THE SYSTEM H₂O—Na₂O—SiO₂ AT 400° C.

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ABSTRACT. A method and an apparatus have been devised which have made possible the analyses of coexisting gas and liquid phases in the system H₂O—Na₂O—SiO₂ at 400° C. and at pressures up to 2500 bars. The isothermal polybaric saturation curves—both gaseous and liquid—of quartz, sodium disilicate, and sodium metasilicate have been determined, and the melting pressure of Na₂O·2SiO₂ found to be 2200 bars. The boundary curve G + L + quartz + sodium disilicate is continuous and does not intersect the critical end-point curve, and probably the boundary curve G + L + sodium disilicate + sodium metasilicate has a similar relationship. There are probably two critical regions surrounded by critical curves, one of which is represented by (G = L) + Na₂O·SiO₂, the other by (G = L) + Na₂O·2SiO₂, although the possibility has not been excluded that these two critical curves intersect, giving rise to a double critical end-point (G = L) + Na₂O·SiO₂ + Na₂O·2SiO₂. There is also a critical region represented by (G = L) + Qtz.

INTRODUCTION

THE complete solubility curve of a salt in water covers the entire composition and temperature range from the melting point of ice to the melting point of the salt. When the melting point of the salt is high, the vapor pressure of the saturated solutions may reach high values, and the solubility of the solid in the gas may become so great as to be not only of theoretical interest but also of practical importance (Morey and Hesselgesser, 1951a, 1951b). There is almost no experimental knowledge of such systems, and the present study is an introduction to an almost new field. This field is important to geochemistry. Knowledge about systems containing water at high temperature and pressure is essential to understanding the mechanism of rock formation, and knowledge about the gas compositions which may coexist with aqueous silicate melts under high pressure is essential to understanding the genesis of vein minerals, pegmatite deposits, and pneumatolytic processes in general.

The first study of a water—silicate system was that by Morey and Fenner (1917) of H₂O—K₂SiO₃—SiO₂. In that system the solubility curves of K₂SiO₃ and K₂Si₂O₆ in water are continuous, and there is no intersection of the critical surface by the solubility surface, except in the region in which quartz is the solid phase. The vapor pressures of the saturated solutions are small, and there is no significant solubility of K₂O and SiO₂ in the gas. Attempts to work out the system H₂O—Na₂O—SiO₂ in a similar manner were unsuccessful, and further work on
the silicate systems was long delayed, chiefly because of the necessity of studying the anhydrous systems before the introduction of water.

The compounds \( \text{Na}_2\text{O} \cdot \text{SiO}_2 \) and \( \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \), prepared hydrothermally, were described by Morey (1914), and the binary system \( \text{Na}_2\text{O} \cdot \text{SiO}_2 - \text{SiO}_2 \) was worked out by Morey and Bowen (1924). Later Kracek (1930) extended the study to the orthosilicate, \( 2\text{Na}_2\text{O} \cdot \text{SiO}_2 \). In 1938 Morey and Ingerson described some work on the lowering of the melting point of \( \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \) by water up to 133 bars pressure. That work indicated that the vapor pressure of a saturated solution of sodium disilicate increased rapidly with decreasing temperature. Other experiments by Morey and Ingerson (Adams, 1941) showed that both \( \text{Na}_2\text{O} \cdot \text{SiO}_2 \) and \( \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \) at lower temperatures had retrograde solubility curves with intersection of the critical curve by the solubility curve at practically the critical temperature of water. In the same publication the first mention was made of the method and apparatus used in the present study. Freidman (1950) made some experiments at the temperature of this work, 400°C, with results somewhat different from those of this paper. His method of study did not include direct determination of the pressure in separation and analysis of both gas and liquid, which may account for the differences observed. He confirmed the retrograde solubility of sodium disilicate.

METHOD AND APPARATUS

The method of study was as follows: A sodium silicate glass or crystalline mixture of known composition was placed in a loosely covered platinum crucible which rested on a pedestal inside a high pressure vessel or bomb. This was attached to the pressure line (fig. 1) and the furnace raised around it. When up to the desired temperature, water was pumped into the hot bomb until the desired pressure was reached. The temperature and pressure were held constant—usually overnight, sometimes for 2 or 3 days—after which the valve connecting the bomb with the pressure line was closed, the furnace lowered, the bomb cooled and opened. On cooling the gas had condensed to a liquid, which was weighed and analyzed. Some gas condensed in the crucible, and this was poured off, weighed and analyzed. The material left in the crucible, which was all
crystals, all liquid, or a mixture of crystals and liquid, also was weighed and analyzed. These three analyses gave the amount and compositions of the coexisting phases, and the amount of water injected into the bomb.

The apparatus is shown diagrammatically in figure 1. It consists of a pump, which pumps distilled water into a pressure line, which includes a pressure reservoir, a pressure measuring and regulating apparatus, and a bomb containing the charge, and suitable valves. The pump, made by the American Instrument Company, is rated at 2000 bars, but it has been used for higher pressures. For higher pressures, a pressure intensifier, not shown, has been used with the pump. This effects a multiplication of pressure of 10 to 1, so that at pressure of 3000 bars the pump pressure is only 300 bars. In using the intensifier the pressure usually is first pumped up to 1000-1500 bars with the pump working directly into the system, after which the intensifier is introduced into the line by a system of valves. The purpose of the pressure reservoir is to increase the volume of the system so that each stroke of

Fig. 1. Diagrammatic representation of the apparatus. Water is pumped into a pressure line in which there is a pressure regulator, a pressure gage, a reservoir, a bomb container, the charge, and suitable valves. The bomb hangs in a furnace with automatic temperature control.

1This can be expressed more briefly by the objectionable expression "liquid and/or crystals;" we commonly refer to it as the "andor," and it will be so designated subsequently.
the pump does not have so much effect. The reservoir used for pressures up to 1500 bars has a volume of 2240 cc.; for higher pressures, 250 cc.

The earlier form of the pressure controller, described in a preceding paper (Morey and Hesselgesser, 1951a), was a Bourdon gage which maintained constant pressure by means of a light and photocell. In the later work a Baldwin Fluid Pressure Cell, the sensitive elements of which are two Baldwin Strain Gages, was used in connection with a special Brown Electronic Indicating Potentiometer. The instrument had a pressure range up to 3300 bars, and a high sensitivity. Pressures were measured on 10-inch Bourdon type pressure gages, made by the Ashcroft Instrument Company, and calibrated against a dead-weight gage.

The temperature of the Nichrome-wound furnace is regulated by a Brown Electronic Indicating Contact Controller. The regulating thermocouple, either iron-constantan or chromel-alumel, was placed in a hole drilled in the cap of the bomb to the level of the top of the chamber, as shown in figure 2. An auxiliary winding, controlled by a separate Variac, was so adjusted that the bottom of the bomb was a degree warmer than the top. Temperatures were determined by a platinum: platinum 10 per cent rhodium couple placed in a position similar to that of the control couple.

