chain ions changes little with total concentration above the critical. The desired quantity is then dC_+^B/dC, the number of small ions bound per mole of colloidal electrolyte added to an infinite amount of solution. From equation (5)

$$\frac{dC_+^B}{dC} = 1 - 2\frac{d(gC)}{dC} \qquad (6)$$

Figure 2 shows a plot of gC *vs.* C for Aerosols MA and OT, and, for comparison potassium laurate.[21,25] It can be seen that slightly above the critical concentration straight lines result, the slopes of which provide values for $d(gC)/dC$ in equation (6). The slopes for the Aerosol-type agents are about 0.16; hence, $dC_+^B/dC = 0.68$, and consequently for each hundred moles of Aerosol added 68 moles of sodium are included in the micelles. For potassium laurate, on the other hand, $dC_+^B/dC = 0.86$. Since nearly all of the potassium is included, this suggests much larger micelles for this substance, although possibly the structure of the micelles may also play a role. This general difference exists between the branched chain salts, to which class most of the efficient wetting agents belong, and the straight chain salts, among which are found the more efficient solubilizing and emulsifying agents.

Acknowledgment.—The authors wish to thank the cyclotron groups at Columbia University and the University of California for the supply of radiotracers. Also, we wish to express our indebtedness to Dr. J. K. Dixon for valuable advice and criticism, and to the Directors of these Laboratories for permission to publish these results.

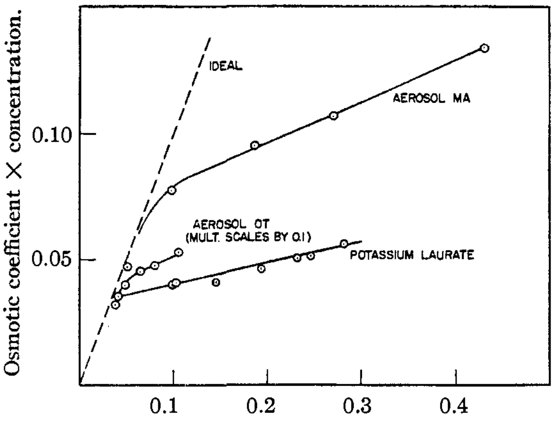

Fig. 2.—Osmotic coefficient times concentration *vs.* concentration for some colloidal electrolytes.

Summary

1. The transference numbers and self-diffusion coefficients for two anionic and two cationic surface active agents were determined using radiotracer techniques.

2. Utilizing the present results and freezing point data extant in the literature, the fraction of the small ions bound to the colloidal aggregates was calculated under consistent assumptions. The values calculated from the three types of measurements agreed well with one another up to several times the critical concentration for micelles. Possible causes for disagreement among the three types of measurements at higher concentrations were discussed.

3. The relationship of the extent of binding to the structure and size of the micelles was briefly considered.

STAMFORD, CONN. RECEIVED MARCH 29, 1947

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[25] Brady, Thesis, Stanford University, 1944, and unpublished work.

[CONTRIBUTION FROM U. S. NAVAL RESEARCH LABORATORY]

Liquid Immiscibility in the System H_2O–Na_2O–SiO_2

BY O. F. TUTTLE[1] AND I. I. FRIEDMAN

Introduction

The dwindling supply of natural quartz for piezoelectric uses, together with the remarkable success attained in growing other crystals for a variety of uses, has stimulated interest on the part of the Armed Forces in the production of synthetic quartz. This work on phase equilibria in a portion of the ternary system H_2O–Na_2O–SiO_2 is a result of efforts to find a commercially feasible method for growing quartz crystals.

The data presented here are incomplete, but publication at this time seems advisable because of the theoretical and practical value of the information. Liquid immiscibility has been observed and investigated in the region $Na_2Si_2O_5$–SiO_2–H_2O. The 250, 300 and 350° isotherms have been worked out at the vapor pressures of the compositions investigated.

Preparation of Materials

All mixtures used in this work were made from a stock solution of sodium hydroxide and quartz or silica glass. The solution was prepared by saturating distilled water with reagent grade sodium hydroxide at 80°. The sodium carbonate precipitated was allowed to settle and the solution decanted through glass wool. The saturated solution was then diluted to approximately 20 *N* and stored in a wax-lined bottle. The composition was determined by titrating a weighed volume against a standard solution of sulfuric acid. The resulting solution contained 388 g. of sodium oxide per 1000 g. and had a specific gravity

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of 1.566 at 25°. After one year, the composition was again determined by titrating with sulfuric acid and was found to be unchanged. A gravimetric check of the sodium oxide and silicon dioxide content gave a sodium oxide content of 386 ± 2 g. per 1000 g. and a silicon dioxide content of less than 0.1%.

Quartz oscillator plates of various sizes were used for all solubility experiments. The rate of solubility was determined using slabs of quartz cut and ground to uniform size. The variation in area of these blocks was less than 0.5%.

Clear silica glass rods were used for all other experiments. The rods were crushed in a diamond mortar and sieved. The material passing the 100 mesh, but not the 250 mesh screen was used after boiling in concentrated hydrochloric acid, washing and igniting at 800° in platinum crucibles. A 0.5 g. sample gave less than 0.0001 g. of residue on treatment with sulfuric acid and hydrogen fluoride.

Analytical Methods

The composition of the two immiscible liquids was determined by chemical analysis. The water content was determined in platinum crucibles by the loss of weight on ignition at bright red heat. As both liquid phases were readily soluble in water, the silicon dioxide was determined by precipitating with hydrochloric acid and igniting as silicon dioxide. It was found necessary to use two precipitations. Evaporation of the filtrate from the silicon dioxide precipitations gave the sodium oxide content as sodium chloride. The sodium chloride was heated to constant weight at 250°.

