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The System Water–Sodium Oxide–Silicon Dioxide at 200, 250, and 300°[1]

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Studies were made of the H_2O–Na_2O–SiO_2 system at its vapor pressure at 200, 250, and 300°. Three different sodium trisilicate hydrates were encountered in the investigation. At 300°, $Na_2Si_3O_7 \cdot 5H_2O$ is found: at 250°, $Na_2Si_3O_7 \cdot 6H_2O$; and at 200°, $Na_2Si_3O_7 \cdot 11H_2O$. The liquid immiscibility previously reported to exist in the system was found to be a quenching phenomenon caused by the decomposition of the hydrates to unstable, supersaturated, viscous liquids. Under conditions where equilibrium is maintained, as temperature is lowered, the hydrates decompose to quartz, sodium disilicate, and liquid. The retrograde solubility of sodium disilicate and its tendency to form supersaturated solutions during heating from 25 to 250° account for higher solubilities reported by others than were found in this study. The solubility of sodium disilicate in water is 26% at 200°, 9% at 250°, and 5% at 300°. Sodium metasilicate solubility is 38% at 200° and 34% at 250°; this compound is incongruently soluble at 300°.

Introduction

Portions of the system H_2O–Na_2O–SiO_2 have been investigated previously by many workers including Morey and Ingerson,[2] Tuttle and Friedman,[3] Baker, Jue, and Wills,[4] Friedman,[5] and Morey and Hesselgesser.[6]

Morey and Ingerson[2] found that sodium disilicate ($Na_2Si_2O_5$) has a strongly retrograde solubility in water. Tuttle and Friedman[3] published isothermal, polybaric sections of the system at 250, 300, and 350° and reported the formation of two immiscible liquids at certain bulk compositions. Butozov and Briatov[7] also reported immiscibility in part of the system H_2O–SiO_2–Na_2CO_3. The results of Tuttle and Friedman[3] were not in agreement with incomplete and unpublished work by Morey, and it was decided to reexamine the system.

Experimental Section

Starting Materials.—Crystalline sodium silicates of the composition of metasilicate, disilicate, $3Na_2O \cdot 8SiO_2$, and trisilicate were prepared by fusing calculated amounts of sodium carbonate (reagent grade) with pure quartz obtained from a large single crystal (99.9% SiO_2). The glassy melts were devitrified by heat treatment. Metasilicate crystallized readily. Disilicate was crystallized by annealing at 800° for several days. Trisilicate[8] and $3Na_2O \cdot 8SiO_2$[9,10] were crystallized by annealing at 700–750°. The crystallinity of all starting materials was verified by optical and X-ray diffraction examination.

Calculated amounts of the various crystalline sodium silicates and distilled water to give desired gross compositions were weighed into silver liners for a modified Morey bomb. NaOH solution of known composition was added to sodium metasilicate to prepare compositions richer in Na_2O than metasilicate.

Equipment.—Modified Morey bombs[3] equipped with silver liners of 15-ml capacity were used in most of the experiments. The liners, covered by silver-disk caps, were removed for weighing before and after each run. Sticking of the silver to the bomb parts was prevented (1) by placing a Teflon washer under the lip of the silver liner and a Teflon disk between the silver cap and the bomb plunger and (2) by placing 1 or 2 drops of water between the silver liner and the main body of the bomb. Each bomb, containing a charge essentially sealed in silver, was placed on a spindle inside an automatically controlled electric resistance furnace and rotated end over end at 1 rpm for at least 24 hr. Temperatures were measured with chromel–alumel thermocouples. During a run, one thermocouple was placed in air close to the bomb near the axis of rotation, and at the conclusion of a run, another thermocouple was inserted into a well in the cap of the bomb. The two thermocouples always agreed to ±0.5°.

To study the reported liquid immiscibility in the system, a method was used by means of which the phases actually present at the temperature and pressure of the run could be directly observed. Charges were sealed in Pyrex tubes (8-mm i.d., 10-mm o.d., 8 cm long) so that the charge filled approximately half the tube. The tubes were then mounted on a shaft in a windowed furnace and rotated end to end at 1 rpm. An intense, focused light directed through the rear window of the furnace provided illumination to view the sample tube as it slowly rotated while at a desired temperature. A magnifier at the front window aided observing changes during heating and cooling. Furnace temperatures were automatically controlled and checked with a chromel–alumel thermocouple. Runs in glass tubes were limited to a few hours at high temperature because the charge slowly dissolved the glass tube. However, for the compositions thus investigated, 1–2 min at temperature was sufficient time to observe the formation of and disappearance of phases. This will be discussed later.