The bomb is connected with the pressure line by a hollow plunger, as indicated in figure 1, and shown in more detail in figure 2. The stem is long enough so that the cone joint connection is about 3 cm. above the top of the furnace. A suitable system of valves enables the bomb to be connected with the pressure line or to blow off to the air. At the end of the run the valve connecting the bomb to the pressure line is closed. After cooling there may be a small residual pressure remaining in the bomb, so the valve opening to the air is opened and whatever is blown out is collected and considered in subsequent analyses.

The pressure vessels and bombs used in this work were similar to that described by Morey and Ingerson (1937), with the differences that the continuous thread is in two diameters, a convenience for putting on and removing the cap, and that the plunger has a longitudinal hole for admitting water and is elongated to connect with the pressure apparatus. Several dif-
Different types of closure were used. The simplest is a flat silver disc pierced through the middle and used with a flat plunger. This is the easiest to use, but cannot be used for long runs or for pressures over 500 bars. A second type of closure is that described by Morey and Ingerson (1937), and Morey (1914). This will hold 1000 bars but at higher pressures there is danger of it leaking during the cooling.

For high pressures, the closure shown in figure 2 has proven most satisfactory. It makes use of the internal pressure to maintain the seal. The head of the plunger fits inside the

![Diagram](image)

**Fig. 2.** The bomb assembly. This consists of a body and a hollow plunger held in place by a follower washer and the cap. The sealing washer is between the head of the plunger and the follower. The initial seal is made by tightening the nut which bears on the top of the cap, but as pressure builds up it makes the seal by compression of the sealing washer between the follower and the head of the plunger.
chamber of the bomb. A follower washer made with a slight taper, held in place by the cap, fits over the stem of the plunger, and the lower-$\frac{1}{4}$ inch fits inside the chamber of the bomb. A washer $\frac{1}{8}$-inch thick fits over the stem of the plunger and is compressed between the head of the plunger and the follower. The washers usually are of silver, but copper and aluminum washers have been used. The initial closure has been made by screwing down the nut bearing on the top of the cap; the final closure, by the action of the pressure in the interior of the bomb. The area of the head of the plunger is 0.60 square inch, that of the silver washer, 0.30 square inch, so that the pressure on the washer is twice the internal pressure. This closure has never leaked, even when subjected to wide changes in pressure and temperature.

Most of the bombs were made of Inconel X, which withstands the corrosive action of highly alkaline gases better than stainless steel. Several stainless steel bombs failed by having a hole drilled through them overnight. For example, if 5 grams Na$_2$O·SiO$_2$ are heated at 400° C. with 100 bars water pressure, the gas will contain about 10 per cent Na$_2$O and will drill a hole in a 303 stainless steel bomb overnight. A study made by the National Bureau of Standards showed that failure was due to stress corrosion, and that the fracture took place across the grains. Several Inconel X bombs have failed from the chemical action of alkaline gases under more drastic conditions. A study made by the International Nickel Company showed that failure was caused by intergranular corrosion.

The platinum crucibles were 17.5 mm. in diameter at the top, tapering to 16 mm. at the bottom, and usually 15 mm. high. This size holds about 5 grams of powdered silicate, and when larger charges were needed, a higher crucible was used. The desired amount of glass of known composition was put in the weighed crucible, loosely covered with a silver disc, and placed in the bomb, resting on a silver pedestal of such height that the crucible was at the top of the chamber, and the bomb was then assembled. The loose cover was to prevent any of the powder from being blown out when water was let into the bomb and this usually was further prevented by about 1 ml. of water placed in the bomb initially, which served to sinter the loose powder. The assembled bomb was attached to the pressure line by means of a standard cone fitting, the regulating and
reading thermocouples inserted, and the furnace raised around the bomb. When it was up to temperature, water was pumped in to the desired pressure.

After a run was over, the valve connecting the bomb with the pressure line was closed, the furnace dropped, and the bomb cooled in air for about 10 minutes, by which time its temperature had fallen to about 250° C. Then the bomb was immersed in water up to the cap and cooled to about 70°. It was then taken off the pressure line and the cap and plunger removed. Most of what was gas at high temperature had condensed on the walls of the bomb outside of the crucible. It was removed with a pipette, weighed and analyzed. Several examples are given in table 2.

If the amount of glass put into the crucible was greater than that which corresponds to the solubility in gas, some remained as crystals, or liquid plus crystals, or liquid only. When there was a liquid at the temperature of the experiment it cooled to a more or less hard glass. The extra gas condensed in the crucible was poured off; the “andor” remaining in the crucible was weighed, examined with the petrographic microscope for the pressure of crystals, and analyzed. Except with mixtures having a SiO₂/(Na₂O + SiO₂) ratio of less than 0.62, the crucible containing the “andor” usually was placed in a large covered crucible and heated. It then puffed up into a pumicious mass. When a small amount of quartz was present it could be quantitatively separated and weighed by heating in a pressure cooker at about 15 pounds steam pressure after adding enough NaOH solution to bring the SiO₂-ratio to 0.4. A systematic error in all of the liquid compositions is caused by some of the condensed gas penetrating the upper layers of the liquid. When the SiO₂-ratio is greater than 0.66, the error probably is small. In such mixtures the liquid forms a hard glass from which the last drops of condensed gas can be soaked up with filter paper strips, and the surface of the glass is not sticky. But with mixtures increased in metasilicate the liquid becomes a stiff paste, and there is enough penetration of the surface to make it sticky. The amount of this error probably is not large, but it is not possible to make allowance for it.

On top of the “andor” was some condensed gas which had had the opportunity to react with it. This extra gas usually weighed 1-2 grams, and was analyzed separately. Since it is
condensed gas which has reacted with "andor" its composition will be intermediate between the reacting phases, and hence the amount of reaction can be calculated. This calculation was made both from the Na$_2$O—content and the SiO$_2$—content, and the agreement between these two gives an idea of the precision of the experiment.

The formulae used in these calculations are:

$$G = \frac{\text{Ex} - \text{Na}_2\text{O}}{x - x'} = \frac{\text{Ey} - \text{SiO}_2}{y - y'}$$

in which E is weight of extra gas which includes both the condensed gas and what has dissolved from the "andor"; G the weight of condensed gas, x and y the weight fractions Na$_2$O and SiO$_2$ in the "andor"; x' and y', the weight fractions Na$_2$O and SiO$_2$ in the gas; and Na$_2$O and SiO$_2$, the weights of these oxides found in the E grams of extra gas.

For the gas of table 2 (1) this gives:

$$\frac{1.104(.192) - .0453}{.192 - .019} \quad \text{and} \quad \frac{1.104(.508) - .01152}{.500 - .037}$$

which give for the weight of gas 0.963 g. and 0.943 g., respectively; mean 0.953 g.; material dissolved by the gas, 0.151 g.