Experimental Methods

As the vapor pressures of the compositions investigated are of the order of magnitude of the vapor pressure of water at the temperatures employed (250, 300, 350°), it was necessary to use a container that was capable of withstanding considerable pressure. A bomb (Fig. 1) described by Morey and Ingerson[2] was found to be satisfactory. For part of the work it was found necessary to modify the seal slightly and to line the chamber by plating with gold (0.01 in.). The seal on the gold-plated bombs is illustrated in Fig. 2. The silver disc welded to the seat during the experiments, and on opening it was necessary to cut out the center of the disc, leaving a silver ring on the shoulder of the pressure chamber. In subsequent runs the silver continued to weld to the previous silver rings and it was necessary to dissolve the excess silver from the shoulder after 10 or 20 runs. The silver disc seal was also used in unlined bombs for much of the work, as it tended to prevent leaking during quenching.

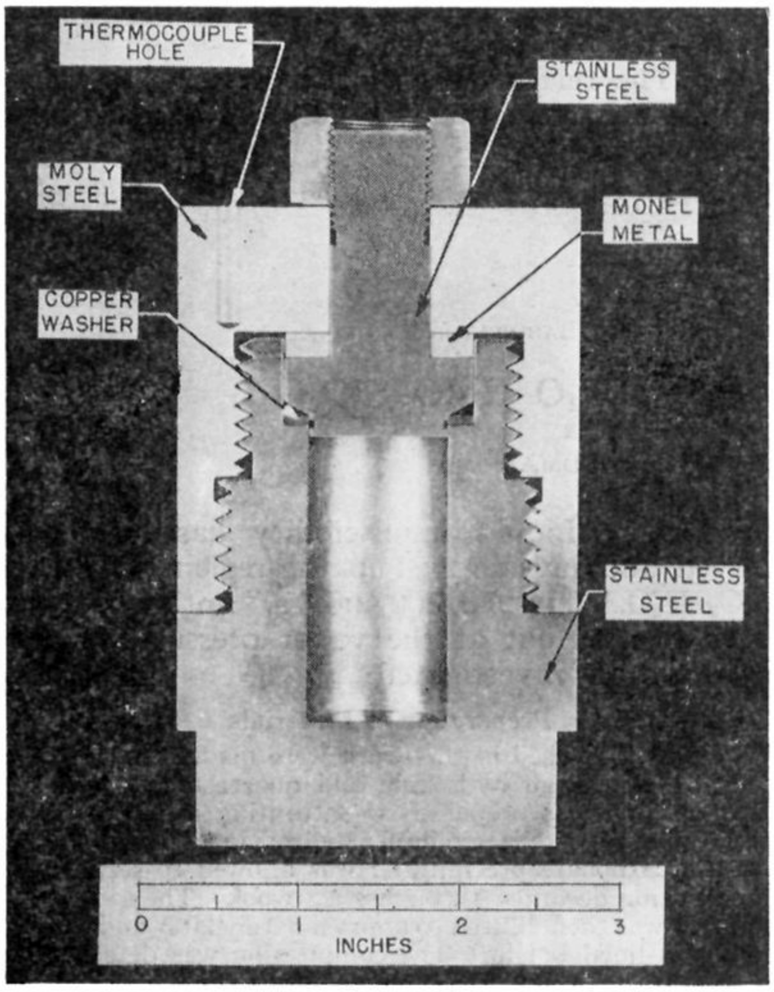

Fig. 1.—Cross-section of bomb used for this work.

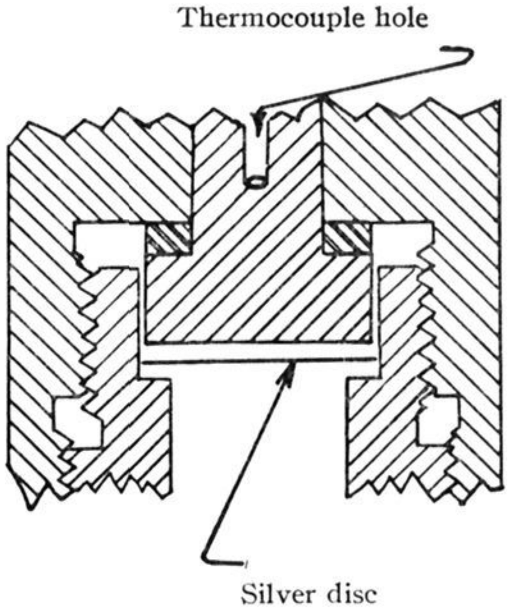

Fig. 2.—Cross-section of a portion of bomb showing construction when used with a silver disc as a seal.

The charges were stirred to hasten equilibrium by rocking the furnaces throughout the experiments (Fig. 3). The cylindrical resistance furnaces were oscillated 60° at 15 cycles per minute about an axis normal to the long axis of the bombs. Furnace temperatures were set manually by regulating the input voltages to the wire-wound heating element by means of a variac. Line voltage variations were kept to a minimum by a constant voltage transformer. It was possible to maintain temperatures at the thermocouple within ±2° by this method, but variations in the gradients between the thermocouple and charge in the different bombs used leads to an estimated uncertainty of ±5°. Temperatures were continually recorded by a Brown Electronik Strip Chart recorder using iron–constantan thermoelements.

Quartz Solubility Determinations.—The solubility of quartz in sodium hydroxide solution was used to establish the boundary of the quartz field. A weighed block of quartz was placed in an 18-cc. bomb together with 10 cc. of a sodium hydroxide solution of known composition, and the bomb was sealed. The bombs were then placed in the rocking furnaces at a predetermined temperature and allowed to attain equilibrium (thirty-six to one-hundred hours, depending upon temperature and composition), after which they were quickly removed and quenched under the cold water tap. The bomb and contents cooled to 100° within forty-five seconds and to room temperature in ninety seconds. The bombs were then opened and the quartz plate removed, washed and reweighed.

The composition of the solution in many of these runs passed through the stability field of sodium disilicate as the silica was being dissolved from the quartz plate; hence, if the length of run was insufficient to reach equilibrium, crystals of sodium disilicate were present on quenching.

