Little attention was given to the adsorption reduction wave occurring at the more positive potential or to the normal reduction wave occurring at the more negative potential, as the main interest was in the desorption wave. It was noted, however, that the potential where the adsorption reduction wave starts shifted to more negative values as the chloride ion concentration was increased, while the potential of the "normal" reduction process changed in the positive direction.

The effect of increasing concentration of chloride ion on the half wave potential for the normal reduction is opposite to the expected behavior for a reversible reduction process. For the irreversible reduction of chloro complexes, the effect of increasing chloride ion concentration is often to diminish the overvoltage, as has been previously observed by Lingane[11] in his study of the chloro complexes of tin and by Lingane and Nishida[12] in their work on the chloro complexes of antimony.

That the normal reduction process is highly irreversible is shown by the fact that the reciprocal slope of the linear plot of log $(i_d - i)/i$ for a solution containing 0.4 millimolar tetrachloroplatinate(II) ion, one molar potassium chloride and 0.01% agar was 0.102. The large overvoltage, shown by the half-wave potential of -1.35 volts, is itself evidence for an irreversible

(11) Lingane, THIS JOURNAL, 67, 919 (1945).
(12) Lingane and Nishida, ibid., 69, 530 (1947).

process. In fact, if the overvoltage were not so large, the phenomenon of the adsorption reduction wave undoubtedly could not have been observed.

Summary

1. It is shown that tetrachloroplatinate(II) ion must be adsorbed on the dropping mercury electrode to be reduced at potentials more positive than about one volt (vs. S.C.E.).

2. The desorption wave is described, and an equation expressing the desorption half-wave potential is derived. The desorption process does not appear to be reversible, although the desorption half-wave potential is independent of the solution tetrachloroplatinate(II) ion concentration.

3. Added adsorbents shift the desorption half-wave potential to more positive values by decreasing the effective area available for adsorption of tetrachloroplatinate(II) ion, and perhaps by changing the free energy and kinetics of adsorption.

4. Tetrachloroplatinate(II) ion in potassium chloride indifferent electrolyte shows a normal irreversible reduction wave which has a half-wave potential of -1.35 volt (vs. S.C.E.) for one molar potassium chloride. The half-wave potential shifts to more positive values as the chloride ion concentration is increased.

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[CONTRIBUTION FROM THE DEPARTMENT OF GEOLOGY, UNIVERSITY OF CHICAGO]

Immiscibility in the System H₂O–Na₂O–SiO₂[1]

BY IRVING FRIEDMAN[2]

Introduction

A previous paper[3] dealing with this system showed that liquid immiscibility existed from about 225° up to the highest temperature investigated, 350°. The unusual character of this system as compared to the H₂O–K₂O–SiO₂ system, plus the fact that an understanding of the relationships in this system is basic to the study of the petrologically important H₂O–Na₂O–SiO₂–Al₂O₃ system, prompted a continuation of this work to temperatures above the critical temperature of water.

Experimental

All of the mixtures used in this research were made from the same materials that were used in the previous

work. The experimental procedures were also quite similar. In order to secure more rapid quenching than had previously been possible, a quenching apparatus was constructed consisting of a coil of $1/2''$ copper tubing, the i. d. of the coil being a little greater than the o. d. of the bombs. The tubing has numerous small holes bored facing the inside of the coil. Both ends of the copper tubing are connected through a valve to the cold water supply. The hot bombs are dropped into the coil and the cold water turned on. The numerous water jets cool the bomb from 450° to below 100° in about fifteen seconds.

The bombs previously used developed cracks, usually longitudinal in direction, when used at the higher temperatures with these alkaline solutions. Most of the cracks were through the thickest part of the bombs, and were not due to pressure failure. In all about 24 stainless steel (303) bombs leaked through material failure. That the alkaline solutions were responsible is shown by the fact that several bombs used by Bowen and Tuttle on the MgO–SiO₂–H₂O system have withstood years of use, while other bombs constructed from the same bar of steel and used on the H₂O–Na₂O–SiO₂ system by Morey have shown cracks after several hours or days of use. Recently, another worker[4] noticed the same failure. It has been suggested that slag inclusions, leached out by the alkaline solutions, has caused the failures.

To overcome the above difficulty, bomb bottoms were

constructed of Hastalloy C.[5] These bombs have proved satisfactory up to 600°. The main drawback to their use, besides difficulty in machining, has been the continual leaching of nickel, in contrast to stainless steel, where a black impervious coating forms a lining on the bomb chamber walls, and effectively stops corrosion. Lately, pure silver cups were spun to fit the chambers, and the solutions are now enclosed entirely in silver.

