of those of Series 5 (in which hydrochloric acid was used), the precipitates were in Series 6 much more difficult to prepare for analysis. Although, like the precipitates of Series 5, they were coarse-grained and quick to settle in the precipitation mixtures, they became fine-grained and slow to settle during the washing, and at the last, on the filters, they were extremely slimy and impervious to the wash-water. This behavior, while unexpected, is nevertheless in good agreement with the conclusion that the iron is carried down in the form of a complex barium sulfato-ferriate. It has already been pointed out that the iron complex in these impure barium sulfate precipitates is slowly dissociated by water in the sense of the equation

$$Ba[Fe(SO_4)_2]_2.nH_2O + \text{Water} = BaSO_4 + Fe_2(SO_4)_3.mH_2O.$$

This dissociation takes place during the washing, and the barium sulfate formed in this way is, as we should naturally expect, very fine-grained and slow to settle. Again it should be emphasized, that analyses of the completely washed precipitates are incapable of furnishing accurate data as to their composition at the time of their actual formation.

One other point should be especially noted in connection with these precipitates, and that is that their losses in weight upon ignition do not of necessity bear any relationship to their iron contents. The truth of this assertion is plainly borne out by the data of Tables VI and VII.

Conclusion.

Barium sulfate precipitates which have been thrown down in solutions containing ferric iron, carry down the latter in varying quantities, not in the form of a solid solution of basic ferric sulfate or other compound, nor adsorbed on the surface of the grains, but in the form of a hydrated complex sulfato-ferriate of barium (or other cation), which is present in intimate mechanical admixture with the barium sulfate.

URBANA, ILL.

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THE TERNARY SYSTEM H_2O–K_2SiO_3–SiO_2.

BY GEORGE W. MOREY.

(MICROSCOPIC STUDY BY C. N. FENNER.)

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K_2SiO_3–SiO_2. *C.* The Binary Systems H_2O–K_2SiO_3, H_2O–$K_2Si_2O_5$, K_2SiO_3–SiO_2 and H_2O–SiO_2. VII. The Critical Region. VIII. The Composition of the Vapor Phase. IX. The Interrelations between Temperature, Pressure and Composition in the Ternary System: *A.* Sequence of P-T Curves around a Quintuple Point; *B.* Application to the Quintuple Points in the Ternary System; *C.* The Solid Models; *D.* The Isobaric Polythermic Saturation Curves. X. The Solubility of Silicates. XI. Summary.

I. Introduction.

When we speak of equilibria between crystalline solids and water, we usually consider only equilibria at low temperatures and at the correspondingly low vapor pressures of the aqueous solutions. Some systems have been followed up to the point at which the vapor pressure of H_2O reaches one atm., *i. e.*, to their boiling points, and a very few have been studied at slightly higher pressures and temperatures. The relations which will be met with at higher temperatures, *e. g.*, at temperatures above the critical temperature of water, have rarely been considered.

The following paper treats of the equilibrium relations in the system H_2O–K_2SiO_3–SiO_2 from 200° to above 1000°. The work comprises a determination of the composition and properties of the various stable solid phases which can coexist with solution and vapor within the above temperature range, of the composition of the solutions in equilibrium with the solid phases, of the change in composition of these solutions with temperature, and the approximate determination of the corresponding 3-phase pressures.

Systems of this type are of considerable interest and importance, both from the theoretical and the practical point of view. They are of fundamental importance in geochemistry, since it is only by consideration of the relations which must exist in systems composed of both volatile and non-volatile components that we can arrive at an adequate explanation of the problems connected with the crystallization of rock magmas.

Systems made up of those substances which are commonly considered as the essential ingredients of a rock magma, namely, the various non-volatile oxides such as CaO, MgO, Al_2O_3 and SiO_2, have been studied in some detail and with considerable accuracy, and at present we are able to orient ourselves fairly well in regard to their mutual saturation and fusion relations. But there is no doubt that magmas originally contained other components, substances such as O, N, H, CO, CO_2, H_2S, SO_2, Cl, HCl, HF, and H_2O, whose critical temperatures lie far below the temperature of anhydrous fusion of the systems composed of the predominant non-volatile components.

The study of the effect of the introduction of volatile components into systems composed of non-volatile substances has scarcely been begun. To be sure, a considerable number of workers have experimented on the production of minerals by the aid of water at high temperature and pressure, but, as was shown in a previous publication on the hydrothermal formation of silicates,[1] this older work has usually been carried out without quantitative determination of essential factors or conditions and but few conclusions of a general nature can be drawn from it. Nor is this surprising. Aside from the experimental difficulties involved, the theoretical consideration of systems composed of volatile and non-volatile components is a field which had not been developed in any detail at the time when most of the earlier work was done; indeed, the relations which must exist in such systems are still but imperfectly understood.

It was in the hope of extending our knowledge of systems which may be considered as more or less similar to rock magmas that a study of the ternary system H_2O–K_2O–SiO_2 was undertaken. These oxides are common rock components, and the system containing K_2O lends itself more easily to study than systems containing a less soluble oxide such as CaO or MgO. A preliminary paper, describing the apparatus used and giving the composition and properties of several of the compounds met with in this system, has already appeared.[2] The present publication gives an account of the equilibrium relations in a portion of the system from comparatively low temperatures, considerably below the critical temperature of water, to temperatures above that of anhydrous fusion of the major portion of the binary system of the non-volatile components. Further work, dealing with the relations in this field from other points of view, and extending our knowledge of the equilibrium diagram, is in progress.

The original plan was to consider the whole of the ternary system H_2O–K_2O–SiO_2, but, for several reasons, the actual work was confined to a portion of this system. If the compound K_2O exists,[3] its dissociation[4] is so great that even at moderately high temperatures its introduction would necessitate the consideration of its dissociation products as components. Moreover, several facts have led to the conclusion that no crystalline K_2O-SiO_2 compound richer in K_2O than the metasilicate is stable in contact with liquid and vapor. Some evidence in regard to this point is presented on page 1193; further evidence in regard to the orthosilicate of several alkali metals is now being obtained.

No general theoretical discussion of the phase relations in systems of this type will be given in this paper, because of the rather involved relationships which are met with when we consider a three-component system existing in solid, liquid and gaseous phases, particularly when critical phenomena are included. Such a treatment is in preparation; in

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[1] Morey and Niggli, THIS JOURNAL, 35, 1086–1136 (1913).

[2] Morey, *Ibid.*, 36, 215–30 (1914); *Z. anorg. Chem.*, 86, 305–24 (1914).

[3] Holt and Sims, *J. Chem. Soc.*, 65, 432–44 (1894).

[4] Rengade, *Ann. chim. phys.*, [8] 11, 420–24 (1907).

the meantime, the reader is referred to the fundamental papers of Smits[1] and Schreinemakers.[2]

II. Preparation of Materials.

As was the case in the preliminary work already published, the materials used in this investigation were water and powdered mixtures, generally glasses, containing SiO_2 and K_2O in various proportions. The obvious method of preparing such mixtures is by fusion of K_2CO_3 with SiO_2 in the required proportions, and this method was used wherever possible. On account of the tendency of the thick viscous melts to froth over during the decomposition of the K_2CO_3, preparations made in this manner were first fused in a large flat-bottomed platinum dish in a Fletcher furnace, then heated in an electric furnace in a CO_2-free atmosphere. This method, however, does not permit of the direct preparation of mixtures of a desired composition. Mixtures rich in SiO_2 require long heating at high temperatures for the complete expulsion of the CO_2 from the melts which are very viscous; under these conditions K_2O is rapidly lost, and the product obtained is always poorer in K_2O than the original mixture. Moreover, mixtures rich in K_2O, containing from 1.0 to 1.5 mol. SiO_2 per mol. K_2O, cannot be prepared CO_2-free in this manner. This is due to the fact, shown by Niggli,[3] that an equilibrium between K_2SiO_3, $K_2Si_2O_5$ and K_2CO_3 tends to be established in the melt, and that the equilibrium pressure of CO_2 is small when the mixture approaches K_2SiO_3 in composition. The great viscosity of the melt makes the escape of CO_2 very slow, so that although the partial pressure of CO_2 in the co-existing vapor phase approximates to zero, the actual expulsion of CO_2 is a very slow process. If the temperature be raised or the charge heated for a long time, K_2O is lost.

These facts are illustrated by the following experiments: A mixture of K_2CO_3 and pure quartz, in equimolecular proportions, was first melted in a Fletcher furnace until a clear melt was obtained, then powdered, sampled, heated in an electric furnace in a CO_2-free atmosphere at the given temperature for the given time, powdered, sampled, and the process repeated. K_2O and CO_2 were determined in each preparation.

Treatment.	% CO_2.	% K_2O.	Mol. ratio SiO_2/K_2O.
Fused 1 hr. in Fletcher furnace........	4.57	56.98	1.053
Fused 1 hr. in electric furnace, 1300°..	1.73	57.38	1.113
Fused 1 hr. in electric furnace, 1400°..	1.52	57.66	1.15

It will be observed that, when the CO_2 content is small, the rate of loss

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[1] See the paper by Smits referred to in THIS JOURNAL, **35**, 1086–1130 (1913); also *Proc. Acad. Sci. Amsterdam*, 18, 793–807 (1916).

[2] See, in particular, the two series of papers, "Equilibria in Ternary Systems," beginning in *Proc. Acad. Sci. Amsterdam*, **15**, 700 (1913); and "In-, Mono-, and Divariant Equilibria," beginning in *Ibid.*, 18, 116 (1916).

[3] Niggli, THIS JOURNAL, **35**, 1694–1727 (1913).

of K_2O is of the same order of magnitude as that of CO_2. The high CO_2 content of the charge after being heated in the Fletcher furnace is also noteworthy; the temperature was probably about 1400–1500°.

It therefore became necessary to devise other methods for the preparation of mixtures intermediate in composition between K_2SiO_3 and $K_2Si_2O_5$. The first method tried consisted in melting the purest obtainable KOH in an atmosphere[1] of steam and adding SiO_2 or a potassium silicate glass rich in SiO_2 and free from CO_2. The steam served a double purpose, providing a CO_2-free atmosphere, and, by solution in the melt, lowering the viscosity and facilitating the melting. It should be mentioned that the platinum crucibles used in this work were not appreciably affected by the molten KOH, even when the temperature was raised above 1000°, provided that the heating was carried out in an atmosphere of steam and that the ratio SiO_2/K_2O was greater than unity.

In the preparation of K_2O-SiO_2 mixtures by either of these methods, it was not practicable to obtain a mixture of a given composition directly, because of the above-mentioned volatility of K_2O. With glasses rich in SiO_2, the high temperatures necessary for complete fusion and complete expulsion of CO_2 make a considerable loss in K_2O inevitable; with glasses rich in K_2SiO_3 the heating in an atmosphere of steam results in a rapid volatilization of K_2O, in spite of the lower temperature. This circumstance led to the devising of a third method for the preparation of K_2O-rich mixtures, one of which is generally applicable to fairly soluble mixtures. It consists in heating a mixture of KOH and SiO_2-rich glass, in the desired proportions, in an autoclave[2] with considerable H_2O at 250–300° until the entire mass is a homogeneous fluid, then, by slightly opening a valve, permitting the H_2O to escape slowly until the pressure falls to about one atmosphere. The charge is then removed, and dehydrated by heating

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[1] The following analyses of various commercial samples of KOH may be of interest. K_2O was determined by evaporation to dryness with HCl and weighing to KCl; no attempt was made to determine separately the amounts of other alkali oxides present. CO_2 was determined by the method described on page 1179. All samples were taken from newly opened bottles, unless otherwise mentioned.

Maker.	K_2O.	CO_2.
B. and A., by baryta	70.41	1.45
J. T. B., C. P. by alcohol (Lot No. 31313)	73.65	0.50 (analysis 0.325)
Mall., U. S. P., by alcohol	74.91	0.47
Squibb, by alcohol	74.20	0.56
Merck, blue label	70.71	0.74
Kahlb., alc. ger. in Stangen	...	0.61
J. T. B., electrolytic, from 5 lb. bottle, $^1/_5$ full, which had been standing, loosely stoppered, for months in the laboratory	...	2.47

[2] See Morey, *J. Wash. Acad.*, 7, 205, for a description of the type of autoclave found advantageous in this work.

to about 700° in a CO_2-free atmosphere. By this method mixtures can be made up of the desired composition, free from CO_2 (except for that in the KOH used), and in considerable quantity.

The impossibility of preparing, free from CO_2, mixtures intermediate in composition between K_2SiO_3 and $K_2Si_2O_5$, and of any mixture with a predetermined SiO_2/K_2O ratio, by fusion of K_2CO_3 and SiO_2 requires further emphasis. It is a fact which appears not to have been sufficiently appreciated by previous investigators. Wallace,[1] working on the binary system K_2SiO_3–Li_2SiO_3, prepared his K_2SiO_3 by direct fusion, but was unable to obtain any result with mixtures containing more than 30% "K_2SiO_3." Pukall[2] describes a considerable series of experiments, on mixtures having SiO_2/K_2O ratios of from 1–6, in which all the mixtures were generally re-fused, but still the components are assumed to be present in the proportion originally weighed out.

It is well known that alkali silicate glasses are difficult to crystallize;[3] this fact is probably connected with their great viscosity. For this reason, previous investigators, working by the fusion method, have been unable to obtain crystalline compounds of K_2O and SiO_2; their melts have merely hardened to amorphous glasses.[4]

The phenomena connected with the "second boiling point" of solutions afforded a means of crystallizing such mixtures. When the equilibrium between a solid, *e. g.*, KNO_3, and water is considered, we know that the solubility usually increases with the temperature; the solubility or fusion curve connects the triple points of the two components. The 3-phase pressure, *i. e.*, the pressure at which equilibrium between solid, liquid and vapor can co-exist, first increases as the temperature increases, reaches a maximum, then falls with increasing temperature, becoming equal to the vapor pressure of the second component at the triple point of the latter. When the maximum lies at a pressure greater than one atmosphere, two points are found at which the vapor pressure of the saturated solution is one atmosphere. The first of these reached as the temperature is raised is the ordinary boiling point of the saturated solution, the second is the "second boiling point." This phenomenon was predicted by Roozeboom[5] and realized experimentally by Smits[5] for several substances, among them KNO_3.

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[1] Wallace, *Z. anorg. Chem.*, **63**, 1–48 (1909).

[2] Pukall, *Silikate-Z.*, **2**, 65–76, 87, 99, 109–118 (1914).

[3] Consult Tammann, "Krystallizieren und Schmelzen," in regard to the "specific crystallizability" and "linear velocity of crystallization" of substances.

[4] *E. g.*, those prepared by Pukall (*Loc. cit.*). That such glasses cannot be considered as compounds appears obvious, yet Pukall designates a series of such glasses by the names "potassium metasilicate, potassium disilicate," etc., to "potassium hexasilicate."

[5] Roozeboom, "Die Heterogenen Gleichgewichte," [1] **2**, 351–2; Smits, *Vers. Akad. Wettenschappen*, Dec., 1901.

The "second boiling point" is easily realized with a glass approximating to K_2SiO_3 in composition. When such a glass is heated to about 1000° in steam and allowed to cool rapidly, it froths or swells up, forming a porous crystalline mass. This is to be ascribed to the pressure of the dissolved H_2O increasing on cooling. The dissolved H_2O then escapes, and at the same time induces crystallization in the liquid. This phenomenon has been utilized in preparing mixtures containing crystals, but, unfortunately, crystals wholly uncontaminated by glass could not be obtained in this way. By careful manipulation, mixtures have been crystallized which had a SiO_2/K_2O ratio as great as 2.20, the crystalline phase in this case being $K_2Si_2O_5$.

III. Analytical Methods.

The methods of analysis used were simple. For the mixtures and products consisting only[1] of K_2O, SiO_2, and small amounts of H_2O and CO_2, special methods could be applied.

K_2O was determined by placing a weighed sample in a platinum dish, dissolving in a few cc. of H_2O, adding HF, and evaporating to dryness on the steam bath. The treatment with HF was then repeated, the residue dried at 150°, and weighed as K_2SiF_6. This method gives excellent results, duplicate determinations repeatedly checking to within the error of weighing, *e. g.*, to 0.01% in a total K_2O content of 50–60% K_2O. The conversion to K_2SiF_6 is rapid and complete, the excess SiO_2, together with any H_2O and CO_2 present, being expelled when the solution is evaporated to dryness, and the K_2SiF_6 formed is stable and easily dried. Its composition was checked many times by conversion to K_2SO_4, with satisfactory results. Care must be taken in this conversion to completely expel all the SiO_2; treatment with dilute acid in the cold results in partial decomposition of the liberated SiF_4, with deposition of SiO_2.

SiO_2 was determined by the HCl method, as given by Hillebrand,[2] with the exception that the separated SiO_2 after the first filtration was again digested with dilute HCl.

Attempts were made to determine H_2O and CO_2 by fusion with an appropriate flux and absorption of the H_2O and CO_2 in P_2O_5 and soda lime, respectively. The choice of a suitable flux is a difficult matter. Borax dissolves the alkali silicate, but the resulting melt is viscous, hence a long time is required to remove all the CO_2. Moreover, because of the high temperature and long heating required, B_2O_3 vapors are evolved in quantity, causing the rapid destruction of the porcelain tubes. Because of this

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[1] The original materials used were, of course, analyzed, and the impurities present were wholly negligible, with the exception of CO_2. This is treated separately.

[2] "The Analysis of Silicate and Carbonate Rocks," U. S. Geological Survey, *Bull.* 422.

fact, total volatile matter cannot be estimated by loss in weight on ignition with borax. Other fluxes give unsatisfactory results. Sodium tungstate,[1] which works so well with many substances, does not appreciably dissolve alkali silicates, and forms 2 liquid layers with them above their melting points, making the complete expulsion of volatile matter an uncertain process. Moreover, tungstic acid is somewhat volatile, leading to troubles similar to those found with borax. Addition of quartz and ignition will effectually expel all volatile matter, but at the high temperature required K_2O is rapidly lost. The method finally used for CO_2 was a wet method, consisting in dissolving the sample in H_2O, acidifying the solution with H_2SO_4, sweeping out the liberated CO_2 with a current of CO_2-free air, and absorbing in soda lime. The absorption train consisted of two soda lime tubes and one P_2O_5 tube; suitable tubes being used on both sides of the absorption train.

H_2O was determined by fusing in a closed tube with anhydrous Na_2CO_3, and absorbing the evolved H_2O in P_2O_5. The H_2O vapor was swept out by a current of air, previously passed through a porcelain tube containing fragments of porcelain, and heated to 1100° in order to remove traces of hydrocarbons.[2] The air stream was dried by concentrated H_2SO_4 and P_2O_5, and the P_2O_5 absorption tube was suitably protected by guard tubes. Frequent blanks were run on the apparatus, and the small correction subtracted from the weight of water obtained.

For convenience in reference, the various mixtures used will be denoted by the letter K, followed by a subscript indicating the ratio SiO_2/K_2O in the mixture. For example, a $K_{2.16}$ glass indicates a mixture containing 2.16 mols. SiO_2 to each mol. K_2O, etc. The composition of the glass mixture in respect to the essential ingredients is given by this method.

Since a total of as many as 60 different glasses was used in the course of this work, it is not practicable to give the complete analysis of each one. Glasses richer in SiO_2 than $K_{2.0}$ were all free from CO_2; glasses containing less SiO_2 usually contained small amounts of CO_2, derived from the original KOH used. In some cases, notably those glasses approaching K_2SiO_3 in composition, the amount is of the order of magnitude of 0.5%. This degree of contamination, which could not well be avoided, probably alters but slightly the position of the saturation surfaces. In some cases the glasses intermediate in composition between K_2SiO_3 and $K_2Si_2O_5$ contained a small amount of H_2O, especially those made by fusion in steam. This was corrected for in calculating the composition of the solutions. For example, the $K_{1.01}$ glass had the following composition:

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[1] Gooch and Kuzirian, *Am. J. Sci.*, 31, 497–500 (1911); Kuzirian, *Ibid.*, 36, 401–5 (1913).