Experimental Procedures.—In the experiments using modified Morey bombs, charges of approximately 10–12 g were enclosed in the silver containers and equilibrated at given temperatures at the vapor pressure generated within the system. Each capped silver liner with enclosed charge was weighed before and after a run. The same weight before and after an experiment indicated no change in bulk composition due to leaks during the run. This procedure also allowed bulk compositions to be precisely changed for successive experiments by adding small amounts of water or solid to the previously investigated charge.

Because of the strongly retrograde solubility of sodium metasilicate and sodium disilicate at the vapor pressure of the system, many bulk compositions at equilibrium yield only liquid at temperatures below 200°, but at appropriate temperatures above 200° they yield mixtures of liquid and crystals. It was found that the nucleation and growth of sodium disilicate crystals from supersaturated solutions is sluggish. Thus, upon heating from 25° to

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] H. L. Adams, Annual Report of the Director of the Geophysical Laboratory, Carnegie Institute of Washington, Washington, D. C., 1941, Year Book 40, p 39.

[3] O. F. Tuttle and I. I. Friedman, *J. Am. Chem. Soc.*, **70**, 919 (1948).

[4] C. L. Baker, L. R. Jue, and H. J. Wills, *ibid.*, **72**, 5369 (1950).

[5] I. I. Friedman, *ibid.*, **72**, 4570 (1950).

[6] G. W. Morey and J. M. Hesselgesser, *Am. J. Sci.*, Bowen Volume, 343 (1952).

[7] V. P. Butozov and L. V. Briatov, *Kristallografiya*, **2**, 670 (1957).

[8] P. P. Budnikov and M. A. Matveev, *Proc. Acad. Sci. USSR, Chem. Sect.*, **107**, 177 (1956).

[9] J. F. Schairer and H. S. Yoder, Annual Report of the Director of the Geophysical Laboratory for 1963–1964, Carnegie Institute of Washington, Washington, D. C., 1964, pp 78, 79.

[10] J. Williamson and F. P. Glasser, *Science*, **148**, 1589 (1965).

the desired temperature of a run, some water-rich bulk compositions would pass from an unsaturated liquid to a saturated liquid and finally to a supersaturated condition owing to the failure of crystals to nucleate and grow. To overcome this difficulty many runs were initially heated to 300°, at which temperature crystallization of sodium disilicate takes place in a few hours. After allowing sufficient time to assure crystallization (determined by previous experiments), the temperature was lowered to the desired value and maintained at that value for the rest of the run.

In some runs an alternate procedure was used. A few crystals of sodium disilicate were placed in a lip at the top of the silver liner, out of contact with the liquid which partially filled the liner. The bomb was heated to temperature without rotation. When the desired temperature was reached rotation was started, which dropped the crystals into the solution. This effectively seeded the solution and promoted the growth of new euhedral sodium disilicate crystals in those solutions which had become supersaturated during heating. Sodium disilicate, metasilicate, and quartz crystals grown in the bomb all were sharply euhedral and could be readily distinguished from the broken and ragged starting materials.

To facilitate the collection of crystals for identification purposes, particularly in composition regions where mostly liquid is present, the following procedure was used. For several minutes before quenching, the bomb was held stationary upside down in the furnace. This allowed crystals to settle onto the silver disk which sealed the liner. The bomb was then quenched upside down in ice water, righted, and opened. Generally upon removing the silver closure disk, many of the crystals were found adhering to this disk. Such crystals were collected and identified with the aid of a polarizing microscope, supplemented by X-ray techniques.

In order to sample the liquid coexisting with crystals at the temperature of the experiment, a small silver cup was formed to fit at the upper end inside the silver liner. The bomb was placed in the furnace in an upright position so that the charge filled part of the liner but did not enter the cup. The temperature was maintained for 16–48 hr during which time the bomb was periodically rocked through a 60° arc to stir the contents. After allowing time for crystals to settle to the bottom of the liner, the bomb was tilted to pour liquid into the cup. The bomb was then returned to an upright position and quenched in ice water.

For the analysis of liquids, a small sample of liquid (approximately 0.1 g) was extracted from the cup, weighed, and diluted for use in the determination of silica by the molybdenum blue method[11] and of Na_2O by flame photometry.