Hydrothermal Quenching Method.—Equilibrium relations were studied by determining, at various constant

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(2) G. W. Morey and Earl Ingerson, *Am. Mineral.*, **22**, 1121–1122 (1937).

temperatures, the presence or absence of crystalline and liquid phases on changing the composition of a series of sodium hydroxide–water solutions varying in composition from 1.5 to 38.8% sodium hydroxide, by adding different amounts of silica. A weighed amount of silica glass was placed in a bomb and 10 cc. of sodium hydroxide solution of known composition added. The bombs were heated, quenched, and examined as in the solubility determinations. All crystalline phases were examined and identified with a petrographic microscope.

The method can be illustrated by an example as follows: To 10 cc. of a solution containing 5.8% sodium oxide and 94.2% water at 300°

0.22 g. silica—one liquid, no crystalline phase
0.33 g. silica—one liquid plus disilicate crystals
1.35 g. silica—two liquids plus disilicate crystals
1.50 g. silica—two liquids no crystalline phase
1.90 g. silica—two liquids plus quartz crystals

Thus it can be seen that, by varying the amount of silica above and below that at which a new phase appears, the limits between which the phase appears can be fixed. These are, then, points on fusion or solubility surfaces of the phases in question.

One disadvantage of the method is that the pressures are not known and cannot be calculated with any reasonable degree of accuracy except in compositions approaching pure water. However, as there is only one pressure at which equilibrium between any of the phases can exist for a given temperature and composition, the results are useful without this information. The data represent what is usually called the condensed system, that is, the solid–liquid relations at the vapor pressure of the system.

Morey and Fenner[3] have discussed in considerable detail two sources of error in the hydrothermal quenching method as used in working out the system H_2O–K_2O–SiO_2. The first source of error described concerns the possibility that the composition of the quenched glass does not represent the composition of the liquid. This error is negligible in the present work because the composition of the liquid or liquids at the liquidus temperatures *is the composition placed in the bomb* with the exception of the amount lost to the vapor phase. This error would increase, then, as the density and amount of the vapor phase increased. Since the density of the vapor increases with pressure, it seems reasonable to assume that this factor would be greatest for compositions approaching water because the vapor pressure at constant temperature for the compositions investigated would be in all cases less than for water. The amount of vapor phase is greatest at the 300° isotherm since 10 cc. of liquid was placed in the 18 cc. bomb for all runs. For water, the amounts in the liquid and vapor phases would be

at 250° 9.85 g. in liquid, 0.12 g. in vapor
300° 9.77 g. in liquid, 0.20 g. in vapor
350° 9.89 g. in liquid, 0.08 g. in vapor

It thus appears to be a reasonable assumption that the greatest error that would arise would be less than 2% of the composition placed in the bomb.

The second source of error in the quenching technique is in the certainty that the quenched phases have not changed composition during the quench. This has been discussed by Morey and Fenner[4] in considerable detail and the possibility of error in this respect seems very remote.

A third error is in being certain that equilibrium conditions have been attained. This possibility was repeatedly checked by making successive runs with increasing time. Consistent results over a wide range of compositions at different temperatures add to the certainty that equilibrium was attained.

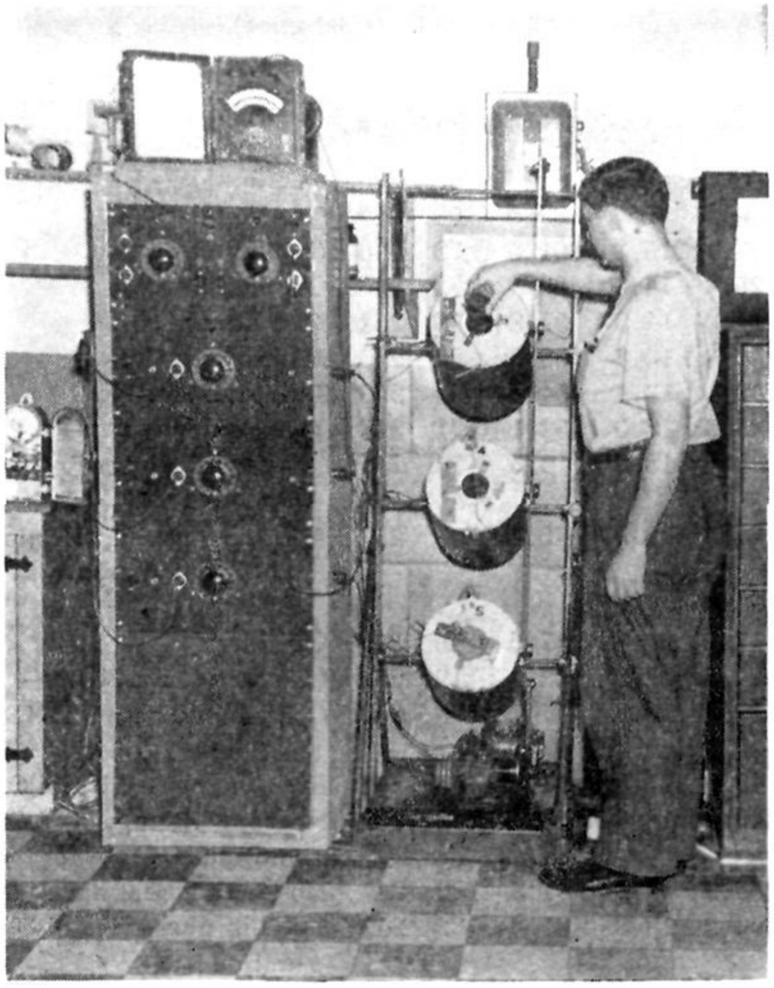

Fig. 3.—Rocking furnaces used for stirring charges at elevated temperatures and pressures.