[2] This was found necessary, probably on account of oil from the air compressor.

K_2O	59.85%
SiO_2	38.65
H_2O	1.06
CO_2	0.43
Total	99.99

IV. Experimental Methods.

A. **Hydrothermal Quenching Method.**—The equilibrium in the system H_2O–K_2SiO_3–SiO_2 was studied by determining, at various constant temperatures, the change in the H_2O content with variation of the SiO_2/K_2O ratio in the saturated solution, *i. e.*, by means of isothermal polybaric saturation curves. Because of the high temperatures and pressures, of the great viscosity of the solutions, and of the fact that glass vessels are attacked by the solutions, none of the usual methods of determining saturation or solubility curves could be applied.

It therefore became necessary to find other methods for carrying out such determinations. The chief method used is based on the fact that when a mixture of K_2SiO_3 and SiO_2, not too rich in the latter component, is heated in a bomb with sufficient H_2O to ensure complete solution, and the hot bomb quickly cooled, the liquid solidifies to a glass, without change in composition. In other words, the equilibrium is frozen—or quenched—and the method has been termed the "hydrothermal quenching method."

The type of bomb used in carrying out determinations by this method is shown in Fig. 1. Each bomb consists essentially of three parts, namely, the body E, the plunger C, and the screw plug B, which are assembled as shown. Closure is effected by means of a copper or silver washer in D; it is essential that the washer be imprisoned in such a manner, otherwise it will flow at the high temperatures and pressures, thus giving rise to a leak. Temperatures are measured by a thermoelement inserted in the hole F. The charge is placed in the gold crucible G. For details of the construction of both bomb and furnace, and for additional details as to the method of carrying out an experiment the reader is referred to a previous paper.[1]

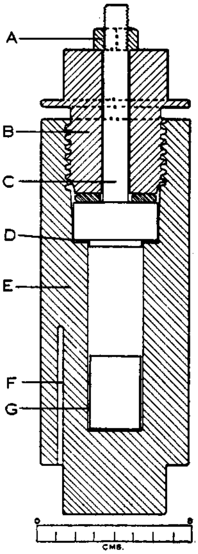

Fig. 1.
Cut showing the construction of the bomb used.

The method of carrying out an experiment is as follows: A weighed mixture of K_2SiO_3 and SiO_2 of known SiO_2/K_2O ratio is heated with H_2O in the bomb at a given temperature, the bomb removed from the furnace, and cooled quickly by plunging into cold water. The charge is then re-

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[1] Morey, This Journal, 36, 215–30 (1914); *Z. anorg. Chem.*, 86, 305–24 (1914).

moved from the furnace, weighed, and subjected to a microscopical examination.

When such a mixture is heated, the product obtained depends on the factors, temperature, pressure (amount of H_2O present) and composition ratio SiO_2/K_2O in the mixture. Consider, *e. g.*, 2 g. of $K_{2\cdot0}$ glass[1] placed in a gold cup in a bomb of about 70 cc. volume, with a quantity of water sufficient to ensure the presence of a liquid phase. As the temperature is increased the vapor pressure of the aqueous solution increases, and an increasing proportion of the H_2O present passes into the vapor phase. As the temperature is increased the concentration of the solution increases and the amount of solid phase decreases. At a certain temperature, determined by the amount of H_2O present,[2] the solid phase will disappear entirely; conditions would be different were the mixture rich enough in SiO_2 so that critical phenomena took place.

Now, by working at constant temperature, with a glass having a known ratio SiO_2/K_2O and varying the amount of water taken above and below that at which crystals are formed, we can fix the limits between which crystals are or are not found. By weighing the glass, we find the amount of H_2O which was present in the hot liquid, hence we know the composition of the solution saturated with the known solid phase at the given temperature.

Let us consider the nature of the product found on opening the bomb after cooling and how it will be affected by the manner in which the cooling is carried out.

When the bomb is allowed to cool very slowly, *e. g.*, inside the furnace (in which case several hours are required), the temperature of the liquid charge in the crucible will be approximately the same as that of the walls of the bomb. Since the vapor pressure of the solution is much less than that of pure water, the vapor condensed as the pressure decreases will be taken up by the charge. Hence, when the bomb is opened the crucible will be found to contain all the components, volatile and non-volatile, originally placed in it; with the alkali silicates it is a liquid, either with or without a residue of hydrolyzed silica. These conclusions have been repeatedly verified by weighing.

Conditions are very different when the hot bomb is suddenly cooled by being totally immersed in cold water and the crucible is caused to cool much more slowly by being placed on a porcelain block. Then the walls of the bomb are quickly chilled, while the temperature of the aqueous melt in the crucible lags behind. As the walls cool quickly, vapor is condensed, and the pressure (*i. e.*, the concentration of H_2O in the vapor

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[1] Critical end points are not met with in a glass of this composition.

[2] With a given SiO_2/K_2O ratio, in a closed space; retrograde solubility does not occur.

phase) in the bomb drops suddenly, becoming much less than the vapor pressure of the warmer melt. The water in the aqueous solution then suddenly vaporizes, expands, and, as a consequence, the non-aqueous portions of the charge froth up and freeze. The product in the crucible in this case will be an anhydrous pumice, the water being all condensed on the walls of the bomb. This phenomenon, which yields a pumiceous mass, has often been observed, and can be reproduced at will.

Between the two extremes mentioned above lies a middle course, which will give a product bearing the same relation to the hot aqueoigneous melt that a glass obtained by quenching bears to the hot charge; and, in this case also, the condition of the charge at the experimental temperature and pressure can be determined by microscopical examination of the quenched product. If all the charge was liquid, under the conditions of the experiment, the bottom of the crucible will be found to be covered with a glass, containing more or less water, depending on the experimental conditions. Microscopical examination will show the absence of crystals. If the hot charge was a mixture of crystals and liquid, the quenched charge will consist of crystals imbedded in a matrix of glass. Moreover, by the application of modern petrographic methods, the crystals present can be positively identified; hence there is no doubt as to the nature of the solid phase. By varying the amount of water present, the crystals can be made to appear or disappear at will. At constant temperature and at constant SiO_2/K_2O ratio, from such a variation in the H_2O concentration the coordinates of the point at which the crystals disappear, and hence a point on the fusion surface of the compound in question, can be determined. The proper manner of cooling in a given case, however, can be learned only by experience, and depends on the temperature of the experiment, the pressure (*i. e.*, the amount of H_2O present) and the composition of the glass. Usually about 3 to 5 minutes are required. Sometimes many experiments were necessary to ascertain the exact rate and manner of cooling which would give satisfactory results.

Since the concentration of one of the components is a function of the pressure, absolute freedom from leaks is essential. That this condition has been fulfilled in these experiments follows of necessity from the weighing experiments, which show directly that all the water originally placed in the bomb was still there after having been heated, and also from the experiments described on page 1185 (Fig. 2).

Two possible sources of error in the points determined by the hydrothermal quenching method should be discussed. First, how closely does the composition of the cooled glass approximate to the composition of the melt, and second, what certainty is there that crystals found in the cooled product were not formed during the cooling?

The first question is obviously one which cannot be answered by direct proof, but only by inference. Experience gained by over 2,000 experiments by this method, however, has shown that, under proper conditions, reproducible and concordant results can be obtained, which are believed to correspond to true equilibrium. The phenomenon of formation of pumiceous glass mentioned above gives a certain indication of loss of water; many experiments have been made in which the bomb was cooled a little too rapidly, and the resulting product was more or less pumiceous. Indeed, a loss of but a few milligrams of H_2O leaves behind in the hardened glass the unmistakable evidence which warns the experimenter that the bomb was cooled too quickly, and, as a consequence of the escape of H_2O from the liquid, the amount of H_2O in the cooled glass is less than the amount corresponding to the equilibrium at high temperature.

While there is no such positive assurance that the charge has not taken up a small amount of water, still many factors exist which together make it possible to feel confidence in the results. In the first place, such a condensation inside the crucible is not probable, unless the cooling takes place very slowly indeed. Usually no pumiceous glass is found if the total duration of cooling is about five minutes, and the bomb is slowly immersed in the water bath. Since the loss of heat takes place on the walls, the water will condense there, not on the inside of the crucible. Condensation in drops in the vapor space of the bomb is highly improbable.

The presence of a small amount of H_2O as such inside the crucible is easily detected. Solution of the hard siliceous glass in the crucible by water in contact with it is a slow matter; a drop of water may lie for some time on the surface and still be plainly visible due to the marked difference in refraction. After the crucible plus contents has been weighed (which is done within a few minutes after removing from the bomb), wiping out with filter paper will remove any water, and that such water has been removed can be detected by diminution in weight. If there has been a loss in weight, the experiment must be repeated until a product is obtained, which satisfies all the criteria applicable.

Another fact which gives weight to this method of determining the saturation concentrations is found in the concordance of results determined by different experimenters. Several of the points at 520° were determined independently by Mr. E. D. Williamson, and agree well with the other determinations. I take this opportunity of expressing my thanks to Mr. Williamson.

Another assurance against error lies in plotting the results of the experiments, the amount of water in the glass against that in the vapor space; *i. e.*, the variation in the amount of water dissolved by the glass with the pressure. Such a plot should give a straight line, in accordance with Henry's law. These plots have been made in all cases, not only as a guard against error, but also to aid in fixing the coördinates of the point sought.

As a further illustration of the method of carrying out an experiment, the detailed results of one are given. The point sought is the point on the isothermal solubility curve at 420°, using 2 g. of glass $K_{2.72}$ in each experiment; the solid phase is $KHSi_2O_5$.

TABLE I.

G. H_2O taken.	G. H_2O in quenched charge.	Condition of quenched product.
6.05	0.476	Glass
5.51	0.441	Glass
5.03	0.413	Glass
4.98	0.412	Glass
4.81	0.400	Glass
4.69	0.388	Glass
4.60	0.386	Glass
4.49	0.375	Crystals and glass
4.40	0.363	Crystals and glass
4.60	0.368	Pumiceous glass
4.55	0.350	Pumiceous glass

Comparison of the table with Fig. 2 shows that the amount of water taken up by the melt decreased with decreasing amount of water added, most of the results lying fairly well on a straight line. The only marked exceptions are the two experiments in which pumiceous glass was formed, in both of which the amount of water in the quenched charge is low. It will also be observed that the product in every case was entirely glass until the amount of water taken was reduced to 4.49 g., when a few well-developed crystals of $KHSi_2O_5$ were found imbedded in the glass. Evidently the solution at its saturation point would contain about 0.380 ± 0.005 g. H_2O, and the amount of water which it would be necessary to take to produce a pressure great enough to keep this amount dissolved would be between 4.49 and 4.55 g. Since the original charge contained 2.000 g. $K_{2.72}$ glass, and this required 0.38 g. H_2O to dissolve it at 420°, the mol. fraction H_2O in the saturated solution is 0.501, of K_2SiO_3 0.134, of SiO_2 0.365. The amount of water in the vapor phase is 4.53—0.37 g., or

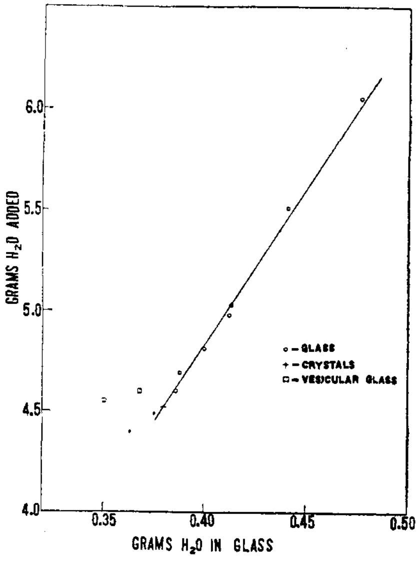

Fig. 2.

Diagram showing the manner in which the amount of H_2O dissolved by a glass varies with the pressure, *i. e.*, the amount of H_2O added.

4.16 g.; since this is at a temperature of 420°, in a volume of 70 cc. (approximately), the pressure is about[1] 84 atmospheres.

The actual accuracy of the results is different at different temperatures and with different SiO_2/K_2O ratios, but the weight of water present at equilibrium can usually be estimated within the limits of ± 5 mg. This is, as an average, about 5% of the total water present, and about 0.5% of the weight of the glass. Expressing the composition of the glass in molecular per cent., K_2SiO_3, SiO_2 and H_2O, this becomes about 2%. A very few points are known with less certainty; many with much more certainty.

In the case of the pressure determinations, other factors enter. The actual amount of H_2O in the vapor space is known, of course, to within the same limits as is the amount of H_2O in the liquid, *i. e.*, to within ± 5 mg. But as, in general, the amount of H_2O in the vapor is greater than in the liquid, the percentage error is less. On the other hand, for the exact calculations of the pressures, the equation of state must be known, and the volume of the bomb at the high pressures and temperatures must be known. The actual volume of the bombs, corrected for the volume of crucible and contents, ranged from 68 to 72 cc.; the mean value of 70 cc. is used in the calculation of the pressures, and the effect of the change in volume due to the temperature and the internal pressure has been ignored. The systematic error thus introduced, however, is less than that necessarily introduced in assuming the equation of state of H_2O, hence a closer determination of the volume would be futile. Moreover, this systematic error affects only the absolute values of the pressure, and not the relative values. A knowledge of the relative values of the vapor pressures of the various solutions, however, is of much greater importance for our present purpose than a knowledge of the absolute pressure.

As stated above, the pressures are calculated by means of van der Waals' equation, using values of a and b, 5.46 and 3.05×10^{-2}, respectively. These values are calculated from Holborn and Baumann's[2] values of 374° and 217.5 atmospheres for the critical temperature and pressure of H_2O.

In this connection it should be emphasized that the pressures which we are considering in this system are the vapor pressures of the saturated solutions. The primary effect of the pressure in systems of this type is to enable the concentration of the H_2O to be kept at the required value. Such an effect of pressure is of great importance, as the concentration of the volatile component is a function of the pressure, and is to be sharply

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[1] The pressure is calculated by means of van der Waals' equation, $p = RT/v-b - a/v^2$, using values of 5.46 and 3.05×10^{-2} for a and b, respectively.

[2] *Ann. Phys.*, [4] 31, 945–70 (1910).

differentiated from the effects due to uniform hydrostatic pressure, which are comparatively small.

The second possible source of error in the determination of points by the hydrothermal quenching method is, what certainty is there that crystals found in the cooled product were in the liquid at the high temperature, and were not formed during the cooling? This question may generally be satisfactorily answered by the microscopical examination. In some cases, especially when the amount of water present was far more than that corresponding to the saturation concentration, crystals actually were formed during cooling, but such secondary growths showed differences of habit. They were usually of small size and showed the feathery or branching or acicular appearance characteristic of crystals of rapid growth, rather than the well-developed forms of slower growth. In some cases of doubt a repetition of the experiment under different conditions of cooling served to dispel the uncertainty.

The "hydrothermal quenching method" outlined above is the one followed. Two grams of a given glass were heated at constant temperature with varying amounts of H_2O, and the product examined under the microscope after each experiment; I am indebted to Dr. C. N. Fenner for carrying out the microscopical part of this work. After the microscopical examination of the products of a given experiment had been made and the phases present identified, the information thus obtained served as a basis for subsequent experiments. For example, in establishing the coördinates of the fusion surface in a given case, the presence or absence of crystals, as shown by the microscope, indicated whether the amount of water to be added should be increased or diminished.

In the above, we have discussed the question of how closely we can determine the condition of the charge at the temperature of the experiment by observations on the quenched product. The importance of whether or not equilibrium was reached at the high temperature itself has not been discussed.

That the melt always reached equilibrium at temperatures above 250° seems certain. The bomb usually was left in the furnace for about 24 hours, only from four to six of which were required to heat it to approximately the temperature of the experiment. Often, however, a longer time, sometimes a week, elapsed before the bomb was removed, but the results of these experiments did not differ from those run for a shorter time. Whenever crystallization took place, the duration of heating was without effect on the result. The occurrence of metastable phases was never observed. The agreement of the results over the extended range of temperature and pressure investigated makes it certain that the results correspond to equilibrium conditions.

At lower temperatures equilibrium was not so easily attained, due to the great tendency toward supersaturation of potassium-silicate solutions. At 200°, great difficulty was met with in inducing crystallization. When a crystalline phase was present, however, reproducible and concordant results could be obtained; the presence of a crystalline phase could be insured by using a mixture containing crystals, instead of a glass, or by heating to a slightly higher temperature, then lowering the temperature. The system was not studied at temperatures below 200° because of this great difficulty in inducing crystallization at low temperatures.

B. **Quenchings in Steam at One Atmosphere Pressure.**—Another method, used in studying the equilibrium at high temperature, consists in heating small charges of known composition, containing both glass and crystals, in an atmosphere of steam, holding at constant temperature for a long enough time for equilibrium to be established, and quenching by sudden cooling.[1] Examination of the product shows whether or not all the crystals have been dissolved, and by repeating the process at various temperatures the exact point at which the known solid phase disappears in a liquid of known SiO_2/K_2O ratio, with a known vapor pressure, but containing an unknown amount of H_2O, can be determined. This is a point on the isobaric polythermal saturation curve of the phase in question. By holding a larger charge at the same or slightly higher temperature for a period of time long enough for it to reach equilibrium with the vapor phase, quenching and determining the H_2O content of the hydrous glass, the amount of H_2O present can be determined. The melting points of anhydrous K_2SiO_3 and $K_2Si_2O_5$ were determined by the quenching method, in a dry, CO_2-free atmosphere, using carefully prepared H_2O-free mixtures.

The curve thus obtained will not differ much from the anhydrous melting-point curve in the binary system K_2SiO_3–SiO_2. The latter curve will lie at a slightly higher temperature than the former; the difference between the two will be determined by the lowering of the melting point of each mixture caused by the amount of water dissolved under a steam pressure of 1 atmosphere. This lowering will not vary much from a SiO_2/K_2O ratio of 1.0, at K_2SiO_3, to 1.3, at the K_2SiO_3-$K_2Si_2O_5$ eutectic, then will decrease slightly up to the ratio 2.0, then will diminish rapidly as the ratio increases to 4.0, at the $K_2Si_2O_5$-SiO_2 eutectic. The portion of the melting-point curve beyond this will be altered very little by the small amount of H_2O taken up by the melt at this pressure.

No attempt was made to determine the melting-point curve in its entirety. The melting points of anhydrous K_2SiO_3 and $K_2Si_2O_5$ were de-

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[1] For a description of the quenching method as applied to silicates, see Shepherd and Rankin, *Am. J. Sci.*, 28, 308 (1909).

termined, and the rest of the curve interpolated, keeping in mind the principles just discussed.

It should be noted that this method enables us to determine melting-point curves in mixtures difficult or impossible to realize by ordinary methods. The interpolation is slight, and, because of the nature of the effects involved, is attended with but slight uncertainty. Methods based on the same principle could doubtless be applied in other cases where the difficulties met with are similar.

C. **Qualitative Determinations by Means of Cup Experiments.**—In addition to the above quantitative methods qualitative results were obtained at 200° and at 285° by another method, called the cup method. It was found, *e. g.*, that at 285° the solubility of the $K_{2.8}$ glass was very small. A given amount of H_2O (18 cc.) was placed in the gold crucible, and a small amount (0.04 g.) of the glass placed in a tiny cup hung about 1 cm. from the bottom of the crucible. On heating to 285° the solution became saturated, leaving a residue in the bottom of the cup. By diminishing the amount of substance present until it was all dissolved, the approximate solubility was determined. The vapor pressure of the solution was assumed to be the same as that of pure H_2O, and, on that basis, correction was made for the amount of H_2O in the vapor space. The solid phase with which the solution was in equilibrium could be determined by microscopical examination. While points determined in this manner have not a high degree of accuracy, they at least give us the order of magnitude of the solubility, and tell us with certainty what the solid phase is. This method cannot be used at high temperatures, because of the uncertainty in the amount of liquid.