The crystalline phases were identified with the aid of the petrographic microscope. As a further check on crystals whose identity was in question, X-ray powder diffraction photographs were taken in several cases. The latter method is especially useful in identifying water-soluble crystals imbedded in a glass.

A discrepancy between the refractive indices of sodium disilicate reported in the literature[6] and crystals obtained in these runs was first observed by Wasserburg.[7] The refractive indices fit those first reported by Bowen[8] who later revised his figures. To check the possibility that Bowen's later values were obtained on material that had inverted to another modification, crystals obtained hydrothermally at 300° were heated in air at 800 ± 50° for fourteen hours. The crystals lost 3% by weight and inverted to another modification, whose indices fit those first reported by Bowen. Kracek[9] reported two arrests in the cooling curve of sodium disilicate, one occurring at 707° and the other at 678°. One or both of these inversions is therefore probably not of the $\alpha-\beta$ type.

Discussion

Degree of Filling.—In order to determine the influence of the degree of filling of the bombs on the equilibrium relations two techniques were used. In the first, several solubility runs were

TABLE I

Group	Degree of filling	Final composition, % SiO₂	Na₂O	H₂O	Temp., °C.
1	0.61	18.6	6.1	75.3	350
1	.47	17.8	6.2	76.0	350
1	.36	18.7	6.1	75.2	350
1	.22	18.9	6.1	75.0	350
2	.67	21.9	6.7	72.4	350
2	.27	21.5	6.7	71.8	350
3	.55	23.6	6.7	69.7	450
3	.22	23.1	6.7	70.2	450

made using the same solution, but filling the bombs to different degrees. As can be seen from Table I, the degree of filling does not influence the final equilibrium composition.

The second check was made by making several solubility runs as before using the same solution, but different degrees of filling, and then separating and analyzing the two immiscible phases. Table II gives the results of the analysis. Again it can be seen that the degree of filling does not greatly affect the equilibrium composition of the phases.

The independence of the equilibrium composition from the degree of filling can be explained by: (1) Immiscibility—The gas and liquid compositions are fixed, and changing the degree of filling only changes the pressure somewhat. The equilibrium is therefore not affected by this small pressure change; or (2) One liquid is in equilibrium with a gas: (a) The composition of the gas is close to that of the liquid, and the composition-pressure curve for the equilibrium is relatively flat in the region under investigation. (b) The liquid and gas differ widely in composition, the gas being low in non-volatiles (SiO_2-Na_2O). In this case the equilibrium concentrations will also be independent of the degree of filling, provided the degree of filling is great enough so that some liquid remains in the bomb at equilibrium, and small enough so that the liquid does not completely fill the bomb.

Critical End-points.—The composition of the "light" liquid at 350° is close to that of pure water. According to Chitarow and Iwanow,[10] such a solution should have a critical end-point at about 380–390°. Therefore, at 400° the phases coexisting at a point between A and C will be (1) a liquid of composition C, (2) a gas of composition A, and (3) crystalline quartz.

If we start out with a mixture of composition H (Fig. 2) and increase the Na₂O content so that the

TABLE II

Group	Degree of filling	Final composition, % SiO₂	Na₂O	H₂O	Composition of, % Glass SiO₂	Na₂O	H₂O	Liquid SiO₂	Na₂O	H₂O	Temp., °C.
1	0.6	21.8	7.0	71.2	56	18	26	5	2	93	350
1	.2	21.1	7.0	71.9	49	18	33	5	2	93	350
2	.48	23.6	6.7	69.7	62	20	18	1	1	98	450
2	.2	23.1	6.8	70.1	63	22	15	1	1	98	450

TABLE III

					Composition of equilibrium phases, %					
Temp., °C.	Total composition, % SiO₂	Na₂O	H₂O	SiO₂	Glass Na₂O	H₂O	Liquid SiO₂	Na₂O	H₂O	
400	22.2	7.4	70.4	59	20	21	7	3	90	
400	14.3	4.9	80.8	59	20	21	4	2	94	
450	22.6	7.4	70.0	60	16	24	8	3	89	
450	15.0	5.0	80.0	61	20	19	5	2	93	

(5) Haynes Stellite Company, Kokomo, Indiana: C, 0.15 max.; Cr, 13–16; Mo, 15–19; W, 3.5–5.5; Fe, 4–7; Ni, balance.

