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THE SYSTEM K_2O—Al_2O_3—SiO_2

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ABSTRACT. Results of quenching experiments at temperatures between the liquidus and that of complete consolidation are reported for 383 synthetic compositions. These locate the liquidus surfaces and the fields of the primary phases cristobalite, tridymite, quartz, mullite, corundum, potash feldspar, leucite, hexagonal $KAlSiO_4$, orthorhombic $KAlSiO_4$, potassium tetrasilicate and potassium disilicate. The temperatures and compositions of ten binary and eleven ternary invariant points within the system K_2O—Al_2O_3—SiO_2 were located and an equilibrium diagram for this ternary system is given. The subsystems leucite—corundum—$KAlSiO_4$, leucite—corundum—silica, leucite—$KAlSiO_4$—potassium disilicate and leucite—potassium disilicate—silica are ternary systems within the larger ternary system K_2O—Al_2O_3—SiO_2. No field of "β-Al_2O_3" was found and, whatever may be its composition, "β-Al_2O_3" is metastable with respect to corundum at the temperatures investigated. Our knowledge of the stability relations of the polymorphs of $KAlSiO_4$ (kaliophilite, kalsilite and orthorhombic $KAlSiO_4$) is still very unsatisfactory, and this matter requires further study. Dry melts of feldspar and silica which approach a granitic composition can dissolve very little aluminous material unless the temperature is very high.

INTRODUCTION

Through the years investigators at the Geophysical Laboratory have been obtaining quantitative information on the melting relations of many of the important rock-forming minerals. Of all the rock-forming minerals, the feldspars are among the most important and interesting. The principal components of natural feldspars are soda feldspar ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ or $NaAlSi_3O_8$), potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$ or $KAlSi_3O_8$) and lime feldspar ($CaO \cdot Al_2O_3 \cdot 2SiO_2$ or $CaAl_2Si_2O_8$). The first paper from the Geophysical Laboratory (Day and Allen, 1905) dealt with the melting relations between the feldspars of soda and of lime, the plagioclases. One of us (Bowen, 1913) determined the liquidus and solidus temperatures for the plagioclase feldspar system and showed that there is an unbroken series of solid solutions between the soda and lime feldspars at high temperatures. At that time it was not possible to crystallize the pure soda feldspar from the extremely viscous glass of its own composition. The complete relations between the lime feldspar anorthite and all other coexisting crystalline phases in the system CaO—Al_2O_3—SiO_2 were presented by Rankin and Wright (1915).

Morey and Bowen (1922) showed that potash feldspar melts incongruently at about 1170°C. to the feldspathoid leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$ or $KAlSi_2O_6$) and a viscous, more siliceous, complementary liquid, and that it became completely liquid only at about 1530°C. Thus it became apparent that the determination of the melting relations of potash feldspar in the system leucite—silica would be difficult experimentally owing to the high melting temperature of pure leucite and to the high viscosity of melts in the composition region between potash feldspar and silica, which would make crystallization difficult or perhaps impossible.

Because of the widespread occurrence of alkali feldspars in rocks, these feldspars are of extreme importance and interest. Feldspars occur with quartz in the granitic rocks and with the feldspathoids leucite and/or nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ or $NaAlSiO_4$), or rarely with kalsilite ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$ or $KAlSiO_4$) or kaliophilite, another polymorph of $KAlSiO_4$, in the alkaline rocks. It should be readily apparent that a knowledge of the melting relations in the ternary systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2, and in the plane $NaAlSiO_4$—$KAlSiO_4$—SiO_2 in the quaternary system Na_2O—K_2O—Al_2O_3—SiO_2 are essential if we are to understand the complex crystallization relations in rock-forming magmas.

During the years between 1929 and 1941 the phase equilibrium relations at or slightly below temperatures where a liquid phase was present, were determined for the ternary systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2 by Schairer and Bowen. Concurrently with the studies of these two systems, the melting relations in $NaAlSiO_4$—$KAlSiO_4$—SiO_2 were investigated. A preliminary report on this last investigation was published (Schairer and Bowen, 1935). More recently the data on the alkali feldspar join $NaAlSi_3O_8$—$KAlSi_3O_8$ were presented (Schairer, 1950), and a revised equilibrium diagram for $NaAlSiO_4$—$KAlSiO_4$—SiO_2 was presented without the data on which it was based. The very large amount of data obtained since 1929 should be presented. It seems desirable, however, to record first of all the data on the systems K_2O—Al_2O_3—SiO_2 and Na_2O—Al_2O_3—SiO_2. Some of the very numerous data were assembled in 1941 and the preparation of diagrams and manuscripts for publication was started, but was interrupted by the war. Because of the general usefulness of the results in petrology and silicate technology, the final diagrams for these two systems were made available (Schairer and Bowen, 1947a), but publication of the data on which the diagrams were based, a full discussion of the preparation of the compositions studied, quenching data, detailed results and some of the applications was deferred. A manuscript presenting the data and complete results for Na_2O—Al_2O_3—SiO_2 is now in preparation. The data on K_2O—Al_2O_3—SiO_2 are presented here.

PREPARATION OF MELTS

Glasses of the desired composition were prepared from pure chemicals by heating in platinum crucibles. As a source of Al_2O_3 a so-called C.P. Al_2O_3 was used, which had been specially treated with NH_4OH in platinum vessels to reduce its alkali content.[1] This product when dry contained only about 0.1 percent alkalies, mostly Na_2O and negligible amounts of other impurities. As a source of K_2O and SiO_2, a series of potassium silicate glasses was prepared from purified quartz (less than 0.03 percent residue by weight after treatment

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[1] Chemically precipitated $Al(OH)_3$ usually contains alkalies. The alkali content can be reduced by treatment in platinum vessels with alkali-free NH_4OH. At the present time a good quality alkali-free Al_2O_3 can be obtained from the Aluminum Company of America, and this tedious purification is unnecessary.

with hydrofluoric and sulfuric acids) and a very pure $KHCO_3$ (Baker and Adamson, lot no. 3772). In the preparation of silicate mixtures containing alkalies, special care must be used to avoid loss of alkali by volatilization and consequent departure from composition.

