1005	$Li_2Si_2O_5$	1.528
125	..	2.99	17.46	79.55	1003	1106	Li_2SiO_3	...
126	..	2.99	21.94	75.06	1089	1091	Li_2SiO_3	1.543
127	..	3.00	25.95	71.05	1146h		Li_2SiO_3	...
			VIII. Ternary Section at 10.0% Na_2O					
131	..	9.97	8.59	81.44	1075	1079	Tridymite	1.509
132	..	10.00	10.00	80.00	954	958	Tridymite	...
133	..	10.00	11.01	78.99	906	908	$Li_2Si_2O_5$	1.518
134	..	9.98	11.97	78.05	914	916	$Li_2Si_2O_5$	1.521
135	..	9.98	18.96	71.06	1054	1056	Li_2SiO_3	1.539
			IX. Ternary Section at 15.0% Na_2O					
141	..	15.00	4.51	80.49	1075	1080	Tridymite	1.501
142	..	14.98	6.49	78.52	904	910	Tridymite	1.510
143	..	14.98	7.69	77.33	805	811	Quartz	1.513
					795	799	Quartz + $Li_2Si_2O_5$	
144	..	14.99	7.99	77.02	802	804	Li_2SiO_3, ($Li_2Si_2O_5$)	1.515

TABLE I (*Continued*)

No.	Wt. % B	Na_2O	Li_2O	SiO_2	Measured limits Liquidus temp. °C. Below	Above	Cryst. phases	Refr. index quenched glass
				X. Ternary Section at 20.0% Na_2O				
151	..	19.97	2.00	78.03	974	980	Tridymite	1.498
152	..	20.0	3.0	77.0	871	874	Tridymite	1.502
153	..	19.98	3.50	76.52	829	833	Quartz	1.506
154	..	19.98	5.00	75.02	688	692	Quartz	...
					642	645	Quartz + $Na_2Si_2O_5$	
					636	638	Ternary eutectic E_2	
155	..	20.28	5.30	74.42	660	663	Li_2SiO_3	1.509
					637	639	Ternary eutectic E_2	
156	..	20.00	6.49	73.51	708	709	Li_2SiO_3	...
157	..	20.00	10.00	70.00	854	856	Li_2SiO_3	...
				XI. Ternary Section at 22.0% Na_2O				
161	..	21.99	2.00	76.01	827	831	Quartz	...
162	..	21.96	3.00	75.04	739	747	Quartz	...
163	..	22.00	3.70	74.30	686	688	Quartz + $Na_2Si_2O_5$	1.507
					686	689	$Na_2Si_2O_5$	...
164	..	21.95	3.99	74.05	684	686	$Na_2Si_2O_5$	...
165	..	21.96	5.00	73.04	677	680	$Na_2Si_2O_5$	...
166	..	22.00	5.59	72.41	675	676	$Na_2Si_2O_5$	>1.510
167	..	21.99	5.98	72.03	688	689	Li_2SiO_3	...
				XII. Ternary Section at 25% Na_2O				
171	..	25.00	1.00	74.00	766	767	$Na_2Si_2O_5$	1.501
172	..	24.99	2.00	73.01	762	764	$Na_2Si_2O_5$	...
173	..	24.99	4.00	71.01	735	737	$Na_2Si_2O_5$	...
174	..	25.00	6.00	69.00	707	711	$Na_2Si_2O_5$	1.517
175	..	25.00	6.50	68.50	714	716	Li_2SiO_3	1.519
				XIII. Ternary Section at 32.5% Na_2O				
181	..	32.50	6.50	61.00	780	782	$(Na_2,NaLi)SiO_3$	1.524
182	..	32.47	7.98	59.55	812	816	$(Na_2,NaLi)SiO_3$	1.528
183	..	32.47	8.99	58.54	828	831	$(Na_2,NaLi)SiO_3$	...
184	..	32.46	9.96	57.58	841	843	$(Na_2,NaLi)SiO_3$	>1.530
185	..	32.40	10.93	56.67	847	849	$(Na_2,NaLi)SiO_3$	...
(9)	..	32.48	11.92	55.60	851	853	$(Na_2,NaLi)SiO_3$	...
186	..	32.45	14.02	53.53	834	842	$(Na_2,NaLi)SiO_3$	...
					836h		$(Na_2,NaLi)SiO_3$	...
				XIV. Miscellaneous Ternary Section from Na_2SiO_3 through Composition 60[d]				
(184)	36.00	32.46	9.96	57.58	841	843	$(Na_2,NaLi)SiO_3$	>1.530
191	37.50	31.75	10.43	57.82	832	834	$(Na_2,NaLi)SiO_3$	1.532
192	39.00	30.98	10.85	58.17	830	832	$(Na_2,NaLi)SiO_3$	...
(60)	40.53	30.20	11.28	58.52	838	841	Li_2SiO_3	>1.530
193	42.00	29.46	11.68	58.86	854	855	Li_2SiO_3	1.534
				XV. Miscellaneous Compositions				
201	..	30.60	6.29	63.11	701	703	Li_2SiO_3 + $(Na_2,NaLi)SiO_3$	
					719	720	$(Na_2,NaLi)SiO_3$	1.523
202	..	30.20	6.30	63.50	696	697	Ternary eutectic E_1	
					699	700	$(Na_2,NaLi)SiO_3$ + Li_2SiO_3	
					707	708	$(Na_2,NaLi)SiO_3$	
203	..	17.03	10.32	72.66	863	864	Li_2SiO_3	1.523
204	..	15.29	7.14	77.57	828	837	Quartz	...
205	..	11.49	9.68	78.83	869	870	Tridymite	1.514
					868	869	$Li_2Si_2O_5$ + tridymite	
206	..	12.35	6.86	80.78	1052	1058	Tridymite	1.506

[a] "h" denotes determination by heating curve analysis. [b] Interpolated from data on Na_4SiO_3–Li_2SiO_3. [c] From data on Li_2SiO_3–SiO_2. [d] B = 27.82% Li_2O, 72.18% SiO_2. > = more than.

TABLE I (*Concluded*)

Polymorphous Transitions in $Na_2Si_2O_5$

Composition, wt. % Na_2O	Li_2O	SiO_2	Transition temp.[e] av., °C. I–II	II–III	Remarks
34.05	...	65.95	706.8	677.0	Pure $Na_2Si_2O_5$
37.5	...	62.5	708.7	677.1	Excess Na_2O
35.8	...	64.2	705.9	678.1	Excess Na_2O
31.7	...	68.3	707.4	678.4	Excess SiO_2
31.0	...	69.0	707.7	677.8	Excess SiO_2
27.0	...	73.0	707.6	677.2	Excess SiO_2
30.61	3.31	66.08	699.5	687.7	90% $Na_2Si_2O_5$ + 10% Li_2SiO_3
28.94	4.98	66.08	698.1	688.5	85% $Na_2Si_2O_5$ + 15% Li_2SiO_3
30.64	1.99	67.37	698.6	688.1	90% $Na_2Si_2O_5$ + 10% $Li_2Si_2O_5$
			Polymorphous Transitions in $Li_2Si_2O_5$		
...	19.92	80.08	(960)h[f]	936.6	Pure Li_2SiO_3
...	22.1	77.9	....	935.4	Excess Li_2O
...	17.7	82.3	(960)h[f]	937.2	Excess SiO_2
	12.6	87.4	....	935.5	Excess SiO_2
3.0	17.5	79.5	....	929.5	
3.4	17.9	79.7	....	929.8	90% $Li_2Si_2O_5$ + 10% $Na_2Si_2O_5$

[e] For method of deducing the average transition temperature see Fig. 3. [f] Faint arrest on first heating only.

mainly eutectics, are given, in connection with the composition for which they were determined. The coördinates of the invariant points for the pressure of one atmosphere are collected in Table III.