(6) Data on Chemicals for Ceramic Use, Bull. National Research Council 107 (1943).

(7) G. J. Wasserburg, personal communication.

(8) A. N. Winchell, "Microscopic Character of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., p. 283, 1931.

(9) F. C. Kracek, This Journal, **61**, 2863 (1939).

composition changes along line H–J–G (Fig. 2) the composition of the gas will change from H to J. At J the concentration of non-volatiles in the gas will increase to a point where a second phase will separate, a liquid whose composition is the same as that of the gas. As the composition is further changed along J–G the compositions of the coexisting gas and liquid will become farther apart.

Unfortunately, the experimental technique employed did not allow the determination of the point at which the critical end-point occurs. A device

(10) N. I. Chitarow and L. A. Iwanow, Zentr. Mineral. Geol., **1936A**, 46 (1936).
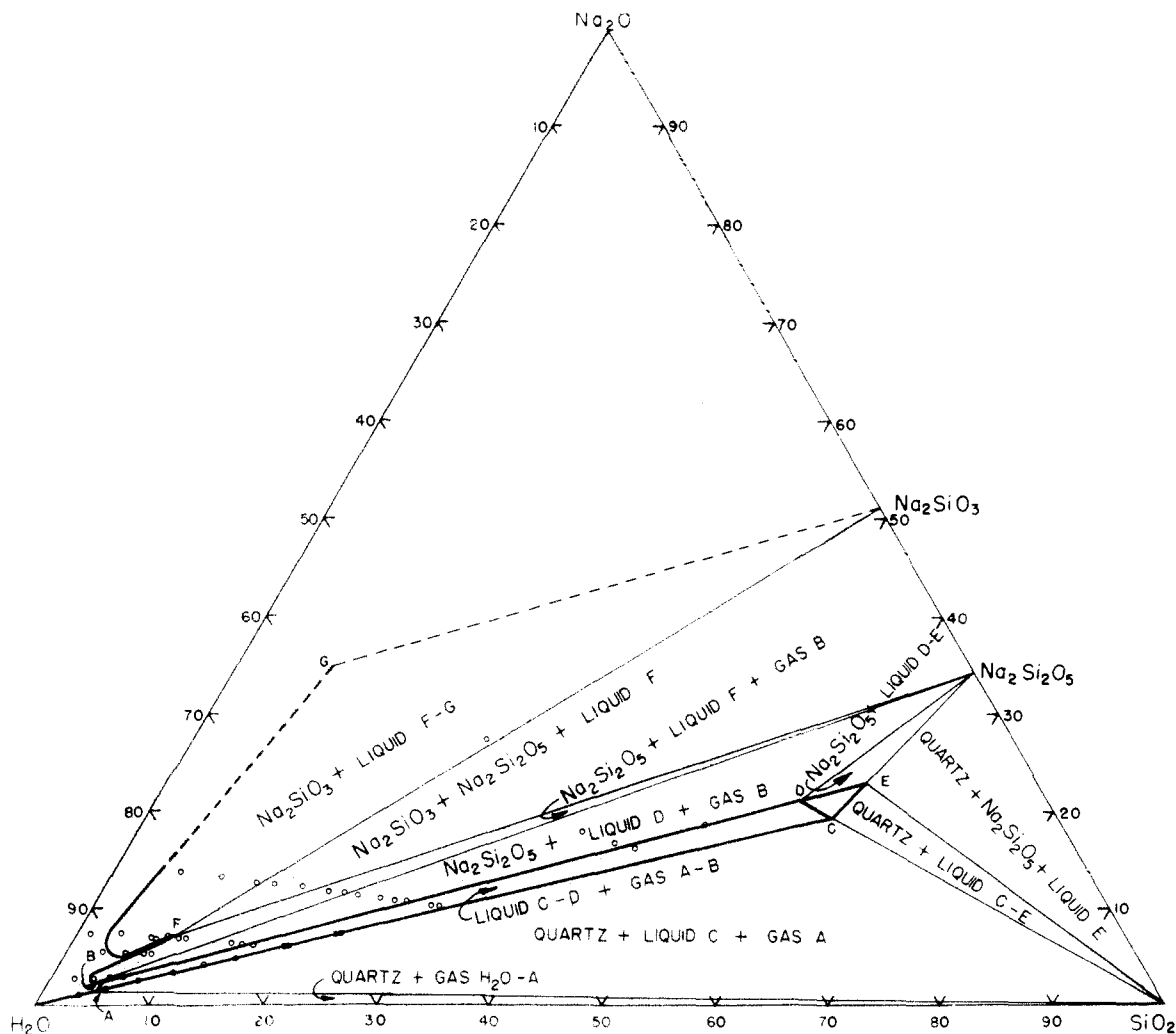
Fig. 1.—Polybaric saturation relations at 400° in the system H₂O–Na₂O–SiO₂.

for accurately measuring pressure in the bombs is being constructed and should help resolve this difficulty.