Results

Approximately 400 runs were made on 286 compositions. A tabulation of the experimental results is on file with the American Documentation Institute.[12] This tabulation does not include duplicate runs and those which did not reach equilibrium. Isothermal sections at 200, 250, and 300° are shown in Figures 1–3. The heavy curves in each of these figures are isothermal polybaric saturation curves. The pressure at any given point along a curve is equal to the vapor pressure of the liquid existing there. Compositions of coexisting gas phases were not determined. The compositions of water-rich liquids saturated with two solid phases are listed in Table I.

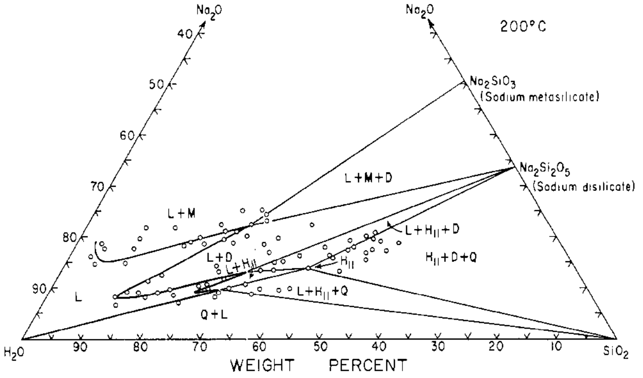

Figure 1.—Isothermal section at 200°. The small circles show bulk compositions that were used in the investigation. The heavy line is the isothermal polybaric saturation curve. The thin lines show the fields of stability of the various phase assemblages as labeled. L = liquid, Q = quartz, D = sodium disilicate, M = sodium metasilicate, and H_{11} = sodium trisilicate undecahydrate.

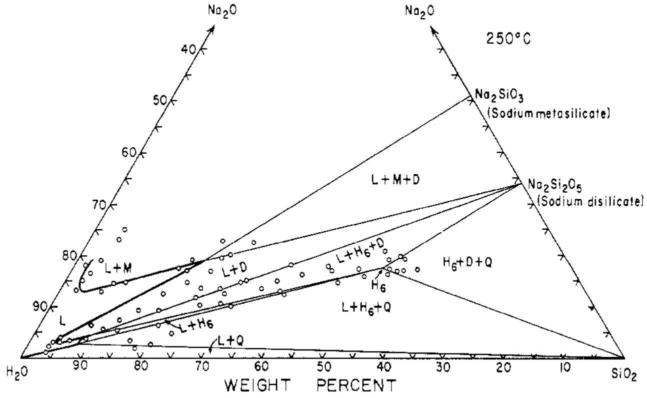

Figure 2.—Isothermal section at 250°. The notation is the same as for Figure 1, except H_6 = sodium trisilicate hexahydrate.

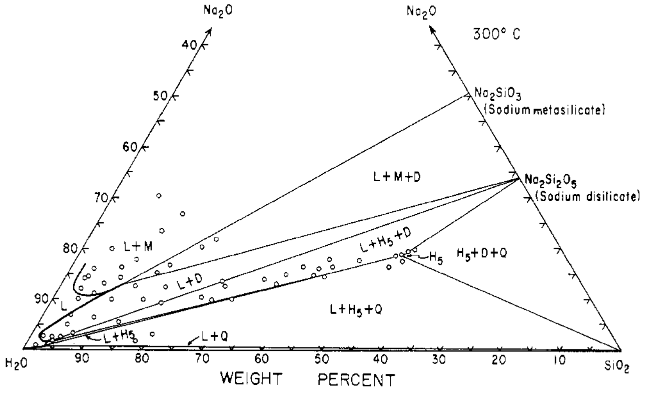

Figure 3.—Isothermal section at 300°. The notation is the same as for Figure 1, except H_5 = sodium trisilicate pentahydrate.

Hydrate Formation and Apparent Liquid Immiscibility.—The most significant result of these experiments was the recognition of the existence of discrete phases believed to be sodium trisilicate hydrates, stable under the conditions of the experiment, but unstable at room temperature and pressure.

Dr. Marshall[13] of the Oak Ridge National Laboratory was the first to observe the formation of a solid at conditions of temperature, pressure, and composition

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[11] W. E. Bunting, *Ind. Eng. Chem., Anal. Ed.*, **16**, 612 (1944).

[12] Tables of experimental results at 200, 250, and 300° have been deposited as Document No. 9375 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[13] W. L. Marshall, private communication, 1962.