The Binary Systems on the Side Lines

Before proceeding to a discussion of the relations brought out in the ternary system, it is necessary to describe the fundamental binary systems on the sides of the triangle, Na_2SiO_3–Li_2SiO_3–SiO_2. It will be noted that one of these, Na_2SiO_3–Li_2SiO_3, is a binary section across the larger triangle, Na_2O–Li_2O–SiO_2.

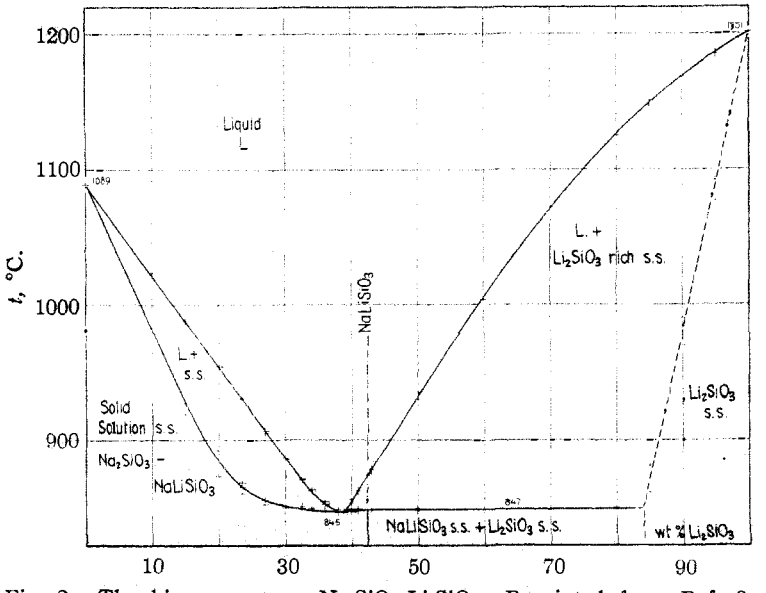

Fig. 2.—The binary system, Na_2SiO_3–Li_2SiO_3. Reprinted from Ref. 3.

1. **The System, Na_2SiO_3–Li_2SiO_3.**—The data on this system have been published recently.[3] This system is of special interest in that sodium metasilicate crystals are capable of exchanging sodium for lithium in solid solution until the composition sodium lithium (1,1) metasilicate is reached. Lithium metasilicate, on the other hand, takes up only a minor proportion of sodium into its lattice. The compound sodium lithium (1,1) metasilicate melts incongruently at 847°, yielding a liquid of 39.3 wt. per cent. lithium metasilicate, and the sodium-bearing lithium metasilicate crystals. The solid solution series, $(Na_2,NaLi)SiO_3$, has a minimum on its liquidus at 845°, 38.5 wt. per cent. lithium metasilicate (binary compositions). The equilibrium relations are illustrated in Fig. 2 (see also Fig. 2 of ref. 3).

2. **The System, Na_2SiO_3–SiO_2.**—This system has been studied by Morey and Bowen,[5] and by Kracek[6] who extended the investigation to include the orthosilicate, Na_4SiO_4.

(a) **Polymorphism of Sodium Disilicate.**—Measurements, supplementing those earlier made by Kracek,[6] of thermal arrests in the sodium disilicate region with the improved apparatus now in use (see ref. 2) were made

(5) G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, **28**, 1167 (1924).

(6) F. C. Kracek, *ibid.*, **34**, 1583 (1930).

on pure sodium disilicate (65.95% silicon dioxide), on two preparations toward sodium metasilicate, at 62.5 and 64.2% silicon dioxide, and on three preparations toward silicon dioxide, at 68.3, 69.0, and 73.0% silicon dioxide. Each of these preparations yielded two arrests, one at 678°, the other at 707° (average temperatures), as illustrated in Figs. 3 and 4. The heat effects are relatively small, probably of the order of 2 cal./g. for the 678° arrest, and 1 cal./g. for the 707° arrest. The 707° arrest had escaped detection previously in preparations containing excess silicon dioxide. An arrest, not included in Fig. 4, previously recorded at 768° in silicon dioxide-rich preparations only, is again recorded in the same region, both of temperature and composition, and probably is due to eutectic melting of small amounts of tridymite and cristobalite present.

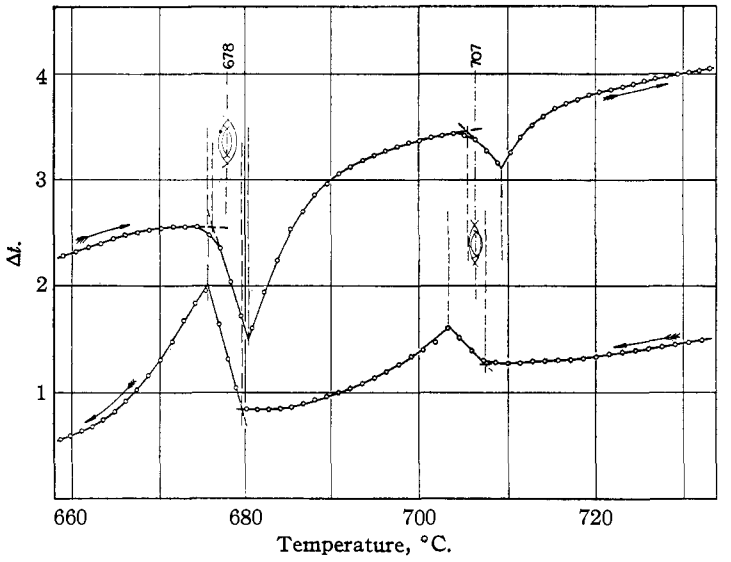

Fig. 3.—Typical differential heating and cooling curves of phase transitions in $Na_2Si_2O_5$, giving geometrical construction for deducing the average transition temperatures.

These measurements lead to the conclusion that sodium disilicate is trimorphous with inversions located at atmospheric pressure at the average temperatures of 678 and 707°. Presence of lithium silicates influences these temperatures, as stated at a later point in the paper (see Figs. 8 and 9).

(b) **The $Na_2Si_2O_5$–Quartz Eutectic.**—The determination of the $Na_2Si_2O_5$–quartz eutectic by heating curves is inexact, yielding an arrest which is spread rather indefinitely over the temperature interval from about 788 to nearly 800°. To verify the location of this eutectic, we have heated completely crystalline preparations of 74.8 and 76.0% silicon dioxide at various temperatures, and quenched. When heated for two days at 786°, the preparations remained powdery. At 788° they sintered to porous lumps, with little or no glass evident under the microscope. At 790° there was much glass, in which were imbedded sharply faceted quartz crystals, and larger eroded quartz grains, with very little unevenly scattered remnants of sodium disilicate crystals. The eutectic temperature is accordingly 789 ± 1°. The quartz liquidus on the 74.8% silicon dioxide preparation (compare Kracek's earlier preparation 571, 74.81% silicon dioxide, 838°) was found by similar procedure to be 822 ± 4°. The intersection of the liquidus curves for sodium disilicate and quartz, at the newly determined eutectic temperature of 789°, is located at 74.2 ± 0.3% silicon dioxide. The former values for the eutectic were 793°, and 73.4% (Morey and Bowen) and 73.9% (Kracek) silicon dioxide.