Results

Isothermal Polybaric Equilibrium Relations.—Table I is a summary of the experiments carried

TABLE I

SiO_2, %	Na_2O, %	H_2O, %	Duration of run, hr.	Temp., °C.	Equilibrium phases
		250° Isotherm			
		Quartz Solubility Runs			
1.4	0.98	97.6	65	253	One liquid
2.4	1.5	96.1	112	248	One liquid
3.3	1.9	94.8	65	253	One liquid
7.5	3.5	89.0	112	251	One liquid
9.8	4.4	85.8	67	247	One liquid
10.5	4.4	85.1	147	247	Small amt. heavy phase
12.6	5.2	82.2	89	251	Small amt. heavy phase
14.3	5.9	79.8	112	248	Approx. 2 ml. heavy phase
16.5	6.2	77.3	118	251	Two liquids
20.2	7.6	72.2	147	247	Two liquids
28.3	10.7	62.0	89	247	Two liquids
		Other Runs			
7.6	4.4	88.0	47	251	One liquid
8.1	4.4	87.5	47	252	Approx. 0.1 ml. heavy phase
8.6	4.4	87.0	47	251	Approx. 0.5 ml. heavy phase
5.0	5.4	89.6	18	248	One liquid
8.5	5.2	86.3	18	248	Approx. 1 ml. heavy phase

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(3) G. W. Morey and C. N. Fenner, THIS JOURNAL, **39**, 1183–1187 (1917).

(4) Ref. 3, p. 1187.

TABLE I (*Continued*)

SiO_2, %	Na_2O, %	H_2O, %	Duration of run hr.	Temp., °C.	Equilibrium phases
8.3	7.1	84.6	98	250	One liquid
9.5	7.0	83.5	98	250	One liquid
23.1	15.2	61.5	72	246	One liquid
25.4	14.8	59.8	72	246	One liquid
27.9	14.3	57.8	18	253	Two liquids
30.3	13.8	55.9	20	250	All heavy phase
32.1	13.4	54.5	22	250	Two liquids
33.9	13.0	53.1	71	248	Two liquids
32.5	18.0	49.5	19	245	One liquid glycerol consist. n_D 1.436
38.6	16.3	45.1	19	250	Approx. 3 ml. liquid, n_D 1.391, heavy phase n_D 1.472
17.6	24.8	57.6	19	250	One liquid
24.3	22.8	52.9	19	252	One liquid, Na_2SiO_3
31.7	20.6	47.7	19	250	One liquid n_D 1.448, $Na_2Si_2O_5$
40.9	17.8	41.3	23	250	No thin phase, $Na_2Si_2O_5$
48.3	18.0	33.7	132	252	No thin phase, $Na_2Si_2O_5$ and quartz
50.9	17.2	31.3	132	247	No thin phase, quartz
48.9	19.8	31.3	132	247	No thin phase, $Na_2Si_2O_5$, and quartz
300° Isotherm Quartz Solubility Runs					
1.6	0.98	97.4	44	298	One liquid
4.2	1.9	93.9	44	298	Small amt. heavy phase
11.3	4.3	84.4	43	294	Two liquids
13.7	5.1	81.2	65	294	Two liquids
17.6	6.4	76.0	43	294	Two liquids
19.6	7.1	73.3	88	292	Two liquids
21.2	7.5	71.3	72	300	Two liquids
21.4	7.5	71.1	16	300	Two liquids
23.0	8.3	68.7	114	297	Two liquids
26.5	9.4	64.1	88	295	Two liquids
29.8	10.4	59.8	88	295	Two liquids
Other Runs					
2.0	2.8	95.2	17	299	One liquid, very small amt. $Na_2Si_2O_5$
3.0	2.8	94.2	17	297	One liquid, small amt. $Na_2Si_2O_5$
5.3	2.7	92.0	17	299	Approx. 0.1 ml. heavy phase
2.0	3.7	94.3	16	299	One liquid
3.0	3.7	93.3	17	297	One liquid, some $Na_2Si_2O_5$
4.0	3.6	92.4	19	298	One liquid, some $Na_2Si_2O_5$
6.0	3.6	90.4	19	298	Approx. 0.5 ml. heavy phase—$Na_2Si_2O_5$
7.6	3.8	88.6	40	299	Approx. 0.1 ml. heavy phase—small amt. $Na_2Si_2O_5$
8.0	3.8	88.2	40	299	Approx. 0.1 ml. heavy phase—small amt. $Na_2Si_2O_5$
8.7	3.8	87.5	115	302	Approx. 0.1 ml. heavy phase
2.0	5.6	92.4	19	302	One liquid
3.0	5.4	91.6	16	300	One liquid
4.0	5.4	90.6	18	300	One liquid, $Na_2Si_2O_5$
8.1	5.2	86.7	19	305	One liquid, $Na_2Si_2O_5$
11.1	5.0	83.9	19	303	Two liquids, some $Na_2Si_2O_5$
14.9	4.8	80.3	19	305	Two liquids, quartz
17.1	8.0	74.9	16	302	Two liquids, some $Na_2Si_2O_5$
19.1	7.8	73.1	16	300	Two liquids, some $Na_2Si_2O_5$
33.0	13.3	53.7	20	296	Two liquids, very small amt. $Na_2Si_2O_5$
33.9	13.0	53.1	49	300	Two liquids
35.1	12.8	52.1	66	298	Two liquids
36.3	12.6	51.1	66	298	One liquid, small amt. quartz
350° Isotherm Quartz Solubility Runs					
2.5	0.97	96.5	44	347	One liquid
5.3	1.9	92.8	44	347	Two liquids
7.5	2.5	90.0	42	353	Two liquids
9.9	3.5	86.6	71	345	Two liquids
12.5	4.3	83.2	162	350	Two liquids
14.7	5.0	80.3	71	345	Two liquids
19.0	6.3	74.7	55	350	Two liquids
22.3	7.4	70.3	118	345	Two liquids
24.2	8.2	67.6	65	350	Two liquids
25.9	8.8	65.3	118	345	Two liquids
27.0	9.3	63.7	56	350	Two liquids
24.0	9.7	66.3	48	353	Two liquids, $Na_2Si_2O_5$
Other Runs					
1.5	1.5	97.0	17	352	One liquid, some $Na_2Si_2O_5$
3.0	1.5	95.5	16	350	One liquid, small amt. $Na_2Si_2O_5$
3.5	1.4	95.1	20	350	Approx. 0.1 ml. heavy phase
1.0	3.8	95.2	17	352	One liquid
2.0	3.7	94.3	16	348	One liquid, small amt. $Na_2Si_2O_5$
4.0	3.6	92.4	19	347	One liquid, small amt. $Na_2Si_2O_5$
7.1	3.6	89.3	19	350	One liquid, $Na_2Si_2O_5$
13.2	3.3	83.5	21	353	Two liquids, quartz
12.6	4.5	82.9	19	348	Two liquids
1.4	5.5	93.1	17	346	One liquid
2.6	5.5	91.9	17	348	One liquid
4.0	5.5	90.5	19	349	One liquid, small amt. $Na_2Si_2O_5$
5.1	5.4	89.5	17	351	One liquid, $Na_2Si_2O_5$
7.7	5.2	87.1	17	347	One liquid, $Na_2Si_2O_5$
12.5	5.1	82.4	21	343	Small amt. heavy phase, some $Na_2Si_2O_5$
12.0	6.1	81.9	17	350	Two liquids, $Na_2Si_2O_5$
18.4	6.3	75.3	19	349	Two liquids
11.1	7.7	81.2	17	355	One liquid, $Na_2Si_2O_5$
17.1	7.9	75.0	67	346	Two liquids, $Na_2Si_2O_5$
25.6	8.7	65.7	18	355	Two liquids
10.2	9.6	80.2	17	348	One liquid, $Na_2Si_2O_5$
16.0	9.7	74.3	67	352	Two liquids, $Na_2Si_2O_5$
20.0	10.0	70.0	21	345	Two liquids, $Na_2Si_2O_5$