At 400° the critical region does not extend very far beyond point A (Fig. 1), and the boundary of the critical field is not marked in the diagram. As the temperature is raised, the area of the diagram in which a gas exists increases. At 450° (Fig. 2) all compositions below and to the left of the curve J–K–L–B–A contain a gas at equilibrium. All compositions above and to the right of this curve contain a gas in equilibrium with a liquid. Since the exact position of the points J along H–G, K along H–F, and L along B–F could not be determined experimentally, the phase boundaries that are determined by these points, the lines J–Na₂SiO₃, K–Na₂SiO₃, and L–Na₂Si₂O₅ are indicated by dotted lines.

Immiscibility.—As was true at lower temperature, a glass and a liquid were found upon quenching many runs made at 400 and 450°. The glasses in runs having a composition falling

in the region A–B–C–D (Fig. 1) and kk (Fig. 2) were hard, brittle and water soluble. Their compositions were determined by analysis as before. Many other runs made at 450° also gave a glass upon quenching. However these glasses were soft, and represent the condensed gas phases outside of the immiscible region. The composition of the immiscible pairs is given in Table II.

Binary Systems.—The Na₂SiO₃–H₂O and the Na₂Si₂O₅–H₂O systems will be binary if all of the phases that can exist when the system is at equilibrium can be expressed as a function of the two components. At 250° the Na₂Si₂O₅ system is not binary since the Na₂Si₂O₅–H₂O join in the ternary system intersects the immiscibility field, and the composition of the two liquids that separate cannot be expressed by the two components. At 400 and 450° both systems appear to be binary, and both possess a critical end-point.

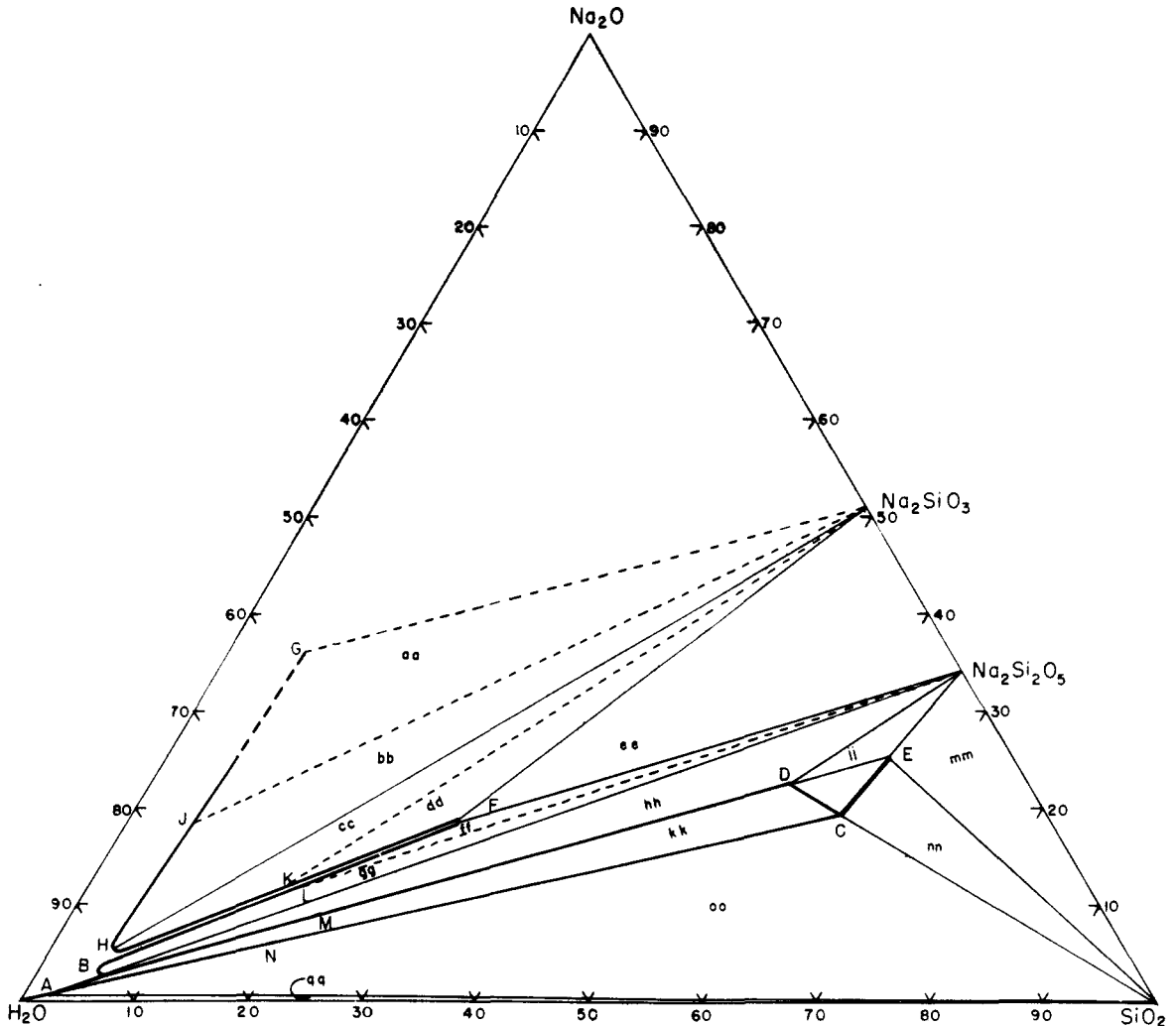In the previous discussion of this system the composition of the gas phase was ignored, since it