In some experiments no liquid was formed; the mixture was in the region gas plus solid. In such experiments the amount of condensed gas remaining in the interstices between the crystals was calculated in the same manner from the gas composition, the composition of the crystals and the gross composition. An example is the gas of table 2 (8) in equilibrium Na$_2$O·SiO$_2$ crystals:

$$\frac{2.76(.5035) - .06598}{.5035 - .242} \quad \text{and} \quad \frac{2.76(.4965) - .2693}{.4965 - .084}$$

which give for the weight of gas 2.791 g. and 2.609 g., respectively; mean 2.73; material dissolved by the gas, 0.03 g.

The sum of the weights of condensed gas weighed directly, and calculated from the extra gas and the gas condensed in interstices between crystals, gives the total weight of gas. The free volume of the bombs depends on the type of closure used, the volume of the crucible and pedestal, and of crystals or liquid. The density of the liquid is not known, and the amount of liquid is different in different runs. However, an approxi-
mate volume can be calculated, and from it and the weight of
gas, an approximate density of the gas can be calculated.
Several densities so calculated are given in table 2.

The sum of Na₂O and SiO₂ found in the analyses of gas,
the extra gas, and the "andor," was compared with the
amounts of Na₂O and SiO₂ put in. There was always some
shortage. The usual shortage was less than 0.1 g. each of
Na₂O and SiO₂; when the shortage was large the run was
usually rejected. A small part of the shortage was due to
reaction with the bomb. Part was due to migration of Na₂O
and SiO₂ back into the pressure line. An estimate of the amount
of this loss was made in a large number of runs by inserting
a valve between the main valve block and the bomb, thus retain-
ing all the material in the stem and tubing up to the valve.
With mixtures high in SiO₂ (.66 or more) the amount in the
stem was less than 10 mg. but with mixtures of composition
near the metasilicate it amounted to as much as 30 mg. This
is a negligible error.

In these experiments the pressure is fixed and known, and
the amount of water used was determined by the pressure. This
amount could be ascertained by subtracting from the total
weight of gas plus extra gas plus "andor," the weight of
sodium silicate taken. It was rarely convenient to use more
than 7 grams of silicate, and the amount of water usually was
over 50 per cent.

The sodium silicate mixtures were powdered glasses, except
for the Na₂O·SiO₂ melt, which always crystallized. Most of
these were made from Laboratory stock of Na₂CO₃ and SiO₂,
but some were commercial glasses obtained from the Phila-
delphia Quartz Company. Mixtures of the desired percentage
of SiO₂ were obtained by mixing stock glasses, powdered to pass
40-mesh screens, and mixed by several screenings. Mixtures
higher in Na₂O than sodium metasilicate were made of Na₂O·
SiO₂ and a stock of solution of NaOH, which contained 35 per
cent of Na₂O, was weighed from a weight burette.

The method of working and the general consistency of the
results are illustrated by several examples in tables 1 and 2.
Table 1 gives the sequence of compositions of gas and liquid
at 1000 bars with increasing amounts of sodium disilicate
glass. With successively 1, 2, and 2.5 grams both the water
content and the SiO₂ content of the liquid decrease. When 2.8
grams were added the liquid (which cooled to a hard glass) contained a small amount of disilicate crystals, and it was assumed that the composition of the liquid of the three-phase triangle gas + saturated solution + Na$_2$O·2SiO$_2$ (G + L + Di) is the mean of the liquids with 2.5 and 2.8 grams. This procedure was used in establishing all of the liquid compositions. The gas composition was taken as the mean of the gases in the same two experiments.

Table 2 (1) and (2) give the details of two of the runs of table 1. First is given the amount of disilicate glass used, the temperature and the pressure. Next is given the weight of the gas removed from the bomb with a pipette, and its composition. In all cases the composition is given in terms of weight fractions H$_2$O, Na$_2$O, and SiO$_2$, followed by the ratio SiO$_2$/(Na$_2$O + SiO$_2$), in square brackets. Then is given the weight of the liquid, or “andor.” This was in the bottom of the crucible and was a hard glass without crystals. Next is the extra gas. This had condensed inside the loosely covered crucible, where it had had opportunity to react with the liquid (hydrous glass). The amount of condensed gas was calculated on the assumption that the liquid poured off was a mixture of condensed gas and dissolved liquid, and the agreement between the amounts calculated on the basis of the amount of Na$_2$O and in the amount of SiO$_2$ is satisfactory. The difference between the total weight and the weight of condensed gas is the weight of the liquid dissolved, 0.111 g. Next is given the

Table 1

Sequence of Gas and Liquid Compositions Determining the Liquid of the Three-phase Triangle G + L + Na$_2$O at 400°, 1000 Bars, Using Sodium Disilicate Glass [0.66 SiO$_2$].

All compositions are given in weight fractions. In mixtures containing all three components, the weight fractions are given in the order (H$_2$O, Na$_2$O; SiO$_2$), and this is usually followed by the weight ratio SiO$_2$/(Na$_2$O + SiO$_2$) in square brackets.

<table>
<thead>
<tr>
<th>Weight glass (grams)</th>
<th>Cond’tion</th>
<th>Gas</th>
<th>I liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liquid only</td>
<td>(0.957; 0.017; 0.026) [0.62]</td>
<td>(0.368; 0.169; 0.463) [0.733]</td>
</tr>
<tr>
<td>2</td>
<td>Liquid only</td>
<td>(0.944; 0.019; 0.037) [0.66]</td>
<td>(0.308; 0.192; 0.500) [0.782]</td>
</tr>
<tr>
<td>2.5</td>
<td>Liquid only</td>
<td>(0.944; 0.020; 0.036) [0.64]</td>
<td>(0.265; 0.215; 0.520) [0.708]</td>
</tr>
<tr>
<td>2.8</td>
<td>Liquid + Di</td>
<td>(0.956; 0.018; 0.026) [0.59]</td>
<td>(0.254; 0.279; 0.517) [0.693]</td>
</tr>
</tbody>
</table>
Table 2
Details of Some Typical Experiments

(1)

2.0 g. (.34; .66) at 400°, 1000 bars

Condensed gas weighed directly ................................. 11.60 g.
Composition (.944; .019; .037) [.68]

Liquid; no crystals ................................................. 1.513 g.
Composition (.308; .192; .500) [.723]

Extra gas 1.104 g.
Na₂O 0.0453 g. = 0.963 g. gas
SiO₂ 0.1152 g. = 0.943 g. gas ............................... 0.953

Total weight of gas ............................................. 12.56

Density (free volume = 16.4 ml.) ............................. .766

Total weight H₂O = 12.21 = 0.859 wt. fraction

(2)

2.8 g. (.34; .66) at 400°, 1000 bars

Condensed gas weighed directly ................................. 10.925 g.
Composition (.956; .018; .026) [.62]

Liquid + few Na₂O·2SiO₂ ......................................... 2.795
Composition (.254; .229; .517) [.693]

Extra gas, 0.639 g.
Na₂O: 0.0639 g. = 0.391 g. gas
SiO₂ 0.1318 g. = 0.402 g. gas ............................... 0.396 g.