V. Identification and Properties of Compounds Formed.

The compounds met with as solid phases in this system are all new, except for the various forms of silica; some of them have been described in the preliminary report to which reference has already been made. In general their characterization has been a matter of considerable difficulty, due to the impossibility of separating the small crystals from their imbedding matrix of deliquescent glass. Various forms of high temperature filtering apparatus were tried, but all proved unsuccessful, due to the considerable viscosity of the melts and the smallness of the crystals.

The identification of the various compounds was made with the petrographic microscope by Dr. C. N. Fenner. The importance of the petrographic microscope for such an investigation cannot be overemphasized. Identification of a given compound is positive and certain; the presence of other compounds or of glass does not diminish the certainty. The fact that a given crystal may appear in different habits, *e. g.*, at one time as short prisms, at another time as tabular growths, or in both forms side by side, is immaterial,[1] since the identification depends on the accurate measurement of optical constants.

While the microscope affords a certain method of identification of a given compound, it is necessary to establish the actual composition of the compound by other means. To one familiar with phase rule work, the actual isothermal saturation curves and boundary curves, as experimentally determined, afford sufficient evidence on this point; analyses of pure compounds are merely corroborative evidence. Nevertheless, the composition has been determined by analyses of pure compounds, or by the method of residues, whenever possible. This evidence is presented in the discussion of the various compounds.

Following is a short description of each compound:

Silica, SiO_2.—Silica exists in several stable forms, the relations between which have been worked out by Fenner.[2] α-Quartz is stable up to 575°, β-quartz from 575° to 870°, β-tridymite from 870° to 1470°, β-cristobalite from 1470° to 1625°. The β-α quartz inversion takes place readily, and hence in preparations obtained above 575° only α-quartz was observed; because of the smallness of the crystals, traces of an inversion could not be distinguished. No experiments were made in the region in which tridymite is stable, nor was it ever observed appearing as a metastable form.

Potassium Hydrogen Disilicate, $KHSi_2O_5$ or $K_2O.H_2O.4SiO_2$.—This compound was described in the preliminary paper already referred to. It is decomposed by H_2O below 420°, and has a congruent melting point at about 515°.

This compound almost always forms sharp, well-bounded crystals. Usual habit, somewhat tabular prisms, but many different faces may be developed; parallel extinction; plane of optic axes parallel to elongation; high birefringence; often shows good cleavage parallel to elongation; twinning quite common. It is biaxial and positive. An average of eleven determinations of the optic axial angle gave $2E = 69^1/_2°$. As observed under the microscope, this compound is practically unattacked by water, and this serves to distinguish it from all other potassium silicates. For a further description and a drawing of a typical crystal see the preliminary paper already referred to.[3]

Potassium Disilicate, $K_2Si_2O_5$ or $K_2O.2SiO_2$.—This compound was described in the preliminary report,[4] but its composition was not definitely

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[1] This fact, obvious though it may appear, is not always recognized; Pukall, *e. g.* (*Ber.*, 49, 397–437 (1916)) considered the fact that in some preparations both plates and needles were present to be evidence that two different compounds were present. $KHSi_2O_5$, *e. g.*, often occurs in both forms.

[2] Fenner, *Am. J. Sci.*, 36, 331–84 (1913).

[3] THIS JOURNAL, 36, 215–30 (1914).

[4] $K_2Si_2O_5$ was also prepared by Niggli, THIS JOURNAL, 35, 1693–1727 (1913); his crystals also were examined by Fenner.

established, and further proof was promised. Following is an analysis of some excellent crystals of this compound, which were practically freed from glass by hand picking under a binocular.

	% by weight.	Mol. ratio.
K_2O	43.73	1.000
SiO_2	55.83	1.995
H_2O	0.59	...
	100.16	

It melts at 1041°, and is not decomposed by water.

This compound usually forms well-bounded crystals of rhomb-like shape, flatly tabular, and with an almost micaceous cleavage parallel to the flat faces. There is also a good cleavage parallel to γ and a less well-defined one parallel to β. When lying on flat faces the crystals show rather low birefringence, and the emergence of an acute negative bisectrix perpendicular to the face. The optic axes lie slightly outside the field of an objective of numerical aperture 0.95.

When a drop of water is placed upon the crystals upon the stage of the microscope they do not dissolve uniformly but are observed to break up into shred-like forms. This is a well-defined characteristic.

A drawing of the usual forms is given in the above-mentioned preliminary paper.

Potassium Disilicate Monohydrate, $K_2Si_2O_5.H_2O$, or $K_2O.H_2O.2SiO_2$. —This compound rarely forms large well-developed crystals, and its separation for analysis proved impossible. It is rapidly decomposed by water at ordinary temperatures.

That it is a disilicate follows from its position in the equilibrium diagram, as does also the fact that it is hydrated. An approximation to its composition was obtained by analysis of a sample of crystals contaminated by glass, and of the glass in equilibrium, contaminated by a small amount of crystals, *i. e.*, by the method of residues. The samples were obtained by heating a charge with the bomb tipped to one side, thereby forming the mass of crystals along one edge of the crucible, and tipping to the other side shortly before removing from the furnace. This method was tried many times before it finally gave a satisfactory separation, but it seemed to be the only method available. The analyses follow:

Crystalline part.			Glassy part.		
	%.	Mol. ratio.		%.	Mol. ratio.
K_2O	40.2	1.000	K_2O	39.2	1.000
SiO_2	51.0	1.98	SiO_2	45.7	1.82
H_2O	8.5	1.12	H_2O	14.8	1.97

These values are plotted in Fig. 3, and from this it is clear that the composition of the solid phase must be $K_2O.H_2O.2SiO_2$.

This compound is decomposed by H_2O below 280°, and at 405° decomposes, with formation of vapor and solution saturated with $K_2Si_2O_5$. It occurs in rounded forms, seldom showing crystal faces. They are biaxial, positive, with small axial angle and high birefringence. The crystals dissolve completely in water.

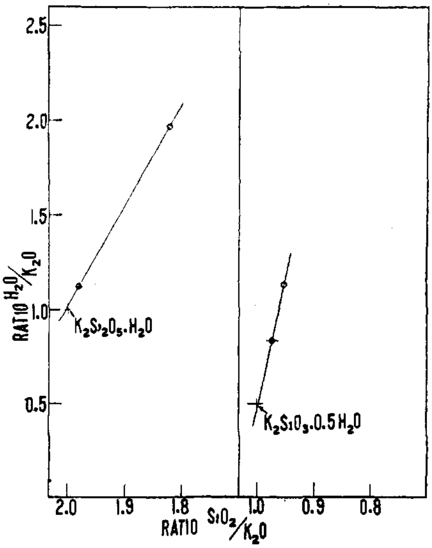

Fig. 3.

Diagram showing the application of the method of residues to the determination of the composition of the compounds $K_2Si_2O_5.H_2O$ and $K_2SiO_3.\frac{1}{2}H_2O$.

Potassium Metasilicate, K_2SiO_3 or $K_2O.SiO_2$.—All the potassium metasilicates possess in a marked degree that property of extreme deliquescence which makes the separation of these compounds such a difficult matter. As a consequence, none of the metasilicates could be obtained in an even approximately pure condition, with the exception of the anhydrous K_2SiO_3. This compound is the stable solid phase in the binary system K_2SiO_3–H_2O from about 610° to its melting point, at about 966°, and hence could be obtained in a fairly pure condition by crystallizing a metasilicate glass at high temperature. Following is an analysis of a preparation so obtained:

	%.	Mol. ratio.
K_2O	60.35	1.000
SiO_2	38.91	1.008
H_2O	0.53	...

Usually in rounded grains without crystal boundaries. Some indication of cleavage parallel to γ; rendered more visible by crushing in mortar. Optic figure is obtained without much difficulty and is marked by a strong dispersion $v > \rho$. The character is biaxial and positive, and the birefringence is high. Measurements of 2E gave $78^1/_2$°. The crystals are very hygroscopic and dissolve rapidly and uniformly in water.

Potassium Metasilicate Hemihydrate, $K_2SiO_3.0.5H_2O$ or $K_2O.0.5H_2O.SiO_2$.—This compound is the stable solid phase in the binary system from 370° to 610°. A fair approximation to its composition was obtained from a tipping experiment, similar to that described with $K_2Si_2O_5.H_2O$. The analysis of the crystals and glass follow: The experiment was carried out with a glass somewhat richer in K_2O than K_2SiO_3, *i. e.*, containing an excess of KOH. It should be noted that at no temperature within the region of stability of the compound is there a very great difference in composition between the crystals and glass, and the small crystals are easily carried along with the viscous liquid, making a separation very difficult. The glass analyzed contained many crystals and the crystals much glass.

Crystalline part.			Glassy part.		
K_2O.........	56.1	1.000	K_2O.........	54.8	1.000
SiO_2.........	34.9	0.973	SiO_2.........	33.4	0.952
H_2O.........	9.0 (by diff.)	0.835	H_2O.........	11.8 (by diff.)	1.128

These results are plotted in Fig. 3, and show that the composition of the compound is $K_2SiO_3.0.5H_2O$. The shape and position of the isothermal solubility curves in Fig. 4, however, is enough to prove the same point.

The crystals of this compound occur, almost without exception, in elongated forms. Terminal faces are sometimes well developed and the interior terminal angle is either about 70° or a little greater than 90°. There is a good cleavage parallel to the elongation, and as a bisectrix also is parallel to the elongation it is difficult to obtain a crystal-fragment which will rest in the proper position to show the emergence of an optic axis. In a few cases it was possible to do this, and it was found that the brush was a nearly straight bar, indicating a large axial angle. There was so little curvature to the bar that one could not be sure whether the character was positive or negative, but it was believed to be positive. Extinction is parallel to the elongation, and the direction of elongation is γ. The birefringence is high. The crystals are completely dissolved by water. Among those compounds which dissolve completely in water this one is distinguished by its elongated habit, both in original crystals and in cleavage fragments, its extinction parallel to γ, and the very large axial angle.

Potassium Metasilicate Monohydrate, $K_2SiO_3.H_2O$ or $K_2O.H_2O.SiO_2$.—All attempts to arrive at the composition of this compound by direct means failed; even tipping experiments did not give a separation of the phases. In this case it is necessary to rely exclusively on the evidence of the saturation curves, but fortunately in this case especially the evidence is conclusive. $K_2SiO_3.H_2$ is decomposed by H_2O at temperatures below 200°, and decomposes at 370° into $K_2SiO_3.{}^1/_2H_2O$, liquid and vapor.

Equant grains. Biaxial, positive, with small axial angle and high birefringence. Crystals dissolve completely in water. The optical and other microscopic characteristics of this compound are so similar to those of the hydrated disilicate that the microscopic examination alone has not been sufficient to distinguish between them. It serves to separate them from all the other compounds in the system, but their distinction from each other was based upon other characteristics.

The question of the existence of a potassium orthosilicate is an interesting one, which has been given some attention, but all attempts to prepare such a compound have failed. For example, several melts were made by heating KOH and SiO_2 in proportions intermediate between $2K_2O.SiO_2$ and $K_2O.SiO_2$ in an atmosphere of steam, the melt being finally heated to well above 1100°, and the resulting products analyzed. In all cases K_2O, SiO_2 and H_2O were found to be present, and the sum of the molecular ratios of SiO_2 and H_2O was always approximately equal to the molecular ration of the K_2O. In other words, the excess of K_2O over that required to form K_2SiO_3 probably was present as KOH, instead of as K_4SiO_4, as would be expected were an orthosilicate formed in the solution. This renders it probable that no such compound as K_4SiO_4 is formed, but statements based on such negative evidence must be made with caution.

Pukall[1] recently described compounds which he claims to have obtained which are not met with in the system. His evidence in regard to their existence, however, is fallacious; much of it, indeed, shows a total disregard for the properties and characteristics necessary to define a compound. An example is the series of "meta-," "di-," "tri-," "tetra-," "penta-" and "hexasilicates" named by him, most of which are described as clear transparent glasses.

VI. Experimental Results.

A. **The Isothermic Polybaric Saturation Curves.**—The summarized results of the various series of experiments are given in the following tables. Only the coördinates of the points on the various saturation isotherms are given; over 2000 experiments were made in determining these points, and it obviously would be impracticable to give the details of all of them. The isotherms are arranged in the order of ascending temperature, and are discussed in the same order, but this was not the order in which the work was carried out. First several glasses were prepared and studied at various temperatures, in order to gain a knowledge of the various fields and the compounds met with therein. After that, the isotherms were determined in the following order: 420°, 285°, 520°, 480°, 500°, 380° and 200°. In addition to the isothermal saturation curves, a number of points were determined at intermediate temperatures, usually for the purpose of assisting in outlining the various fields; these are given under the sub-head "miscellaneous;" these points are not plotted in the figures.

In Table II are given the data for the construction of the isothermal polybaric saturation curves. In the first column, headed "K," is given the SiO_2/K_2O ratio of the glass used; in the second, headed "x," the total amount of H_2O, in g., which it is necessary to place in the bomb,[2] with 2 g. of the glass, in order that the composition of the solution shall be that of the point of the isothermal saturation curve, having the given ratio SiO_2/K_2O;

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[1] W. Pukall, *Silikate Z.*, 2, 65–76, 87–99, 109–118 (1914); *Ber.*, 49, 397–437 (1916).

[2] Of the given capacity, *i. e.*, about 70 cc.

in the third, headed "*y*," the amount of H_2O in the solution in g.; in the fourth, headed "Mol. fraction H_2O," the mol. fraction H_2O in the mixture of H_2O, K_2SiO_3 and SiO_2, calculated from "*y*;" in the fifth, headed "$x - y$," the difference, corresponding to the amount of H_2O in the vapor space; and in the sixth, headed "solid," the composition of the solid phase in equilibrium with the solution.

TABLE II.

K $\left(= \frac{SiO_2}{K_2O}\right)$.	*x* (= total g. H_2O).	*y* (= g. H_2O in solution).	Mol. fraction H_2O.	$x - y$.	Solid phase.
200° isotherm.					
1.01	0.64	0.62	0.726	0.02(*a*)	$K_2SiO_3.H_2O$
1.14	0.72	0.66	0.724	0.05(*a*)	$K_2Si_2O_5.H_2O$
1.34	0.95	0.75	0.731	0.20(*a*)	$K_2Si_2O_5.H_2O$
1.68	1.85	1.56	0.835	0.29(*a*)	$KHSi_2O_5$
285° isotherm.					
1.01	0.53	0.42	0.637	0.11	$K_2SiO_3.H_2O$
1.14	0.43	0.35	0.613	0.09	$K_2Si_2O_5.H_2O$
1.24	0.68	0.46	0.636	0.22	$K_2Si_2O_5.H_2O$
1.34	0.89	0.51	0.649	0.38	$K_2Si_2O_5.H_2O$
1.53	1.09	0.55	0.650	0.54	$K_2Si_2O_5.H_2O$
1.67	1.32	0.57	0.654	0.75	$K_2Si_2O_5.H_2O$
1.91	1.37	0.55	0.621	0.82	$K_2Si_2O_5.H_2O$
2.06	1.36	0.50	0.596	0.86	$K_2Si_2O_5.H_2O$(*b*)
2.19	1.96	0.63	0.644	1.36	$KHSi_2O_5$
2.26	2.51	0.81	0.697	1.70	$KHSi_2O_5$
360° isotherm.					
1.01	0.44	0.30	0.561	0.14	$K_2SiO_3.H_2O$
1.04	0.39	0.28	0.540	0.11	$K_2SiO_3.H_2O$
1.11	0.37	0.26	0.512	0.11	$K_2SiO_3.0.5H_2O$
1.14	0.35	0.26	0.508	0.09	$K_2SiO_3.0.5H_2O$
1.20	0.33	0.25	0.491	0.08	$K_2SiO_3.0.5H_2O$
1.34	0.44	0.24	0.465	0.20	$K_2Si_2O_5$
1.39	0.44	0.25	0.471	0.19	$K_2Si_2O_5$
1.44	0.52	0.27	0.485	0.25	$K_2Si_2O_5.H_2O$
1.48	0.97	0.34	0.539	0.62	$K_2Si_2O_5.H_2O$
1.67	1.17	0.37	0.545	0.80	$K_2Si_2O_5.H_2O$
1.91	1.35	0.36	0.523	0.99	$K_2Si_2O_5.H_2O$
2.02	1.32	0.33	0.496	0.99	$K_2Si_2O_5.H_2O$
2.19	1.15	0.29	0.454	0.86	$K_2Si_2O_5.H_2O$(*c*)
2.37	3.05	0.46	0.561	3.6	$KHSi_2O_5$
2.60	4.9	0.61	0.620	4.3(*a*)	$KHSi_2O_5$
2.66	5.9	0.72	0.658	5.2(*a*)	$KHSi_2O_5$
380° isotherm.					
1.01	0.44	0.27	0.535	0.17	$K_2SiO_3.0.5H_2O$
1.34	0.50	0.22	0.444	0.28	$K_2Si_2O_5$

(*a*) Not shown in Fig. 5.

(*b*) This point is very close to the invariant (T) point $K_2Si_2O_5.H_2O$–$KHSi_2O_5$–L–V, as shown by the fact that both phases are found on slightly diminishing the H_2O concentration.

(*c*) This point is not far from the invariant (T) point $K_2Si_2O_5.H_2O$–$KHSi_2O_5$–L–V.

TABLE II (*continued*).

K (= SiO_2/K_2O).	x (= total g. H_2O).	y (= g. H_2O in solution).	Mol. fraction H_2O.	$x - y$.	Solid phase
1.44	0.59	0.26	0.476	0.33	$K_2Si_2O_5$
1.56	0.81	0.30	0.501	0.51	$K_2Si_2O_5$
1.68	1.26	0.33	0.516	0.93	$K_2Si_2O_5.H_2O$
2.72	7.5	0.52	0.579	7.0(*a*)	$KHSi_2O_5$
420° isotherm.					
1.01	0.48	0.24	0.502	0.24	$K_2SiO_3.0.5H_2O$
1.08	0.45	0.23	0.484	0.22	$K_2SiO_3.0.5H_2O$
1.13	0.44	0.21	0.456	0.23	$K_2SiO_3.0.5H_2O$
1.26	0.40	0.18	0.404	0.21	$K_2SiO_3.0.5H_2O$
1.35	0.59	0.21	0.432	0.38	$K_2Si_2O_5$
1.48	0.79	0.26	0.473	0.53	$K_2Si_2O_5$
1.67	1.08	0.30	0.493	0.78	$K_2Si_2O_5$
1.91	1.07	0.28	0.460	0.79	$K_2Si_2O_5$
2.19	1.06	0.24	0.408	0.82	$K_2Si_2O_5$
2.37	1.02	0.22	0.379	0.80	$K_2Si_2O_5$(*b*)
2.60	3.51	0.35	0.485	3.26	$KHSi_2O_5$
2.72	4.51	0.38	0.501	4.13	$KHSi_2O_5$
3.29	8.33	0.40	0.496	7.93(*a*)	$KHSi_2O_5$
3.59	9.50	0.34	0.426	9.2(*a*)	$KHSi_2O_5$
4.05	21.0	0.27	0.375	20.7(*a*)	Quartz
480° isotherm.					
2.19	1.31	0.21	0.376	1.10	$K_2Si_2O_3$
2.37	1.19	0.19	0.346	1.00	$K_2Si_2O_3$
2.60	2.16	0.23	0.378	1.93	$KHSi_2O_5$
3.29	4.07	0.25	0.384	3.82	$KHSi_2O_5$
3.34	4.43	0.26	0.385	4.17(*a*)	$KHSi_2O_5$
4.27	4.86	0.26	0.396	4.60(*a*)	Quartz
4.49	5.82	0.35	0.442	5.47(*a*)	Quartz
500° isotherm.					
2.06	1.58	0.20	0.372	1.38	$K_2Si_2O_5$
2.19	1.36	0.19	0.354	1.17	$K_2Si_2O_5$
2.26	1.32	0.18	0.338	1.14	$K_2Si_2O_5$
2.37	1.26	0.17	0.321	1.09	$K_2Si_2O_5$
2.72	0.86	0.14	0.270	0.72	$K_2Si_2O_5$
3.44	2.44	0.18	0.307	2.26	$KHSi_2O_5$
3.58	3.3	0.20	0.375	3.10	$KHSi_2O_5$
4.27	4.81	0.22	0.334	4.6(*a*)	$KHSi_2O_5$
4.49	5.42	0.32	0.420	5.1(*a*)	Quartz
4.63	8.9	0.36	0.446	8.6(*a*)	Quartz
520° isotherm.					
1.01	0.36	0.16	0.406	0.20	$K_2SiO_3.0.5H_2O$
1.04	0.32	0.16	0.401	0.16	$K_2SiO_3.0.5H_2O$
1.11	0.31	0.15	0.378	0.16	$K_2SiO_3.0.5H_2O$
1.20	0.22	0.12	0.320	0.14	$K_2SiO_3.0.5H_2O$
1.34	0.57	0.16	0.357	0.43	$K_2Si_2O_5$
1.57	1.41	0.21	0.412	1.20	$K_2Si_2O_5$

(*a*) Not shown in Fig. 5.