Preparation of potassium silicate glasses.—When mixtures of $KHCO_3$ and SiO_2 are heated rapidly to high temperatures in a platinum crucible, extensive foaming occurs as water and CO_2 are evolved and the frothy melts foam out of the crucible. At the same time a considerable portion of the K_2O is lost by volatilization before combination with SiO_2 is effected. A satisfactory procedure was found for the preparation of $K_2O—SiO_2$ glasses of the precise desired composition, and several hundred grams of each of 22 different glasses of this type were prepared during the course of the studies of the $K_2O—Al_2O_3—SiO_2$ system.

Twenty-gram batches of a series of potassium silicate glasses were prepared in 40 cc platinum crucibles. Calculated amounts of dry powdered silica (quartz ignited overnight at 1500° and crushed to a fine powder) and $KHCO_3$ were weighed into a platinum crucible, mixed with a platinum spatula, then covered with a platinum cover and heated in a nichrome-wound pot furnace for about 24 hours at 700°C. (a temperature at which no liquid is present but reaction rate is rapid). A combination of $KHCO_3$ and SiO_2 is effected with evolution of water and CO_2 and no loss by volatilization, spattering and frothing. Then the temperature of the pot furnace is raised to 800°, 900° and then 1000° for successive 24-hour periods. The contents of the crucible melt down slowly without violent evolution of gas. Finally the crucible is placed in a platinum-wound electric furnace on a clean, smooth corundum disk and heated to 1200°C., or higher if the liquidus temperature of the particular potassium silicate requires it for complete melting. By cooling rapidly to room temperature in a desiccator with a tight-fitting cover on the crucible to prevent any loss of glass particles by decrepitation, a clear glass is obtained.

Careful weighing showed that, for compositions between potassium disilicate and those with silica contents up to about 85 percent, with a 20-gram sample the weight was deficient by only 10 to 20 mg, if the operations just described were conducted with care. For those compositions with 85 to 95 percent silica, where the temperature must be raised to 1500°C. or more for complete melting of the charge, the K_2O losses were only slightly higher (30 to 50 mg). The calculated amount of $KHCO_3$ to make up this small deficiency was added to the crushed glass, which is first held overnight at 800°C. and then completely melted three times in the platinum-wound furnace with intermediate cooling and crushing in a steel mortar (small steel chips accidentally introduced during the crushing operation are removed with a magnet). This procedure gives a homogeneous glass. These observations confirm those of Kracek (1932, p. 2529-2530).

Since all these powdered potassium silicate glasses are more or less hygroscopic, they were crystallized completely by holding the crushed glass for 24-hour periods at 750°C., with intermediate crushing, until the powder no longer fritted at this temperature and crystallization was complete. There is no segregation of crystals in these viscous glasses. Such a crystallized product of the desired composition remains dry in a desiccator over KOH sticks and can be weighed without difficulty in the preparation of the ternary K_2O—Al_2O_3—SiO_2 glasses.

Preparation of the ternary glasses.—Ten grams of each of the desired ternary K_2O—Al_2O_3—SiO_2 glasses were prepared by weighing on watch glasses appropriate amounts of dry Al_2O_3 and dry crystallized K_2O—SiO_2 compositions, the preparation of which has just been described. These ingredients were mixed with a platinum spatula on glazed paper and transferred to a 15 cc platinum crucible, which was heated in a vertical platinum-wound electric furnace with the crucible placed on a refractory pedestal in the "hot" zone of the furnace. The first heating of several hours' duration was always conducted at about 1200°C. The crucible was removed from the furnace with tongs and the charge quenched by placing the crucible in a shallow pan of water with a cover on the crucible to prevent loss by decrepitation. The charge is remelted several times with intermediate crushing to mix the charge thoroughly and obtain a homogeneous glass.

Experience has shown that at least three, and usually four or five, fusions with intermediate crushings are necessary to obtain a homogeneous glass of most silicate melts. The final fusions must be made at temperatures above the liquidus temperature for the particular composition. Al_2O_3 is very difficult to dissolve in silicate melts. No matter what type of Al_2O_3 is used it is rapidly converted to corundum (α-Al_2O_3) at high temperatures, and this is very difficult to dissolve, particularly in compositions which yield very viscous melts. Because of this difficulty most of the mixtures in the system K_2O—Al_2O_3—SiO_2 required six or seven fusions to obtain a homogeneous glass free from undissolved Al_2O_3. In most of the melts which lie on the line leucite—silica, as many as ten or eleven fusions at 1600°C. were required in order to effect the complete solution of Al_2O_3 and obtain a homogeneous glass, even though some of these compositions have liquidus temperatures as low as 990°C.

Too much emphasis cannot be placed on the importance of obtaining a homogeneous glass before starting equilibrium studies. Erratic and unreliable phase data are obtained when the composition of the charge is not uniform. Index of refraction of the glass is a very sensitive test of homogeneity. When a small sample of powdered glass is immersed in an oil with an index of refraction about 0.005 above that of the glass and examined under the petrographic microscope, any undissolved Al_2O_3 or crystals of any kind can be seen at a glance. If there are no crystalline phases the homogeneity of the glass can be tested in a very sensitive manner by warming the sample in the immersion oil over the microscope lamp, replacing the slide on the stage of the microscope and observing the sample as it cools to room temperature. At some point during the cooling process the index of the oil and the index of the glass match exactly, and all grains of a homogeneous glass seem to disappear simultaneously. Even slight inhomogeneity in the glass can be detected by this method.

EQUILIBRIUM STUDIES

Investigation of the melting relations of the ternary mixtures was carried out by the method of quenching (Shepherd, Rankin and Wright, 1909), which consists of holding a small charge of known composition at a measured temperature for a period of time adequate for attainment of equilibrium between the several phases, and then chilling instantly to room temperature to "freeze" the equilibrium assemblage. Quenched charges are examined with a petrographic microscope to determine the nature and number of crystalline and liquid phases. Most silicate liquids quench to a glass. Even if some devitrification occurs during the rapid quenching of the small samples, microscopic examination easily distinguishes primary crystals from the feathery crystals formed during the quenching.

In order to employ the method of quenching on these ternary compositions it is necessary to crystallize the melts first, and precautions should be taken to have only small crystals present in order to hasten the attainment of equilibrium between crystals and liquid. The time necessary for equilibrium between crystals and liquid for various ternary compositions must be determined by experiment. The time required for equilibrium is a very crude qualitative measure of the viscosity of the melt. The selection of ternary compositions for study and their crystallization will be discussed in the next section of this paper.