(c) **The Na_2SiO_3–$Na_2Si_2O_5$ Eutectic.**—Precrystallized preparations of 61.5 and 62.5% silicon

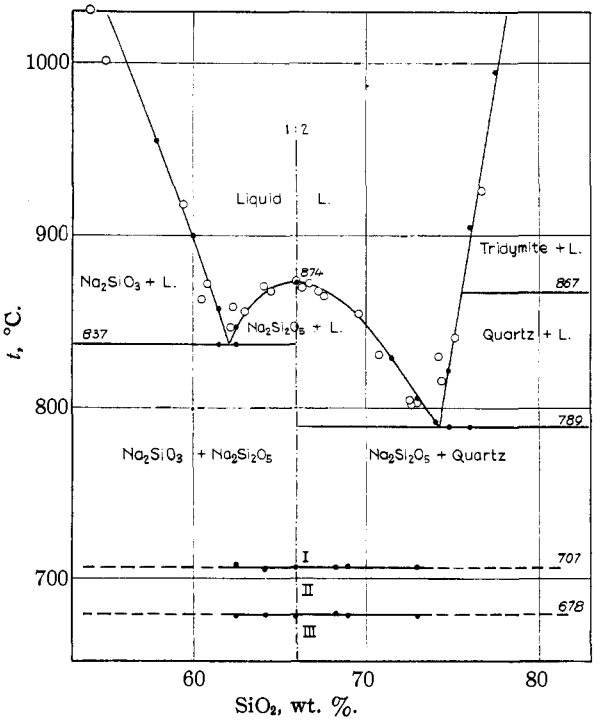

Fig. 4.—The disilicate region of the system, Na_2SiO_3–SiO_2: open circles by Morey and Bowen,[5] and Bowen, Schairer and Willems (unpublished); black dots, Kracek.

dioxide remained unsintered at 836°, and contained much glass at 838°. If 837 ± 1° is taken as the eutectic temperature, the eutectic composition is 62.1 ± 0.2% silicon dioxide. The former values were 840°, 60.8% silicon dioxide (Morey and Bowen), and 846°, 62.1% silicon dioxide (Kracek).

(d) **The Cristobalite Liquidus.**—The liquidus temperatures published earlier by the writer[7] for cristobalite in the system, Na_2O–SiO_2, are slightly higher than those determined in the present work. The high values in the earlier determinations can be ascribed only to the existence of a temperature gradient in the quenching furnace then used. The newly determined values are: 1532 ± 5° at 91.5, 1580 ± 3° at 95.0, and 1628 ± 3° at 97.5% silicon dioxide.

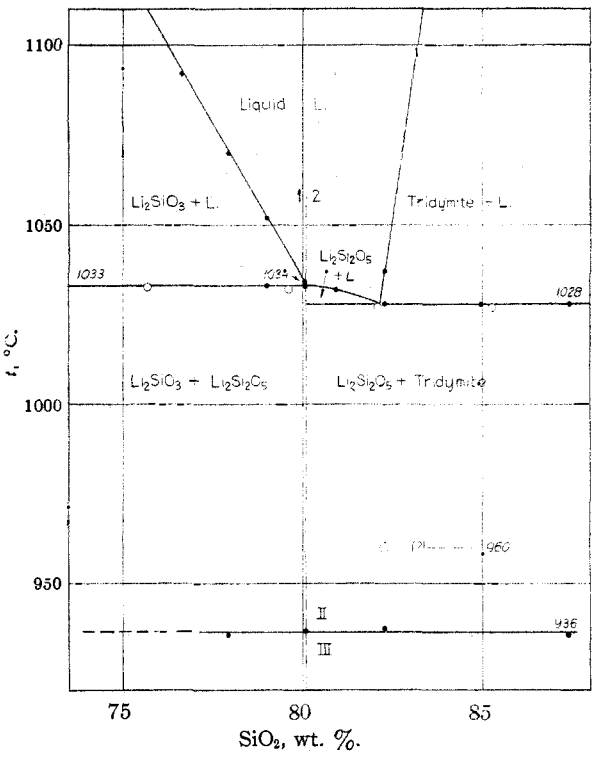

Fig. 5.—The disilicate region of the system, Li_2SiO_3–SiO_2: open circles, Jaeger and van Klooster; black dots and dotted circles, Kracek.

The revisions discussed above have been incorporated in Fig. 4, which represents the phase relations in the system, Na_2SiO_3–SiO_2, for the region in the neighborhood of sodium disilicate.

3. The System, Li_2SiO_3–SiO_2.—The equilibrium relations in this system were studied by Jaeger and van Klooster[8] and by Kracek,[7,9] among others.

(a) **The Cristobalite Liquidus.**—A redetermination was made of the liquidus temperatures for cristobalite as the primary phase. It was found that the published temperatures[7] in this system also are slightly high; the new values are 1508 ± 4° at 92.5, 1561 ± 3° at 95.0, and 1605 ± 3° at 97.0% silicon dioxide.

(b) **Polymorphism of Lithium Disilicate.**—To verify the former[9] thermal analysis measurements in the lithium disilicate region of the system, we have made new determinations on crystallized preparations of 77.9, 80.08 ($Li_2Si_2O_5$), 82.3, and 87.4% silicon dioxide. A small arrest, with a thermal effect of 1 to 2 cal./g. in pure lithium disilicate, was found in all the preparations, at the average temperature of 936°. This arrest has the characteristics associated with typical polymorphic inversions, with hysteresis.

The very small irregularity in differential temperature, formerly noted at 960°, could not be reproduced with certainty. It was noted once, but only during the first heating, in the 80.08 and 82.3% silicon dioxide preparations. It did not reappear during subsequent heat treatments, or in any of the other preparations; hence, its significance remains unexplained.

Addition of sodium silicates to lithium disilicate lowers the 936° inversion to 930° (see the section, $Na_2Si_2O_5$–$Li_2Si_2O_5$).

The phase relations in the neighborhood of lithium disilicate for the system Li_2SiO_3–SiO_2 are illustrated in Fig. 5.

The Ternary System

The only ternary compound in the system is sodium lithium (1,1) metasilicate. This compound is an end-member of the $(Na_2,NaLi)SiO_3$ series of solid solutions, and has no separate field of its own in the ternary system. Hence, the primary phases at the liquidus are the $(Na_2,NaLi)SiO_3$ solid solutions, Li_2SiO_3, $Na_2Si_2O_5$, $Li_2Si_2O_5$, and silica in its three major modifications. The compounds Li_2SiO_3, $Li_2Si_2O_5$, and $Na_2Si_2O_5$ all form limited series of solid solutions with small mutual replacements of lithium and sodium.

Only one section within the system, namely, $Na_2Si_2O_5$–Li_2SiO_3, is binary at the liquidus; the other possible binary section, $Na_2Si_2O_5$–$Li_2Si_2O_5$,

(7) F. C. Kracek, THIS JOURNAL, 52, 1436 (1930).

(8) F. M. Jaeger and H. S. van Klooster, *Proc. Amst. Acad. Sci.*, 16, 857 (1914).

(9) F. C. Kracek, *J. Phys. Chem.*, 34, 2641 (1930).