(*b*) This point is very close to the invariant (T) point $K_2Si_2O_5$–$KHSi_2O_5$–L–V.

TABLE II (*continued*).

K $\left(= \frac{SiO_2}{K_2O}\right)$.	x (= total g. H_2O).	y (= g. H_2O in solution).	Mol. fraction H_2O.	x — y.	Solid phase.
1.91	1.67	0.21	0.390	1.46	$K_2Si_2O_5$
2.19	1.56	0.18	0.342	1.38	$K_2Si_2O_5$
2.60	1.21	0.14	0.273	1.07	$K_2Si_2O_5$
2.72	0.91	0.13	0.256	0.78	$K_2Si_2O_5$
3.29	0.32	0.08	0.165	0.24	$K_2Si_2O_5$
4.49	3.82	0.21	0.368	3.6	Quartz
			600° isotherm.		
1.01	0.55	0.14	0.364	0.41	$K_2SiO_3.0.5H_2O$
1.04	0.31	0.12	0.335	0.19	$K_2SiO_3.0.5H_2O$
1.11	0.19	0.12	0.328	0.07	K_2SiO_3
1.20	0.13	0.10	0.282	0.03	K_2SiO_3
1.34	0.26	0.11	0.285	0.15	$K_2Si_2O_5$
1.44	0.94	0.15	0.334	0.78	$K_2Si_2O_5$
2.19	1.60	0.17	0.327	1.33	$K_2Si_2O_5$
2.60	1.21	0.13	0.258	1.08	$K_2Si_2O_5$
4.49	1.52	0.16	0.266	1.36	Quartz
4.76	10.5	0.22	0.328	10.3(*a*)	Quartz
T.			Miscellaneous.		
345°	1.33	0.42	0.602		$K_2Si_2O_5.H_2O$
337	1.53	0.41	0.582		$K_2Si_2O_5.H_2O$
339	1.80	0.34	0.514		$K_2Si_2O_5.H_2O$
340	2.06	0.38	0.527		$K_2Si_2O_5.H_2O$
343	2.02	0.33	0.494		$K_2Si_2O_5.H_2O$
409	1.53	0.28	0.486		$K_2Si_2O_5$
510	1.53	0.23	0.434		$K_2Si_2O_5$
405	1.68	0.28	0.475		$K_2Si_2O_5$
403	2.02	0.30	0.483		$K_2Si_2O_5$
430	2.02	0.25	0.402		$K_2Si_2O_5$
438	2.06	0.23	0.425		$K_2Si_2O_5$
440	2.26	0.21	0.362		$K_2Si_2O_5$
346	2.26	0.41	0.537		$KHSi_2O_5$

(*a*) Not shown in Fig. 5.

The results given in Table II are presented graphically in Fig. 4; the points determined are shown by circles. The curves as a whole are most readily conceived as projections on the basal plane of successive sections, at various temperatures, of the solid prismatic model,[1] in which composition in mols. is represented in the usual triangular projection, and temperature along the vertical axis.

Let us consider a typical saturation curve, *e. g.*, the first one determined, at 420°. At this temperature, if 2 g. of K_2SiO_3 are placed in a bomb[2] with more than 0.48 g. of H_2O, the product is a clear glass; microscopical examination shows the absence of crystals. In other words, at the temperature of the experiment the solution was unsaturated. As the amount of water present is reduced, the amount dissolved by the liquid diminishes.

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[1] See page 1221.

[2] Of the given capacity (= 70 cc.)

If less than 0.48 g. of H_2O is present, the product appears partly crystalline; microscopical examination shows the solid phase to be $K_2SiO_3.0.5H_2O$. When the total amount of H_2O present is 0.48 g., the solution is just saturated; the amount of water in the liquid phase is then 0.24 g. Expressed in mol. fractions, this becomes 0.512 mol. H_2O, 0.488 mol. K_2SiO_3.

As the mol. ratio SiO_2/K_2O in the glass is increased, the "solubility"[1] of $K_2SiO_3.0.5H_2O$ increases; in other words, the mol. fraction of H_2O diminishes. This continues until an H_2O content of 0.39 is reached, at a SiO_2 K_2O ratio of 1.27 (see Table IV). At this point a new crystalline phase, $K_2Si_2O_5$, makes its appearance; we then have four phases, two solid, a liquid and a vapor, in equilibrium; in other words, we are at a constant temperature invariant point in the ternary system.

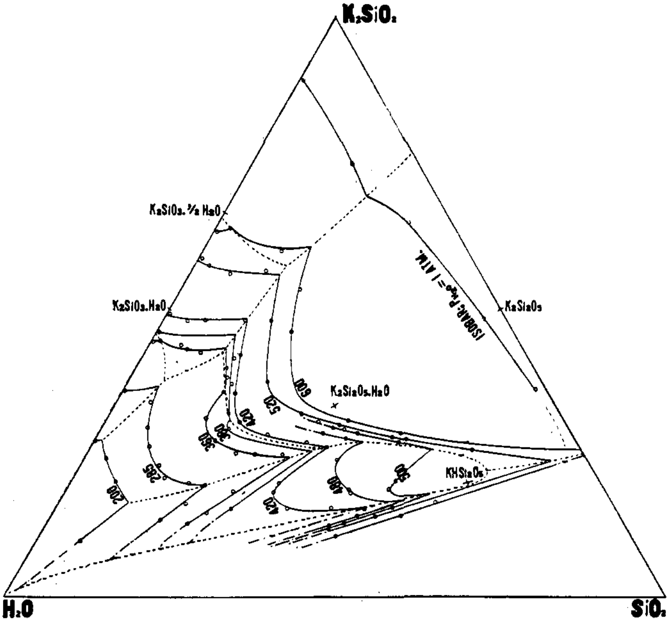

Fig. 4.

The isothermal polybaric saturation curves and the isobaric polythermal saturation curve at 1 atmosphere pressure of H_2O vapor. The temperature of each isotherm is indicated; the dotted lines are the boundary curves (cf. Fig. 8). The circles represent the experimental results given in Table II.

Further increase of SiO_2 results in the disappearance of $K_2SiO_3.0.5H_2O$, and the solution traces the saturation curve of $K_2Si_2O_5$ at constant temperature under its own vapor pressure, *i. e.*, the isothermal polybaric saturation curve of $K_2Si_2O_5$. This compound remains the solid phase until the mol. fraction H_2O reaches 0.379, at a SiO_2/K_2O ratio of 2.38, at which

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[1] The term "solubility" is here used in a loose sense; this matter is further discussed subsequently (page 1226).

point the compound $KHSi_2O_5$ appears, and we have the invariant (T) point $K_2Si_2O_5$-$KHSi_2O_5$-L-V.

It will be observed that the mol. fraction H_2O along this isothermal saturation curve increases from the invariant (T) point, $K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$-L-V to a maximum of 0.495 at a SiO_2/K_2O ratio of about 1.66, then falls to a minimum of 0.379 at the invariant point $K_2Si_2O_5$-$KHSi_2O_5$. The point corresponding to the composition of the solid phase, $K_2Si_2O_5$, is no special point on the saturation curve; this is in harmony with theory, as will be shown in a later paper.

Further increase of the SiO_2/K_2O ratio results in the disappearance of $K_2Si_2O_5$, the solution tracing the saturation curve of $KHSi_2O_5$. At 420° this compound is not decomposed by H_2O, and its saturation curve can be followed up to the invariant (T) point $KHSi_2O_5$-SiO_2-L-V, at which point the mol. fraction H_2O is 0.381, the SiO_2/K_2O ratio, 4.02. It will be noticed that the minimum mol. fraction H_2O along this isothermal saturation curve is found at a SiO_2/K_2O ratio considerably less than that of the compound.

With further increase of SiO_2, quartz becomes the crystalline solid phase; the saturation curve of quartz could only be followed a short distance, as will be explained later.

Let us now consider the variation of pressure along this isothermal polybaric saturation curve. When a charge is heated, a portion of the water is dissolved in the melted silicates; the remainder passes into the vapor phase, developing a pressure whose magnitude is easily calculated. With a given SiO_2/K_2O ratio, the vapor pressure of the saturated solution is, of course, fixed; change in the SiO_2 content naturally changes the pressure.

The pressure-concentration curves for the various isotherms are shown in Fig. 5; the amount of water in the vapor space, the value experimentally determined, being plotted against the SiO_2 content, expressed as ratio SiO_2/K_2O. As previously stated, from these data the approximate pressure at each point can be calculated by means of van der Waals' equation. Values so calculated are given in the discussion; they are assembled for the several monovariant systems in Table VI. The curve for 420° is indicated; the coördinates of the left-hand group of Fig. 5 refer to the 420° isotherm.

We saw before that when 2 g. of K_2SiO_3 were heated to 420° with 0.48 g. H_2O, 0.24 g. went into the liquid phase, hence the remainder, 0.24 g., was in the vapor phase. This corresponds to a pressure of 10.7 atmospheres. As shown in Fig. 5, increasing the amount of SiO_2 in the liquid diminishes the pressure, until at the invariant (T) point the amount in the vapor is 0.19 g. (8.8 atm.). From the eutectic point the pressure increases to a maximum of 0.83 g. (37.7 atm.) at a SiO_2/K_2O ratio of 2.0. This is in accord with theory; Gibbs[1] showed that the maximum pressure along an isothermal is at the point where the compositions of the reacting phases lie on a straight line in the concentration diagram. As the compound here

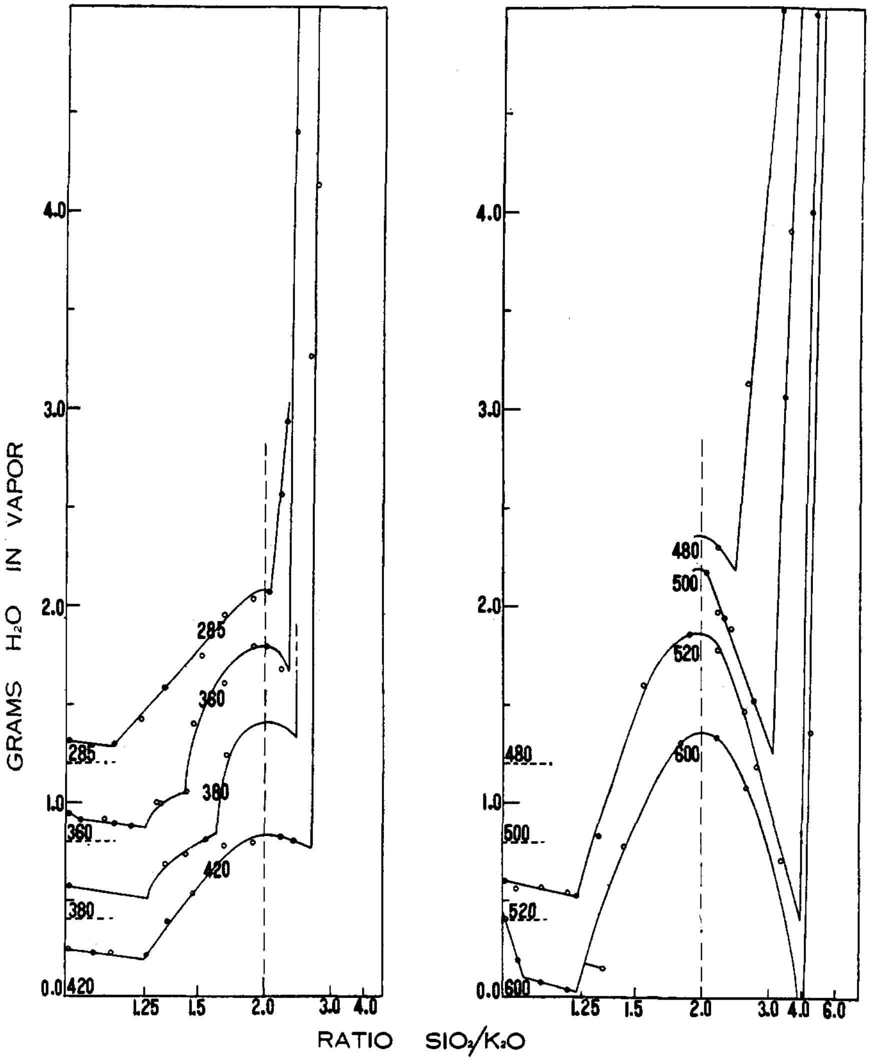

Fig. 5.

Diagram showing the variation of vapor pressure with change of SiO_2/K_2O ratio along the isotherms. Pressures are represented by the amount of H_2O in the vapor phase, the quantity experimentally determined. All curves are drawn to the same scale; the numbered scale is indicated only for the two bottom curves, *i. e.*, the 420° and 600° isotherms. To avoid confusion of curves, each successive curve has been shifted vertically by 0.4 g.; the line of zero pressure is shown for each curve by the dotted line to the left of the diagram.

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[1] "The Scientific Papers of J. Willard Gibbs," 1, 99.

is $K_2Si_2O_5$, and the vapor phase is H_2O, the pressure maximum should lie at the point where the SiO_2/K_2O ratio is 2.0. This matter will be discussed more fully from a theoretical standpoint in a later publication.

From this maximum the pressure falls until the $K_2Si_2O_5$-$KHSi_2O_5$ invariant point is reached, then rises to a maximum at a SiO_2/K_2O ratio of 4.0, corresponding to the compound $KHSi_2O_5$. At this point the vapor phase contains about 21 g. H_2O, corresponding to a pressure of about 350 atmospheres. As the scale of Fig. 5 is such that at 420° the maximum pressure which can be represented is that equivalent to 5.0 g., this point is not shown. Further increase in SiO_2 brings us to the $KHSi_2O_5$-SiO_2 invariant point, at 20.0 g. H_2O (340 atm.), after which quartz is the stable phase, and the pressure again rises.

Reference to Fig. 5 shows that the pressure is not greatwh en K_2SiO_3.-$0.5H_2O$ is the solid phase, and is not greatly affected by increase in the SiO_2 content. As soon as $K_2Si_2O_5$ becomes the solid phase the pressure rises rapidly, until the rather flat portion of the curve near the composition ratio of $K_2Si_2O_5$ is reached. When $KHSi_2O_5$ appears, the pressure increases very rapidly indeed, only to flatten out again at a SiO_2/K_2O ratio corresponding to $K_2O.H_2O.4SiO_2$. When the $KHSi_2O_5$-quartz invariant point is passed, increase in the SiO_2 content results in an enormous increase in pressure, the curve being practically vertical.

The saturation curve of quartz could not be followed further because of this fact; since the critical volume of H_2O is about $^1/_3$, it was not considered wise to fill the bomb more than one-third full of H_2O, as the thermal expansion would then completely fill the bomb with liquid, with possibly disastrous results.

Let us now consider an isotherm at a slightly lower temperature, say 360°. Starting with a K_2SiO_3 glass, and diminishing the amount of water present, we find that crystals appear when less than 0.44 g. of H_2O are added. These crystals, however, are different from those found at 420°, being $K_2SiO_3.H_2O$, instead of $K_2SiO_3.0.5H_2O$. This temperature, then, lies below the transition temperature, $K_2SiO_3.H_2O = K_2SiO_3.0.5H_2O + 0.5H_2O$ in the binary system H_2O–K_2SIO_3.

As the SiO_2/K_2O ratio is increased, the "solubility" increases; at a SiO_2/K_2O ratio of 1.04 the compound $K_2SiO_3.0.5H_2O$ appears. We are now at the invariant (T) point $K_2SiO_3.H_2O$-$K_2SiO_3.0.5H_2O$-L-V, a point on the boundary curve between the two forms of metasilicate.

On further increase in the SiO_2/K_2O ratio $K_2SiO_3.H_2O$ disappears, and the solution traces the saturation curve of $K_2SiO_3.0.5H_2O$. · At a SiO_2/K_2O ratio of 1.29 the invariant (T) point $K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$-L-V is reached, just as at 420°.

On further increase of SiO_2, $K_2Si_2O_5$ becomes stable, but only for a short interval. At a SiO_2/K_2O ratio of 1.43, the invariant (T) point $K_2Si_2O_5.H_2O$-

$K_2Si_2O_5$-L-V is reached. In other words, at this temperature two "disilicate" compounds are found, one anhydrous, the other containing one molecule of water. This transition point is similar to the $K_2SiO_3.H_2O$-$K_2SiO_3.0.5H_2O$ transition; it is a point on the boundary curve $K_2Si_2O_5.H_2O$-$K_2Si_2O_5$. These boundary curves will be discussed in detail later.

$K_2Si_2O_5.H_2O$ is stable up to the invariant (T) point $K_2Si_2O_5.H_2O$-$KHSi_2O_5$-L-V, at a SiO_2/K_2O ratio of 2.27; then $KHSi_2O_5$ becomes the stable phase. Reference to Fig. 4 will show that the "solubility" of this compound falls off rapidly with increasing SiO_2/K_2O ratio; its saturation curve was not determined up to its end at the SiO_2-$KHSi_2O_5$-L-V invariant (T) point, but cup experiments[1] showed that it lay at a SiO_2/K_2O ratio of 3.3. In other words, at this temperature $KHSi_2O_5$ is decomposed by H_2O, SiO_2 (quartz) being the stable phase.

The saturation curve of quartz at this temperature was not followed, because of the very small solubility of SiO_2 in H_2O. There is no doubt, however, that the solubility of SiO_2 in H_2O is very small at 360°, and from the nature of the components it is highly probable that the saturation curve of quartz will be practically a straight line, joining the invariant point with H_2O apex.

We have seen that, at each of the two temperatures, 420° and 360°, the isothermal saturation curve consisted of several parts, along each of which only one solid phase is stable. Corresponding to each concentration curve is a pressure curve, giving the change in pressure with concentration. In both cases the intersection of the curves gives rise to the invariant (T) points, at which two solids can co-exist in equilibrium with liquid and vapor.