Quenching experiments were conducted in platinum-wound electric furnaces whose temperature was controlled (± 2°C.) with a temperature regulator, the Geophysical Laboratory furnace thermostat (Roberts, 1925), somewhat modified from the original design, but identical in principle.

The temperature was measured with a thermocouple placed nearly in contact with (about 1 mm distant from) the small charge wrapped in a tiny platinum envelope, which is suspended in that part of the furnace determined as the "hot point." In the well insulated furnace there is a range of about 5 mm on either side of this point where the temperature falls off only about one-half degree. The small platinum envelope containing the charge hangs entirely within this zone.

The Pt-Pt 90 Rh 10 thermoelements were calibrated frequently at one or more of the several fixed points, defined in degrees Centigrade as follows: pure palladium melting point, 1549.5°; pure diopside ($CaO \cdot MgO \cdot 2SiO_2$) melting point, 1391.5°; pure gold melting point, 1062.6°; pure NaCl melting point, 800.4°C. (Sosman, 1910; Adams, 1919; Roberts, 1924).

METHOD OF ATTACK AND CRYSTALLIZATION OF MELTS

Many experimental difficulties could be expected in the study of the system $K_2O—Al_2O_3—SiO_2$. Geological interest in this system was focused chiefly on those compositions with 40 weight percent or more of silica. Previous studies by one of us (Bowen, 1917) on the composition $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ had shown that its melting point must lie well above 1700°C. and that some K_2O was volatilized during attempts to prepare this high-melting composition. Such temperatures are above the practical upper temperature limit of the platinum-wound electric furnace. Pure leucite was prepared and its congruent melting point at 1686° ± 5°C. was determined (Bowen and Schairer, 1929). Its preparation had been difficult, expensive and time consuming owing to the short life of the furnaces at the temperatures required.

Fortunately, the glass crystallized readily at high temperatures.

All previous reconnaissance attempts at the Geophysical Laboratory to crystallize synthetic glasses of several different compositions in that portion of the system leucite—silica between the composition of potash feldspar and silica had resulted in failure to obtain crystals in these viscous glasses. When no crystals are present, a study of crystal-liquid equilibrium is impossible. If mixtures of natural materials such as feldspar and quartz were used, we could hope for little success. Experiment had shown that natural crystals of potash feldspar can be heated well above the incongruent melting point of this compound for many hours or days before appreciable melting occurs and equilibrium might not be attained in several months or even years. In order to attain equilibrium between crystals and liquid, even at and near liquidus temperatures, and in order to obtain reliable phase equilibrium data it was essential to have well distributed, small crystals in the glasses before quenching experiments were initiated.

As mentioned in the introduction to this paper, the system $NaAlSiO_4$—$KAlSiO_4$—SiO_2 was concurrently under investigation. The system $KAlSiO_4$ ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$)—$SiO_2$ is one of the limiting binary systems. With $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ and SiO_2 as components, leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) and potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) become binary compounds between these two components. A series of melts in the siliceous portion of this binary system had been prepared. Most of them would not crystallize. Fortunately cristobalite, as small, well distributed crystals, was obtained in a glass of the composition $KAlSiO_4$ 10, SiO_2 90, in a few days at about 1500°C. (all compositions in this paper are given in weight percent). The cristobalite liquidus temperature at 1558°C. was determined on this material. At these high temperatures with small cristobalite crystals, only about five hours were adequate for attainment of equilibrium between crystals and liquid. The first data in the silica-rich portion of K_2O—Al_2O_3—SiO_2 had been obtained!

As the study of three additional binary compositions progressed (those with 85, 80 and 75 percent SiO_2), it was found that crystallization was much more difficult at the lower temperatures required and that many weeks or months were necessary to obtain crystals. Only cristobalite crystallized below 1470° ± 10° even though temperatures were in the stability range of tridymite (Fenner, 1912, 1913). It was not possible to crystallize tridymite from these viscous binary melts. It became apparent that the best approach to the binary system leucite—silica might be from melts in that portion of the ternary system K_2O—Al_2O_3—SiO_2 between the join leucite—silica and the $K_2O \cdot 2SiO_2$—SiO_2 portion of the limiting binary system K_2O—SiO_2.

Series of glasses with increasing amounts of Al_2O_3 were prepared on joins (straight lines connecting two arbitrarily selected compositions) between a particular K_2O—SiO_2 composition and Al_2O_3. These joins are sections through the system K_2O—Al_2O_3—SiO_2. The first joins selected for study crossed the silica-rich portion of this system. The K_2O—SiO_2 glasses (without Al_2O_3) presented little difficulty in crystallization, particularly if such glasses were held at temperatures 50° to 75°C. below the liquidus temperatures (Kracek, Bowen and Morey, 1929; Kracek, 1930). Tridymite crystallized readily from appropriate glasses. Thus it was possible to follow the liquidus surface of cristobalite and of tridymite from the $K_2O—SiO_2$ side of the diagram toward the binary system leucite—silica by studying mixtures progressively richer in Al_2O_3 on the several appropriate joins which cross the fields of these crystalline phases, and, finally, to delimit completely the primary fields of these crystalline phases. In a similar manner it was possible to crystallize mullite, to determine the mullite liquidus surface at high temperatures, and, eventually, to follow it through successive lower temperatures and to completely outline its field of primary crystallization. By progressing in a similar manner we were able to obtain liquidus data for the fields of potash feldspar, leucite, corundum, etc., to define that portion of the system $K_2O—Al_2O_3—SiO_2$ between $K_2O \cdot 2SiO_2$, Al_2O_3 and SiO_2.