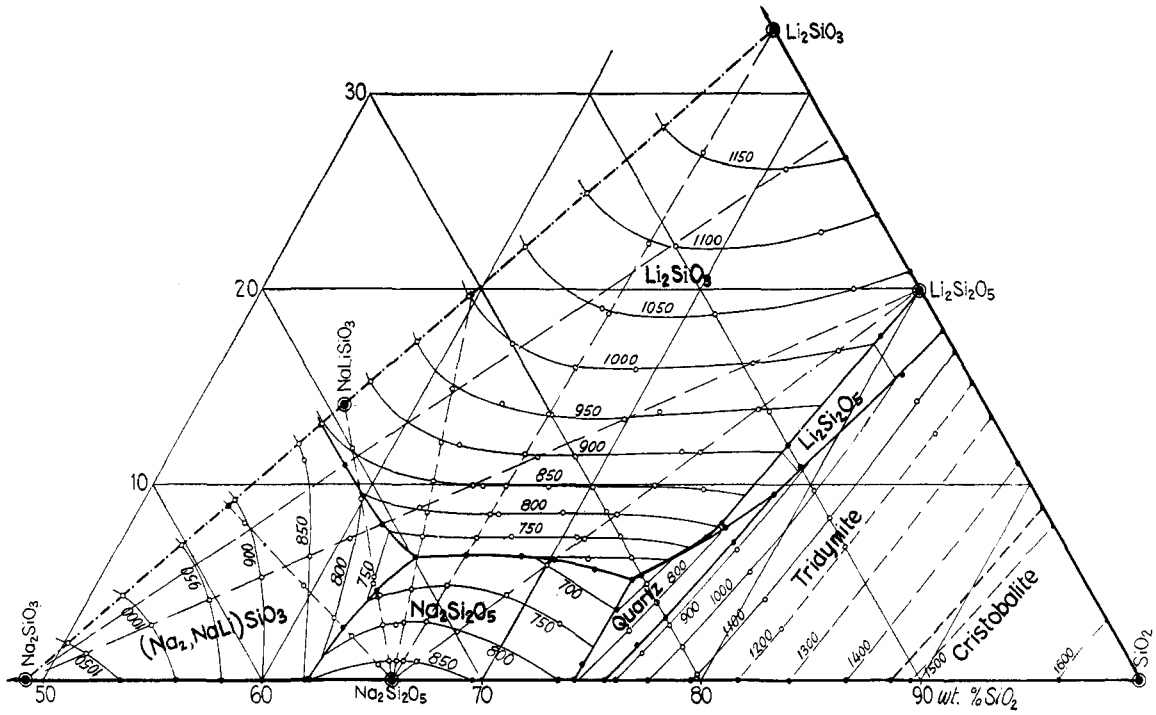

Fig. 6.—Equilibrium diagram with isotherms, of the system, Na_2SiO_3–Li_2SiO_3–SiO_2. Open circles represent interpolated temperatures corresponding to the various isotherms. Black dots give the location of boundary curves as measured or deduced by interpolation from the data on the various cross-sections in the system.

is partly ternary at the liquidus; this is due to the incongruent melting relations of lithium disilicate.

Method of Interpolation in Deriving Isotherms.—The data for each of the sections I to VI across the system, as indicated in Fig. 1, were plotted on a sufficiently large scale to allow for interpolation with a precision of ±0.5°. The compositions corresponding to even temperatures at 50° intervals were then read off from the graphs, and plotted in the ternary system, as indicated in Fig. 6 by the open circles.

Cross interpolation was employed for the remaining sections, VII to XIV. For this purpose the temperatures of intersection of these sections with the sections I to VI were read off from the above graphs, and were then plotted, together with the data for preparations on the individual sections, as indicated in Fig. 7, the abscissa being progressively shifted so as to bring the metasilicate composition for each of the sections VII to XIII upon the vertical line at the left of the diagram. This was done by adding to the lithium oxide content for each section the quantity

$$\%\ Li_2O \text{ added} = \%\ Na_2O \text{ along the section} \times \frac{Li_2O \text{ in } Li_2SiO_3}{Na_2O \text{ in } Na_2SiO_3}$$
$$= 0.6541 \times \%\ Na_2O \text{ along the section}$$

The resulting figure, Fig. 7, represents a t–x (temperature–composition) projection of a part of the system upon the plane of the side system, Li_2SiO_3–SiO_2. To avoid confusion in the diagram, only sections up to 25% sodium oxide are represented. The sections I, V, and VI, appear as curved dotted lines, with the interpolated loci of the intersections marked by crosses. Other t–x projections of the system were constructed to facilitate cross-interpolations in regions not covered by Fig. 7. The data so obtained are plotted in Fig. 6.

The Boundary Curves.—The coördinates of the boundary curves between the various primary phases, as deduced by interpolation from the graphs, or directly from the experimental data, are given in Table II. The boundary curves meet at the invariant points, which are collected for reference in Table III.

1. **The System, $Na_2Si_2O_5$–Li_2SiO_3.**—The relations in this system are illustrated in Fig. 8. The system is simply eutectoid; both the end-members are present in limited solid solution. The extent of the solid solution in lithium metasilicate is approximately the same as in the system Na_2SiO_3–Li_2SiO_3, as judged from the values of the refractive indices of the crystals. The solid solution