TABLE I (*Concluded*)

SiO_2, %	Na_2O, %	H_2O, %	Duration of run, hr.	Temp., °C.	Equilibrium phases
21.9	9.8	68.3	21	350	Two-liquids, $Na_2Si_2O_5$
25.3	9.4	65.3	19	357	Two liquids, $Na_2Si_2O_5$
14.8	12.4	72.8	67	350	One liquid, $Na_2Si_2O_5$
17.2	12.1	70.7	21	348	One liquid, $Na_2Si_2O_5$
29.8	10.3	59.9	19	343	Two liquids, small amt. quartz
30.9	10.1	59.0	18	350	Two liquids, quartz
34.2	13.1	52.7	41	350	Two liquids, $Na_2Si_2O_5$
36.1	12.6	51.3	64	347	Two liquids
37.8	12.3	49.9	41	353	Two liquids, quartz
50.9	19.0	30.1	40	353	Two liquids, $Na_2Si_2O_5$, quartz
55.0	17.4	27.6	40	353	Two liquids, quartz

out to determine the equilibrium conditions for the 250, 300, and 350° isotherms. The three isothermal sections are shown graphically in Figs. 4, 5, and 6. Compositions investigated are shown by small circles.

Equilibrium relations can perhaps best be illustrated by discussing, in some detail, the 250 and 350° isothermal sections. (The 300° and 350° are essentially alike.)

At 250° (Fig. 4) the area investigated is divided into two principal regions by the complicated curve H_2O–A–B–C–D–E–F. All compositions to the left of the curve are unsaturated at 250°, and all mixtures to the right of the curve consist of two liquids or of one liquid and one or more crystalline phases. The composition of all liquids that can coexist with crystalline phases is represented by the curve itself with the exception of the portion A–B–C. Mixtures in the area A–C–B consist of two liquids whose compositions vary along A–B and C–B. All other mixtures are partly crystalline at 250°, with the exception of compositions along the SiO_2–Na_2O side of the diagram which are completely crystalline at 250°,