SOME OBSERVATIONS ON THE GLASSES AND ACCURACY OF RESULTS

Powdered potassium silicate glasses are very hygroscopic. As Kracek, Bowen and Morey (1937, p. 1191-1192) have indicated, the moisture in these glasses is not merely adsorbed on the surfaces of the grains, as is the case with most ordinary glasses, but penetrates into the interior of the grains as a consequence of the high solubility of water in these glasses. Even when stored in containers in desiccators over sticks of fused KOH, these powdered alkali-silica glasses gradually absorb moisture. As noted previously in the discussion of the preparation of mixtures, the $K_2O—SiO_2$ glasses to be used for the preparation of ternary $K_2O—Al_2O_3—SiO_2$ melts were crystallized promptly. A temperature just below that of the lowest binary eutectic was selected for the crystallization. The crystals are small and there is no local inhomogeneity introduced because of the presence of large crystals of a different composition from that of the total composition of the mixture produced when hydrous glasses crystallize. These completely crystallized preparations remain dry and can be weighed rapidly with no increase in weight by moisture absorption during the weighing.

Similarly, the $K_2O—Al_2O_3—SiO_2$ glasses are hygroscopic, particularly those with a silica content of less than about 75 percent. It was necessary to begin the crystallization of the glasses immediately after their preparation, in order to keep them dry and on composition. This precaution was necessary particularly for those compositions with less than about 60 percent of silica. When the powdered glasses were kept in a desiccator for some months they took up water slowly. When they were examined under the petrographic microscope it was observed that the refractive index had changed and was not uniform from the center to the exterior of a grain. In any particular join studied, consistent results were obtained and the liquidus temperatures were found to lie on smooth curves only when the mixtures were crystallized immediately after preparation of the homogeneous ternary glasses, and only when they were kept dry in a crystallizing furnace until the quenching runs were completed. When partially crystallized glasses were stored in a desiccator and allowed to absorb moisture slowly, difficulties were encountered when subsequent quenching runs were made in some cases to check the previous runs. The charge puffed up when the moisture was evolved on heating, crystals grew too large for prompt attainment of equilibrium between crystals and liquid, and the runs indicated that the composition of the mixtures had shifted slightly owing to loss of K_2O when the moisture was expelled during the heating.

During the preparation of this manuscript a very careful study of all the quenching data was made. Considering the difficulties and pitfalls encountered in this investigation, most of the data are remarkably consistent. When proper precautions are observed it is possible to prepare a selected composition in this system by synthesis as closely as its composition can be verified by a chemical analysis. This is certainly true for the siliceous compositions. A glass (K907) was made from appropriate amounts of a dry crystalline potassium silicate preparation, K_2O 10, SiO_2 90, and Al_2O_3 to have the composition K_2O 9.3, Al_2O_3 7.0, SiO_2 83.7. A careful chemical analysis by one of our colleagues, J. Allen Crocker, whose assistance is gratefully acknowledged, gave the values K_2O 9.5, Al_2O_3 7.1, SiO_2 83.4 for this glass.

Melts were prepared and quenching experiments made in that portion of the join $K_2O \cdot 2SiO_2$—Al_2O_3 between $K_2O \cdot 2SiO_2$ and $KAlSiO_4$ before all the pitfalls enumerated above had been discovered. A new study of this join and the adjacent portion of the ternary system should be made. With the "know-how" now available and with modern X-ray techniques for the identification of crystals and detection of solid solution when present, much additional information can be obtained on the relations between the polymorphous forms of $KAlSiO_4$.

LIMITING BINARY SYSTEMS

The three binary systems K_2O—SiO_2, Al_2O_3—SiO_2 and K_2O—Al_2O_3 limit the ternary system K_2O—Al_2O_3—SiO_2.

The system K_2O—SiO_2.—That portion of this system between $K_2O \cdot SiO_2$ and SiO_2 was studied by Kracek, Bowen and Morey (1929) and Kracek (1930). During the course of the investigation of the ternary system K_2O—Al_2O_3—SiO_2 31 different glasses between $K_2O \cdot SiO_2$ and SiO_2 were prepared. Twenty-two of these were prepared in sufficient quantities to use as a source of K_2O and SiO_2 in the preparation of ternary glass compositions in the 22 joins studied. Quenching runs were made on all the potassium silicate compositions prepared, in order to gain experience in crystallization and to tie in the data on the ternary glass compositions with those on the binary system K_2O—SiO_2. These results were used by Kracek, Bowen and Morey (1937) to obtain their final revised diagram for the system K_2SiO_3—SiO_2. Their phase equilibrium diagram is given here as figure 1. The melting point of cristobalite (SiO_2) at 1713° ± 5° is from Greig (1927, p. 7-12).

The system Al_2O_3—SiO_2.—This system was studied by Bowen and Greig (1924), who found only one binary compound at elevated temperatures, mullite ($3Al_2O_3 \cdot 2SiO_2$), which melts incongruently at 1810° ± 10°C. to corundum and liquid and becomes completely liquid only at about 1920°C. They placed the eutectic between cristobalite and mullite at 1545° ± 5°C. at the composition Al_2O_3 5.5, SiO_2 94.5. In our studies of the system K_2O—Al_2O_3—SiO_2 several compositions were prepared and studied to locate the positions