Fig. 2.—Polybaric saturation relations at 450° in the system H₂O–Na₂O–SiO₂: explanation of figure:

aa, Na₂SiO₃ + liquid G–J

bb, Na₂SiO₃ + gas J–H

cc, Na₂SiO₃ + gas H–K

dd, Na₂SiO₃ + liquid K–F

ee, Na₂SiO₃ + Na₂Si₂O₅ + liquid F

ff, Na₂Si₂O₅ + liquid L–F

gg, Na₂Si₂O₅ + gas L–B

hh, Na₂Si₂O₅ + liquid D + gas B

jj, Na₂Si₂O₅ + liquid D–E

kk, liquid C–D + gas A–B

mm, quartz + Na₂Si₂O₅ + liquid E

nn, quartz + liquid C–E

oo, quartz + liquid C + gas A

pp, quartz + gas H₂O–A

was assumed that the concentration of non-volatiles in the gas was low enough so that the system could be treated as a condensed system. This assumption becomes less true as the temperature is raised. At 450° the gas can be fairly dense, and may contain a considerable concentration of non-volatiles. If the Na₂O–SiO₂ ratio in the gas differs appreciably from that in the coexisting liquids, the total composition lying on the Na₂SiO₃–H₂O or Na₂Si₂O₅–H₂O joins, then the corresponding Na₂SiO₃–H₂O and Na₂Si₂O₅–H₂O systems will not be binary. At the critical end-point, the systems will be binary.

Stability Relations.—Again, as at 300 and 350°, the area investigated is divided by the curve

H₂O–A–C–D–B–F–G (Fig. 1) into regions to the left of the curve representing mixtures that are unsaturated with respect to a solid phase, and a region to the right of the curve containing one or more crystalline phases in equilibrium with a liquid and a gas, or a gas. The compositions of the liquids or gases coexisting with the crystalline phases are given by the curve, with the exception of the section A–C–D–B. Along this section liquids of compositions C–D will be in equilibrium with gases of composition A–B, plus either quartz or sodium disilicate. Point F is a point on the eutectic line.