TABLE II

COÖRDINATES OF THE BOUNDARY CURVES IN THE SYSTEM Na_2SiO_3–Li_2SiO_3–SiO_2

	Section no. and identification	Wt. % Na_2O	Wt. % Li_2O	Wt. % SiO_2	t, °C.
	A. Boundary between $(Na_2,NaLi)SiO_3$ and $Na_2Si_2O_5$ (s. s.)[a]				
...	Na_2SiO_3–$Na_2Si_2O_5$	37.9	..	62.1	837 ± 1
II	$Na_2Si_2O_5$–$(Na_4Li_2Si_3O_9)$[b]	35.0	2.7	62.3	782
III	$Na_2Si_2O_5$–$NaLiSiO_3$	32.5	4.5	63.0	741
XIII	32.5% Na_2O	32.5	4.6	62.9	741
...	30.0% Na_2O	30.0	6.30	63.7	700
...	Ternary eutectic E_3	29.9	6.2	63.9	697 ± 3
	B. Boundary between $(Na_2,NaLi)SiO_3$ and Li_2SiO_3 (s. s.)				
...	Na_2SiO_3–Li_2SiO_3	30.8	13.1	56.1	847 ± 1
XIV	Na_2SiO_3–72.19% SiO_2 on Li_2SiO_3–SiO_2	30.7	11.0	58.3	831
III	$Na_2Si_2O_5$–$NaLiSiO_3$	30.8	9.5	59.7	799
VI	Na_2SiO_3–$Li_2Si_2O_5$	30.6	7.9	61.5	759
...	30.0% Na_2O	30.0	6.4	63.6	700
...	Ternary eutectic E_1	29.9	6.2	63.9	697 ± 3
	C. Boundary between $Na_2Si_2O_5$ (s. s.) and Li_2SiO_3 (s. s.)				
...	Ternary eutectic E_1	29.9	6.2	63.9	697 ± 3
IV	$Na_2Si_2O_5$–$(Na_2Li_4Si_3O_9)$	29.7	6.3	64.0	698
I	$Na_2Si_2O_5$–Li_2SiO_3, eutectic	27.5	6.4	66.1	709 ± 3
XII	25.0% Na_2O	25.0	6.3	68.7	705
V	$Na_2Si_2O_5$–$Li_2Si_2O_5$	23.7	6.0	70.3	693
XI	22.0% Na_2O	22.0	5.7	72.3	674
...	Quint. point Q_1	20.5	5.2	74.3	641 ± 3
	D. Boundary between $Na_2Si_2O_5$ (s. s.) and $Li_2Si_2O_5$ (s. s.)				
...	Quint. point Q_1	20.5	5.2	74.3	641 ± 3
...	Ternary eutectic E_2	20.5	5.1	74.4	637 ± 3
	F. Boundary between $Na_2Si_2O_5$ (s. s.) and Quartz				
...	$Na_2Si_2O_5$–SiO_2	25.8	...	74.2	789 ± 1
XII	25.0% Na_2O	25.0	0.8	74.2	770
XI	22.0% Na_2O	22.0	3.6	74.4	688
...	Ternary eutectic E_2	20.5	5.1	74.4	637 ± 3
	G. Boundary between Li_2SiO_3 (s. s.) and $Li_2Si_2O_5$ (s. s.)				
...	Quint. point Q_1	20.5	5.2	74.3	641 ± 3
X	20.0% Na_2O	20.0	5.4	74.6	660
IX	15.0% Na_2O	15.0	8.0	77.0	803
VIII	10.0% Na_2O	10.0	12.0	78.0	915
VII	3.0% Na_2O	3.0	17.6	79.4	1008
...	Li_2SiO_3–SiO_2	..	19.9	80.1	1033 ± 1
	H. Boundary between $Li_2Si_2O_5$ (s. s.) and Tridymite				
...	$Li_2Si_2O_5$–SiO_2	...	17.8	82.2	1028 ± 1
VII	3.0% Na_2O	3.0	15.7	81.3	1001
VIII	10.0% Na_2O	10.0	10.8	79.2	904
...	Quint. point Q_3	11.9	9.5	78.6	867 ± 3
	K. Boundary between $Li_2Si_2O_5$ (s. s.) and Quartz				
...	Quint. point Q_2	11.9	9.5	78.6	867 ± 3
IX	15.0% Na_2O	15.0	7.8	77.2	801
X	20.0% Na_2O	20.0	5.3	74.7	657
...	Ternary eutectic E_2	20.5	5.1	74.4	637 ± 3
	L. Boundary for Inversion of Quartz to Tridymite				
...	Na_2SiO_3–SiO_2	24.5	...	75.5	867 ± 3
XI	22.0% Na_2O	22.0	1.8	76.2	867
X	20.0% Na_2O	20.0	3.1	76.9	867
IX	15.0% Na_2O	15.0	7.0	78.0	867
...	Quint. point Q_2	11.9	9.5	78.6	867

[a] (s. s.) = solid solutions. [b] Formula in parentheses signifies a theoretical compound.

TABLE III

INVARIANT POINTS FOR THE PRESSURE OF ONE ATMOSPHERE IN THE SYSTEM Na_2SiO_3–Li_2SiO_3–SiO_2

Phases	Type	Na_2O	Li_2O	SiO_2	t, °C.
Na_2SiO_3	Melting	50.79	...	49.21	1089 ± 1
$Na_2Si_2O_5$	Melting	34.04	...	65.96	874 ± 3
Li_2SiO_3	Melting	...	33.22	66.78	1201 ± 1
$Li_2Si_2O_5$	Peritectic	...	19.9	80.1	1033 ± 1
	Liquidus	...	19.92	80.08	1034 ± 1
$NaLiSiO_3$ and Li_2SiO_3	Peritectic	30.82	13.05	56.13	847 ± 1
$(Na_2,NaLi)SiO_3$	Minimum	31.25	12.79	55.96	845 ± 1
Na_2SiO_3 and $Na_2Si_2O_5$	Eutectic (binary)	37.9	...	62.1	837 ± 1
$Na_2Si_2O_5$ and quartz	Eutectic (binary)	25.8	...	74.2	789 ± 1
$Li_2Si_2O_5$ and tridymite	Eutectic (binary)	...	17.8	82.2	1028 ± 1
$Na_2Si_2O_5$ and Li_2SiO_3	Eutectic (binary)	27.5	6.4	66.1	709 ± 3
$(Na_2,NaLi)SiO_3$, Li_2SiO_3, and $Na_2Si_2O_5$	Eutectic (ternary) E_1	29.9	6.2	63.9	697 ± 3
$Na_2Si_2O_5$, $Li_2Si_2O_5$, and quartz	Eutectic (ternary) E_2	20.5	5.1	74.4	637 ± 3
$Na_2Si_2O_5$, $Li_2Si_2O_5$, and Li_2SiO_3	Peritectic limit, Q_1	20.5	5.2	74.3	641 ± 3
$Li_2Si_2O_5$, quartz, and tridymite	Inversion point, Q_2	11.9	9.5	78.6	867 ± 3
Quartz and tridymite	Inversion	...	...	100.0	867 ± 3
$Na_2Si_2O_5$ I and $Na_2Si_2O_5$ II	Inversion	34.04	...	69.56	707 ± 3
$Na_2Si_2O_5$ I and $Na_2Si_2O_5$ II in solid solutions	Inversion	...	...	...	699 ± 3
$Na_2Si_2O_5$ II and $Na_2Si_2O_5$ III	Inversion	34.04	...	65.96	678 ± 3
$Na_2Si_2O_5$ II and $Na_2Si_2O_5$ III in solid solutions	Inversion	...	...	...	688 ± 3
$Li_2Si_2O_5$ II and $Li_2Si_2O_5$ III	Inversion	...	19.92	80.08	936 ± 3
$Li_2Si_2O_5$ II and $Li_2Si_2O_5$ III in solid solutions	Inversion	...	...	...	930 ± 3

in sodium disilicate is approximately 5 ± 3% lithium metasilicate, as indicated in the diagram; the 678° transition in sodium disilicate is raised to 688°, while the 707° transition is lowered to 699°, as measured by thermal analysis on preparations 31 and 32 (see Table I). The binary eutectic is at 709 ± 3°, 19.20% lithium metasilicate in the binary system (6.38% lithium oxide, 27.50% sodium oxide, 66.12% silicon dioxide in ternary compositions).

2. **The Section, $Na_2Si_2O_5$–$Li_2Si_2O_5$.**—The phase relations along this section are only partly binary at the liquidus. Lithium disilicate melts incongruently at 1033 ± 1°, the primary phase at the liquidus, 1034 ± 1°, being lithium metasilicate. Additions of sodium disilicate to lithium disilicate lower the peritectic temperature more rapidly than the liquidus, as shown in Fig. 9, so that lithium metasilicate continues to be the primary phase down to the boundary with sodium disilicate, 693°. Beyond this boundary the liquidus relations are binary, sodium disilicate being the primary phase, but the sub-liquidus relations remain ternary to 641 ± 3°, at which temperature the last of the lith-