TABLE I

COMPOSITIONS OF WATER-RICH LIQUIDS AT INVARIANT POINTS

Temp, °C	Starting compn, wt %			Compn of liquid, wt %			
	SiO_2	Na_2O	H_2O	SiO_2	Na_2O	H_2O	Coexisting phases
200	29.76	10.24	60	27.5	10	62.5	Liquid + quartz + hydrate
250	16.4	3.6	80	7.44	3.02	89.54	Liquid + quartz + hydrate
	20	3	77	7.39	3.1	89.49	Liquid + quartz + hydrate
	29.76	10.24	60	6.9	2.97	90.13	Liquid + quartz + hydrate
				Av 7.24	3.03	89.72	
	21	9	70	11	5.3	83.7	Liquid + disilicate + hydrate
	27.2	12.8	60	9.9	5.4	84.7	Liquid + disilicate + hydrate
				Av 10.45	5.35	84.2	
300	29.76	11.24	60	2.5	1.0	96.5	Liquid + quartz + hydrate
	27.2	12.8	60	3.0	1.5	95.5	Liquid + disilicate + hydrate

which had been reported by Tuttle and Friedman[3] to yield only two immiscible liquids. Using apparatus[14] which he had previously used for the visual observation of liquid immiscibility in the system UO_3–SO_3–N_2O_5–H_2O, Dr. Marshall examined a sample (26.25 wt % SiO_2, 10.5 wt % Na_2O, 63.25 wt % H_2O) which we sent to him. Part of the sample was placed in Pyrex tubes (2-mm i.d.) and part in pure silica glass tubes (0.8-mm i.d.). The tubes were sealed and placed in liquid salt baths at various temperatures from 150 to 252° for 10 sec to 15 min. Above 160° a white solid formed within 10 sec after placing a tube in a salt bath. Upon removing the tube from the bath the white solid liquefied within 10 sec yielding a gellike material in contact with a watery liquid. However, if the process was repeated several times with one tube or if a tube was held at high temperature for 10–15 min, enough reaction of the charge with the tube occurred to prevent the reliquefication of all of the solid dispersed in the liquid. Presumably a solid silica phase formed in addition to the hydrate. This behavior was not found to occur when we used 8-mm i.d. tubes. Below 150–160° a single liquid appeared to be stable.

Using Pyrex tubing of much larger diameter (8-mm i.d.) and the equipment already described, the authors confirmed the observation of Dr. Marshall. Bubbles evolve from the immediate vicinity of the white solid just as that solid liquefies to a viscous material. At 250° the white solid is more dense than the liquid and settles to the bottom of the container. However, at 200° the solid is less dense than the liquid and floats to the top of the container. This explains certain results found after quenching charges contained in Morey bombs. Runs of appropriate composition quenched from 250 and 300° yield a hard viscous material at the bottom of the container. Runs quenched from 200° yield a gelatinous material as a skin on top of the watery liquid. Because the hydrate floated at 200°, attempts to isolate the liquid in contact with that hydrate by pouring the liquid into an internal cup did not succeed. Therefore, the analysis of the water-rich liquid at 200°, shown in Table I, is suspect. The liquid may have been contaminated during and after the quench by reaction with the liquefied hydrate.

To determine the amount of silica which may have been dissolved from the glass tube, a run was made at 300° using a sealed Pyrex glass tube containing a charge of composition 25.4% SiO_2, 9.6% Na_2O, and 65% H_2O. Upon heating the charge from room temperature to 300°, a white precipitate formed and settled to the bottom of the tube. After 1 hr at 300° the temperature was reduced to 150° and the tube was rotated to provide a homogeneous liquid as the white precipitate completely dissolved. The Pyrex tube was then cooled to room temperature and analysis showed that the charge had gained 1% SiO_2. Considering the concentration of SiO_2 in the starting liquid, this does not represent a great change in composition and would change the bulk composition only slightly.

One long run was made in a tube of alkali-resistant glass (Corning 7280) in which a charge of the same composition as that listed above was heated without rotation. During the initial heating a white precipitate formed and floated to the top of the container at a temperature above 160° and then settled to the bottom of the container at about 227°. The sample then was maintained for 17 hr at 250°. At the end of this time the white material at the bottom of the container still showed no sign of forming an immiscible liquid layer or even of being composed of independent globules of liquid. Finally the tube was inverted and the white material was closely observed through a telescope as it settled as discrete particles through the clear liquid. However, upon quenching, this white material immediately changed to a coalescing, viscous, glassy semisolid. An important point is that this reaction is reversible. Upon reheating the charge, the white precipitate forms again.