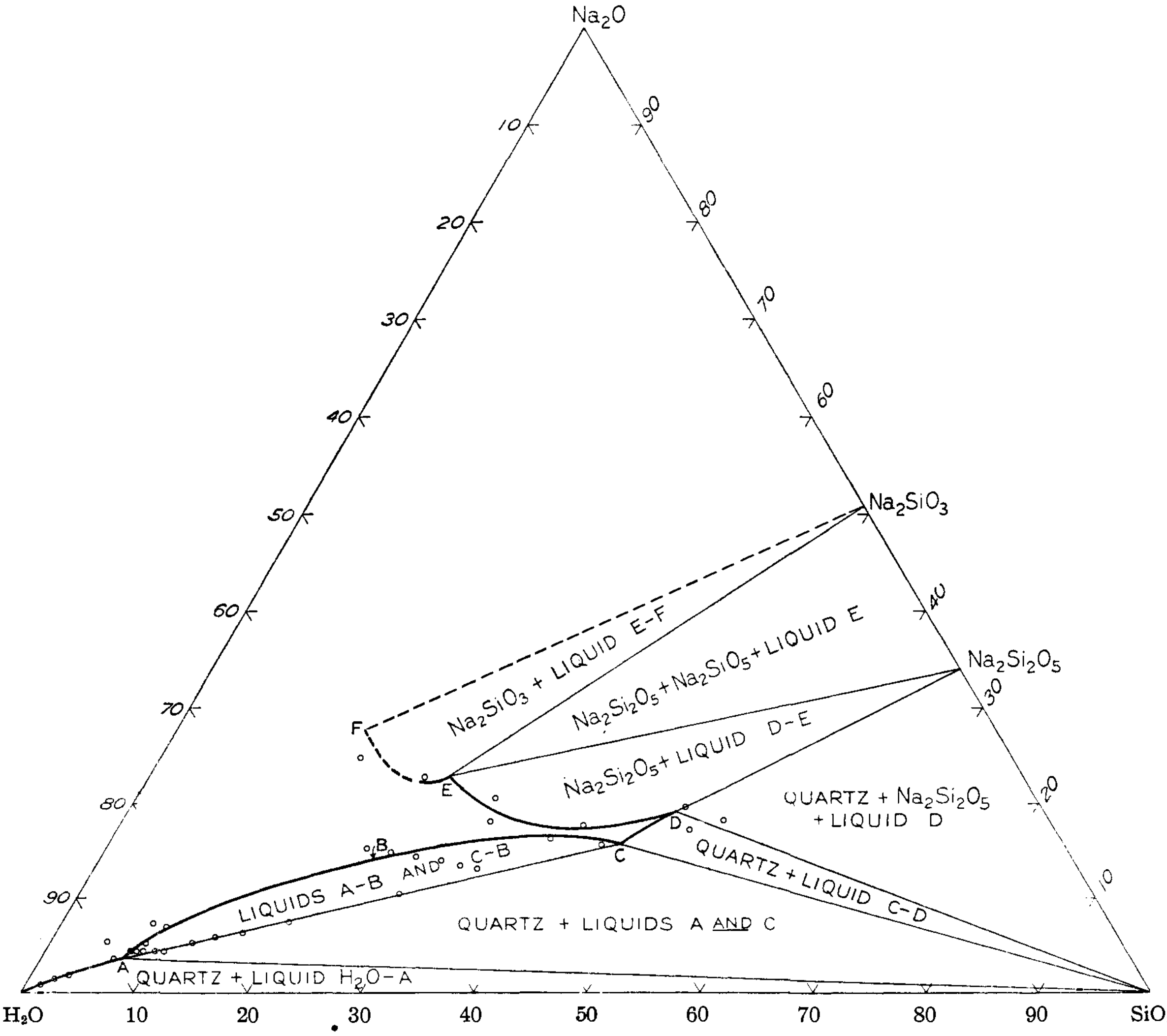

Fig. 4.—Polybaric saturation relations at 250° in the system H_2O–Na_2O–SiO_2.

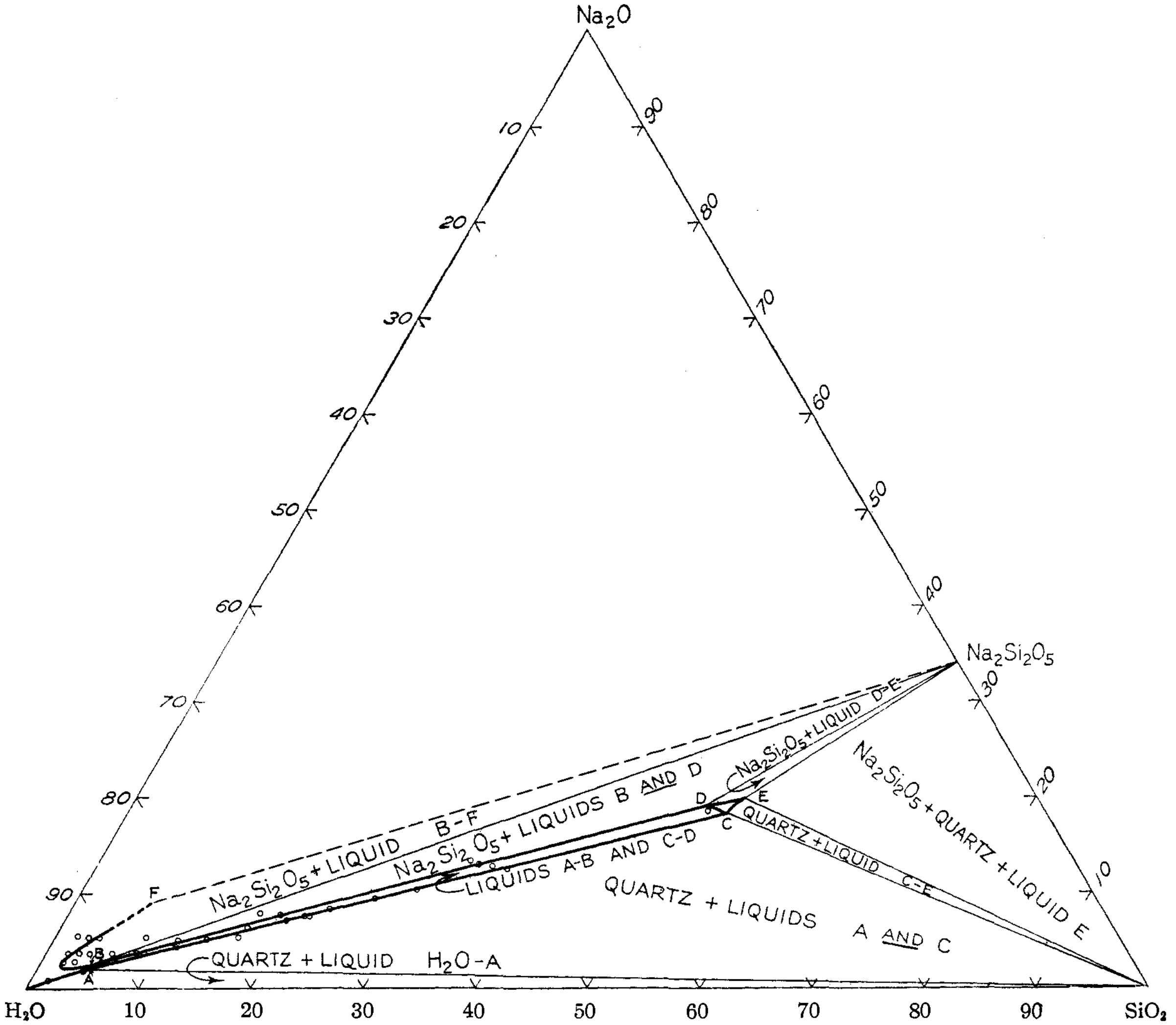

Fig. 5.—Polybaric saturation relations at 300° in the system H_2O–Na_2O–SiO_2.