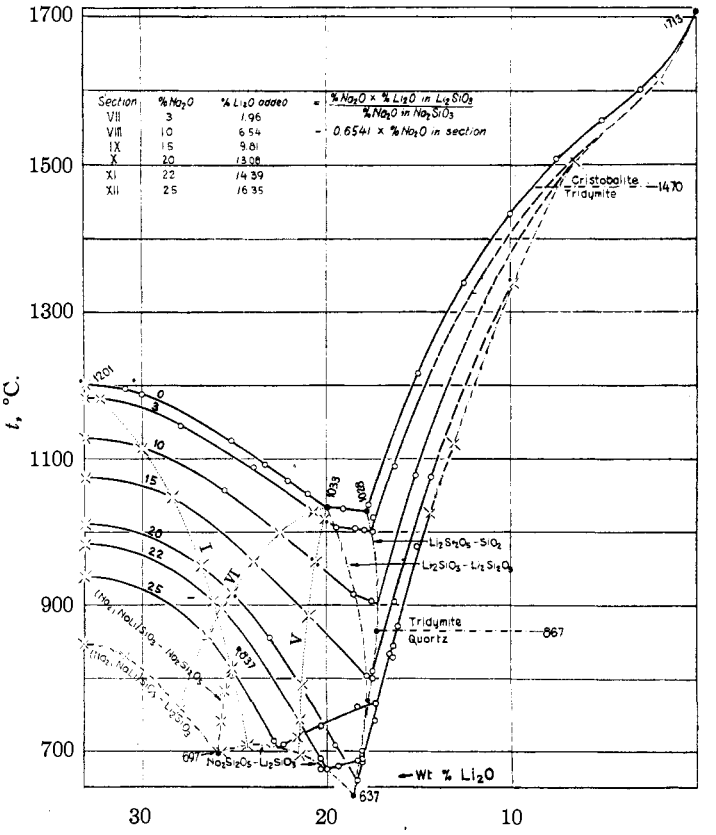

Fig. 7.—Temperature–composition projection of part of the system upon the t–x plane of the system, Li_2SiO_3–SiO_2. Open dots are experimental points. Crosses give intersections of the sections VII to XIII with sections I, V and VI. Dot and dash curves represent phase boundaries, and black circles, intersections of phase boundaries.

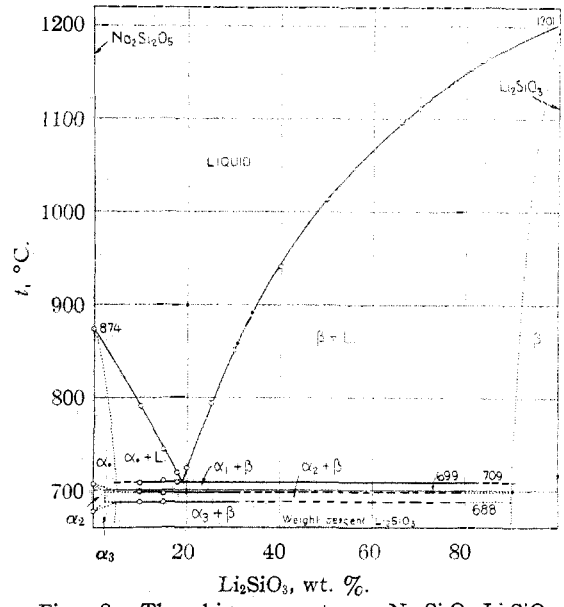

Fig. 8.—The binary system, $Na_2Si_2O_5$–Li_2SiO_3. Solid solution relations, as estimated, are indicated by dotted lines.

ium metasilicate crystals, and liquid, disappear.

The solid solution relations for sodium disilicate and lithium disilicate are indicated in Fig. 9 by dotted lines, the extent in either constituent being estimated to be 5 ± 3% of the other, as based on measurements of the transition temperatures. As already mentioned in discussing the binary system, $Na_2Si_2O_5$–Li_2SiO_3, additions of lithium silicates to sodium disilicate lower the 707° inversion to 699°, and raise the 678° inversion to 688°. On the other hand, the 936° inversion in lithium disilicate is lowered by additions of sodium disilicate to 930°.

The Quartz–Tridymite Inversion.—The temperature of this sluggish, but reversible, transformation is given by Fenner as 870 ± 10°, from measurements made in the presence of sodium tungstate, Na_2WO_4, as flux.[10] Many other substances, such as phosphorus pentoxide, lithium carbonate, potassium carbonate, sodium carbonate, and tungsten trioxide, have been suggested as fluxing agents for accelerating the inversions in silica. Among these, only lithium carbonate holds, *a priori*, any promise of being a more efficient "catalyst" than the sodium tungstate used by Fenner. Van Nieuwenburg[11] reports the conversion of quartz to tridymite in the presence of 1% of lithium carbonate, but he apparently has made no effort to measure the equilibrium temperature closer than about ±30°. Since carbon dioxide is displaced rapidly from such mixtures, the action depends on the speed of reaction between the quartz and the small quantity of crystalline lithium disilicate formed. Fluxing action becomes important only above 1028° (see Fig. 4). For this reason, additions of lithium carbonate to quartz are actually less efficient than those of sodium tungstate in promoting the inversion to tridymite (unpublished experiments by the writer). However, since lithium ions, presumably because of their small dimensions, tend to act as efficient devitrifying agents, it is reasonable to suppose that the inversion would be accelerated by lithium-bearing melts, fluid below the inversion temperature. Compositions in the present system, in the silica field, with liquidus temperatures above 900° fulfil this requirement, and it was

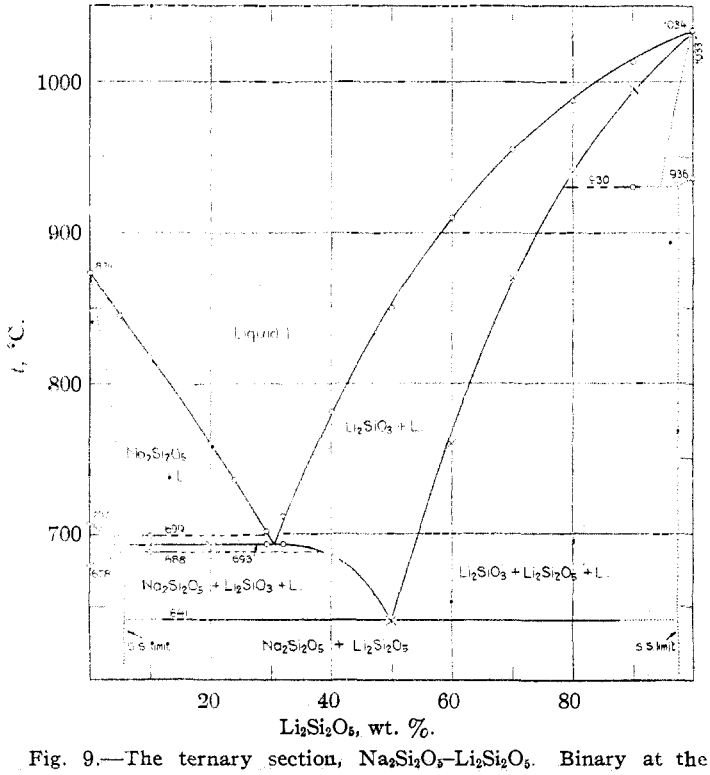

Fig. 9.—The ternary section, $Na_2Si_2O_5$–$Li_2Si_2O_5$. Binary at the liquidus of $Na_2Si_2O_5$, and below 641°. Estimated solid solution relations are indicated by dotted lines.

(10) C. N. Fenner, *Am. J. Sci.* **36**, 331 (1913).