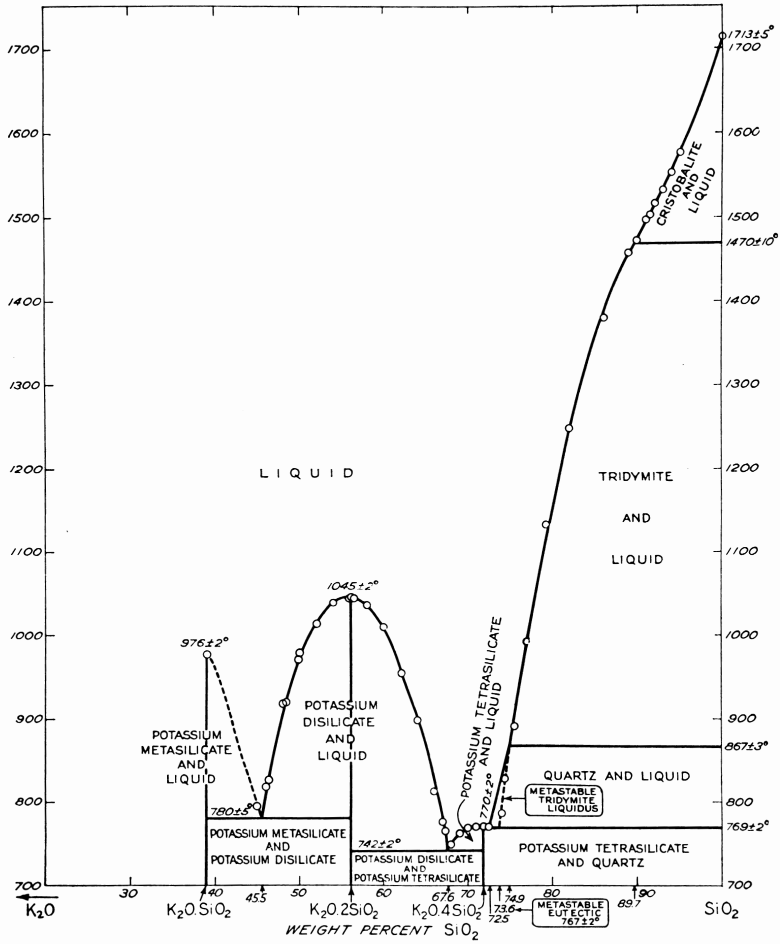

Fig. 1. Equilibrium diagram of the binary system K_2SiO_3—SiO_2 (after Kracek, Bowen and Morey).

of isotherms in the cristobalite field, the position of the ternary invariant point cristobalite + tridymite + mullite + liquid (1470° ± 10°) and the boundary curve between the fields of cristobalite and mullite. Studies of these compositions indicated that the eutectic temperature of Bowen and Greig at 1545° ± 5°C. between cristobalite and mullite in the binary system Al_2O_3—SiO_2 must be too low. Quenching studies on the composition K_2O 1.0, Al_2O_3 6.5, SiO_2 92.5 gave a cristobalite liquidus temperature at 1555°C. with the appearance of mullite as a second solid phase at 1543°C. A careful study of the locations of isotherms and temperatures along the boundary curve suggests that the binary eutectic in Al_2O_3—SiO_2 lies at 1585° ± 10°.[2] The equilibrium diagram of Bowen and Greig with this change is given here as

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[2] The value 1595° ± 10° was given by Schairer (1942, p. 274, footnote 57).

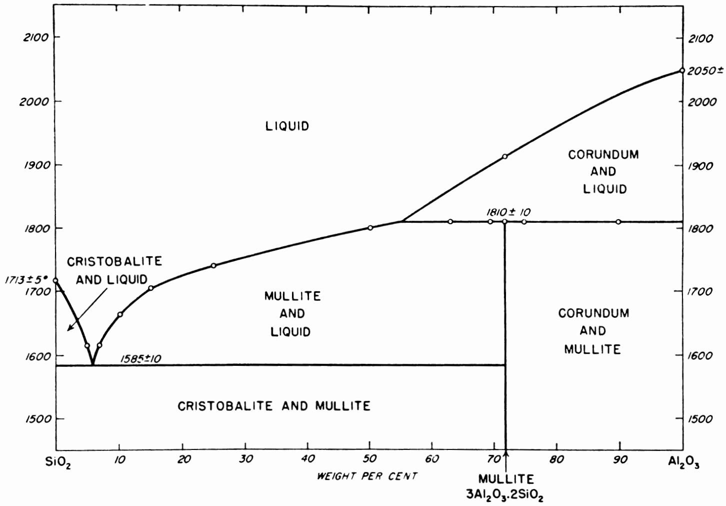

Fig. 2. Equilibrium diagram of the binary system Al_2O_3—SiO_2 (after Bowen and Greig). The eutectic temperature between cristobalite and mullite has been changed to 1585° ± 10°. There is evidence that the compound $3Al_2O_3 \cdot 2SiO_2$ may contain more Al_2O_3 than is indicated by the ratio 3:2. A revision of this portion of the diagram awaits determination of the exact composition (alumina content) of the mullite crystals present at the binary invariant point corundum + mullite + liquid.

figure 2. The melting point of cristobalite at 1713° ± 5° is from Greig (1927, p. 7-12) and that of corundum at 2050° ± 20° from Kanolt (1913, 1914) who used for calibrations the same value 1755°C. for the melting point of pure platinum as was used by Bowen and Greig in their determinations in Al_2O_3—SiO_2. On the International Temperature Scale the value for the melting point of pure platinum is 1773.5°C. Geller and Yavorsky (1945) made a critical review of previous determinations of the melting point of pure Al_2O_3 (corundum) and the nature of the uncertainties in the determinations. On the basis of seven new measurements they indicate that the melting point is within the range 2000° to 2030°C. (on the International Temperature Scale) and that a more accurate determination of the true value must involve prevention of contamination of the alumina specimen by vapors of other elements in the furnace atmosphere.

Bowen and Greig (1924) showed that crystals of mullite take up no excess SiO_2 over the Al_2O_3:SiO_2 ratio 3:2. Posnjak and Greig (1933) showed that mullite crystals with some excess Al_2O_3 in solid solution formed, and homogeneous crystals with 75 weight percent of Al_2O_3 were prepared and studied. Rooksby and Partridge (1939) studied synthetic mullite crystals with excess Al_2O_3 in solid solution and found that the maximum amount of Al_2O_3 in mullite is 77.6 percent Al_2O_3 or possibly a little higher. A sample with 80 percent Al_2O_3 contained corundum as well as mullite. Bauer and Gordon (1951) grew large single crystals of mullite by a flame-fusion technique, and chemical analyses of the boules indicated that the amount of Al_2O_3 in mullite may be even greater than 78 percent.

Recently, Shears and Archibald (1954) gave an excellent review of all the data on the system $Al_2O_3—SiO_2$ and on aluminosilicate refractories. They presented a revised diagram for $Al_2O_3—SiO_2$ which purports to take into account all the pertinent data in the literature. This revised diagram is not in accord with all the data presented. Until it is possible to ascertain the exact composition (alumina content) of the mullite crystals which are present at equilibrium at the binary invariant point corundum + mullite + liquid, no satisfactory revised diagram can be given.

In the investigation of the ternary system $K_2O—Al_2O_3—SiO_2$ the field of mullite was delimited but no information was obtained on the exact composition of the small mullite needles present in the glasses.