Total weight of gas ............................................. 11.321

Density (free volume 14.9 ml.) .............................. .76

Total H₂O = 11.56 g. = 0.805 wt. fraction

(3)

Condensed gas weighed directly ................................. 7.66 g.
Composition (.881; .049; .070) [.592]

Liquid; no crystals ................................................. 3.44 g.
Composition (.315; .211; .474) [.691]

Extra gas, 2.35 g.
Na₂O: 0.1432 g. = 2.271 g. gas
SiO₂: 0.2384 g. = 2.170 g. gas ............................. 2.17 g.

Total gas .......................................................... 9.83 g.

Density (free volume = 10.4 ml.) ............................ 0.945

Total wt. H₂O = 9.93 g. = 0.739 wt. fraction


**Table 2 (Cont.)**

Details of Some Typical Experiments

(4)  
5.0 g. (24.; 66), 400°, 2000 bars

Condensed gas weighed directly 8.02 g.
Composition (.853; .059; .088)[.599]

Liquid, trace Na₂O·2SiO₂ crystals 4.69 g.
Composition (.312; .224; .464)[.675]

Extra gas, 1.94 g.
Na₂O: 0.0829 g. = 2.13 g. gas  
SiO₂: 0.2308 g. = 1.78 g. gas  
Total gas 9.80 g.

Density (free volume 10.4 ml.) 0.942
Total wt. H₂O = 9.65 g. = 0.659 wt. fraction

(5)  
2 g. (26.; 74), 400°, 247 bars

Condensed gas weighed directly 2.50 g.
Composition (.997; .002; .001)[.37]

Liquid; no crystals 2.36 g.
Composition (.229; .200; .571)[.741]

Extra gas, 0.47 g.
Na₂O: 0.0352 g. = 0.335 g. gas  
SiO₂: 0.1006 g. = 0.321 g. gas  
Total gas 2.828 g.

Density (free volume = 17 ml.) 0.166
Total wt. H₂O = 3.366 g. = 0.631 wt. fraction

(6)  
5 g. (255.; 745), 400°, 2000 bars

Condensed gas weighed directly 6.30 g.
Composition (.728; .161; .111)[.721]

Liquid no crystals 4.06 g.
Composition (.318; .161; .521)[.764]

Extra gas, 0.83 g.
Na₂O: 0.0645 = 0.813 g. gas  
SiO₂: 0.1631 = 0.829 g. gas  
Total gas 7.12 g.

Density (free volume = 9.6 ml.) 0.742
Total wt. H₂O = 6.482 = 0.565 wt. fraction
The System H₂O—Na₂O—SiO₂ at 400° C.

<table>
<thead>
<tr>
<th>TABLE 2 (Cont.)</th>
<th>Details of Some Typical Experiments</th>
</tr>
</thead>
</table>

(7)  
1.5 g. (.44; .56) at 400° C., 700 bars

<table>
<thead>
<tr>
<th>Composition</th>
<th>11.185 g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensed gas weighed directly</td>
<td>11.185 g.</td>
</tr>
<tr>
<td>Condensed gas + Na₂O·2SiO₂ crystals</td>
<td>0.90 g.</td>
</tr>
<tr>
<td>Na₂O: 0.2509 g. = gas</td>
<td></td>
</tr>
<tr>
<td>SiO₂: 0.4724 g. = 0.429 g. gas</td>
<td>0.432 g.</td>
</tr>
<tr>
<td>Extra gas, 1.445 g.</td>
<td>1.238 g.</td>
</tr>
<tr>
<td>Na₂O: 0.0964 g. = 1.220 g. gas</td>
<td></td>
</tr>
<tr>
<td>SiO₂: 0.1281 g. = 1.256 g. gas</td>
<td></td>
</tr>
<tr>
<td>Total weight of gas</td>
<td>12.855 g.</td>
</tr>
<tr>
<td>Density (free volume = 17 ml.)</td>
<td>0.756</td>
</tr>
<tr>
<td>Total weight H₂O = 12.04 g. = 0.889 wt. fraction</td>
<td></td>
</tr>
</tbody>
</table>

(8)  
6 g. (.7; .3), 400° C., 2000 bars

<table>
<thead>
<tr>
<th>Composition</th>
<th>11.27 g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensed gas weighed directly</td>
<td>11.27 g.</td>
</tr>
<tr>
<td>Condensed gas with Na₂O·SiO₂ crystals, 2.56 g.</td>
<td></td>
</tr>
<tr>
<td>Na₂O: 0.7847 = 1.005 g. gas</td>
<td></td>
</tr>
<tr>
<td>SiO₂: 0.6135 = 1.017 g. gas</td>
<td>1.01 g.</td>
</tr>
<tr>
<td>Extra gas, 2.76</td>
<td></td>
</tr>
<tr>
<td>Na₂O: 0.6598 = 2.791</td>
<td></td>
</tr>
<tr>
<td>SiO₂: 0.2693 = 2.669</td>
<td></td>
</tr>
<tr>
<td>Total gas</td>
<td>15.01 g.</td>
</tr>
<tr>
<td>Density (free volume = 11 ml.)</td>
<td>1.36</td>
</tr>
<tr>
<td>Total weight H₂O = 12.04 g. = 0.889 wt. fraction</td>
<td></td>
</tr>
</tbody>
</table>

The total weight of gas, the sum of that weighed directly and the extra gas, and its approximate density. This is obtained by dividing the total weight of gas by the free volume of the bomb. The last line gives the total weight of water in the bomb and its weight fraction.

Table 2 (3) and (4) give similar details for two runs at 2000 bars. In (4) the weight of gas calculated from the Na₂O is high and was discarded. This discrepancy would be explained by some loss of Na₂O.
Table 2 (5) is a run with glass near the disilicate-quartz boundary, at a pressure near the boundary pressure, but with too little solid present to give crystals, and (6) is a similar one at 2000 bars. Each of these is in a bivariant region above the three-phase pressure.

Table 2 (6) and (7) are experiments in which no liquid is formed; the mixtures were both in the field of gas plus crystals, and in each case the crystals were large and well formed with many crystal faces. There was some condensed gas held in the interstices between the crystals after the supernatant liquid was poured out of the crucible, and the amount of gas was calculated as shown. The calculated density of gas in (8), 1.36, is noteworthy.

THEORETICAL DISCUSSION

The complete system.—The results here presented consist of a series of isothermal polybaric saturation curves at 400° C. The complete representation of this system, with two composition variables, pressure, and temperature, would require a hyperprism of four dimensions. In such a hyperprism the liquid solubility or saturation regions of each solid phase would be represented by a hypersurface and the corresponding gaseous solubility regions by a second hypersurface. The intersection of the two liquid saturation hypersurfaces would give a boundary curve in four-dimensional space between the two saturation regions. The complete representation of the system requires consideration of the critical hypersurface which, stably or metastably, joins the critical points of the three components. It is known that this critical hypersurface is intersected by saturation hypersurfaces, at which points the gaseous and liquid surfaces fold into each other, and this intersection is a critical end-point curve. In this paper the critical end-point curves will be mentioned only briefly.