The formation of the solid was also observed using a heating stage mounted on a petrographic microscope. The white precipitate was too finely grained to exhibit birefringence. However, the white material was not present as globules as would be the case if it were a silica-rich liquid phase dispersed in a water-rich liquid.

Despite many attempts, no hydrate was isolated for study or analysis at 25° and 1 atm total pressure. This is understandable from Marshall's observation that a white solid (presumably a hydrate) liquefied upon quench even when the container was taken from 250 to 25° in 10 sec. Similarly, the hydrate was not pre-

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(14) C. J. Barton, G. M. Hebert, and W. L. Marshall, *J. Inorg. Nucl. Chem.*, **21**, 141 (1961).

served when charges contained in sealed silver tubes were quenched at 5000 psi of externally applied pressure. Using an even higher pressure probably would not help because the hydrate which forms at 200° is less dense than the coexisting liquid. Increasing the water pressure allows the hydrate to decompose at higher temperature. Therefore, the composition of each hydrate was obtained by finding the point of intersection of the boundary curves separating the fields of quartz + disilicate + hydrate, disilicate + hydrate + liquid, and quartz + hydrate + liquid. At 300° $Na_2Si_3O_7 \cdot 5H_2O$ is present. At 250° the hydrate contains $6H_2O$, and at 200°, $11H_2O$.

For conditions at the vapor pressure of the system from 25 to 300°, nowhere in this range were two immiscible liquid phases found to be stable together. The observed viscous liquid that forms by liquefication of hydrated sodium trisilicate is completely miscible with the less viscous liquid given enough time and stirring of the system. Upon slow cooling, if the temperature is maintained at which a hydrate first is observed to liquefy (about 150–160°), as soon as the viscous liquid forms, that liquid starts to react with the less viscous liquid. The two liquids dissolve into each other and finally one liquid results.

The Pressure–Temperature Diagram for a Portion of the System.—Within the portion of the ternary system $H_2O–Na_2O–SiO_2$ bounded by H_2O, $Na_2Si_2O_5$, and SiO_2, seven phases were encountered in this study. They are gas, quartz, sodium disilicate, liquid, sodium trisilicate pentahydrate, sodium trisilicate hexahydrate, and sodium trisilicate undecahydrate.[15]

In the ternary system containing only these seven phases there are theoretically 21 possible invariant points in pressure–temperature–composition dimensional space. At each invariant point, five phases coexist and five curves, representing divariant reactions among the five phases, radiate.[16] Using techniques explained by Morey and Williamson,[17] Schreinemaker,[18] Niggli,[19,20] and Morey,[21] it is possible to determine the sequence of divariant curves that radiate about an invariant point, with pressure and temperature as coordinates. This was done for each of the 21 invariant points defined by the combinations of five-phase assemblages shown in Table II. These 21 invariant points plus divariant curves were positioned on a single *P–T* diagram and the points having a reaction in common were connected by the appropriate divariant curve for that reaction. A network of curves was thus built up which enclosed areas where specific assemblages of phases are stable or metastable at limiting temperature–pressure conditions. The complexity of this diagram is such that it would be incomprehensible at a scale necessary for reproduction.

Table II

Possible Invariant Points in the Portion of the System $H_2O–Na_2O–SiO_2$ Bounded by $H_2O–Na_2Si_2O_5–SiO_2$

No.	Invariant assemblage[a]		No.	Invariant assemblage[a]	
1	$GQDLH_{11}$	Stable	12	$GDLH_6H_5$	Stable
2	$GQDLH_6$	Metastable	13	$GQH_{11}H_6H_5$	Metastable
3	$GQDLH_5$	Metastable	14	$GDH_{11}H_6H_5$	Metastable
4	$GQDH_{11}H_6$	Stable	15	$GLH_{11}H_6H_5$	Metastable
5	$GQH_{11}H_5$	Metastable	16	$QDLH_{11}H_6$	Stable
6	$GQDH_6H_5$	Stable	17	$QDLH_{11}H_5$	Metastable
7	$GQLH_{11}H_6$	Stable	18	$QDLH_6H_5$	Stable
8	$GQLH_{11}H_5$	Metastable	19	$GDH_{11}H_6H_5$	Metastable
9	$GQLH_6H_5$	Stable	20	$QLH_{11}H_6H_5$	Metastable
10	$GDLH_{11}H_6$	Stable	21	$DLH_{11}H_6H_5$	Metastable
11	$GDLH_{11}H_5$	Metastable			

[a] G = gas, Q = Quartz, D = $Na_2O \cdot 2SiO_2$, L = liquid, H_{11} = $Na_2O \cdot 3SiO_2 \cdot 11H_2O$, H_6 = $Na_2O \cdot 3SiO_2 \cdot 6H_2O$, and H_5 = $Na_2O \cdot 3SiO_2 \cdot 5H_2O$.