The system $K_2O—Al_2O_3$.—Brownmiller (1935) studied eight compositions in the system $K_2O—Al_2O_3$. He found that no melting occurred in any of these preparations when heated to 1600°C. Microscopic examinations of all but two of the preparations heated at 1600°C. showed the presence of the two phases $K_2O{\cdot}Al_2O_3$ and "β-Al_2O_3." When the ratio of K_2O to Al_2O_3 was 1:1 only the compound $K_2O{\cdot}Al_2O_3$ was present. It crystallized as isometric crystals (octahedra) with an index of refraction of 1.603 ± 0.005 for artificial white light. The interplanar spacings were measured by X-ray techniques. No melting or observable dissociation of $K_2O{\cdot}Al_2O_3$ was found at 1650°C.,

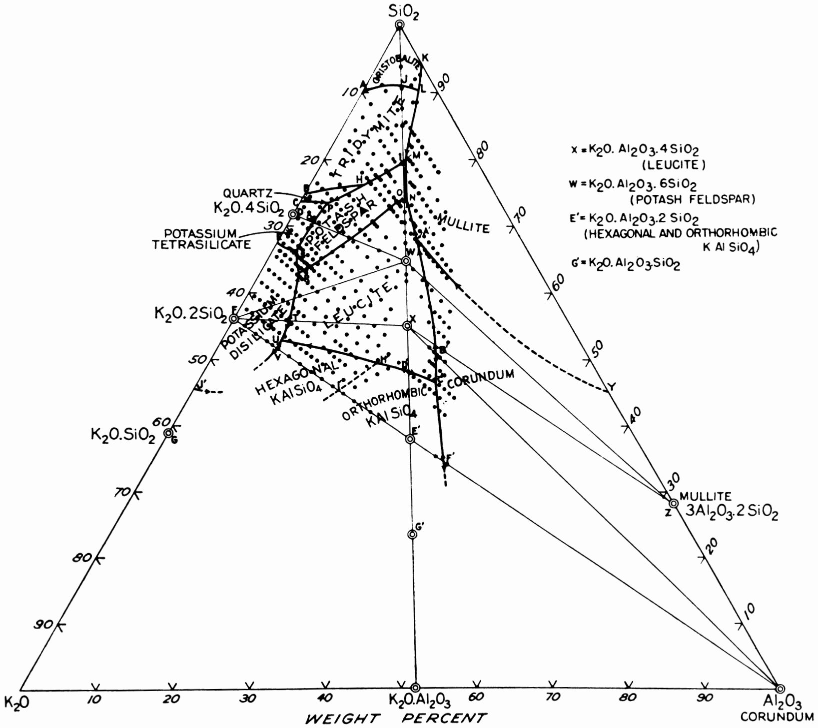

Fig. 3. Equilibrium diagram of the system $K_2O—Al_2O_3—SiO_2$ showing compositions studied and the fields of the primary crystalline phases.

the highest temperature available in the study. This compound was extremely hygroscopic. When the composition 96.5 weight percent Al_2O_3 with 3.5 percent K_2O was heated at 1550°C. corundum and "β-Al_2O_3" crystallized. No evidence for the composition of "β-Al_2O_3" was obtained by Brownmiller.

Strokov *et al.* (1940) studied the reaction between alkali (Na_2O or K_2O) carbonates with Al_2O_3. When the mol. ratio of K_2CO_3:Al_2O_3 was 1:1 only $K_2O \cdot Al_2O_3$ was formed on fusion between 900° and 1100°C., and when the ratio was 2:1 or 3:1 the excess K_2O evaporated and only $K_2O \cdot Al_2O_3$ was present. Kato and Yamauchi (1943) prepared several mixtures from K_2CO_3 and Al_2O_3, heated them between 1640° and 1700°C. and obtained "β-Al_2O_3" by treating the product with a 6N solution of HCl.

There is considerable evidence from many investigators that the so-called "β-Al_2O_3" is not a polymorph of Al_2O_3 but a compound of Al_2O_3 with an alkali or alkaline earth oxide. This evidence will be presented later in this paper.

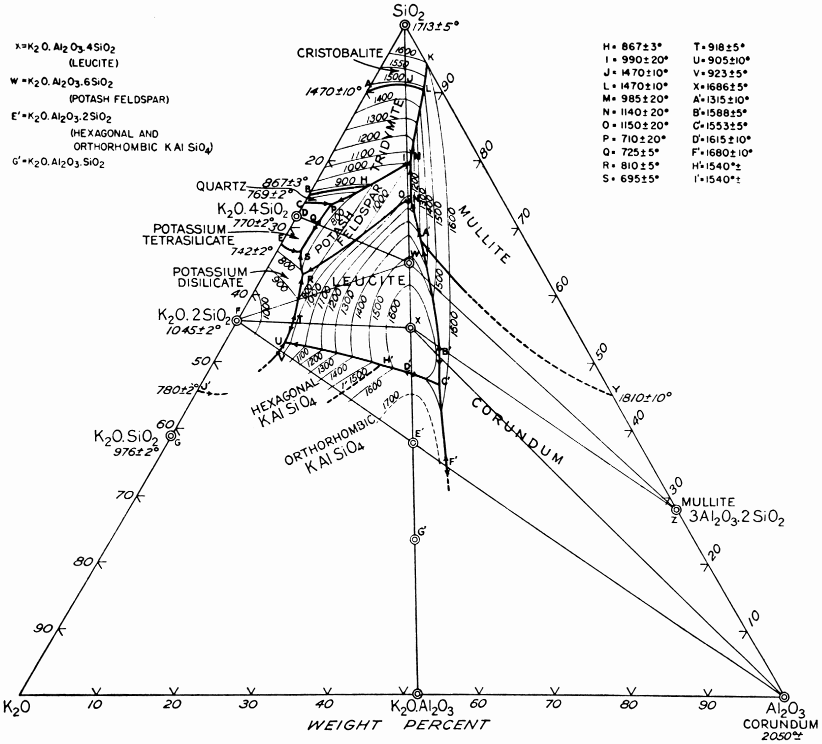

Fig. 4. Equilibrium diagram of the system K_2O—Al_2O_3—SiO_2 with fields of the primary crystalline phases, isotherms and temperatures of binary and ternary invariant points.

QUENCHING DATA AND THE EQUILIBRIUM DIAGRAM FOR K_2O—Al_2O_3—SiO_2

The results of quenching experiments on compositions in this system are given in table 1 and presented graphically in two diagrams (figs. 3 and 4). Metastable solid phases are marked with an asterisk in table 1.