Schreinemakers[2] has shown that in condensed systems the conditions of equilibrium require that at such invariant (T) points as we are now considering the angles between the intersecting curves must lie between certain limits. He defines the "conjugation angle" as the angle at the invariant point between the lines joining the composition of each of the two solid phases with the invariant point in the concentration diagram. He then shows that the tangents to two saturation curves whose intersection gives rise to the invariant point must both be either inside or outside the conjugation angle or its opposite angle. One cannot be outside, the other inside. These conclusions can easily be shown to apply to systems of the type in which a vapor phase is present.

This theorem affords a valuable aid in the study of ternary systems. It will be observed that all the curves in Fig. 4 are drawn in conformity with it. Its applications may be illustrated by the SiO_2-$KHSi_2O_5$-L-V invariant (T) point at 360°. Here we find that the saturation curve of

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[1] Described on page 1189.

[2] Roozeboom-Schreinemakers, "Die Heterogenen Gleichgewicht," III [1], 297.

$KHSi_2O_5$ lies outside the conjugation angle; the saturation curve of SiO_2 must also lie outside this angle, and hence must be a practically straight line from the H_2O apex (since SiO_2 is insoluble in pure H_2O) to the transition point. Similarly, the curves at the $KHSi_2O_5$-$K_2Si_2O_5$-H_2O invariant point both lie inside the conjugation angle, those at the $K_2Si_2O_5$-$K_2Si_2O_5$-H_2O invariation point, both outside, those at the $K_2Si_2O_5$-$K_2SiO_3.0.5H_2O$ invariant point, both inside, but almost both tangent with the conjugation lines.

Further lowering of temperature results in similar changes; a detailed discussion of the 285° and 200° isotherms is unnecessary. It is evident that the region of unsaturated solution contracts rapidly as the temperature is lowered; this contraction is due not only to a decrease in the saturation concentration of the various compounds, but also to the fact that as the temperature is lowered the mass effect of the H_2O results in an increased hydrolysis, shifting the stability regions of all the compounds. For example, we have already seen that at 420° $KHSi_2O_5$ was stable in contact with H_2O, and that at 360° it was decomposed. Further decrease in temperature results in a continued shifting of the SiO_2-$KHSi_2O_5$ invariant (T) point towards regions of greater K_2O content, until at 200° it lies at a SiO_2/K_2O ratio of close to 2.0. This is not evident from the saturation curves, but was determined by cup experiments.

Similarly, decrease in temperature results in a shifting of the stability region of $K_2Si_2O_5.H_2O$. At 285°, this compound is stable in contact with H_2O; at about 280° the invariant (T) point $K_2Si_2O_5.H_2O$-$KHSi_2O_5$-L-V lies on the conjugation line H_2O-$K_2Si_2O_5$, and at lower temperatures $K_2Si_2O_5.H_2O$ is decomposed by H_2O. At 200° the invariant point $K_2Si_2O_5.$-H_2O-$KHSi_2O_5$ lies at a SiO_2/K_2O ratio of 1.66. The metasilicate region, it will be observed, tends to disappear from the diagram. The $K_2Si_2O_5.$-H_2O-$K_2SiO_3.H_2O$ invariant (T) point at 285° lies at a SiO_2/K_2O ratio of 1.13; at 200° it is at 1.04, and at slightly lower temperatures the metasilicate is decomposed by H_2O.

This shifting of the stability regions toward the side H_2O-K_2SiO_3 of the component triangle with decreasing temperature results in an apparen contradiction of the rule[1] that the temperature increases along a boundary curve as we approach the side of the component triangle. The reason for the apparent contradiction lies in the fact that in the derivation of the above rule both the crystalline phases coexisting along the boundary curve are assumed to have compositions such as can be expressed by points lying on the side of the component triangle. This is not true for the boundary curve $K_2SiO_3.H_2O$-$K_2Si_2O_5.H_2O$, for example, which will cut the com-

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[1] von Alkemade, A., *Z. physik. Chem.*, 11, 289 (1893); Schreinemakers, *Ibid.*, 12, 73 (1893). This is merely a special case of the general rule enunciated by Gibbs, "Scientific Papers," 1, p. 99.

ponent triangle a little below 200°, and along which the temperatures decrease. It is obvious that below the temperature at which $K_2SiO_3.H_2O$ is decomposed by H_2O, K_2SiO_3 can no longer be chosen as a component, since the SiO_2/K_2O ratio in the liquid phase becomes less than unity. The apparent contradiction of the above rule is, consequently, not a real one.

Let us now consider the effect of increasing the temperature above 420°. We will first consider the field of the compound $KHSi_2O_5$. We have seen that at 200°, it is stable between the SiO_2/K_2O ratios of 2.0 and 1.66, and that as the temperature was increased its field of stability swept toward regions of greater SiO_2 concentration. At 420°, it had just become stable in contact with H_2O.

Further increase in temperature results in rapid changes in this field. At 480° its solubility has greatly increased; still more so from 480° to 500°; the saturation curve of $KHSi_2O_5$ is nearing a maximum, evidently due to the occurrence of a congruent melting point. This is confirmed by the fact that at 520° this compound has disappeared; the fields of SiO_2 and of $K_2Si_2O_5$ now come together.

$K_2Si_2O_5$ remains stable over a large portion of the field, up to its melting-point curve in the binary system K_2SiO_3–SiO_2. $K_2SiO_3.0.5H_2O$ is stable at 520°; at 600°, the anhydrous compound K_2SiO_3 is stable until the SiO_2/K_2O ratio in the liquid is only 1.04, when $K_2SiO_3.0.5H_2O$ becomes stable. The transition temperature $K_2SiO_3.0.5H_2O$-K_2SiO_3 in the binary system H_2O–K_2SiO_3 lies at a slightly higher temperature.

The effect of temperature change is readily grasped by a consideration of the boundary curves, but before considering these effects let us first consider the isobaric polythermal saturation curve at one atmosphere H_2O pressure, and the equilibrium relations in the limiting binary systems K_2SiO_3–SiO_2, H_2O–K_2SiO_3, and H_2O–SiO_2.

B. **The Isobaric Polythermic Saturation Curve at One Atmosphere Pressure of H_2O Vapor, and the Binary System** K_2SiO_3–SiO_2. When small charges of K_2SiO_3 were heated in steam at atmospheric pressure, as explained on page 1188, crystals were found at all temperatures below 942°, while above this temperature the product was glass. After this point had been determined, a charge of about 0.3 g. was held at 945° for various periods of time, quenched, and the amount of water determined. It was found that the glass contained 1.3 wt. % H_2O, corresponding to a mol. fraction H_2O of 0.101. When K_2SiO_3 was first completely dehydrated, and then heated at various temperatures in an atmosphere of dry CO_2-free air, its melting point was found to be 976°. Hence the presence of 0.142 mol. H_2O to 0.858 mol. K_2SiO_3 (the vapor pressure at this concentration is one atmosphere) lowered the melting point of the latter from 976° to 942°.

Similarly the melting point of $K_2Si_2O_5$ was found to be 1041°;[1] at one atmosphere H_2O pressure its melting point is lowered to 1025° by the presence of 1.0% water, or 0.066 mol. H_2O to 0.934 mol. $K_2Si_2O_5$.

The various experiments of this type are summarized in Table III The first part of the table gives the amount of H_2O dissolved by the various mixtures at the "melting point" in one atmosphere of steam; these values are plotted in Fig. 4.

The second portion of Table III gives the corresponding changes of temperature with SiO_2 content. The temperatures given are the mean of the highest temperature at which crystals were found, and the lowest at which they disappeared; the limits also are given. The temperature for $K_{4.0}$ is taken from the isothermal saturation curves. In addition, the melting point of the anhydrous compounds K_2SiO_3 and $K_2Si_2O_5$ are given.

TABLE III.

Variation in H_2O Content along Isobaric Polythermic Saturation Curve.

K.	Wt. % H_2O.	Mol. fraction H_2O.	Solid phase.
1.01	1.3	0.101	K_2SiO_3
1.20	1.5	0.104	K_2SiO_3
1.44	1.0	0.066	$K_2Si_2O_5$
2.00	0.54	0.031	$K_2Si_2O_5$
2.72	0.30	0.017	$K_2Si_2O_5$

Variation of Temperatures on Isobaric Polythermic Saturation Curve.

K.	Temp.	Solid.	K.	Temp.	Solid.
1.01	942 ± 1	K_2SiO_3	1.34	820 ± 4	$K_2Si_2O_5$
1.06	936 ± 2	K_2SiO_3	1.78	1022 ± 2	$K_2Si_2O_5$
1.21	842 ± 4	K_2SiO_3	2.00	1034 ± 2	$K_2Si_2O_5$
1.27	806 ± 4	$K_2Si_2O_5$	2.21	1025 ± 2	$K_2Si_2O_5$
			2.72	860 ± 4	$K_2Si_2O_5$
			4.00	...	$K_2Si_2O_5$ + SiO_2

Melting Points of Anhydrous Compounds.

K_2SiO_3	976°
$K_2Si_2O_5$	1041°

The data in the second portion of Table III are presented graphically in Fig. 6. The full line represents the isobaric polythermal saturation curve at one atmosphere pressure of steam. The melting-point curve in the binary system K_2SiO_3–SiO_2 will be parallel to the former curve, and will lie at a slightly higher temperature, the temperature difference between the two being determined by the lowering of melting point caused by steam at one atmosphere. This difference was only determined for the compounds K_2SiO_3 and $K_2Si_2O_5$, where it is 34° and 16°, respectively. The melting-point curve for the binary system has been drawn on this basis; it is the broken curve in Fig. 6. The eutectic K_2SiO_3-$K_2Si_2O_5$ is at about 775° and a SiO_2/K_2O ratio of 1.30, the $K_2Si_2O_5$-SiO_2 eutectic at 525°

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[1] Niggli (THIS JOURNAL, 35, 1710 (1913)) gives 1015 ± 10° for the melting point of $K_2Si_2O_5$.

and a SiO_2/K_2O ratio of 4.0. The broken curve representing the equilibrium of melts containing small amounts of $K_2Si_2O_5$ with SiO_2 in one of its forms as solid phase is wholly an extrapolation. Its end points at the $K_2Si_2O_5$-α-quartz eutectic, and the melting temperature of pure silica are known, however, and the true curve cannot deviate much from its assumed course. It also must show breaks corresponding to the change from α-quartz to β-quartz at 575°, and from β-quartz to tridymite at 870°; the inversion tridymite-cristobalite at 1470° has also been considered, though this point does not lie inside the diagram as given.

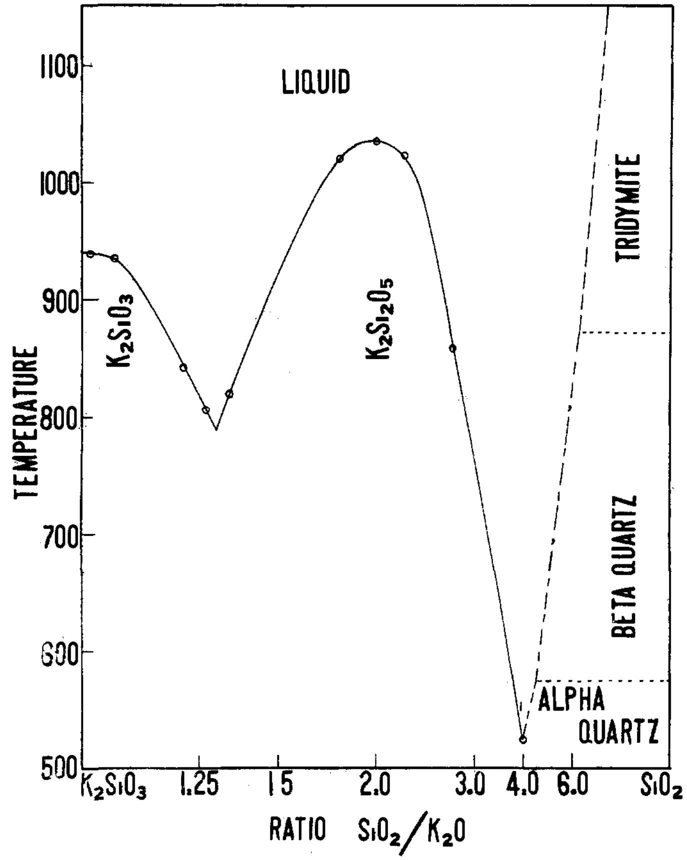

Fig. 6.

Diagram showing the variation of melting point with SiO_2/K_2O ratio on the one atmosphere isobar (cf. Fig. 4).

C. **The Binary Systems H_2O–K_2SiO_3, H_2O–$K_2Si_2O_5$, K_2SiO_3–SiO_2 and H_2O–SiO_2.**—The ternary system H_2O–K_2SiO_3–SiO_2 is limited by the binary systems K_2SiO_3–SiO_2, H_2O–SiO_2, and H_2O–K_2SiO_3. The first of these has already been discussed; its components are sufficiently non-volatile to allow of its being treated as a condensed system without appreciable error. This is not true of the other binary systems which we have to consider.

The binary system H_2O–SiO_2 is considered in detail in the discussion of the critical region (p. 1209.)

The systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$ are similar in type. The solubility data for both have been assembled in Table IV, and are presented graphically in Fig. 7. The corresponding P-T curves are the Curves 555 and 333, respectively, in Fig. 9.

TABLE IV.

Solubility in Binary Systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$.

Temp.	Mol. fraction H_2O.	Pressure (atmospheres).	Solid phase.
		H_2O–K_2SiO_3.	
200°	0.727	..	$K_2SiO_3.H_2O$
285	0.648	4.3	$K_2SiO_3.H_2O$
360	0.555	6.1	$K_2SiO_3.H_2O$
380	0.537	7.4	$K_2SiO_3.0.5H_2O$
420	0.512	10.7	$K_2SiO_3.0.5H_2O$
520	0.420	10.8	$K_2SiO_3.0.5H_2O$
600	0.365	(?)	$K_2SiO_3.0.5H_2O$
942	0.142	1.0	K_2SiO_3
976	0.00	0.0	K_2SiO_3
		H_2O–$K_2Si_2O_5$.	
200°	Decomposed by H_2O at this temp..........		$KHSi_2O_5$
285	0.760	29.5	$K_2Si_2O_5.H_2O$
360	0.668	38.6	$K_2Si_2O_5.H_2O$
380	0.650	39.0	$K_2Si_2O_5.H_2O$
420	0.619	37.7	$K_2Si_2O_5$
480	0.584	54.1	$K_2Si_2O_5$
500	0.561	66.1	$K_2Si_2O_5$
520	0.555	71.3	$K_2Si_2O_5$
600	0.520	73.9	$K_2Si_2O_5$
1034	0.070	1.0	$K_2Si_2O_5$
1041	0.000	0.0	$K_2Si_2O_5$

Invariant (Quadruple) Points in Binary Systems.

Phases.	Temp.	Mol. fraction H_2O.	Pressure (atmospheres).
System H_2O–K_2SiO_3.			
$K_2SiO_3.H_2O$-$K_2SiO_3.0.5H_2O$-L-V..........	370°	0.53	6.2
$K_2SiO_3.0.5H_2O$-K_2SiO_3-L-V..............	610°	0.345	9.0
System H_2O–$K_2Si_2O_5$.			
$K_2Si_2O_5.H_2O$-$K_2Si_2O_5$-L-V................	410°	0.628	36.0

In each of these systems we have compounds between the volatile and non-volatile components, and hence we have several quadruple points, at which two solid phases, liquid and vapor, can exist in equilibrium.

In the P-T diagram, four curves proceed from each quadruple point. One of these curves gives the change in transition point with pressure, and is practically vertical. A second is the "dissociation pressure curve" of the higher hydrate. The course of these two curves is well known. The two remaining curves represent the vapor pressures of the solutions in equilibrium with solid and vapor. The general shape of these curves has been treated theoretically by van der Waals and demonstrated experimentally by Roozeboom.[1]

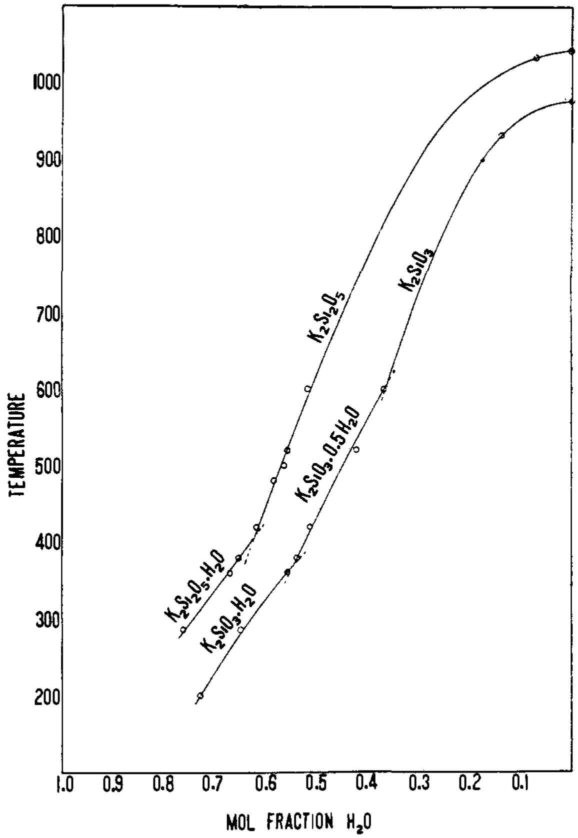

Fig. 7.

The solubility or melting-point curves of the binary systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$.

When the compound formed has a congruent melting point, the pressure of the solution saturated with it increases to a maximum, then decreases. In general, it will have both a horizontal and a vertical tangent; as pointed out by Smits,[2] neither of these is a special point in the T-X-diagram. From the vertical tangent both pressure and temperature fall to the eutectic between the compound and a phase poorer in volatile component *i. e.*, the, anhydrous salt or a lower hydrate. The pressure then rises to a maximum, and falls.

When the compound has an incongruent melting point, *i. e.*, a transition point, the relations are similar, and may easily be conceived by assuming the higher temperature curve intersecting the lower temperature curve at different points. Thus, if the intersection occurs at a point below the vertical tangent, the P-T curve will still show a point of maximum pressure and one of maximum temperature; if the intersection is between the two tangents, the P-T curve will still possess a pressure maximum, and if the intersection takes place at a lower temperature than the maximum,

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[1] *Z. physik. Chem.*, 4, 31–65 (1889).

[2] A. Smits, *Ibid.*, 78, 708–24 (1912).

the curve will merely show a break. Examples of some of these cases are to be found in a recent paper by Derby and Yngve.[1]

Examination of the Curves 5 and 3 in Fig. 9 shows that these curves are in harmony with theory. In Curve 3, the pressure rises with decreasing temperature, reaches a maximum, falls to the transition point $K_2Si_2O_5$-H_2O-$K_2Si_2O_5$, rises to a maximum, then falls again. Curve 5 is similar.

Mixtures of H_2O and $K_2Si_2O_5$ can no longer be treated as a binary system at temperatures below 280°, because of the fact that $K_2Si_2O_5$-H_2O is decomposed by H_2O at this temperature. Similarly, the binary system H_2O–K_2SiO_3 passes into a ternary system at a temperature slightly below 200°, due to K_2SiO_3-H_2O being decomposed by H_2O below this temperature.

VII. The Critical Region.

In the system H_2O–SiO_2 we have an interesting relation which we have not as yet considered. The solubility of SiO_2 in H_2O is very slight; so slight, in fact, that its amount is not enough to affect the ordinary fixed points in the binary system H_2O–SiO_2, such as the triple point, boiling point, or critical point. Hence, as we heat up a mixture of H_2O and SiO_2, at the critical temperature of the former, 374°, the solution will show critical phenomena; the amount of SiO_2 in both liquid and vapor phases at the critical point is approximately zero. The first critical end point in the system H_2O–SiO_2 therefore coincides with the critical point of H_2O.