From the relationships encountered in the abovementioned diagram, it was concluded that only 9 of the 21 invariant points represent stable-phase assemblages; the other 12 points[22] represent metastable-phase assemblages (see Table II). Assemblages 2 and 3 in Table II were concluded to be metastable because the respective penta- and hexahydrates decompose directly to liquid + quartz + sodium disilicate in the field of stability of the undecahydrate. The other metastable assemblages involve either the undeca- and pentahydrates without any hexahydrate or all three hydrates together. A hypothetical and schematic *P–T* diagram for the 9 stable invariant points is shown in Figure 4. In constructing this diagram the following considerations were kept in mind: (1) The slope of a divariant reaction involving a gas phase is positive. (2) For reactions forming a gaseous phase, the gas is on the high-temperature and low-pressure side of the divariant curve. (3) The hydrates were formed from liquid + quartz + sodium disilicate upon heating and were decomposed upon cooling. (4) The undecahydrate was assumed to be less dense than the associated liquid because it apparently floated on that liquid. Thus the slope of the curve for the reaction

$$\text{liquid} + \text{quartz} + \text{disilicate} \rightleftharpoons \text{undecahydrate}$$

is positive. The slope may be much less steep than that shown in Figure 4. (5) The assemblages found experimentally at 200° are in the area bounded by the reactions

$$L + Q + D = H_{11}$$

$$H_{11} + Q + D = H_6$$

$$G + Q + D = H_{11}$$

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(15) It is possible that other hydrates exist at temperatures and pressures intermediate to those investigated here. However, provided that such possible phases are hydrates of sodium trisilicate, they can be worked into a pressure–temperature diagram for the abbreviated system fairly readily. Also, many hydrates have been found to exist in the system at temperatures below 90°.[3] All of these previously reported hydrates appear to be unstable in the temperature, pressure, and composition range of this investigation.

(16) In some special circumstances the stable portions of the *P–T* curves for two divariant reactions may coincide. In such instances the number of radiating curves about an invariant point is reduced from five to four.

(17) G. W. Morey and E. D. Williamson, *J. Am. Chem. Soc.*, **40**, 49 (1918).

(18) F. A. H. Schreinemaker, "In-, mono- and divariant equilibria," *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B18-B28** (1915–1925) (29 separate articles in the series).

(19) P. Niggli, *Chem. Erde*, **5**, 201 (1930).

(20) P. Niggli, "Rocks and Mineral Deposits," translated by R. L. Parker, W. H. Freeman, San Francisco, Calif., 1954, pp 364–416.

(21) G. W. Morey, *Am. J. Sci.*, **255**, 461 (1957).

(22) Actually there are only 10 metastable invariant points because metastable points 13, 14, and 15 of Table II were found to coincide.