TABLE 1

Results of Quenching Experiments for the Ternary System Potash—Alumina—Silica

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
Points in Cristobalite Field							
1.467	3.0	3.2	93.8	1555	8 hr.	Rare cristobalite in glass	152
				1560	8 hr.	All glass	
1.469	1.0	6.5	92.5	1555	4 hr.	Very rare cristobalite in glass	x7
				1560	4 hr.	All glass	
				1540	4 hr.	Cristobalite and very rare mullite in glass	
1.468	6.9	1.0	92.1	1510	4 hr.	Small amount cristobalite in glass	K1301
				1515	6 hr.	All glass	
1.467	2.0	6.0	92.0	1525	6 hr.	Very rare cristobalite in glass	x2
				1480	40 hr.	Cristobalite in glass	
				1475	17 hr.	Cristobalite and rare mullite in glass	
1.468	6.9	2.0	91.1	1485	2 hr.	Small amount cristobalite in glass	K1302
				1490	2 hr.	All glass	
1.468	3.0	6.0	91.0	1500	5 hr.	Very rare cristobalite in glass	x1
				1505	7 hr.	All glass	
Points in Tridymite Field							
1.468	4.5	4.8	90.7	1455	24 hr.	Rare cristobalite* in glass	154
				1460	24 hr.	All glass	
1.468	6.8	3.0	90.2	1460	12 hr.	Rare tridymite in glass	K1303
				1465	16 hr.	All glass	
1.470	4.0	7.5	88.5	1420	6 days	Rare tridymite in glass	x5
				1425	2 days	All glass	
				1360	3 days	Tridymite in glass	
				1350	4 days	Tridymite and small amount mullite in glass	
1.469	6.6	5.0	88.4	1385	24 hr.	Rare tridymite in glass	K1305
				1390	2 days	All glass	
1.472	9.8	2.0	88.2	1405	24 hr.	Small amount tridymite in glass	K902
				1410	3 hr.	All glass	
1.470	6.0	6.4	87.6	1345	7 days	Very rare cristobalite* in glass	153
				1350	3 days	All glass	
1.470	6.6	6.0	87.4	1345	2 days	Rare tridymite in glass	K1306
				1350	8 hr.	All glass	
1.473	9.6	4.0	86.4	1335	4 hr.	Rare tridymite in glass	K904
				1340	4 hr.	All glass	

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* Metastable solid phase (see text).

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt.%)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.474	11.8	2.0	86.2	1355	4 hr.	Rare tridymite in glass	K2502
				1360	3 hr.	All glass	
1.472	6.4	8.0	85.6	1282	10 days	Very rare cristobalite* in glass	K1308
1.473	7.9	7.0	85.1	1250	7 days	Rare tridymite in glass	K2907
				1255	4 days	All glass	
1.474	9.4	6.0	84.6	1250	3 days	Very rare tridymite in glass	K906
				1255	4 days	All glass	
1.472	6.4	9.0	84.6	1272	10 days	Very rare tridymite in glass	K1309
1.475	11.5	4.0	84.5	1270	5 hr.	Rare tridymite in glass	K2504
				1275	4 hr.	All glass	
1.472	7.5	8.0	84.5	1215	7 days	Rare cristobalite* in glass	167
				1220	4 days	All glass	
1.476	13.7	2.0	84.3	1290	2 hr.	Rare tridymite in glass	K802
				1295	2 hr.	All glass	
1.474	9.3	7.0	83.7	1210	7 days	Rare tridymite in glass	K907
				1215	3 days	All glass	
1.480	15.2	2.0	82.8	1245	3 hr.	Rare tridymite in glass	K1502
				1250	3 hr.	All glass	
1.474	9.2	8.0	82.8	1155	6 days	Rare tridymite in glass	K908
				1160	2 days	All glass	
1.476	11.3	6.0	82.7	1180	18 hr.	Rare tridymite in glass	K2506
				1185	16 hr.	All glass	
1.477	13.4	4.0	82.6	1205	2 days	Rare tridymite in glass	K804
				1210	3 days	All glass	
1.476	11.2	7.0	81.8	1125	7 days	Small amount tridymite in glass	K2507
				1130	7 days	All glass	
1.481	16.7	2.0	81.3	1180	2 days	Rare tridymite in glass	K1202
				1185	4 hr.	All glass	
1.480	14.9	4.0	81.1	1150	2 days	Rare tridymite in glass	K1504
				1155	2 days	All glass	
1.476	11.0	8.0	81.0	1095	2 days	Rare tridymite in glass	K2508
				1100	24 hr.	All glass	
1.477	13.2	6.0	80.8	1105	4 hr.	Rare tridymite in glass	K806
				1110	2 hr.	All glass	
1.476	10.9	9.0	80.1	1045	10 days	Rare tridymite in glass	K2509
				1050	8 days	All glass	
1.481	16.3	4.0	79.7	1080	15 hr.	Very rare tridymite in glass	K1204
				1085	15 hr.	All glass	
1.477	10.9	9.5	79.6	1025	18 days	Very rare tridymite in glass	K2509-1/2
1.480	14.6	6.0	79.4	1040	6 hr.	Very rare tridymite in glass	K1506
				1045	17 hr.	All glass	

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* Metastable solid phase (see text).