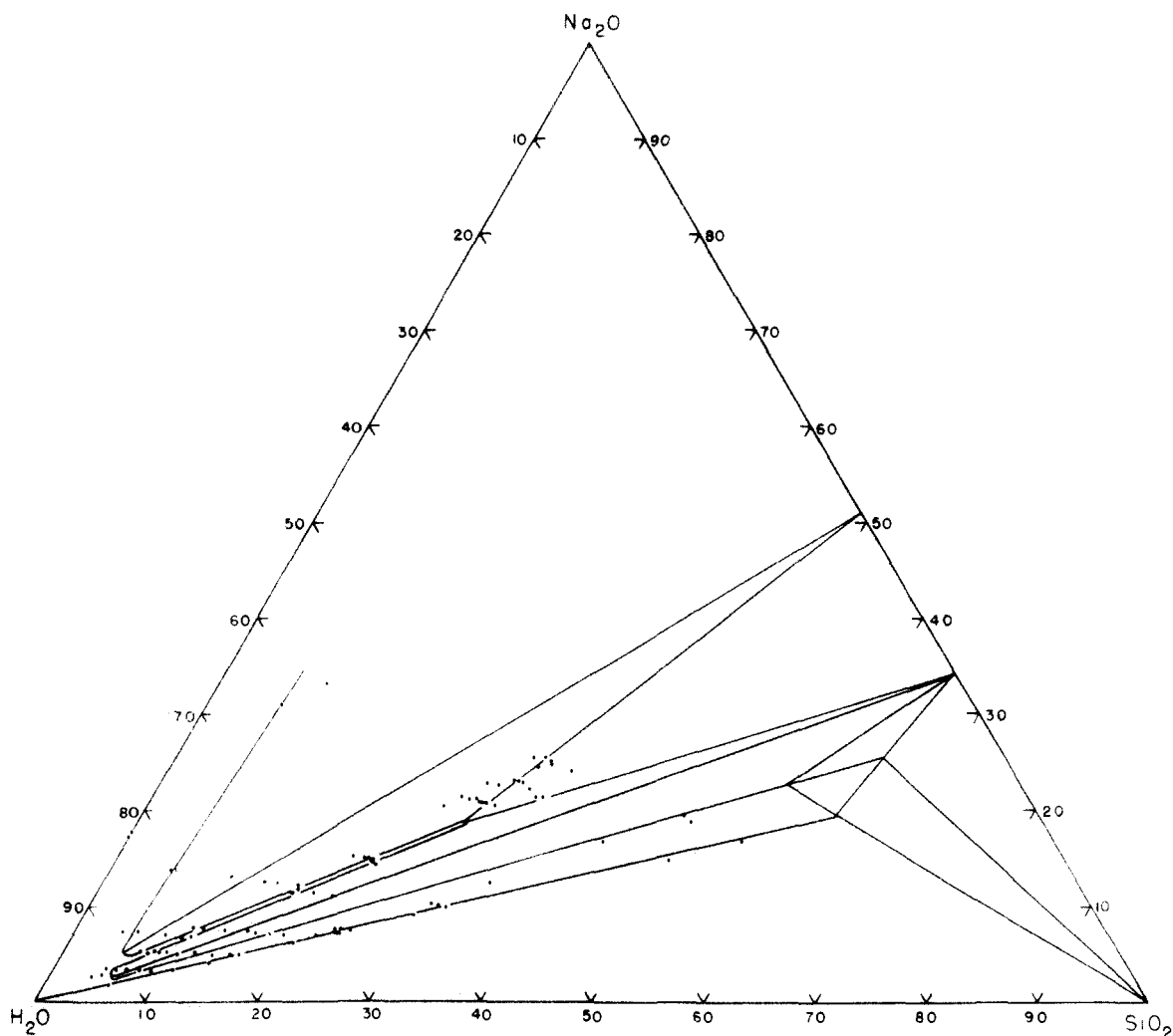The saturation relations at 450° are illustrated in Fig. 2. The major changes as the temperature

Fig. 3.—Equilibrium relations at 450°, showing experimental points.

is raised from 400° is the shift of the point F to-
ward the right of the diagram. Within the area
bounded by the line B–F–H mixtures will consist
either of one liquid plus gas, or a gas. The critical
end-point at which the gas composition and den-
sity becomes equal to that of the coexisting liquid
is given by the experimentally undetermined
curve K–L. All mixtures in the area B–L–K–H
contain a gas, and all those in the area L–F–K
contain a liquid plus a gas.

Points E and F are monovariant, since four
phases, two crystal, a liquid, and a gas, coexist
at each of these points. The area C–D–E, as at

300° and 350°, represents a region of one liquid.

Summary

Polybaric equilibria in the system H_2O–Na_2O–
SiO_2 was investigated at 400 and 450°. One
member of the immiscible pair reported at 250 to
350° has a critical end-point with its coexisting
gas at about 390°. Therefore, at 400 and 450°
the term liquid immiscibility no longer applies,
although immiscibility still exists since the coexist-
ant liquid and gas compositions are independent of
the initial composition within the immiscible region.