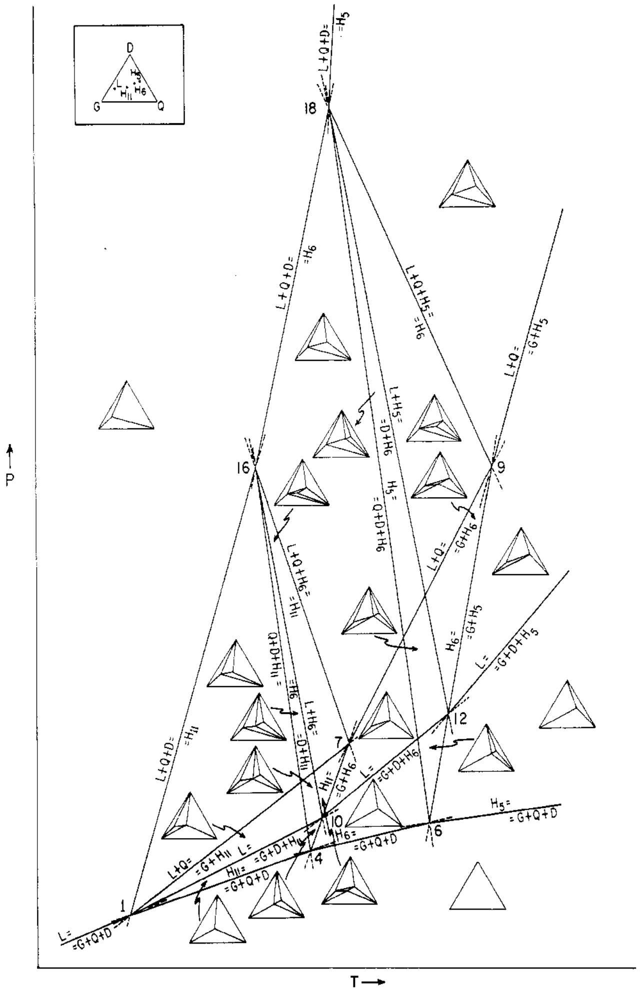

Figure 4.—Schematic and hypothetical pressure–temperature diagram for the portion of the system H_2O–Na_2O–SiO_2 bounded by H_2O–$Na_2Si_2O_5$–SiO_2 and at temperatures greater than 100°. The numbers refer to invariant points with five-phase assemblages as listed in Table II. The letter notation is the same as that for Figures 1–3.

The assemblages found at 250° are in the area bounded by the reactions

$$L + Q + D = H_6$$
$$H_{11} = L + Q + H_6$$
$$H_{11} = G + H_6$$
$$G + Q + D = H_6$$
$$H_6 + Q + D = H_5$$

The assemblages found at 300° are in the area partly bounded by the reactions

$$L + Q + D = H_5$$
$$H_6 = L + Q + H_5$$
$$H_6 = G + H_5$$
$$G + Q + D = H_5$$

(6) The liquid phase is of variable composition. However, the liquid composition does not cross any tie line connecting any other two phases; *i.e.*, the liquid remains within the triangle gas–undecahydrate–disilicate. Under this circumstance, the liquid may be treated as if it were of constant composition. (7) The gas phase is considered to be pure H_2O.

The density relations for given bulk reactions may be such that in Figure 4 the curves $H_{11} + Q + D = H_6$ and $H_{11} = G + H_6$ do not intersect. Similarly the curves $H_6 + Q + D = H_5$, $H_6 = G + H_5$, and $H_5 = G + Q + D$ may not intersect. In this event, all these curves plus the curve $L + Q + D = H_{11}$ would sweep asymptotically to zero pressure and points 1, 4, and 6 would not be encountered. The resulting diagram would be more similar to diagrams for *P–T* projections of hydrate systems commonly shown in textbooks.

It is apparent from Figure 4 that the undecahydrate should decompose to liquid plus quartz plus sodium disilicate as the temperature is lowered. However, when the temperature is lowered quickly, quartz and disilicate do not nucleate as the hydrate decomposes and an unstable or metastable viscous layer of supersaturated liquid results. However, given enough time and stirring at the temperature of decomposition, this viscous material merges with the liquid initially in equilibrium with the hydrate, and a single liquid results. This liquid also is supersaturated and, given more time and stirring, quartz and disilicate should finally precipitate. For some bulk compositions, lowering the temperature further may bring the liquid into a field of unsaturation owing to the retrograde solubility exhibited by the system.

At appropriately high pressure either the hexa- or the pentahydrate may decompose to liquid + quartz + sodium disilicate as the temperature is lowered. However, in sealed bombs with no externally applied pressure, such as were used in this study, the internal pressure simultaneously drops as the temperature is lowered. Provided equilibrium is maintained as the temperature and pressure decrease, a pentahydrate should react with other phases until a hexahydrate is present which in turn goes to an undecahydrate. However, when the pressure vessels are quickly cooled from high temperatures, equilibrium is not maintained. When cooled rapidly, both the penta- and hexahydrates may become slightly supercooled and then decompose directly to a metastable or unstable viscous liquid.

Discussions and Conclusions

Morey[23,24] discussed the meaning of solubility and saturation. For any given bulk composition in a ternary system, the amount of material in solution coexisting with solid material, under the conditions of the experiment, can be depicted as a saturation curve. For the system of interest here, all compositions can be shown by a triangular diagram in which the apices are H_2O, SiO_2, and Na_2O. For any given compound, *e.g.*, sodium metasilicate, if a straight line from that compound to the water apex cuts the saturation curve of the compound, then that compound possesses a true solubility in water at the specified temperature and pressure. The solubility is given by the composition at the point of intersection of the straight line with the saturation

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[23] G. W. Morey, *J. Soc. Glass Technol.*, **6**, 20 (1922).