All mixtures in the area H_2O–A–SiO_2 consist of one crystalline phase (quartz) and one liquid whose composition lies along the curve H_2O–A. Compositions in the triangle A–C–SiO_2 consist of quartz and two liquids A and C. The remainder of the diagram is largely self-explanatory and it seems unnecessary to describe each stability field separately.

The saturation relations at 350° are illustrated in Fig. 6. The relations here are similar to those at 250° with the exception that the $Na_2Si_2O_5$ stability field intersects the immiscible area. All mixtures, then, lying in the area A,B,D,C consist of two liquids A–B and C–D. Compositions in the triangle A–C–SiO_2 consist of quartz and two liquids A and C as at 250° and compositions in the triangle B–D–$Na_2Si_2O_5$ consist of $Na_2Si_2O_5$ crystals and two liquids B and D. The small area C–D–E represents a region consisting of one liquid only and was not realized experimentally; but from theoretical considerations such a relation appears necessary.

The Binary System $Na_2Si_2O_5$–H_2O.—A portion of this system has been studied by Morey and Ingerson.[5] They worked out the pressure–temperature relations at saturation from the melting point of $Na_2Si_2O_5$ (874°) down to 730° and 2000 lb./sq. in.[2] This portion of the system is apparently binary.

At 250° (Fig. 4) the system is binary in part, but where the $Na_2Si_2O_5$–H_2O join intersects the immiscible field, the two liquids formed do not lie on the join, hence the system is not binary from this point to A. From H_2O to point A, quartz crystallizes from $Na_2Si_2O_5$–H_2O mixtures and therefore this part of the system is not binary. There is some uncertainty as to whether or not the system is binary at 300 and 350° because the precision with which point B (Figs. 5 and 6) is located does not permit a decision as to whether $Na_2Si_2O_5$ will form two liquids or one. If two liquids are formed the system will not be binary, as the com-

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(5) G. W. Morey and Earl Ingerson, *Am. J. Sci.*, [5] **35A**, 217–225 (1938).

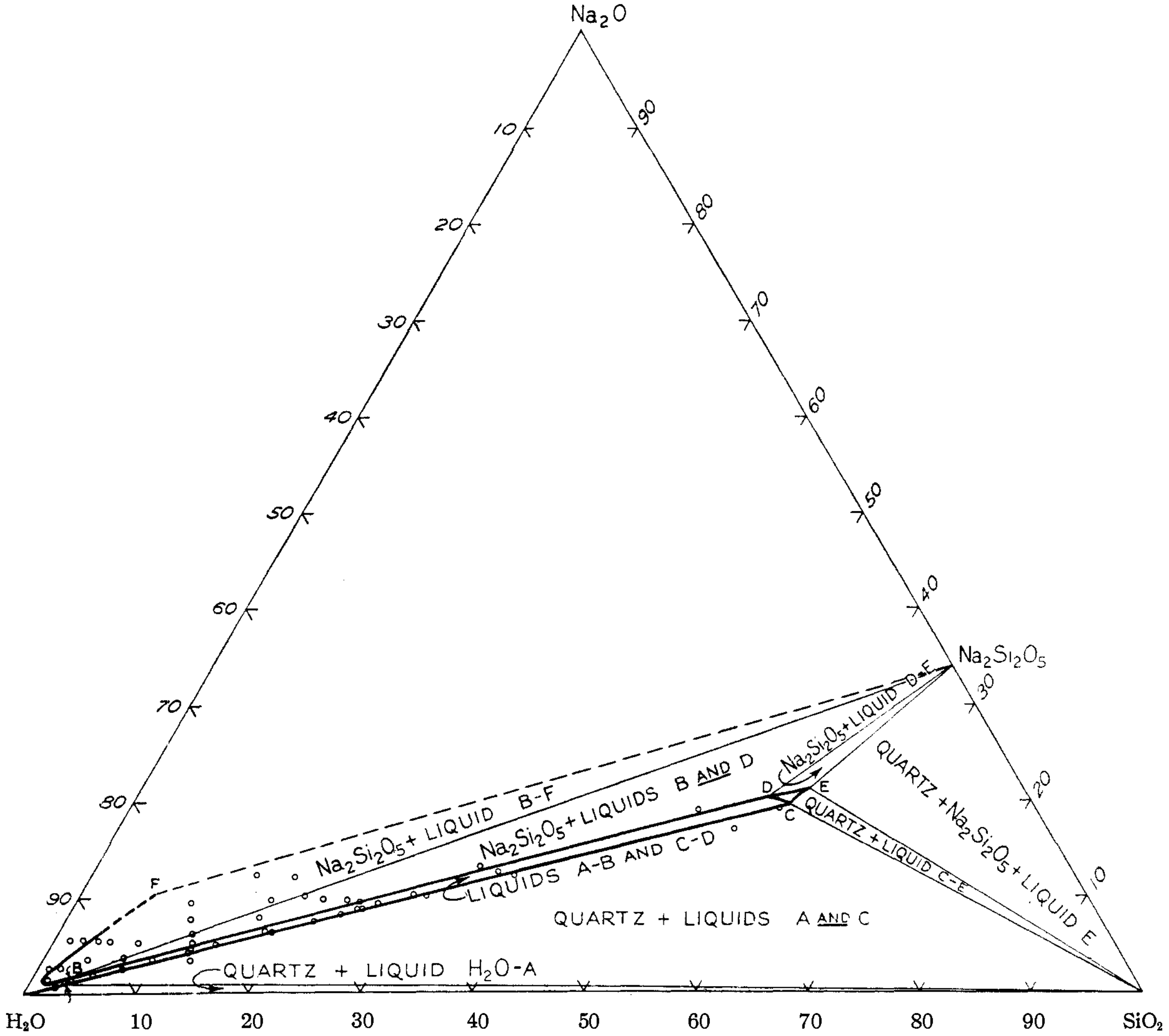

Fig. 6.—Polybaric saturation relations at 350° in the system H_2O–Na_2O–SiO_2.

position of the heavy liquid will not lie on the $Na_2Si_2O_5$–H_2O join. At 300° it is probable that the quartz field crosses the $Na_2Si_2O_5$–H_2O join at low $Na_2Si_2O_5$ concentrations, in which case this portion of the system will not be binary.