A section through the hyperprism at constant temperature gives a triangular prism with the composition triangle as base, pressure as ordinate. The experimental results may be considered as a determination of the pressure necessary to dissolve in each Na₂O—SiO₂ mixture enough water to lower its melting point to 400° C., the identification of any crystals, and the analyses of the gaseous and liquid phases. The melting point of Na₂O·SiO₂ is 1089°, of the eutectic between Na₂O·
The System $H_2O-Na_2O-SiO_2$ at $400^\circ$ C.

$SiO_2$ and $Na_2O\cdot2SiO_2$, $846^\circ$, of $Na_2O\cdot2SiO_2$, $874^\circ$ and of the eutectic between $Na_2O\cdot2SiO_2$ and quartz, $793^\circ$. It was convenient to make a series of runs at constant pressure, increasing the amounts of sodium silicate added until the compositions of the gas and saturated solution of the three-phase triangle $G + L + S$ could be determined.

The isothermal isobaric section.—The discussion of these experiments is aided by figure 3 which is a diagrammatic representation of a projection of a section at constant pressure through a solid model representing the relations at constant temperature between pressure and composition; that is, through the $(P-X-Y)_T$ model. Part of the side $Na_2O-SiO_2$ is indicated, and $Di$ represents the composition of $Na_2O\cdot2SiO_2$. The broken lines $E L_1$ and $E L_2$ are the saturation curves of quartz and of $Na_2O\cdot2SiO_2$, metastable except at the points $L_1$ and $L_2$. These are points of the three-phase triangles $G_1-L_1-Qtz$ and $G_2-L_2-Di$, and represent invariant equilibrium at constant pressure and temperature. The portions of the saturation curves $E L_1$ and $E L_2$ represent solutions of vapor pressure lower than that of the diagram; the prolongations of these curves represent pressures higher than that of the diagram. The curve $L_1L_2$ represents solutions unsaturated with respect to solid at this temperature and pressure.

![Diagram](image)

**Fig. 3.** Diagrammatic representation of part of a section at constant pressure through a solid model representing the relations between pressure and composition at constant temperature. On part of the side $Na_2O-SiO_2$ is indicated the composition of sodium disilicate, $Di$. The lines 1, 2, 3 go to the $H_2O$ apex.
The lines $\text{H}_2\text{O} - \text{Di}$, $\text{H}_2\text{O} - 1$, $\text{H}_2\text{O} - 2$ and $\text{H}_2\text{O} - 3$ join the $\text{H}_2\text{O}$-apex with mixtures on the side $\text{Na}_2\text{O} - \text{SiO}_2$ of the indicated composition. The gross composition of every ternary mixture which can be formed by adding $\text{H}_2\text{O}$ to the given $\text{Na}_2\text{O} - \text{SiO}_2$ mixture will be on this line, and when both a gaseous and a liquid phase are formed the line joining their compositions cuts the line from the $\text{H}_2\text{O}$-apex at a point corresponding to the percentage of water injected.

When a small amount of disilicate is put into the crucible it will all be dissolved by the gas. If just enough is added to give a liquid, the gas will have a composition indicated by $a$ on the line $\text{H}_2\text{O} - \text{Di}$ and the liquid will be on the curve $L_1$, $L_2$, as indicated by the tie-line. If more disilicate is added, the gas composition follows the curve $G_1$, $G_2$, the liquid the curve $L_1$, $L_2$, until the gross composition $b$ is reached. The liquid has now reached the composition $L_2$, crystalline sodium disilicate is formed, and the coexisting phases now are fixed in composition. If the original silicate mixture was of composition $1$, there would be the same sequence of phases, $G \rightarrow G + L \rightarrow G + L + \text{Di}$, but more of the mixture would have to be added before the three-phase triangle was entered; that is, the percentage of the water is less. If the mixture had the composition $2$, no crystalline phase could be obtained; a mixture of this composition forms only unsaturated solution at this temperature and pressure.

With a mixture of composition $3$, the sequence of phases will be different. The mixture will pass from the region of unsaturated gas to that of gas + quartz. The line $G_1$, $G_2$ represents the solubility of $\text{SiO}_2$ in gases of changing $\text{Na}_2\text{O}$-content, in equilibrium with quartz. In this region the $\text{Na}_2\text{O}$ dissolves in the gas in greater proportion than $\text{SiO}_2$, leaving crystalline quartz. With larger amounts of $3$, the three-phase triangle $G + L_1 + \text{Qtz}$ is reached, liquid of composition $L_1$ is formed, and the phases become of fixed composition, their proportions changing as more solid is added.

The three-phase triangle $G + L_2 + \text{Di}$ is entered from a region of $G + L_1$, at the point where the tie-line $\text{H}_2\text{O} - \text{Di}$ or $\text{H}_2\text{O} - 1$ cuts the side $G_2$, $L_2$. The three-phase triangle $G + L_1 + \text{Qtz}$ is entered from a region of $G + \text{Qtz}$, at the point where the tie-line $\text{H}_2\text{O} - 3$ cuts the side $G_1$, $\text{SiO}_2$. In the first case the phase sequence is $G \rightarrow G + L \rightarrow G + L + \text{crystals}$; in the second it is $G \rightarrow G + \text{crystals} \rightarrow G + L + \text{crystals}$. 
If the area of the three-phase triangle \( G_1 + L_1 + \text{quartz} \) is calculated, writing the compositions of the phases in this order, the area will be found to have a positive sign, and it is circumscribed clockwise. If the area of the three-phase triangle \( G_2 + L_0 + \text{Di} \) is calculated, writing the phases in the same order, the area will be found to have a negative sign, and the three-phase triangle will be circumscribed counterclockwise. In general, a three-phase area of positive sign will result from a phase sequence \( G \rightarrow G + \text{crystals} \rightarrow G + L + \text{crystals} \), and one of negative sign will form a phase sequence \( G \rightarrow G + L \rightarrow G + L + \text{crystals} \).

EXPERIMENTAL RESULTS

Preliminary work had indicated that the second critical endpoint curve of sodium disilicate probably is below \( 400^\circ \) C. and accordingly \( 400^\circ \) was chosen as a desirable temperature for the first isotherm. The saturation pressures at \( 400^\circ \) over much of the system are greater than at higher temperatures; consequently the effect of the gaseous solubility is more important. The summarized results of the various saturation curves are given in tables 3 to 6, and shown in figures 4 to 6. Figure 7 shows the isothermal polybaric saturation curves, both gas and liquid. It will be discussed in more detail subsequently.