[24] J. G. Vail, "Soluble Silicates, Their Properties and Uses. Vol. 1: Chemistry," Reinhold Publishing Corp., New York, N. Y., 1952, p 126.

curve. Thus it can be seen in Figure 5 that sodium metasilicate possesses a true solubility at 200 and 250°. However, at 300° the line from sodium metasilicate to water cuts the field of sodium disilicate. Therefore, sodium metasilicate does not possess true solubility under these conditions; it is incongruently soluble at 300° and will decompose in water to form sodium disilicate in equilibrium with a more Na_2O-rich liquid.

In Figure 5 the isothermal polybaric saturation curves at various temperatures are superimposed. The heavy line shows the locus of liquid compositions that coexist with sodium metasilicate plus sodium disilicate at various temperatures and the vapor pressure of the solution. The straight dashed line from sodium metasilicate to water intersects the boundary curve at 270°. Therefore, at the vapor pressure of the solution, sodium metasilicate has a true solubility in water only at temperatures below about 270°.

Tuttle and Friedman[3] reported that at 250° the join sodium disilicate–water is not a binary system because a field of two immiscible liquids crosses the join. At 250°, rather than a field of two immiscible liquids, we found (1) sodium disilicate + liquid, (2) sodium disilicate + liquid + sodium trisilicate hydrate, and (3) a field containing only one liquid + a sodium trisilicate hydrate.[25] The field of liquid + hydrate is narrow between the field containing sodium disilicate and that containing quartz and it does not intersect the join sodium disilicate–water. We conclude that sodium disilicate dissolves congruently in water at the vapor pressure of the solution at all temperatures up to 300°.

At 250° Tuttle and Friedman[3] indicate much greater solubilities for sodium disilicate than we found at the same temperature. These differences in results are probably due to the readiness with which supersaturation occurs during heating of sodium silicate solutions; the nucleation of sodium disilicate in moderately supersaturated solutions is extremely sluggish. In the present study a well-formed sodium disilicate crystal 5 mm long was grown in 22 days from a charge (6.6% SiO_2, 3.4% Na_2O, 90% H_2O) having a bulk composition lying in a field shown by Tuttle and Friedman as unsaturated liquid. Tuttle and Friedman used silica glass or quartz plus NaOH solution as starting materials for the preparation of compositions in the system. We used crystals of quartz, sodium disilicate, and sodium metasilicate in an effort to minimize nucleation problems.

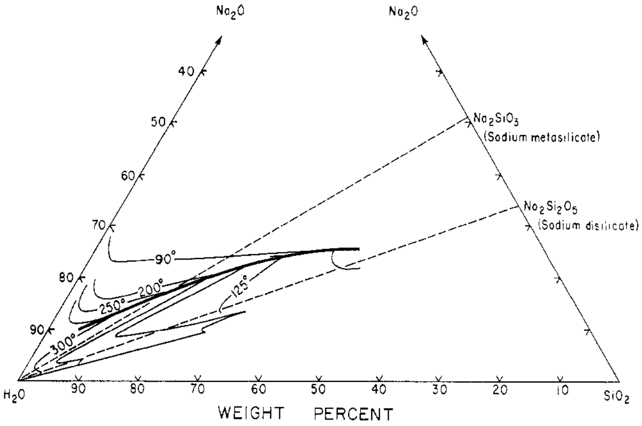

Figure 5.—Isothermal polybaric saturation curves at the vapor pressure of the solution. The curve at 125° is taken from work of Morey as reported by Vail.[24] The curve at 90° is drawn from data by Baker, Jue, and Wills.[4] The heavy line is the boundary between a field of sodium metasilicate + liquid and a field of sodium disilicate + liquid.

At 300°, where sodium disilicate nucleates fairly readily, the present results and those of Tuttle and Friedman are in close agreement. The saturation curves coincide very well and the heavy, viscous second member of the "two immiscible liquids" shown by Tuttle and Friedman has a composition close to our 300° hydrate, $Na_2Si_3O_7 \cdot 5H_2O$.

As the temperature is lowered the hydrates should decompose to liquid + quartz + sodium disilicate. However, upon quenching certain bulk compositions to room temperature and pressure, a viscous glassy liquid is found in contact with a watery liquid owing to the failure of quartz and disilicate to nucleate when a hydrate decomposes. This viscous material is entirely a quench product and is not due to liquid immiscibility at the temperature of the run.

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(25) The basic experimental results of the present study bearing on immiscibility in the system are very similar to those of Tuttle and Friedman.[3] However, because of additional types of experiments, a different interpretation has been given these results.