Liquid Immiscibility.—Many of the quartz solubility runs were characterized by the presence of a clear water-soluble glass together with a thin liquid upon quenching and opening. The amount of glass increased as the Na_2O concentration was increased. The glass was shown to be a liquid at the temperature of the experiment by quenching the bomb in different positions and observing that the glass always occupied the lowest point in the bomb.

The presence of a small amount of glass, which represented a liquid phase containing 30 to 40% H_2O, in a run whose total composition was 90% water, established the fact that two liquids must coexist at the temperature of the experiment. The question arises, is it possible that the glass represents a liquid phase and the thin liquid the vapor phase? A simple calculation shows that at 350°, for example, less than 1% of the volume of the 18-cc. bomb could be occupied by the vapor phase and the thin phase present on quenching may occupy as much as *8 or 9 cc. at room temperature.* It is obvious, then, that the thin phase represents a liquid phase at the temperature of the experiment plus a small amount of material that was in the vapor phase.

Character of the Heavy Phase.—Quartz solubility determinations at 250° yielded a glass whose composition is represented by point C (Fig. 4). This glass has a hardness of about 2.5 and is readily soluble in water. At 300° the glass had a composition shown by point C (Fig. 5) and is noticeably harder and less soluble than the 250° glass. The 350° glass is very brittle, has a hardness of approximately 5, and is slowly soluble in water (C, Fig. 6). As the composition of the heavy phase approached the critical point (B,

Fig. 4), the viscosity of the quenched material changed continuously from a glass at C to a liquid with the approximate consistency of SAE 20 lubricating oil.

Table II is a summary of analyses of the two phases, together with the original composition. The composition of the two immiscible liquids cannot be determined with great accuracy without elaborate equipment for sampling under the pressure–temperature conditions encountered. However, the heavy phase quenches readily to a glass which, with some caution, can be sampled with little or no contamination from the light phase, but the latter cannot be sampled nearly so accurately because of contamination from the condensed vapor phase and solution of some of the heavy phase.

TABLE II

Temp., °C.	Initial composition, % SiO$_2$	Na$_2$O	H$_2$O	Composition of light phase, % SiO$_2$	Na$_2$O	H$_2$O	Composition of heavy phase, % SiO$_2$	Na$_2$O	H$_2$O
250	33.9	13.0	53.1	21.8	9.0	69.2	45.5	17.5	37.0
300	35.1	12.9	52.0	17.2	6.7	76.1	51.0	18.0	31.0
350	36.1	12.6	51.3	12.1	4.5	83.4	55.4	20.1	24.5

The analysis of the heavy phase was used in locating the boundary of the immiscible area on the high silica end of the region. The boundary of the immiscible area in the low silica region was defined by allowing the bombs to remain inverted in the furnace a few minutes prior to removal, and quenching in the inverted position for forty-five seconds, after which the bombs were turned right side up and opened. The heavy phase collects on the silver washer, and amounts as small as 0.05 g. of the glass can easily be detected.

The Immiscible Region.—In the three-dimensional temperature–composition prism the region of liquid immiscibility in a ternary system in which there is no solubility gap in the liquid phases of the binary systems has the shape of a spheroid when it is not intersected by the stability field of a crystalline phase. Theoretically, this spheroid may be cut off by the stability fields of crystalline phases in almost any manner. In most examples the lower portion of the spheroid is intersected by one or more stability fields of crystalline phases. The present system is unusual in that the upper portion of the spheroid is apparently cut off by stability fields of $Na_2Si_2O_5$ and quartz. Immiscibility has not been found in several runs at 200°, hence the lower consolute point on the immiscibility spheroid is probably between 200 and 250°. The upper extent of the immiscible region has not been reached.

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Summary

A portion of the system Na_2O–SiO_2–H_2O was investigated. Equilibrium relations were determined at 250, 300 and 350°. The system possesses liquid immiscibility with a lower consolute temperature between 200 and 250°. The immiscible region is intersected at 250° by the quartz stability field, and at 300 and 350° by the stability fields of quartz and $Na_2Si_2O_5$.

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The Methanolysis of 3,4-Epoxy-1-butene

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Introduction

Kadesch[2] reported that the allylic epoxide, 3,4-epoxy-1-butene, was attacked by methanol at the primary position in the presence of sodium methoxide and at the secondary position in the presence of sulfuric acid. In an attempt to prepare the resulting isomeric ether–alcohols we repeatedly obtained products from both acid and alkaline treatments yielding the same 3,5-dinitrobenzoate (m. p. 75.5–76°). Furthermore, the yield of this derivative was highest in the case of the acid-catalyzed methanolysis from which Kadesch reported only a 3,5-dinitrobenzoate melting at 107–109°. As a result of these discrepancies we have made a more careful study of the reaction than was at first intended, with the following conclusions: The product of the acid-catalyzed methanolysis is the primary alcohol 2-methoxy-3-buten-1-ol (II) as reported by Kadesch, although its 3,5-dinitrobenzoate melts at 75.5–76° and not at 107–109°. The alcohol is accompanied by a small amount of crotonaldehyde and by a larger amount of a dimolecular product, probably the 2-erythryl ether of 2-methoxy-3-buten-1-ol (VIII). The low-boiling product of the base-catalyzed methanolysis is a mixture of II and 1-methoxy-3-buten-2-ol (I) which could not be separated and from which only the 3,5-dinitrobenzoate of II could be crystallized. We obtained neither the dinitrobenzoate of I nor any compound resembling the dinitrobenzoate of Kadesch melting at 107–109°. Our results and their relation to the results of Kadesch are summarized in the flow sheet and in Table I.

Discussion of Results

Kadesch[2] has given an able discussion of the

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[1] Pittsburgh Plate Glass Fellow, 1945–1946.

[2] Kadesch, THIS JOURNAL, 68, 41 (1946).