The boundary, sodium disilicate—quartz.—The coexistence of \( G + L + \text{Di} + \text{Qtz} \) is an invariant point at constant temperature. It represents the point at \( 400^\circ \) of the boundary between the regions of \( \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \) and quartz, which starts at the eutectic in the binary system at \( 793^\circ \) C. and 0.793 \( \text{SiO}_2 \). Its coordinates are \( p = 240 \) bars; gas (0.998, 0.001, 0.001) [0.37]; liquid (0.229, 0.200, 0.571) [0.741]. At 233 bars there was no liquid, only gas, crystalline disilicate and quartz. At 247 bars the phases were gas, solution, and a trace of quartz; the experimental details are given in table 2 (5). The pressure at the invariant point is taken as the mean of 233 and 247, or 240 bars, and gas and liquid compositions are assumed to be the same as at 247 bars. The density of the gas is 0.165; that of water at the same temperature and pressure is 0.152. The ratio \( \text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2) \), 0.741, is essentially the same as at the binary eutectic.

The isothermal polybaric saturation curve of quartz.—As the pressure of water is increased at \( 400^\circ \) above that of the
boundary between disilicate and quartz, the composition of both the gas and the liquid in equilibrium with quartz changes. The three-phase triangle $G + L + Qtz$ is of positive area, and the sequence of the phases as the amount of sodium silicate is increased is $G \rightarrow G + Qtz \rightarrow G + L + Qtz$. In other words, a small amount of sodium silicate, say of ratio 0.76, is all dissolved by the steam. When more silicate is added, the ratio $\text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2)$ in the gas is smaller than in the liquid, $\text{Na}_2\text{O}$ is extracted, and some $\text{SiO}_2$ is left behind as quartz. With still more silicate, liquid is formed, and the mixture enters the three-phase triangle $G + L + Qtz$. On further increase in the amount of silicate, the compositions of gas and liquid remain fixed and the proportions of gas, liquid and solid change. At lower pressures the difference between the $\text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2)$ ratio of gas and liquid is larger than at higher pressures; at 400° it is 0.37 at 240 bars, and 0.72 at 2000 bars, not very different from the ratio in the liquid, 0.76. This was found to be true in every case. At low pressure sodium oxide is extracted by the gas, but as pressure is increased the $\text{SiO}_2$—ratio in the gas approaches that in the liquid. The same effect was found with albite (Morey and Hesselgesser, 1951b).

The gaseous and liquid composition of the three-phase equilibrium at 400° C. are given in table 3 and shown graphically in figure 4. The ordinate is pressure in bars. The first pair of curves gives the weight fraction of $\text{H}_2\text{O}$ in gas and liquid; the middle pair, the weight fraction $\text{SiO}_2$ in gas and liquid; and the

<table>
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<tr>
<th>Pressure bars</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{Na}_2\text{O}$</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Na}_2\text{O} + \text{SiO}_2$</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{Na}_2\text{O}$</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Na}_2\text{O} + \text{SiO}_2$</th>
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</thead>
<tbody>
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<td>0.001</td>
<td>0.001</td>
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<td>0.200</td>
<td>0.571</td>
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<td>0.005</td>
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<td>0.192</td>
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<td>0.060</td>
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<td>0.179</td>
<td>0.540</td>
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<td>0.045</td>
<td>0.115</td>
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<td>0.161</td>
<td>0.521</td>
<td>0.76</td>
</tr>
<tr>
<td>2500</td>
<td>0.77</td>
<td>0.062</td>
<td>0.168</td>
<td>0.73</td>
<td>0.35</td>
<td>0.156</td>
<td>0.494</td>
<td>0.76</td>
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</table>

Table 3
Composition of Gas and Liquid of the Three-phase Triangle with Quartz at 400° C.
third pair, the ratio $\text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2)$ in gas and liquid.

At the highest pressure used, 2500 bars, the gas and liquid are still far apart in composition. Table 2 (6) gives details of a determinative run. Five grams of 0.745 glass were taken, and a total of 6.48 g. $\text{H}_2\text{O}$ or 56.5 per cent was injected, and the weights and compositions of the condensed gas (solution in the bomb outside of the crucible), the liquid solution (glass) in the bottom of the crucible, and the extra gas poured out of the crucible are given. The glass contained a small amount, less than 0.1 per cent, of quartz.

At a sufficiently high pressure the gas and liquid will become identical in composition and the critical end-point will be reached. This line will extend into the P-T-X-Y hyper prism,
from the first critical end-point in the system H₂O—SiO₂, which is practically identical with the critical point of water; and will end at the second critical end-point in the system H₂O—SiO₂, if such an end-point exists. The critical end-point line at 400°C will be at pressures greater than 2500 bars.

The isothermal polybaric saturation curve of sodium disilicate. (a) Negative side. As the pressure of water increases at 400°C above the boundary between sodium disilicate and quartz, the composition of both gas and liquid in equilibrium with disilicate change. At each pressure the three-phase triangle gas + solution + disilicate is of negative area, and the phase sequence as the quantity of sodium silicate is increased is $G \rightarrow G + L \rightarrow G + L + Di$. Two thousand bars is not enough to obtain a liquid on the join H₂O—disilicate, but at 2250 bars 7 grams of a 0.63 glass gave no crystals, gas (.806; .081; .113) [.584], liquid (.339; .224; .487) [.661]. The melting pressure of Na₂O ·2SiO₂ accordingly is taken as 2200 bars. At 2500 bars the same charge gave a gas of composition (.77; .093; .135) [.588] and a liquid (.347; .222; .431) [.66]. With 6 g. of a 0.66 glass the liquid composition was (.445; .170; .385) [.695]. The compositions of gas and liquid are approaching each other, and the critical region will be met with on further increase in pressure.

Several of the experimental details of tables 1 and 2 refer to this saturation curve. Table 1 gives the sequence of gas and liquid compositions by which the gas and liquid of the three-phase triangle were determined at 1000 bars, and table 2 (1) and (2) give details of two of the experiments. Table 2, (3) and (4), give similar details for 2000 bars.

The compositions of the gases and liquids of the three-phase triangle $G + L + Di$ at 400°C C. and at various pressures are given in table 4, and shown graphically in figure 5. The ordinate is pressure in bars. The first pair of curves gives the weight fraction of H₂O in gas and liquid; the middle pair, the weight fraction SiO₂ in gas and liquid; and the third pair, the ratio SiO₂/(Na₂O + SiO₂) in gas and liquid. Comparison with figure 4 shows that at 2000 bars, gas and liquid are farther apart than in the saturation curve of quartz. The gas saturation curve of quartz shows a much greater decrease in water and increase in SiO₂ from 1000 to 2000 bars than does the disilicate curve; and
the ratio of $\text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2)$ in gas and liquid is little changed with increase in pressure.

(b) Positive side. The three-phase triangle $G + L + Di$ which goes from the boundary $G + L + M + Di$ is of positive area, and the sequence of phases as the amount of sodium silicate is increased is $G \rightarrow G + Di \rightarrow G + L + Di$. This liquid curve was difficult to determine. The gas which condensed inside the crucible reacted rapidly with crystals and the liquid reaction product was a pasty mass. It was hard to tell when liquid began to form and to separate the extra gas, and successive experiments under the same conditions were much less concordant than on the negative side of the disilicate curve or even of the metasilicate curve.