Similar relations are met with when we start at the triple point of SiO_2 and add H_2O. When molten SiO_2 is placed in an atmosphere of water vapor, a certain amount of the latter will dissolve, and will depress the freezing point of the SiO_2. If the pressure of H_2O vapor is increased, more will be dissolved, and a greater temperature lowering will result; the solution will follow the melting point or solubility curve for the binary system H_2O–SiO_2. This process, however, cannot go on indefinitely; a point will be reached where, no matter what the pressure of H_2O vapor, enough H_2O cannot be held in the liquid to cause a further depression of melting point; in other words, to keep H_2O in the liquid phase. The solution will then have reached the second critical end point in the system H_2O–SiO_2.

The question of critical end points in binary and ternary systems cannot be discussed in this place. For a short discussion of this subject the reader is referred to a previous paper;[2] for further information the reader is referred to the papers of Smits,[3] to whom is due most of our knowledge, both theoretical and practical, of this interesting and difficult subject.

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[1] Derby and Yngve, THIS JOURNAL, 38, 1439–51 (1916).

[2] Morey and Niggli, *Ibid.*, 35, 1086–1130 (1913).

[3] A. Smits, *Z. Elektrochem.*, 46, 427 (1903); *Z. physik. Chem.*, 51, 193 (1905); 52, 498 (1905); 54, 498, 512 (1906); 67, 454, 464 (1909); 76, 445 (1911); also in *Proc. Acad. Sci. Amsterdam.* In addition to the above Professor Smits has been so kind as to discuss in detail the phenomena of critical end points in ternary

About the coördinates of the second critical end point in the system H_2O–SiO_2 we know nothing. In the various figures and in the solid model it has been assumed to lie at 550° and practically zero SiO_2 concentration. There is some justification for this assumption; at the critical end-point both phases must have the same composition, and since it is highly improbable that, no matter how high the total pressure, the SiO_2 content of the vapor can be appreciable it follows that both phases must approach pure H_2O in composition. But in this case the temperature must be fairly low; 550° seems, indeed, to be a probable upper limit. This assumption, also, is in harmony with certain geological evidence.

Addition of K_2O will cause an immediate disappearance of the critical field; this field will therefore be very small, so small, in fact, as not to occupy an appreciable area in a projection such as Figs. 4 or 8. Hence the solubility relations in SiO_2-rich mixtures will be as shown in Figs. 4 and 8, and in the solid model. The pressures in this region will be enormous, however, and it is doubtful if it can be experimentally realized. This is evident from a consideration of the variation of pressure with increasing SiO_2 content along the isotherm when quartz is the solid phase. For example, at 600°, when we increased the SiO_2/K_2O ratio from 4.49 to 4.76, *i. e.*, the mol. fraction SiO_2 in the binary system K_2O–SiO_2 from 0.741 to 0.752, the pressure increased from 93 to 560 atmospheres. This is the highest pressure determined in the system. What the magnitude of the pressure will be when we approach the binary system H_2O–SiO_2 can only be imagined.

VIII. The Composition of the Vapor Phase.

Throughout the above discussion we have assumed the vapor phase to be pure H_2O. At low temperatures, up to, say 500°, this is certainly justifiable over the entire field. But under some conditions the volatility of K_2O (or KOH) is not to be neglected. We have seen that K_2O is lost rapidly from anhydrous melts, above 1000°, and also from melts in steam at lower temperatures. Moreover, in bomb experiments some evidence of a volatility of K_2O under certain conditions has been obtained. For example, when glass containing an excess of K_2O over the 1 : 1 ratio is heated with H_2O at 500–600°, the condensed liquid outside of the crucible is found to be alkaline. In a study, now being carried out, of the system H_2O–K_2O–Fe_2O_3, conclusive evidence of a volatility of K_2O is shown by the iron walls of the bomb being attacked, with formation of a K_2O-Fe_2O_3 compound. But in the present system, while under certain conditions, some K_2O is undoubtedly present in the vapor phase, its amount is small, probably only a small fraction of one per cent. No evidence of the presence

systems, with special reference to this system, in *Proc. Acad. Sci. Amsterdam,* **18,** 793–807 (1916). I wish to take this occasion to express my gratitude to Professor Smits for his kindness in discussing this difficult question.

of SiO_2 in the vapor phase has been obtained, though numerous experiments with this end in view have been made.

Hence, the assumption that the vapor phase consists of H_2O only is a justifiable one; the amounts of other components in the vapor are so small as to be without effect on the general course of equilibrium as outlined above.

IX. The Interrelations between Temperature, Pressure and Composition in the Ternary System.

The influence of temperature change on the composition of the solid and liquid phases, and on the pressure in the various monovariant systems, is summarized in Tables V and VI, and presented graphically in Figs. 8 and 9. In Table V are given the coördinates of the invariant (T) points

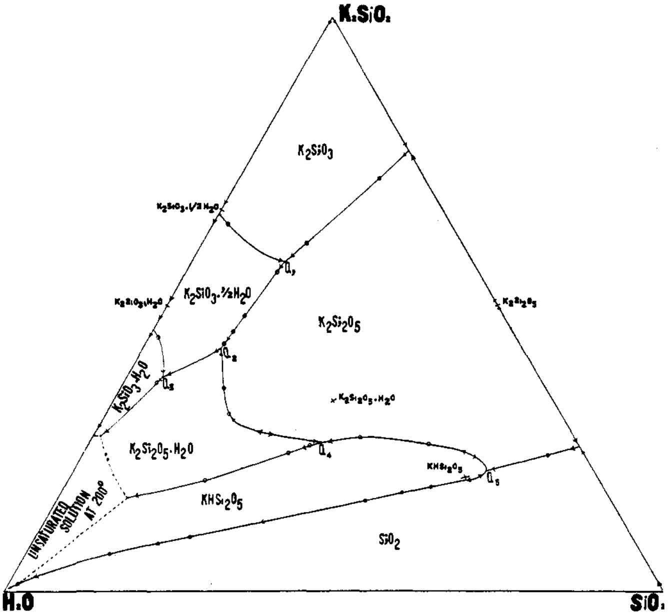

Fig. 8.

Diagram showing the boundary curves. The compound stable in contact with liquid in each field is shown by the large letters, the point representing the composition of the compound, by the small letters. Arrows show the direction of the falling temperature. The broken line is the isotherm at 200°.

at various temperatures, and of the quintuple points. These boundary curves in Fig. 8 are plotted from the data of Table V; the same curves are shown dotted in Fig. 4. In Table VI are summarized the simultaneous values of pressure and temperature for the various monovariant systems, both binary and ternary.

Before discussing these curves in detail, let us consider some general

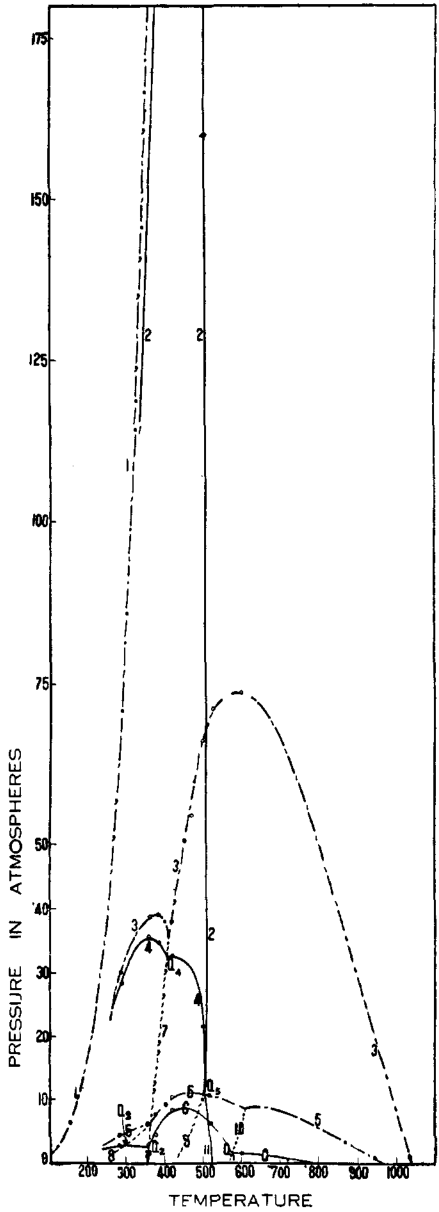

Fig. 9.

The P-T curves for the monovariant systems. The dot-dash curves represent binary systems; Curve 1 being the P-T curve for the binary system H_2O–SiO_2 (identical with the vapor-pressure curve of H_2O), Curve 3 the binary system H_2O–$K_2Si_2O_5$, Curve 5 the binary system H_2O–K_2SiO_3. The full curves are the ternary monovariant systems 2 solids–liquid–vapor; Curve 2 is the system $KHSi_2O_5$–SiO_2–L–V; Curve 4 the system $KHSi_2O_5$–$K_2Si_2O_5$ (or $K_2Si_2O_5.H_2O$)–L–V; Curve 6 the system $K_2Si_2O_5$ (or $K_2Si_2O_5.H_2O$)–K_2SiO_3 (or $K_2SiO_3.0.5H_2O$ or $K_2SiO_3.H_2O$)–L–V. The dotted curves are the monovariant system 3 solids–L–V, *i. e.*, the dissociation pressure curves.

relationships which must exist between the various curves which proceed from a quintuple point.

A. **Sequence of Pressure-Temperature Curves around a Quintuple Point.**—In a three-component system, five phases existing in equilibrium constitute an invariant system; the pressure, temperature, and composition of each of the phases are completely defined. When one of these factors is changed, one of the phases must disappear; we then have a four-phase complex, which has one degree of freedom. For example, if at a quintuple point three solid phases, a liquid phase and a vapor phase exist in equilibrium, we can make any one of these disappear by appropriate change in the conditions. In other words, from each quintuple point proceed five curves representing monovariant equilibria. These curves are most easily conceived in the P-T diagram.

The relative positions of the curves representing the various monovariant equilibria proceeding from a quintuple point are completely determined by the entropy and volume changes which take place in the neighborhood of the point, and can be deduced directly from them. But, as Schreinemakers[1] has shown, cer-

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[1] Schreinemakers, in the series of papers on "In-, Mono-, and Divariant Equilibria," *Proc. Acad. Sci. Amsterdam*, beginning with 18, 116 (1916).

tain relations may be deduced from the composition of the phases in equilibrium.

When we consider the composition, in the ordinary triangular projection, of the 5 phases which coexist at a quintuple point, we see that when these points are connected by lines, the outline of the figure formed is either a pentagon, a quadrilateral or a triangle. Schreinemakers proceeds as follows to construct a pentagon in each of the above cases, to distinguish sides and diagonals of the pentagons formed, and to number the phases.

When the five phases have compositions such that the figure formed is a convex pentagon, as shown in Fig. 10, A, the sides and diagonals are easily distinguished. The phases are numbered as follows: Starting from any phase, called (1), proceed along either diagonal to phase (2), thence along the other diagonal to (3), to (4), to (5).

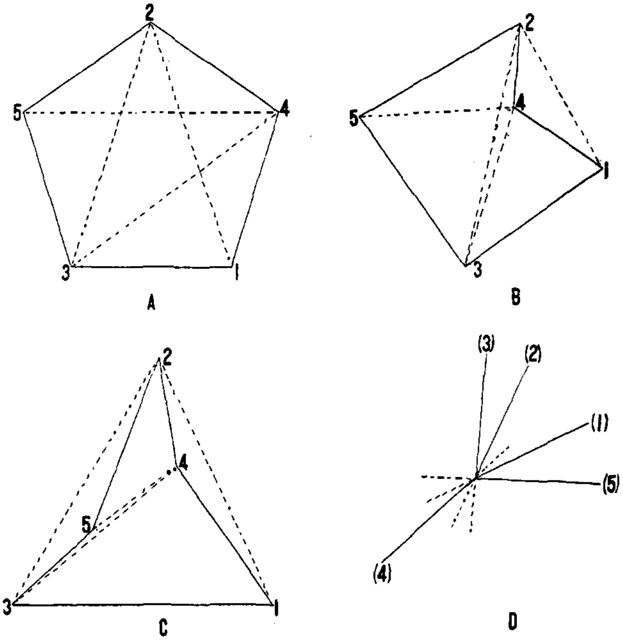

Fig. 10.

A, B and C are non-re-entrant, singly re-entrant and doubly re-entrant pentagons, respectively. D shows the sequence of P-T curves proceeding from a quintuple point corresponding to a concentration diagram of type B.

If the figure formed is a quadrilateral (Fig. 10, B), when the diagonals of the quadrilateral are drawn we see that the 5th phase lies inside one of the triangles formed; *e. g.*, phase (4). Replace side 12 with 24 and 41, making the singly re-entrant pentagon 14253. The phases are numbered as before, in diagonal sequence.

When the figure formed is a triangle (Fig. 10, C), two points will be inside. When a line is passed through the two internal points, two of the sides will be intersected internally; *e. g.*, sides 12 and 15 are intersected by the line 34. Sides 12 and 15 are replaced by 14 and 24, and 13 and 55, respectively, forming the doubly re-entrant pentagon 14253. The phases are numbered in diagonal succession as before.

When the five phases are connected so as to form a pentagon, as outlined above, and numbered in diagonal succession, the sequence of the P-T curves proceeding from the quintuple point follows a very simple law. If we denote each of these univariant equilibria by the phase which is absent, *i. e.*, the equilibrium $2 + 3 + 4 + 5$ by (1), etc., Schreinemakers has shown that the P-T curves proceed from the quintuple point in the order (1), (2), (3), (4), (5). This is equivalent to the statement that when the conditions are progressively altered in the neighborhood of a quintuple point the phases disappear in a diagonal succession, a fact which follows at once from a consideration of the ζ-surfaces in a ternary system. An illustration will be given presently.

These considerations fix the sequence of the P-T curves. Schreinemakers then defines the term "bundle of curves" as meaning a group of curves which follow one another without being separated by the metastable projection of another curve. For example, a "3-curve bundle"[1] is one in which three curves follow in sequence, with no metastable prolongations of other curves in between. Schreinemakers then shows that around every invariant point in a P-T diagram the number of bundles is at least 3, and is an odd number. Further, in a 3-component system, when the phases form a regular pentagon in the concentration-diagram, five 1-curve bundles are formed in the P-T diagram; if the phases form a singly re-entrant polygon, two 2-curve and one 1-curve bundles are formed; and if the pentagon is doubly re-entrant one 3-curve and two 1-curve bundles are formed.

When 2 of the 5 phases are liquid (L) and vapor (V), certain other conclusions may be drawn.

Consider a quintuple point at which the phases have the position shown in Fig. 10, B, and let phases 1, 2 and 5 be solid phases, phase 3, vapor, and phase 4, liquid. The sequence of curves around the quintuple point will then be (1), (2), (V), (L), (5). Since the System V is a condensed system, its P-T curve will, as is well known, be almost vertical, hence will be as shown in Fig. 2. The equilibrium (L) is the vapor-pressure curve of the 3 solids, hence proceeds from the quintuple point to lower temperature and pressures, as shown. Since the pentagon is singly re-entrant, we will have two 2-curve and one 1-curve bundles. Hence the curves must lie as shown in Fig. 10, D. Since each of the other phases involves forma-

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[1] Schreinemakers uses the form "3-curvical bundle."

tion of L, they will proceed to higher temperature, as shown; the pressure will usually increase along each of them. When the phase inside the pentagon is a liquid, the reaction is of the type 1 + 2 + 5 = L, which Schreinemakers has termed "monogenetic;"[1] when the phase inside is a solid, *e. g.*, 5, the reaction is of the type 5 = 1 + 2 + L, which Schreinemakers has termed "trigenetic."

Certain special cases are of importance, particularly those in which 3 of the phases in question lie on a straight line, and also the case that 2 of the phases have the same composition.

In general, when 3 phases lie on the same straight line the P-T curves for all equilibria involving these 3 phases coincide. When the order of the figure remains unchanged, *i. e.*, a convex pentagon remains a convex pentagon, or a quadrilateral remains a quadrilateral, a stable and a metastable portion coincide; when the order of the figure becomes changed, the stable portions coincide.

The second case mentioned, *i. e.*, that the composition of two of the phases is identical, may be considered as a special case of the above. We then see that the P-T curves for every equilibrium which contains the 2 phases in question will coincide. These later points will be deduced and discussed in a subsequent publication.

The above considerations will serve to give the relative position and directions of the curves proceeding from a quintuple point, both in the P-T and T-X representations. To fix the actual positions of the curves, and their quantitative relations in any specific case, a knowledge of the entropy and volume changes would be required in addition; that phase of the question will not be discussed.

B. **Application to the Ternary System.**—Let us now apply these considerations to the quintuple points in the system $H_2O-K_2SiO_3-SiO_2$. Fig. 8 shows the composition of the phases in equilibrium at the various quintuple points, Fig. 9 gives the P-T curves. In Fig. 9 no condensed systems are represented; their P-T curves are all practically vertical, as is well known. It may therefore be assumed that in all cases the vapor consists only of pure H_2O. The validity of this assumption is discussed on page 1210; it is certain that it is so near the truth that the conclusions based on it in the following will not be affected.

At quintuple point Q_1, K_2SiO_3, $K_2SiO_3.0.5H_2O$, $K_2Si_2O_5$, liquid and vapor co-exist; the liquid, of course, has the composition of point Q_1. When the phases are connected up as explained above, the figure formed is a singly re-entrant pentagon, hence in the P-T representation (Fig. 9), two 2-curve and one 1-curve bundles; the P-T curves will lie in the sequence (V) (K_2SiO_3) (L) ($K_2SiO_3.0.5H_2O$) ($K_2Si_2O_5$), where the curves are designated by the missing phases. Curve V will be vertical and is not

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[1] Roozeboom-Schreinemakers, "Die Heterogene Gleichgewichte," [1] 2, p. 90.

TABLE V.

Invariant Points in the Ternary System H_2O–K_2SiO_3–SiO_2.

Invariant (T) Points.

Solid.	Mol. fraction H_2O.	Mol. ratio SiO_2/K_2O.	Pressure (atmospheres).
200°.			
$K_2SiO_3.H_2O$	0.727	0.00	..
$K_2SiO_3.H_2O$-$K_2Si_2O_5.H_2O$	0.715	1.04	..
$K_2Si_2O_5.H_2O$-$KHSi_2O_5$	0.733	1.65	..
$KHSi_2O_5$-SiO_2	0.99	2.00	..
285°.			
$K_2SiO_3.H_2O$	0.648	0.00	4.3
$K_2SiO_3.H_2O$-$K_2Si_2O_5.H_2O$	0.581	1.14	2.7
$K_2Si_2O_5.H_2O$-$KHSi_2O_5$	0.595	2.06	29.3
$KHSi_2O_5$-SiO_2	0.805	3.03	±70.0
360°.			
$K_2SiO_3.H_2O$	0.567	0.00	6.1
$K_2SiO_3.H_2O$-$K_2SiO_3.0.5H_2O$	0.540	1.03	—4.0
$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$	0.436	1.27	—4.1
$K_2Si_2O_5$-$K_2Si_2O_5.H_2O$	0.482	1.43	2.9
$K_2Si_2O_5.H_2O$-$KHSi_2O_5$	0.492	2.27	35.3
$KHSi_2O_5$-SiO_2	0.720	3.28	160.0
380°.			
$K_2SiO_3.0.5H_2O$	0.537	0.00	7.4
$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$	0.414	1.26	4.2
$K_2Si_2O_5$-$K_2Si_2O_5.H_2O$	0.505	1.61	18.3
$K_2Si_2O_5.H_2O$-$KHSi_2O_5$	0.406	2.33	37.2
$KHSi_2O_5$-SiO_2	0.670	3.51	200.0
420°.			
$K_2SiO_3.0.5H_2O$	0.512	0.00	10.7
$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$	0.390	1.27	8.4
$K_2Si_2O_5$-$KHSi_2O_5$	0.379	2.38	32.5
$KHSi_2O_5$-SiO_2	0.381	4.02	340.0
480°.			
$K_2Si_2O_5$-$KHSi_2O_5$	0.320	2.53	47.0
$KHSi_2O_5$-SiO_2	0.344	4.17	190.0
500°.			
$K_2Si_2O_5$-$KHSi_2O_5$	0.218	3.03	21.5
$KHSi_2O_5$-SiO_2	0.320	4.26	160.0
520°.			
$K_2SiO_3.0.5H_2O$	0.420	0.00	10.8
$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$	0.305	1.25	6.2
K_2SiO_5-SiO_2	0.50	4.00	15.0
600°.			
$K_2SiO_3.0.5H_2O$	0.380	0.00	23.3(?)
$K_2SiO_3.0.5H_2O$-K_2SiO_3	0.335	1.04	
K_2SiO_3-$K_2Si_2O_5$	0.230	1.26	1.4
$K_2Si_2O_5$-(L)	0	2.85	0
(L)-SiO_2	0	4.08	0

TABLE V (*Continued*).