(11) C. J. van Nieuwenburg, *Rec. trav. chim. de Pays-Bas*, **48**, 402 (1929); summary.

found that the most suitable were those whose liquidus lies in the range between 900 and 1000°. The melts of compositions still richer in silicon dioxide tend to be too viscous to act efficiently as fluxes. In the region mentioned (see Fig. 6) quartz is converted into tridymite almost completely (only the larger grains remaining undissolved, but rounded) in twenty-four hours at 869°, and in forty-eight hours at 868°. In the reverse direction, tridymite is converted into sharply faceted crystallites of quartz in twenty-four hours at 866°, and in less than twenty-four hours at 865°. Similar conversions were obtained with all the following compositions: nos. 131, 132, 141, 142, 151, 152. It is concluded that the inversion temperature at one atmosphere pressure is 867 ± 3°, as measured by thermoelements calibrated at the sodium chloride (800.4°) and gold (1062.6°) points. This confirms Fenner's temperature of 870 ± 10°. The temperature 867° is used in presenting the experimental results of this paper.

The liquidus fields of the various primary crystalline phases are smooth sheets pointing down to two ternary eutectics E_1 and E_2 (Table III).

Eutectic E_1 represents the junction of the boundaries between the fields of Li_2SiO_3, $Na_2Si_2O_5$ and $(Na_2,NaLi)SiO_3$, at 697 ± 3°. Of these boundaries, the one between Li_2SiO_3 and $(Na_2,NaLi)SiO_3$ has some theoretical interest. Within the triangle, Na_2SiO_3–$Na_2Si_2O_5$–$NaLiSiO_3$, this boundary is a peritectic (reaction) curve and represents the lowering of the incongruent melting point of sodium lithium (1,1) metasilicate (847° in the pure compound) with the changing compositions of the melts in equilibrium with the crystals. There is no eutectic, but only a minimum on the liquidus of the solid solutions $(Na_2,NaLi)SiO_3$ in the binary system, Na_2SiO_3–Li_2SiO_3 (see also Fig. 2 of ref. 3). As the boundary curve crosses the join, $Na_2Si_2O_5$–$NaLiSiO_3$, this minimum coincides with the curve, which then takes on the character of a eutectoid trough, within the larger triangle, Na_2SiO_3–$Na_2Si_2O_5$–Li_2SiO_3, and finally ends at the ternary eutectic.

The boundary between sodium disilicate and lithium metasilicate, beginning at the ternary eutectic E_1, 697°, rises to the temperature of the binary eutectic between these two compounds, 709 ± 3°, and then descends to the quintuple point Q_1, 641 ± 3°, which is the lowest temperature on the peritectic curve for the incongruent melting relations between lithium disilicate and lithium metasilicate. The ternary eutectic E_2, at 637 ± 3°, practically coincides with the quintuple point Q_1; similarly, the two boundary curves, one between lithium disilicate and lithium metasilicate, the other between lithium disilicate and quartz, lie very close to each other for a considerable portion of their lengths. However, they cannot coincide, since the ternary eutectic E_2 is located within the triangle, $Na_2Si_2O_5$–$Li_2Si_2O_5$–SiO_2, so that the eutectic relations demand that lithium disilicate, and not lithium metasilicate, be one of the eutectic constituents. This will be made clear also by a study of the crystallization relations in Figs. 6 and 9.[11a]

Refractive Indices of the Glasses

Each preparation studied in the course of this work was obtained in the form of a homogeneous glass. A measurement was made of the refractive index of the glass of each composition represented by a black dot in Fig. 1. These measurements were made on crushed, quenched glasses only, by the immersion method, and are estimated to be accurate to ±0.003. The measured values are recorded in Table I, and values along several of the ternary sections in the system are plotted in Fig. 10. This figure also includes published values for Li_2O–SiO_2 glasses,[9] and an interpolated curve for annealed Na_2O–SiO_2 glasses.[12,13]

Cocrystallization of Sodium and Lithium Compounds in Solid Solutions.—Mutual replacement of sodium and lithium plays a sufficiently important part in the crystalline phases of this system (see Figs. 2, 8, 9) to make it desirable to inquire into the general problem of solid solution formation between other sodium and lithium compounds, particularly since it appears to be held by some writers that no such solid solutions have been established[14] for these and other pairs of compounds with cations of the helium and neon-like structures. This view is based on a consideration of the ionic radii, and the differences between the structures of the cations.

(11a) The principles involved in this and the immediately preceding paragraph are discussed in standard books on heterogeneous equilibria, *e. g.*, Rudolf Vogel, "Die heterogenen Gleichgewichte," Akademische Verlagsgesellschaft m. b. H., Leipizig, 1937, pp. 410 *et seq.*

(12) C. A. Faick and A. N. Finn, *Bur. Standards J. Research*, **6**, 993 (1931).

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

(14) See H. G. Grimm and H. Wolff in "Handb. der Physik," **24**, part 2, Verlag von Julius Springer, Berlin, 1933, p. 1097, Table 78.

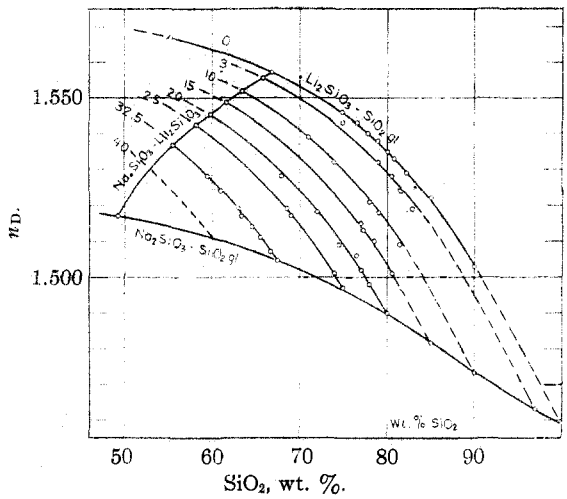

Fig. 10.—Refractive indices of quenched glasses in the system, Na_2SiO_3–Li_2SiO_3–SiO_2. Numbers identifying the curves denote percentage content of Na_2O. The curve for Na_2SiO_3–SiO_2 interpolated from data of Faick and Finn, and of Morey and Merwin, on annealed glasses.

Sodium and lithium compounds probably present the only exception to the rule, and, for that reason, a discussion of the known experimental data is desirable at this point.

The existence of solid solutions in systems of sodium and lithium compounds having the same anion is quite general. The following systems have been studied: LiCl–NaCl,[15] LiBr–NaBr,[16] Li_3AlF_6–Na_3AlF_6,[17] $LiNO_3$–$NaNO_3$,[18] Li_2SO_4–Na_2SO_4,[19] $LiBO_2$–$NaBO_2$,[20] Li_2CO_3–Na_2CO_3,[21] Li_2MoO_4–Na_2MoO_4,[22] Li_2WO_4–Na_2WO_4.[22] The experimental data are indecisive or insufficient for the nitrates, borates, carbonates, molybdates, and tungstates; in all the other cases, considerable miscibility is found at the liquidus, the chlorides, bromides, and the fluoaluminates forming continuous series with a minimum, while the sulfates present two series with an intermediate compound, analogous in principle to the system Na_2SiO_3–Li_2SiO_3[3] (Fig. 2). On the basis of lattice dimensions, it is probable that the iodides also would present a complete series of solid solutions. In the chlorides unmixing occurs below the critical temperature, 270–300°, 58 mole per cent. lithium chloride, the minimum on the liquidus being 553°, 72 mole per cent. lithium chloride; the fluorides may thus be expected to yield continuous solid solutions with unmixing very near the minimum on the liquidus, or actually above it, that is, two series with eutectoid relations. The carbonates, molybdates and tungstates are especially interesting. The sodium compounds are all three, at least partially, miscible with sodium sulfate; among the corresponding lithium compounds only the carbonate is known to be miscible with lithium sulfate; the tungstate and molybdate have not yet been investigated, and crystal structure information is also lacking. It is highly probable that miscibilities analogous to those in the sodium compounds will be found, and that, consequently, small amounts of solid solution will be found also, by sufficiently sensitive methods, in the corresponding systems of lithium and sodium compounds. The data on these systems, as they stand, are decidedly insufficient to deny the existence of such small amounts of solid solutions as exist between crystalline sodium and lithium disilicates (Fig. 9); on the other hand, it is certain that the miscibility, if it exists, must be very limited.