The end-points of this curve are the metasilicate-disilicate

---

**Fig. 5.** The gas and liquid saturation curves of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. The ordinate is pressure in bars. The first pair of curves gives the weight fraction $\text{H}_2\text{O}$ of gas and liquid in equilibrium with $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; the second pair, the weight fraction of $\text{SiO}_2$ of gas and liquid; and the third pair the ratio $\text{SiO}_2/(\text{Na}_2\text{O} + \text{SiO}_2)$ in gas and liquid.
boundary, at 380 bars, discussed subsequently, and the congruent saturation curve of Na$_2$O·2SiO$_2$, at 2200 bars. The coordinates of the curve are in table 4 b. Experiments were made at 400 and 500 bars, but the results were too discordant to interpret. At higher pressures the results are somewhat better, and the points given are the mean of several experiments.

The boundary, sodium metasilicate-sodium disilicate.—The coexistence of gas, liquid, Na$_2$O·SiO$_2$ and Na$_2$O·2SiO$_2$ is an invariant point at constant temperature. It represents the point at 400° of the boundary between the regions of Na$_2$O·SiO$_2$ and Na$_2$O·2SiO$_2$, which starts at the eutectic in the binary system at 846° and 0.621 SiO$_2$.

This invariant (T) point, and the univariant curves leading from it, were difficult to locate. At 360 bars and at lower pressures all mixtures from .60 to .64 SiO$_2$ give only gas + crystals. At 400 bars there is an undoubted formation of liquid with 4 g. of a mixture containing 0.52 SiO$_2$; with 2 g. the phases are gas + Na$_2$O·SiO$_2$ + Na$_2$O·2SiO$_2$. The pressure at the univariant

<table>
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<th>Pressure (bars)</th>
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<th>Liquid S:O$_2$</th>
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<td>H$_2$O Na$_2$O SiO$_2$ Na$_2$O + SiO$_2$</td>
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<td>0.866 0.076 0.118 0.31</td>
<td>0.5 0.340 0.224 0.436 0.661</td>
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<td>b. Positive Side</td>
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<th>Pressure (bars)</th>
<th>Gas S:O$_2$</th>
<th>Liquid S:O$_2$</th>
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<td></td>
<td>H$_2$O Na$_2$O SiO$_2$ Na$_2$O + SiO$_2$</td>
<td>H$_2$O Na$_2$O SiO$_2$ Na$_2$O + SiO$_2$</td>
</tr>
<tr>
<td>380</td>
<td>0.96 0.027 0.013 0.03</td>
<td>0.32 0.265 0.294 0.441 0.600</td>
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<tr>
<td>700</td>
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<tr>
<td>2200</td>
<td>0.806 0.074 0.120 0.14</td>
<td>0.61 0.340 0.224 0.436 0.661</td>
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</tbody>
</table>
(T) point is accordingly assumed to be 380 ± 20 bars. The compositions of the gaseous and liquid phases were estimated by extrapolation of the curves for \( G \pm L + Na_2O \cdot SiO_2 \) down to 380 bars.

The isothermal polybaric saturation curve of \( Na_2O \cdot SiO_2 \).

This saturation curve at 900° C. goes from the boundary with disilicate at 380 bars to the melting pressure of sodium metasilicate, if a critical region is not met with first. Our experiments go only to 2500 bars, and only two runs were made at that pressure; in one of these were no crystals, in the other only a few. The gas composition given for this pressure (0.61, 0.197, 0.193) [497] is in part an extrapolation; the runs agreed in the \( SiO_2/(Na_2O + SiO_2) \) ratio but the percentages of \( H_2O \) were far apart and one was disregarded. The liquid composition (0.427, 0.268, 0.305) [532] is the average of the two runs. The water content and the \( SiO_2/(Na_2O + SiO_2) \) ratios of gas and liquid are approaching each other, and it is probable that a critical region is not far distant. A water pressure which will melt sodium disilicate will not melt metasilicate. The experimental details are given in table 5 and shown graphically in figure 6.

The saturation curve is of negative area and the phase sequence is \( G \rightarrow G + L \rightarrow G + L + S \). At the lower pressures it was hard to determine the first appearance of crystals, but at higher pressures the liquid of the three-phase equilibrium could be determined with more certainty. Work with this material was stopped because of its extremely corrosive action on the bombs, even on bombs made of Inconel X.

The more alkaline regions.—The regions containing more \( Na_2O \) than corresponds to the metasilicate (0.5035: 0.4965) have not been cleared up. Sodium orthosilicate has the composition (0.6737: 0.3263) but it was never found in any of the experiments. Mixtures containing 0.30 \( SiO_2 \) are in the divariant region of \( gas + crystalline metasilicate \) from 400 to 2000 bars: table 4 gives a summary of gas compositions at various pressures in equilibrium with \( Na_2O \cdot SiO_2 \) with an original composition containing 0.30 \( SiO_2 \). The ratio \( SiO_2/Na_2O + SiO_2 \) increases from 0.1 at low pressure to 0.26 at 2000 bars; at low pressure \( Na_2O \) is extracted; at high pressure the material is practically dissolved as such. Details of the experiments at 2000
bars are in table 2, example 8. This gas has a content of dissolved Na₂O + SiO₂ of 32.6 per cent, and a density of 1.35. It will eat through 3/4 inch of stainless steel overnight, and even Inconel X cannot withstand its corrosive action for long. Stainless steel fails by stress corrosion, Inconel X by intergranular corrosion. It was because of this extremely corrosive nature of these highly alkaline gases that the studies have not been pushed to the critical end-point curve, which cannot be far away.

When 5 g. of a mixture containing 0.10 SiO₂ was heated at 100 bars, it was in the region of gas + metasilicate; the gas composition was (0.583, 0.410, 0.007) [.016]. The high-pressure steam extracted most of the Na₂O, leaving metasilicate crystals; the density of the gas was 0.49, that of the H₂O at the same temperature and pressure is 0.38. When 5 g. of the same mixture was heated at 1200 bars, there were no crystals. The composition of the gas was (0.756; .225; .020) [.083], that of the mixture of the liquid and condensed gas in the crucible, (0.722; .223; .053) [0.196]. The proportions of gas and liquid are unknown, but the possible range of the proportion is limited by the known behaviour of the mixture containing 0.30 SiO₂. If the proportion is 6 gas: 4 liquid, the liquid composition would be (0.679; .221; .108) [0.33] which is about the highest probable proportion. In any case, liquid and gas are approaching each other in composition, and a point on the critical surface is not far distant.

Several runs were made with NaOH at 80 bars. Lump NaOH

**Table 5**

Composition of Gas and Liquid of the Three-phase Triangle with Sodium Metasilicate at 400° C.