Invariant (Quintuple (= Q, Fig. 9)) Points in Ternary System.

I. K_2SiO_3-$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$-L-V.
Mol. fraction H_2O = 0.285 Mol. ratio SiO_2/K_2O 1.24
t = 575° P = 1.5 atm.

II. $K_2SiO_3.0.5H_2O$-$K_2Si_2O_5.H_2O$-$K_2Si_2O_5$-L-V.
Mol. fraction H_2O = 0.460 Mol. ratio SiO_2/K_2O 1.30
t = 350° P = 2.4 atm.

III. $K_2SiO_3.0.5H_2O$-$K_2SiO_3.H_2O$-$K_2Si_2O_5.H_2O$-L-V.
Mol. fraction H_2O = 0.57 Mol. ratio SiO_2/K_2O 1.14
t = 300° P = 2.7 atm.

IV. $K_2Si_2O_5.H_2O$-$K_2Si_2O_5$-$KHSi_2O_5$-L-V.
Mol. fraction H_2O = 0.40 Mol. ratio SiO_2/K_2O 2.33
t = 405° P = 32.3 atm.

V. $K_2Si_2O_5$-$KHSi_2O_5$-SiO_2-L-V.
Mol. fraction H_2O = 0.16 Mol. ratio SiO_2/K_2O 4.00
t = 510° P = 12 atm.

TABLE VI.

Pressure-Temperature Curves for Univariant Systems.

	$x - y$.	P.	Solid phase.
Binary System H_2O–K_2SiO_3.			
285°	0.12	4.3	$K_2SiO_3.H_2O$
360°	0.15	6.1	$K_2SiO_3.H_2O$
380°	0.18	7.9	$K_2SiO_3.0.5H_2O$
405°	0.20	8.7	$K_2SiO_3.0.5H_2O$
420°	0.24	10.7	$K_2SiO_3.0.5H_2O$
520°	0.21	10.8	$K_2SiO_3.0.5H_2O$
600°	0.42	23.3[1]	$K_2SiO_3.0.5H_2O$
Ternary System H_2O–K_2SiO_3–$K_2Si_2O_5$.			
285°	0.08	2.9	$K_2SiO_3.H_2O$-$K_2Si_2O_5.H_2O$
360°	0.07	2.9	$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5.H_2O$
380°	0.10	4.2	$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$
420°	0.19	8.4	$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$
520°	0.12	6.2	$K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$
600°	0.02	1.4	K_2SiO_3-$K_2Si_2O_5$
Binary System H_2O–$K_2Si_2O_5$.			
285°	0.86	29.5	$K_2Si_2O_5.H_2O$
360°	1.00	38.6	$K_2Si_2O_5.H_2O$
380°	1.00	39.0	$K_2Si_2O_5.H_2O$
420°	0.90	37.7	$K_2Si_2O_5$
480°	1.17	54.1	$K_2Si_2O_5$
500°	1.40	66.1	$K_2Si_2O_5$
520°	1.47	71.3	$K_2Si_2O_5$
600°	1.37	73.9	$K_2Si_2O_5$
Ternary System H_2O–$K_2Si_2O_5$–$KHSi_2O_5$.			
285°	0.86	29.3	$K_2Si_2O_5.H_2O$-$KHSi_2O_5$
360°	0.86	35.3	$K_2Si_2O_5.H_2O$-$KHSi_2O_5$
380°	0.93	37.2	$K_2Si_2O_5.H_2O$-$KHSi_2O_5$
420°	0.75	32.5	$K_2Si_2O_5$-$KHSi_2O_5$
500°	0.43	21.5	$K_2Si_2O_5$-$KHSi_2O_5$

[1] This pressure is believed to be too high; it is omitted from Fig. 9 on that account.

TABLE VI (*Continued*).

t.	x — y.	P.	Solid phase.
Ternary System H_2O–$KHSi_2O_5$–SiO_2..			
360°	6.0	160	$KHSi_2O_5$-SiO_2
380°	9.0	200	$KHSi_2O_5$-SiO_2
420°	20.0	340	$KHSi_2O_5$-SiO_2
500°	5.1	160	$KHSi_2O_5$-SiO_2

shown. Curve K_2SiO_3 will go to regions of lower temperature; it is the Curve Q_1Q_1; the maximum is, of course, at the point where the entropy change in the reaction

$$K_2SiO_3.0.5H_2O + K_2Si_2O_5 + V = L$$

passes through zero. This is analogous to the maximum pressure observed on the P-T curve in a binary system.

Curve $K_2SiO_3.0.5H_2O$ goes to regions of higher temperature and higher pressure ending at the eutectic K_2SiO_3-$K_2Si_2O_5$ in the binary system K_2SiO_3–SiO_2. The pressure along it also rises to a maximum, then falls, as in the case of the Curve K_2SiO_3. Curves K_2SiO_3 and $K_2SiO_3.0.5H_2O$ are both numbered "6" in Fig. 9.

Curve $K_2Si_2O_5$ represents the boundary curve between $K_2SiO_3.0.5H_2O$ and K_2SiO_3; it also goes to regions of higher temperature, and along it the pressure also increases. Its end point is at the transition point $K_2SiO_3.0.5H_2O$-K_2SiO_3 in the binary system. Both pressure and temperature increase along the curve as we approach the side of the triangle, but neither reaches a maximum. The reaction along the Curve $K_2Si_2O_5$ is

$$K_2SiO_3.H_2O + L = K_2SiO_3 + V.$$

As explained above, because of the fact that the three phases, $K_2SiO_3.0.5H_2O$, K_2SiO_3 and V, lie on a straight line, the P-T curve of this reaction will coincide with that of the reaction in the binary system:

$$K_2SiO_3.0.5H_2O = K_2SiO_3 + V,$$

the "dissociation pressure curve of $K_2SiO_3.0.5H_2O$." Moreover, since the fifth monovariant system proceeding from Q_1, the system (L) in which the phase reaction is

$$K_2SiO_3.0.5H_2O + K_2Si_2O_5 = K_2SiO_3 + V,$$

contains these same three phases, its P-T curve will coincide with that of the binary dissociation pressure curve of $K_2SiO_3.0.5H_2O$. The Curves L and $K_2Si_2O_5$ will coincide in their metastable portions, and both will coincide with the stable dissociation pressure curve of $K_2SiO_3.0.5H_2O$.

In Fig. 8 the Curve $K_2Si_2O_5$ is shown; in Fig. 9, Curve 10 above Q_1 is the curve $K_2Si_2O_5$, below Q_1, the Curve L, and both portions represent the dissociation pressure curve of $K_2SiO_3.0.5H_2O$.

The quintuple point Q_3 is completely analogous to Q_1, and the same considerations will apply to it. The order of curves is (V), ($K_2SiO_3.0.5$-

H_2O), (L), ($K_2SiO_3.H_2O$), ($K_2Si_2O_5.H_2O$). As before, (V) (not shown in Fig. 9) is practically perpendicular; ($K_2SiO_3.0.5H_2O$) goes to lower temperatures, and is numbered 6 in Fig. 9; ($K_2SiO_3.H_2O$) is the Curve Q_2Q_2 in both Fig. 8 and Fig. 9, and is also part of Curve 6 in the latter figure; Curves L and $K_2Si_2O_5.H_2O$ coincide in their metastable portions and also coincide with the dissociation pressure curve of $K_2SiO_3.H_2O$. Curve 8 in Fig. 9 represents these complexes.

Quintuple points Q_2 and Q_4 are similar in type. Both form singly reentrant pentagons; around Q_2 the sequence of curves is (V), ($K_2SiO_3.0.5H_2O$), (L), ($K_2Si_2O_5.H_2O$), ($K_2Si_2O_5$); around Q_4, (V), ($K_2Si_2O_5$), (L), ($K_2Si_2O_5.H_2O$), ($KHSi_2O_5$).

Let us first consider Q_2. The Curve $K_2Si_2O_5.H_2O$ is the Curve Q_2Q_1 in Figs. 8 and 9, Curve $K_2Si_2O_5$, the Curve Q_2Q_3, both of which have already been discussed. Curve V is, of course, vertical.

Along the two remaining curves (L and $K_2SiO_3.0.5H_2O$), we have the phases $K_2Si_2O_5.H_2O$, $K_2Si_2O_5$, $K_2SiO_3.0.5H_2O$, V, and $K_2Si_2O_5.H_2O$, $K_2Si_2O_5$, L, V, respectively. Since the phases $K_2Si_2O_5.H_2O$, $K_2Si_2O_5$, V lie on a straight line, the P-T curves of the equilibria (L and $K_2SiO_3.0.5H_2O$) will coincide, and also coincide with the dissociation pressure curve of $K_2Si_2O_5.H_2O$. The Curve L will proceed from Q_2 to lower temperatures; it is the portion of Curve 7 in Fig. 9 below Q_2. Curve $K_2SiO_3.0.5H_2O$ will proceed to higher temperatures, it is the portion of Curve 7 in Fig. 9 above Q_2, and the portion of Curve Q_2Q_4 in Fig. 8 from Q_2 to the point of maximum temperature, at the intersection of Curve 7 with Curve 3.

The two curves just discussed also are coincident, in part, with the Curves L and $KHSi_2O_5$, which proceed from Q_4; the Curve L in this case is the portion of Curve 7 in Fig. 8 below Q_4; the Curve $KHSi_2O_5$, the portion of Curve Q_2Q_4 in Fig. 6 from Q_4 to the point of maximum temperature, in Fig. 8, the portion of Curve 7 above Q_4. It should be remembered that Curve 7, in its entirety, is also the dissociation pressure curve of $K_2Si_2O_5.H_2O$. The above may perhaps be expressed more simply as follows: When we consider Curve Q_2Q_4 in Figs. 8 and 9, we see that both pressure and temperature increase to a maximum at the transition point $K_2Si_2O_5$-H_2O-$K_2Si_2O_5$ in the binary system H_2O–$K_2Si_2O_5$, then both pressure and temperature fall to Q_4. In Fig. 9, pressure and temperature increase along Curve 7 to a maximum at the transition point, then fall, along the same curve, to Q_4.

The other curves proceeding from Q_4 are (V), ($K_2Si_2O_5$), and ($K_2Si_2O_5.H_2O$). The Curve V is approximately vertical. The Curve $K_2Si_2O_5$ goes to regions of lower temperature; it is shown in both Figs. 6 and 8 and is the portion of Curve 4 below Q_4 in the latter figure. The Curve $K_2Si_2O_5.H_2O$ goes to regions of higher temperature, and is also the higher temperature portion of Curve 4. It will be discussed in greater detail later.

Quintuple point Q_5 differs from the other quintuple points found in this system in two particulars. In the first place, it is the only one in which the liquid lies inside the triangle formed by the solid phases in equilibrium, hence the only eutectic. Second, the points around Q_5 form a doubly reentrant pentagon. Hence we have in the P-T curves one 3-curve and two 1-curve bundles. The sequence of P-T curves is (V), (L), ($KHSi_2O_5$), (SiO_2), ($K_2Si_2O_5$); the Curves SiO_2, $K_2Si_2O_5$, V, constitute the 3-curve bundle.

The Curve V, is as usual, almost vertical. The Curve $\bar{L}$ coincides with the dissociation pressure curve of $KHSi_2O_5$, which is not shown in either figure. The Curve $KHSi_2O_5$ is the boundary curve between the SiO_2 and $K_2Si_2O_5$ fields in Fig. 8; along it the temperature increases to its end point in the $K_2Si_2O_5$-SiO_2 eutectic in the binary system K_2SiO_3–SiO_2, but the pressure probably decreases, as shown by Curve 11 in Fig. 9.

It has been assumed that the phases V, $KHSi_2O_5$ and L lie on a straight line. The exact position of Q_5 could not be determined, but it must lie very close to its assumed position, and very probably does lie on the line V-$KHSi_2O_5$. Hence, the Curves SiO_2 and $K_2Si_2O_5$, representing the monovariant equilibrium of $KHSi_2O_5$-L and V with SiO_2 and $K_2Si_2O_5$, respectively, will coincide near the quintuple point, and will also coincide with the dissociation pressure curve of $KHSi_2O_5$. The first of these curves is the boundary curve between SiO_2 and $KHSi_2O_5$, the second between $K_2Si_2O_5$ and $KHSi_2O_5$ in Fig. 8. In Fig. 9, the Curve SiO_2 is the Curve 2. From Q_5 it rises very steeply. It first passes through a temperature maximum corresponding to the point of maximum temperature in Fig. 8, where the line $KHSi_2O_5$-SiO_2 intersects the boundary curve; at this point it has a vertical tangent. It then rises with decreasing temperature to a pressure maximum at about 420° and 340 atmospheres. Both pressure and temperature then fall; the maximum is not shown in Fig. 8, but it can easily be seen that the maximum in Curve 2 lies at about twice the height of the diagram.

Curve SiO_2 is the Curve Q_5Q_4 in Fig. 8, the upper portion of Curve 4 in Fig. 9. At Q_5 it coincides with $K_2Si_2O_5$, has a vertical tangent at a temperature corresponding to the point where in Fig. 8, the line K_2Si_2-O_5-$KHSi_2O_5$ intersects the boundary curve, and at a point of maximum pressure.

C. **The Solid Models.**—In a system of three components we have, in general, to consider the variables, pressure, temperature, and three masses, *i. e.*, five variables. By imposing the restriction that the sum of the mols of the components is unity (or one hundred) we reduce the variables to four. By imposing further restrictions we can reduce the degrees of freedom to three, two, one, or zero. We have already considered the variation of pressure with temperatures in monovariant systems containing two solids, liquid and vapor, *i. e.*, the P-T curves (Fig. 9), and of the composition of liquid in equilibrium, with solid and vapor at constant temperature and variable pressure (concentration of H_2O in the vapor phase), the isothermal polybaric saturation curves (Fig. 4). These latter may be regarded as sections, at constant temperature, of the solid T-X model.

Since we have four variables, it is not possible to construct a solid model showing directly the variation of pressure, temperature, and composition. However, we can construct models showing the simultaneous variation of any three, the change in the fourth not being shown. Two such models, in one of which the variables shown are pressure and composition, in the other, temperature and composition, will completely represent the possible variations in the system.

Photographs of the T-X and P-X models for this system are shown in Figs. 11 and 12. Fig. 11 is the T-X model. The field for each compound is represented by a surface; the intersection of two such surfaces gives the variation in composition with temperature of the liquid in equilibrium with the two solids and vapor; of three surfaces, the invariant point three solids-liquid-vapor. The projections of these lines on the base gives Fig. 8. In this model, the base is the isotherm at 200°. It will be noticed that all the fields slope toward the region of unsaturated solution at 200° shown in Fig. 8.

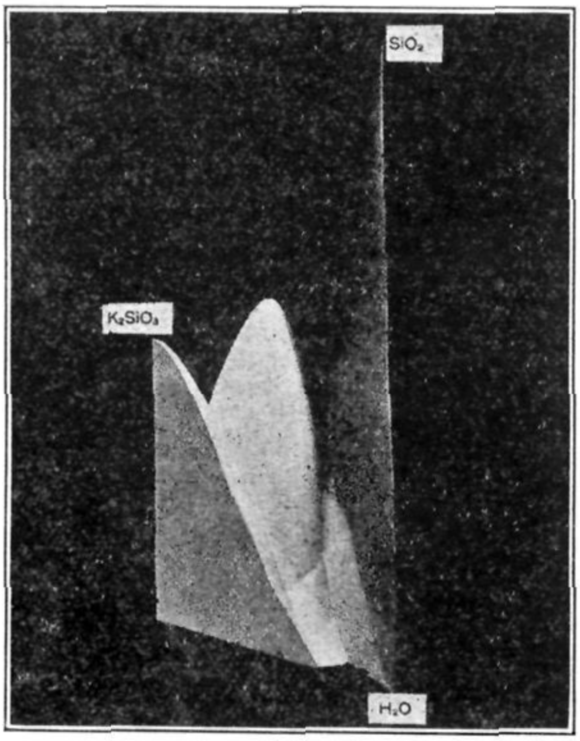

Fig. 11.
Photograph of the solid T-X model.

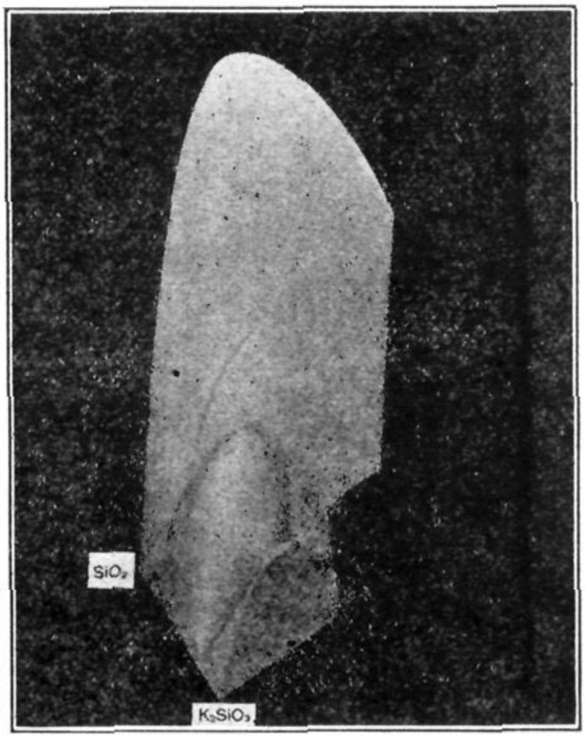

Fig. 12.
Photograph of the solid P-X model.

The sections at constant temperature of this model have already been discussed in considering the experimental isothermal polybaric curves (Fig. 4); the corresponding pressure changes are shown in Fig. 5.

The base in the case of the P-X model (Fig. 12) is zero pressure, and this model differs strikingly from the T-X model because of the fact, already discussed, that in each binary system H_2O–silicate the pressure increases with decreasing H_2O concentration, reaches a maximum, then falls to the vapor pressure of the anhydrous silicate, *i. e.*, to practically zero. Hence the pressure is zero at all points in the binary system K_2SiO_3–SiO_2, rises on addition of H_2O, then falls. To each compound belongs a surface, and, as before, intersection of two surfaces gives a boundary curve, of three surfaces, an invariant point. On account of the extreme range of pressure in this system, it was necessary to use a variable scale.