One further case requires consideration. The minerals jadeite ($NaAlSi_2O_6$) and spodumene ($LiAlSi_2O_6$) are found by crystal structure methods to be isomorphous with diopside ($CaMgSi_2O_6$).[23] The symmetry is that of the monoclinic pyroxenes, of which diopside is the type, but the spodumene structure is somewhat distorted by the substitution Li Al for Ca Mg, allowing the Si–O chains to pack somewhat closer together. It is to be expected, therefore, that spodumene will be only partially miscible with the other pyroxenes.

Summary

The phase equilibrium relations in the system, Na_2SiO_3–Li_2SiO_3–SiO_2 are described in this paper. The work was carried out by the method of quenching supplemented by thermal analysis.

There is one ternary compound, $NaLiSiO_3$, which is an end-member of the solid solution series $(Na_2,NaLi)SiO_3$. It melts incongruently at 847°. At the liquidus in the system, the pri-

(15) S. Zemczuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 403 (1910); W. Schaeffer, *Neues Jahrb. Mineral. Geol.*, Beilage Bd., **43**, 145 (1920).

(16) Kellner, *Z. anorg. Chem.*, **99**, 137 (1917).

(17) P. Drossbach, *Z. Elektrochem.*, **42**, 65 (1936).

(18) Thermal data by H. R. Carveth, *J. Phys. Chem.*, **2**, 209 (1898); calculations by P. de Cesaris, *Atti accad. Lincei*, **20-I**, 749 (1911).

(19) R. Nacken, *Neues Jahrb. Mineral. Geol.*, Beilage Bd., **24**, 1 (1907).

(20) H. S. van Klooster, *Z. anorg. Chem.*, **69**, 122 (1911).

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

(22) F. Hoermann, *ibid.*, **177**, 145 (1928).

(23) B. E. Warren and J. Biscoe, *Z. Krist.*, **80**, 391 (1931).

mary phases are $(Na_2,NaLi)SiO_3$ solid solutions, Li_2SiO_3, $Na_2Si_2O_5$ and $Li_2Si_2O_5$, all three of which form solid solutions of limited extent, and the three modifications of silicon dioxide, namely, quartz, tridymite, and cristobalite. The liquidus fields meet at two ternary eutectics: one at 697°, with $(Na_2,NaLi)SiO_3$, Li_2SiO_3 and $Na_2Si_2O_5$, the other at 637°, with $Li_2Si_2O_5$, $Na_2Si_2O_5$ and quartz as the eutectic constituents. $Li_2Si_2O_5$ melts incongruently throughout its region of existence in the system, the reaction temperature descending from 1033° in the binary system, Li_2SiO_3–SiO_2, to 641°, the peritectic end-point in the ternary system, with $Li_2Si_2O_5$, Li_2SiO_3, $Na_2Si_2O_5$ and liquid in coexistence.

The inversion temperature of quartz and tridymite has been redetermined. The temperature of 870 ± 10°, given by Fenner in 1913, is confirmed, the value obtained being 867 ± 3°.

Refractive indices of glasses of various compositions in the system were measured.

A discussion of solid solution relationships of sodium and lithium compounds in general is given, with particular reference to the theoretical aspects of the subject.

Minor revisions of the phase relations in the systems, Na_2SiO_3–SiO_2 and Li_2SiO_3–SiO_2, particularly with respect to the polymorphic behavior of $Na_2Si_2O_5$ and $Li_2Si_2O_5$, are presented.

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Pressure–Volume–Temperature Relations in Solutions. III. Some Thermodynamic Properties of Mixtures of Aniline and Nitrobenzene

BY R. E. GIBSON AND O. H. LOEFFLER

A few months ago we noted[1] that the absorption of light by mixtures of aniline and nitrobenzene was strongly influenced by pressure changes. In investigating this effect we thought it desirable to examine thoroughly the volume changes which take place when these two liquids are mixed in different proportions at different pressures and temperatures. Furthermore, we have noticed in the pure liquids[2] that, whereas the internal pressure $(\partial E/\partial V)_T$ varies with temperature at constant volume, another quantity, P_A, computed from the P–V–T data is independent of temperature at constant volume and is expressible as a'/V^n. We have tentatively identified P_A as the attractive internal pressure of the liquid. In this paper we shall give data from which the volumes of aniline–nitrobenzene mixtures may be determined at all concentrations, between 25 and 85° and between 1 and 1000 bars, and we shall examine the behavior of P_A in these solutions.

Experimental Results

The solutions were all made up independently from weighed amounts of samples of aniline and nitrobenzene purified to a degree which already has been described.[2] The specific volumes of these solutions were determined at 25.00° in 55-ml. U-tube pycnometers, and the thermal expansions were measured[3] at 10° intervals from 25 to 85° in a weight dilatometer of 18 ml. capacity made of vitreous silica.

The volumes of the solutions were expressed as functions of the temperature by empirical equations of the form

$$v = v_{55} + a(t - 55) + b(t - 55)^2 + c(t - 55)^3 \quad (1)$$

We already have published for the pure components such equations whose coefficients we may call a_1^0, a_2^0, b_1^0, b_2^0, etc. From them we computed[4] $\Delta_T v_1^0$ and $\Delta_T v_2^0$ at each temperature, using 55° as the base temperature, and thence the quantity $\Delta_T v - (x_1\Delta_T v_1^0 + x_2\Delta_T v_2^0) \equiv \delta_T$. This function measures the departures of the thermal expansions

(1) R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).

(2) R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, 2515 (1939).

(3) For details of the procedure in these measurements the reader is referred to the second paper of this series (ref. 2).

(4) The symbols used here are as follows. The subscripts 1 and 2 refer to nitrobenzene and aniline in solution, respectively, the superscript 0 implies the pure components, and symbols without subscripts refer to the solutions. The weight and mole fractions are given by x and X, respectively, $R_2 = X_2/X_1$, and v and V mean the specific and molal volumes. For a solution $V = v/(x_1/M_1 + x_2/M_2)$, M being the molecular weight. Φ is the apparent molal volume of a component. Δv and ΔV are the volume changes on mixing per gram and per mole of solution. All volumes are given in milliliters.

The pressure in kilobars is given by P, the temperature by t (centigrade scale) or T (absolute), and the total energy by E. Δ_T and Δ_P denote the finite changes with temperature and pressure, respectively, of the quantities to which they are prefixed. $k = -\Delta_P v/v\Delta_P = 0$. $z_1 = 1/(1 + R_2V_2^0/V_1^0)$, $z_2 = (1 - z_1)$ are the volume fractions of the components.