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<tr>
<th>Pressure bars</th>
<th>H₂O</th>
<th>Na₂O</th>
<th>SiO₂</th>
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<th>H₂O</th>
<th>Na₂O</th>
<th>SiO₂</th>
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The System $\text{H}_2\text{O}—\text{Na}_2\text{O}—\text{SiO}_2$ at 400° C.

was put into the crucible, and analyses made as usual. On cooling, the condensed gas usually formed a mush of NaOH·H$_2$O crystals. The average gas composition was (.503, .497), the mixed condensed gas + liquid in the crucible (.492; .518), or gas, 0.641 NaOH, condensed gas + liquid, 0.668 NaOH. There is no way of estimating the proportion of condensed gas in the mixture.

*The isothermal polybaric saturation curve.—* This is shown in figure 7. Consider again the complete representation by means of the hyper prism X-Y-P-T. The consideration of this may be simplified by a separate consideration of the X-Y-T prism and the X-Y-P prism, which by transformation through a fourth dimension unite to form the hyper prism. The X-Y-T prism is similar to the triangular prism commonly used to represent

![Diagram of saturation curves](image)

Fig. 6. The gas and liquid saturation curves of $\text{Na}_2\text{O}·\text{SiO}_2$. The ordinate is pressure in bars. The first pair of curves gives the weight fraction of H$_2$O of gas and liquid in equilibrium with $\text{Na}_2\text{O}·\text{SiO}_2$; the second pair the weight fraction of SiO$_2$ of gas and liquid; and the third pair the ratio SiO$_2/(\text{Na}_2\text{O}+\text{SiO}_2)$ in gas and liquid.
phase equilibrium relations in the ternary systems, except that it is two-leaved. We commonly think of the liquid leaf, which gives the compositions of the liquids which can coexist with crystalline phases. But when the compositions of the coexisting gas phases must be considered, there must be a second leaf or set of surfaces representing the compositions of those gases. The pressures of these saturated solutions will not be constant but will range between wide limits. A second triangular prism must be considered, the X-Y-P prism. This, of course, must also be two-leaved, and composition is the connecting link between the two prisms. If a given composition is chosen, a perpendicular at the composition will give in the X-Y-T prism the melting point of that mixture, in the X-Y-P prism the vapor pressure of that saturated solution, or the pressure of water plus the dissolved material which must be developed to liquify the mixture at the temperature in question.

At every temperature there is a range of pressures required to melt the various compositions, so that an \((X-Y-P)_T\) model can be constructed for each temperature, and the projection of

Fig. 7. The isothermal polybaric saturation curves at 400° C. The curve \(E_1L_1\) is the liquid saturation curve of quartz; \(G_2E_2\) the coexisting saturation curve; and the triangle \(G_1L_1SiO_2\) is the three-phase triangle at 2500 bars. \(E_1E_2\) and \(G_1G_2\) are the gas and liquid saturation curves of \(Na_2O:2SiO_2\). \(E_1L_1\) and \(GE_2G_2\) are the saturation curves of \(Na_2O:SiO_2\), and \(G_1L_1\) \(Na_2O:SiO_2\) is the three-phase triangle at 2500 bars.
such model on the base will give a representation of the results of this study. Figure 7 is such a projection at 400° C.

The intersection of the saturation curves of quartz and disilicate is at E₁; the pressure at this point is 240 bars. The coexisting gas is at G₁. The curve E₁ L₁ is the isothermal polybaric saturation curve of quartz, and along it pressure increases to 2500 bars. G₁—L₁—SiO₂ is the three-phase triangle at 2500 bars.

The curve E₁ E₂ is the liquid saturation curve of sodium disilicate, and G₁ G₁; G₁ E₂ is the coexisting gaseous saturation curve. Liquid of the ratio of SiO₂/(Na₂O + SiO₂) of sodium disilicate, [0.66], is in equilibrium with a gas containing a larger proportion of Na₂O, of ratio [.61]. The three-phase triangle at this pressure is gas—sodium disilicate—liquid so that the point of maximum water content, the point of tangency of a line parallel to the side Na₂O—SiO₂, will not be exactly 0.66 but will be displaced to be on the line G—Na₂O·2SiO₂. This will be at a ratio of about 0.65. This gas contains less dissolved material than that in equilibrium with the liquid saturation curve of quartz at the same pressure.

E₂ is the point on the boundary between metasilicate and disilicate, and from it the saturation curve of metasilicate rises to the three-phase triangle at 2500 bars. G₂—M—L₂ is the three-phase triangle at this pressure. Gas and liquid are approaching each other, and the critical end-point curve probably would be reached in another thousand bars. It is noteworthy that the melting pressure of sodium metasilicate is greater than that of sodium disilicate.

The line G + M (0.30) represents the gases in equilibrium with metasilicate crystals at pressures up to 2000 bars, with an initial silica ratio of 0.3 (table 6). A higher pressure than 2000 bars is necessary to obtain a liquid with this composition. A mixture with a silica ratio of 0.10 was in the region gas + metasilicate crystals at 100 bars, and the gas contained 42 per cent dissolved material. At 1200 bars unsaturated liquid was obtained.

When the system as a whole is considered it is evident that some such results are inevitable. Sodium metasilicate and sodium disilicate are surrounded by a critical curve, representing the intersection of the critical hypersurface joining the critical points of the three components by the saturation hypersurface.
The metasilicate critical region will extend toward the side \( \text{H}_2\text{O} - \text{Na}_2\text{O} \), which it cannot reach. Similarly, the boundary between disilicate and quartz is a continuous curve which does not intersect a critical curve. The disilicate and the metasilicate critical regions thus will be surrounded by closed curves. These curves either may be separate closed curves, or they may intersect, giving rise to upper and lower double critical end-points. Which of these possibilities represents the facts cannot be said for certain until other work which is under way can be completed, but at present it seems probable that the critical surface is not intersected by the boundary \( \text{G} + \text{L} + \text{metasilicate} + \text{disilicate} \). Each critical region will then be surrounded by a closed curve. These critical regions are remarkable in that the temperature difference across them is so small. The first critical end-point on the join \( \text{G} + \text{L} + \text{Di} \) cannot be much above 374°, with a pressure near 212 bars, and the second critical end-point must be below 400°, with a pressure greater than 2250 bars. The end-point on the join \( \text{G} + \text{L} + \text{M} \) must be at a higher pressure, possibly a higher temperature. It may be true in general that systems of the type water-salt which show critical end-points will have similar relationships between the first and second critical end-points, namely, a small difference in temperature and a very great difference in pressure.

Other work on this system is under way, at both higher and lower temperatures and will be reported before long.

**Table 6**

Composition of Gases in Equilibrium with Crystalline Sodium Metasilicate at 400° C.

The original charge was 5 g. of a (0.7:0.3) mixture.

<table>
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<tr>
<th>Pressure (bars)</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{SiO}_2 )</th>
<th>( \frac{\text{SiO}_2}{\text{Na}_2\text{O} + \text{SiO}_2} )</th>
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The System $H_2O$—$Na_2O$—$SiO_2$ at 400° C.

References


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Carnegie Institution of Washington
Washington, D. C.