Up to 10 atmospheres pressure, which include all the region in which a metasilicate compound is stable, the scale of the model is 1 cm. = 1 atmosphere. From this pressure up to 75 atmospheres, the maximum pressure on the $K_2Si_2O_5$ surface, the scale is 1 cm. = 10 atmospheres. Above this, the model is purely schematic. The maximum pressure in the $KHSi_2O_5$ field is about 360 atmospheres, in the SiO_2 field, probably several thousand atmospheres. In making this model, it has been assumed that the pressure at the second critical end point in the binary system H_2O–SiO_2 lies at about 1000 atmospheres.

D. **The Isobaric Polythermic Saturation Curves.**—When planes parallel to the base, *i. e.*, constant pressure planes, are passed through the solid P-X model, one or more surfaces are intersected, depending on the pressure chosen. Projections of the intersections on the basal plane are isobaric polythermal saturation curves. A series of isobaric curves, or isobars, are shown in Fig. 13. They have been drawn to show plainly the effect of varying water pressure (concentration of H_2O in the vapor phase) on the equilibrium relations. The pressures chosen are those which will best show the principles involved; in order to make the relations more evident, the curves have not been drawn true to scale, but some features have been exaggerated.

When only one surface is cut by the pressure plane, the isobaric saturation curve obtained is a single closed curve. When more than one surface is intersected, the saturation curves of the different compounds may be wholly separate closed curves, or they may intersect. Since the projection on the base of the intersection of two surfaces is the boundary curve between the two compounds, shown in Fig. 8, intersection of two saturation curves belonging to a given isobar will take place on the boundary curve. The boundary curves are shown by broken lines in Fig. 13.

We will first consider a section at a very high pressure,[1] higher than the assumed second critical end point in the binary system H_2O–SiO_2, but lower than the maximum pressure in this system. We will assume that a pressure of 1500 atm. fulfils this condition.

The only surface cut by the 1500 atm. isobar will be that of SiO_2, in one of its polymorphic forms. That this is true is evident from Fig. 12; the projection of the intersection is the curve marked "1500 atm." in Fig. 13. The arrows give the direction of falling temperature. At the pressure considered, points inside the area enclosed by this isobar and the side H_2O-SiO_2 of the component triangle represent complexes of solid quartz with vapor and saturated solution of a composition lying on the isobar itself. This area, then, is the field for SiO_2 at 1500 atm., the rest of the triangle is the field of unsaturated solutions.

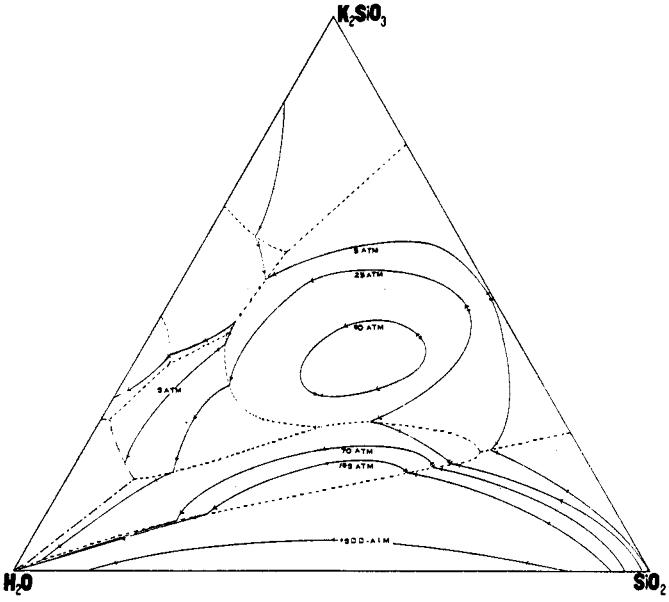

Fig. 13.

The isobaric polythermal saturation curves. The arrows show the direction of falling temperature.

The next isobar considered is at the much lower pressure of 175 atmospheres. This pressure is below the point of maximum pressure along the boundary Curve $KHSi_2O_5$-SiO_2; the variation of pressure with temperature in this monovariant equilibrium is shown by Curve 2 in Fig. 9.

Since the pressure, 175 atmospheres, is less than that of the first critical end point in the binary system H_2O–SiO_2, the saturation curve of SiO_2

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[1] Naturally, the temperature must be raised above the critical temperature of H_2O before a pressure of water vapor greater than about 200 atm. can be realized.

at 175 atmospheres ends at the H_2O apex of the triangle. This is the lowest temperature along the 175 atm. isobar at which SiO_2 can co-exist with liquid and vapor. The highest temperature will correspond to the lowering of the melting point of SiO_2 by the amount of H_2O dissolved by the liquid under this pressure. On lowering the temperature, SiO_2 remains stable until the invariant (P) point SiO_2-$KHSi_2O_5$-L-V is reached. The isobar then follows the saturation curve of $KHSi_2O_5$.

At a pressure higher than the maximum pressure on the $KHSi_2O_5$-SiO_2 boundary curve (Curve 2 in Fig. 9), but lower than the maximum pressure on the $KHSi_2O_5$ surface, the saturation curve of $KHSi_2O_5$ would be a closed curve, enclosing the $KHSi_2O_5$ field. Along such a closed curve, in accordance with the theorem of Gibbs already mentioned, a temperature minimum is found on the line connecting the compositions of solid and vapor, toward the vapor side, and a temperature maximum on the same line, on the side away from the vapor.

At the lower pressure of the 175 atm. isobar, the $KHSi_2O_5$ saturation curve is no longer a closed curve. Starting from the highest temperature invariant (P) point $KHSi_2O_5$-SiO_2 the temperature first increases to a maximum on the line H_2O-$KHSi_2O_5$, then falls to the second invariant (P) point $KHSi_2O_5$-SiO_2. At the pressure we are considering the second invariant (P) point lies at a smaller SiO_2/K_2O ratio than that of the compound $KHSi_2O_5$. This is due to the fact that the boundary Curve $KHSi_2O_5$-SiO_2 has crossed the conjugation line H_2O-$KHSi_2O_5$. Hence the minimum temperature along the isobaric polythermic saturation curve of $KHSi_2O_5$ at 175 atm. lies on the metastable portion of this curve, and the temperature decreases as we pass along the $KHSi_2O_5$ saturation curve to the SiO_2 curve.

It will be observed that the field of the compound $KHSi_2O_5$ does not extend over the point representing the composition of the compound. Schreinemakers[1] has termed the saturation curves enclosing fields which do not extend over the composition of the compound "exphased," those which do, "circumphased."

The next isobar drawn in Fig. 13 corresponds to a pressure a little below that of the maximum pressure of the $K_2Si_2O_5$ surface, *i. e.*, at about 70 atmospheres (cf. Fig. 9). The plane now cuts, in addition to the SiO_2 and $KHSi_2O_5$ surfaces, the $K_2Si_2O_5$ surface. The SiO_2 and $KHSi_2O_5$ fields have extended over a larger portion of the component triangle, and in addition a field, bounded by a closed curve, in which $K_2Si_2O_5$ is stable, has appeared. This is, of necessity, exphased, and shows both a temperature maximum and a temperature minimum.

A section at a pressure of about 25 atmospheres (cf. Fig. 9) is shown by the corresponding isobar in Fig. 13. At this pressure the surfaces of

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[1] Schreinemakers, *Proc. Roy. Acad. Amsterdam*, 15, 707 (1912).

SiO_2, $KHSi_2O_5$, $K_2Si_2O_5$ and $K_2Si_2O_5.H_2O$ are intersected by the cutting plane. The chief point of difference between the 25 atm. and the 70 atm. isobars is the appearance of the field of $K_2Si_2O_5.H_2O$, and the consequent disappearance of the point of minimum temperature in the $K_2Si_2O_5$ field. Also the isobar chosen is one in which the minimum temperature of the $K_2Si_2O_5.H_2O$ field has also disappeared. This is due to decomposition of $K_2Si_2O_5.H_2O$ by H_2O, $KHSi_2O_5$ being stable phase in a mixture having a SiO_2/K_2O ratio of 2.

The last curve drawn corresponds to a pressure above that of Q_1, Q_2 and Q_3 in Fig. 9, but below the maximum pressure at which $K_2SiO_3.H_2O$ can co-exist with liquid and vapor, *i. e.*, about 5 atmos. The pressure is also below that of Q_5, so that as the temperature is decreased along the SiO_2 curve, $K_2Si_2O_5$ becomes stable solid phase. Along the $K_2Si_2O_5$ curve temperature rises to a maximum along the line H_2O-$K_2Si_2O_5$, then falls to the intersection of the $K_2Si_2O_5$ surface with the $K_2SiO_3.0.5H_2O$ surface, *i. e.*, the boundary Curve $K_2Si_2O_5$-$K_2SiO_3.0.5H_2O$. Temperature rises along the $K_2Si_2O_5.0.5H_2O$ saturation curve as the SiO_2/K_2O ratio is decreased, until the boundary curve between $K_2SiO_3.0.5H_2O$ and K_2SiO_3 is reached, when the latter compound becomes the solid phase.

Separated from the above portion of the 5 atmosphere isobar by the $K_2SiO_3.0.5H_2O$ surface is a second portion of the same isobar representing lower temperature equilibria. Starting from the side H_2O-K_2SiO_3 of the component triangle, temperature rises along the saturation curve of $K_2SiO_3.H_2O$ until the invariant (P) point $K_2SiO_3.H_2O$-$K_2SiO_3.0.5H_2O$ is reached. The temperature continues to rise along the saturation curve of $K_2SiO_3.0.5H_2O$, which ends at the invariant (P) point $K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$-L-V. It will be observed that these same solids can co-exist with vapor and liquid of another composition at a higher temperature; there are two invariant (P) points $K_2SiO_3.0.5H_2O$-$K_2Si_2O_5$-L-V on this isobar. Temperature then falls along the saturation curve of $K_2Si_2O_5$, to the invariant (P) point $K_2Si_2O_5$-$K_2Si_2O_5.H_2O$-L-V, and continues to fall along the saturation curve of $K_2Si_2O_5.H_2O$. The pressure on this isobar is less than that found for the invariant (T) point $K_2Si_2O_5.H_2O$-$KHSi_2O_5$-L-V at 200°, hence the saturation curve of $K_2Si_2O_5.H_2O$ at this pressure ends on the isothermal polybaric saturation curve of $K_2Si_2O_5.H_2O$ at 200°.

There are many other questions whose discussion would be of interest, not only because of the physico-chemical relationships involved, but also because of many important applications of similar processes to technical and geological problems. Some of these questions whose discussion would be of interest are the course of crystallization of any mixture of constant temperature and slowly falling pressure, the course of crystallization of any mixture at constant pressure and falling temperature, the course of crystallization with simultaneous change of pressure and temperature.

Such questions, however, can easily be answered from a consideration of the isobaric polythermal and isothermal polybaric saturation curves, in connection with the P-T curves and the boundary curves, but their discussion must be omitted from the present paper.

X. The Solubility of Silicates.

In the preliminary paper to which reference has already been made, the following remarks were made:[1]

"As we have noted above, $KHSi_2O_5$ and $Na_2Si_2O_5$ are not readily affected by H_2O, while $K_2Si_2O_5$ and Na_2SiO_3 are decomposed very rapidly. But from these facts one can draw no necessarily valid conclusions as to their real solubility, *i. e.*, as to the equilibrium between a solid of definite composition and the same substance in a solution saturated with it. The process is one of decomposition, the rate of which differs from one to another of the above four substances." Let us consider the question more fully, in the light of the equilibrium relations which have now been experimentally ascertained.

The term "solubility" is one so often used in a loose sense that its precise meaning is frequently lost sight of. Its original meaning, indeed, was a loose one, merely indicating that some substance, usually solid, disappeared, wholly or in part, the material passing into a co-existent liquid phase. In this sense we often speak of the solubility of metals in acids, our conception being usually one of relative rate of solution merely.

When we try to assign quantitative values to solubility, it becomes necessary to define our terms precisely. Moreover, we usually have a slightly different conception of solubility according to the nature of the phases, *e. g.*, gas in liquid, liquid in liquid, a solid in liquid. But in each case, the solubility of the one phase in the other is defined by the relative amounts of the two substances which are in equilibrium in the phase in question; in other words, the saturation concentration. It should be emphasized that in each of the above cases the restriction is placed on the system as a whole that at constant temperature the equilibrium is invariant. When we are dealing with a gas and a liquid, we specify the pressure of the gas. When we are dealing with a liquid–liquid system, two liquid layers are necessary to give invariance. In systems solid–liquid, we have co-existence of three phases—solid, liquid and vapor—which gives us an invariant point at constant temperature in a two-component system, and the solubility is fixed. In all the above cases solubility has a definite meaning.

When we come to apply the term solubility to systems of more than two components we find that additional restrictions are necessary. Co-existence of solid, liquid and vapor at constant temperature in a ternary system leaves one degree of freedom. For example, in the case of a double

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[1] THIS JOURNAL, 36, 224; *Z. anorg. Chem.*, 86, 317 (1914).

salt in contact with H_2O, the compound can exist in equilibrium with a whole series of solutions. For the term solubility to mean anything in such a case it is necessary to impose a further restriction, for example, to fix the proportions of some of the components in the liquid phase, or to fix the pressure of the solution.

In the case of aqueous solutions we must, in general, distinguish between compounds which are stable in presence of the solvent and those which are decomposed by water. In the first case we can speak of the solubility of the compound in water; imposition of the restriction that the ratio of the anhydrous components in the liquid phase is the same as in the solid is tantamount to assuming a binary system.

When excess of either of the anhydrous components is added, the solution follows the saturation curve of the compound, and the ratio between the amount of solid phase in the solution to that of solvent (*i. e.*, H_2O), varies. Thus, the saturation concentration may diminish on addition of one component and increase on addition of the other, or it may increase in both cases, if it happens to be at a minimum. An example of a compound stable in the presence of H_2O is $K_2Si_2O_3.H_2O$ at 360°. Here the saturation concentration is diminished by addition of K_2SiO_3, increased by addition of SiO_2. It is obvious, however, that the saturation concentration in a mixture containing any particular excess of K_2SiO_3 is no special point; the saturation concentration in this particular mixture is merely one point on the isothermal polybaric saturation curve of the compound.

When the compound is decomposed by H_2O it is no more proper to speak of its solubility in H_2O than to speak of the solubility of brass in nitric acid. In both cases the solid phase disappears, the material passing into the liquid. In neither case is any equilibrium between solid and liquid attainable. To be sure, if there is enough brass, a point will be reached at which the limited quantity of liquid will dissolve no more. When the decomposed compound is treated with H_2O, another solid phase appears, and if there is enough of the original compound the solution will finally attain the composition of the invariant (T) point at which the two compounds can co-exist in presence of liquid and vapor. For example, at 200° $K_2Si_2O_5.H_2O$ is decomposed by H_2O, the stable solid phase being $KHSi_2O_5$. Depending on the relative amounts of $K_2Si_2O_5.H_2O$ and H_2O originally present, the equilibrium condition will either be a saturated solution of $KHSi_2O_5$ or the solution represented by the invariant (T) point $KHSi_2O_5$-$K_2Si_2O_5.H_2O$-L-V. It is obviously improper to speak of any of these points as the solubility of $K_2Si_2O_5.H_2O$.

These considerations evidently were not realized by Vesterberg,[1] who

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[1] *Z. anorg. Chem.*, **88**, 341–8 (1914); also in *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **2**, 235–9. Vesterberg also confuses the integral with the differential heat of solution; he says, "the salt dissolves easily in water with rather great cooling. Thus

says, "On account of the hydrolysis I have examined the solubility not in pure H_2O but in caustic soda solution of about 0.5 *N*." In this connection it is interesting to examine the isothermals along which $KHSi_2O_5$ is stable phase (see Fig. 3). These show plainly what an enormous effect the change in the SiO_2/K_2O ratio may have on the concentration along an isothermal saturation curve.

The case of a compound such as $KHSi_2O_5$ is similar. At ordinary temperatures this compound is far outside of its stability region. It will be decomposed with separation of SiO_2; in this particular case, the SiO_2 will not separate as a crystalline solid, but as an amorphous precipitate of indefinite composition. This will continue until all the $KHSi_2O_5$ has been completely decomposed, and the end result will be an alkaline solution, containing but little SiO_2. The actual equilibrium probably would correspond to a solution containing a vanishingly small amount of SiO_2, in equilibrium with crystalline quartz, but the attainment of the equilibrium is hindered by the fact that some of the SiO_2 tends to be dispersed in the liquid, forming a colloidal mixture whose mass concentration is determined in part by factors other than those which we are considering.

Several authors have determined a so-called "solubility" of various minerals in water at ordinary and slightly elevated temperatures. That the results are usually merely poorly-defined rates of reaction, is obvious. Equilibrium between orthoclase and water, at ordinary temperature would not be reached until the mineral was completely decomposed, the end condition being an alkaline solution, containing vanishingly small amounts of Al_2O_3 and SiO_2. This case, as is that of most minerals, is complicated by the fact that, instead of the Al_2O_3 and SiO_2 separating as crystalline solids, of definite composition,[1] the end result, in a finite time, is a "colloidal" material of indefinite composition and properties, co-existing with a liquid containing dispersed Al_2O_3 and SiO_2.

XI. Summary.

The ternary system $H_2O–K_2SiO_3–SiO_2$ has been studied over the temperature range from 200° to over 1000°. The work comprised a determination of the composition and properties of the various stable solid phases which can co-exist with solution and vapor within the above temperature range; of the composition of the solutions in equilibrium with the solid phases; of the change in composition of these solutions with temperature; and the approximate determination of the corresponding 3-phase pressures.

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the coefficient of temperature for solution is positive, and the solubility increases notably with temperature." Here it obviously is the integral heat of solution that is referred to, while the differential heat is the one which determines the change in solubility with temperature.

[1] While the stable solid phases are referred to as Al_2O_3 and SiO_2, this is done only for convenience. No inference in regard to the existence of definite compounds formed by either or both with H_2O is intended.

In addition to quartz and the compounds $K_2Si_2O_5$ and $KHSi_2O_5$, the following new compounds occur as solid phases: *Potassium disilicate monohydrate*, $K_2Si_2O_5.H_2O$; *potassium metasilicate*, K_2SiO_3; *potassium metasilicate hemihydrate*, $K_2SiO_3.0.5H_2O$; and *potassium metasilicate monohydrate*, $K_2SiO_3.H_2O$.

The data obtained are presented by means of tables, and graphically by means of curves and solid models. Curves are given showing the solubility relations in the binary systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$ (Fig. 7), the isothermal polybaric saturation curves (Fig. 4), the variation of pressure with SiO_2/K_2O ratio along the isotherms (Fig. 5), the isobaric polythermal saturation curves (Fig. 13), the P-T curves of the various monovariant systems (Fig. 9), and the boundary curves of the different solid phases in the ternary system (Fig. 8). In addition, photographs are given of the solid models showing the variation in the composition of the saturated solutions with temperature, under the corresponding 3-phase pressure (Fig. 11), and the variation of the composition of the saturated solutions with pressure, at the corresponding 3-phase temperatures (Fig. 12).

Brief mention is made of some of the theoretical relations governing the equilibrium in binary and ternary systems containing a volatile component, and a short discussion of the proper application of the term "solubility" is given.

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ON THE DIETERICI EQUATION OF STATE.

BY F. H. MACDOUGALL.

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In a recent article[1] I discussed at some length the Dieterici equation of state, $p = \frac{RT}{v-b} e^{-a/vRT}$ and applied it to a number of substances, among which may be mentioned isopentane, carbon dioxide and hydrogen. Various methods were developed of calculating the values of a and b (two of the "constants" of the equation) below, at, and above the critical temperature; and formulas were deduced connecting the pressure of saturated vapor and the latent heat of vaporization with the densities of liquid and saturated vapor.

In the present paper I desire to bring forward an additional method of calculating a and further to urge strongly the advantages, both theoretical and practical, which the Dieterici equation has over any equation of the van der Waals type.

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[1] THIS JOURNAL, 38, 528–555 (1916).