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.477	12.9	8.0	79.1	985	7 days	Rare tridymite in glass	K808
				990	7 days	All glass	
1.480	14.4	7.0	78.6	980	7 days	Rare tridymite in glass	K1507
				985	7 days	All glass	
1.478	12.7	9.0	78.3	935	7 days	Rare tridymite in glass	K809
				940	7 days	All glass	
1.482	16.0	6.0	78.0	975	7 days	Rare tridymite in glass	K1206
				980	8 days	All glass	
1.484	20.3	2.0	77.7	1015	24 hr.	Rare tridymite in glass	K702
				1020	24 hr.	All glass	
1.481	14.3	8.0	77.7	935	7 days	Rare tridymite in glass	K1508
				940	7 days	All glass	
1.482	15.8	7.0	77.2	925	7 days	Very rare tridymite in glass	K1207
				930	7 days	All glass	
1.482	15.7	7.5	76.8	900	7 days	Rare tridymite in glass	K1207-1/2
				905	7 days	All glass	
1.486	22.8	1.0	76.2	930	7 days	Rare tridymite in glass	K2601
				935	7 days	All glass	
1.485	19.9	4.0	76.1	880	2 days	Rare tridymite in glass	K704
				885	24 hr.	All glass	
1.487	22.5	2.0	75.5	865	4 days	Rare tridymite in glass	K2602
				870	4 days	All glass	
Points in Quartz Field							
1.486	19.7	5.0	75.3	805	10 days	Very rare tridymite* in glass	K705
				810	14 days	All glass	
1.488	22.3	3.0	74.7	785	14 days	Small amount tridymite* in glass	K2603
				790	14 days	All glass	
1.488	24.7	1.0	74.3	785	14 days	Rare tridymite* in glass	K1101
				790	14 days	All glass	
Points in Potassium Tetrasilicate Field							
1.488	24.5	2.0	73.5	745	7 days	Very rare potassium tetrasilicate in glass	K1102
				750	24 hr.	All glass	
1.492	26.2	1.0	72.8	755	7 days	Rare potassium tetrasilicate in glass	K3101
				760	24 hr.	All glass	
1.488	24.2	3.0	72.8	725	7 days	Small amount potassium tetrasilicate in glass	K1103
				730	7 days	All glass	
1.492	26.0	2.0	72.0	745	7 days	Small amount potassium tetrasilicate in glass	K3102
				750	24 hr.	All glass	

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* Metastable solid phase (see text).

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.492	25.7	3.0	71.3	730	7 days	Rare potassium tetrasilicate in glass	K3103
				735	7 days	All glass	
1.494	27.9	1.0	71.1	755	7 days	Rare potassium tetrasilicate in glass	K601
				760	7 days	All glass	
1.494	27.6	2.0	70.4	745	7 days	Very rare potassium tetrasilicate in glass	K602
				750	7 days	All glass	
1.493	27.3	3.0	69.7	730	21 days	Rare potassium tetrasilicate in glass	K603
				735	21 days	All glass	
1.496	29.7	1.0	69.3	750	7 days	Rare potassium tetrasilicate in glass	K1401
				755	2 days	All glass	
1.496	29.4	2.0	68.6	740	7 days	Very rare potassium tetrasilicate in glass	K1402
				745	2 days	All glass	
1.496	30.7	1.0	68.3	745	7 days	Very rare potassium tetrasilicate in glass	K3501
				750	7 days	All glass	
1.495	29.1	3.0	67.9	715	28 days	Small amount potassium tetrasilicate in glass	K1403
				720	28 days	All glass	
1.496	30.4	2.0	67.6	725	7 days	Small amount potassium tetrasilicate in glass	K3502
				730	7 days	All glass	
1.498	31.7	1.0	67.3	730	7 days	Potassium tetrasilicate and rare potassium disilicate in glass	K1801
				735	21 days	Rare potassium tetrasilicate in glass	
				740	7 days	All glass	
1.496	30.1	3.0	66.9	715	28 days	Rare potassium tetrasilicate in glass	K3503
				720	7 days	All glass	
1.498	31.4	2.0	66.6	710	21 days	Potassium tetrasilicate and very rare potassium disilicate in glass	K1802
				715	14 days	Potassium tetrasilicate in glass	
				720	27 days	Rare potassium tetrasilicate in glass	
				725	7 days	All glass	
Points in Potassium Disilicate Field							
1.498	31.0	3.0	66.0	710	28 days	Lots disilicate and rare tetrasilicate in glass	K1803
				715	28 days	Disilicate in glass	
				720	10 days	Very rare disilicate in glass	
				725	11 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.501	33.7	1.0	65.3	815	4 days	Rare disilicate in glass	K1901
				820	3 hr.	All glass	
1.501	32.0	3.0	65.0	770	21 days	Small amount disilicate in glass	K3403
				775	14 days	All glass	
1.501	33.3	2.0	64.7	815	4 days	Small amount disilicate in glass	K1902
				820	3 days	All glass	
1.501	31.7	4.0	64.3	770	21 days	Small amount disilicate in glass	K3404
				775	14 days	All glass	
1.501	33.0	3.0	64.0	815	4 days	Small amount disilicate in glass	K1903
				820	3 days	All glass	
1.502	35.6	1.0	63.4	900	3 hr.	Very rare disilicate in glass	K501
1.501	32.6	4.0	63.4	815	4 days	Very rare disilicate in glass	K1904
				820	3 days	All glass	
1.502	35.3	2.0	62.7	900	3 hr.	Very rare disilicate in glass	K502
1.501	32.3	5.0	62.7	810	5 days	Very rare disilicate in glass	K1905
				815	4 days	All glass	
1.501	34.9	3.0	62.1	895	3 hr.	Small amount disilicate in glass	K503
				900	3 hr.	All glass	
1.503	37.6	1.0	61.4	950	3 hr.	Rare disilicate in glass	K2101
				955	2 hr.	All glass	
1.501	34.6	4.0	61.4	885	3 hr.	Very rare disilicate in glass	K504
				890	2 hr.	All glass	
1.503	37.2	2.0	60.8	945	3 hr.	Small amount disilicate in glass	K2102
				950	2 hr.	All glass	
1.501	34.2	5.0	60.8	865	3 hr.	Small amount disilicate in glass	K505
				870	2 hr.	All glass	
1.503	36.9	3.0	60.1	935	3 hr.	Small amount disilicate in glass	K2103
				940	3 hr.	All glass	
1.503	36.5	4.0	59.5	935	3 hr.	Very rare disilicate in glass	K2104
1.505	39.6	1.0	59.4	1000	3 hr.	Very rare disilicate in glass	K1601
				1005	2 hr.	All glass	
1.502	36.1	5.0	58.9	925	3 hr.	Small amount disilicate in glass	K2105
				930	2 hr.	All glass	
1.504	39.2	2.0	58.8	990	3 hr.	Small amount disilicate in glass	K1602
				995	2 hr.	All glass	
1.502	35.7	6.0	58.3	910	6 hr.	Small amount disilicate and very rare leucite in glass	K2106
				915	3 hr.	Rare disilicate in glass	
				920	3 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.504	38.8	3.0	58.2	980	3 hr.	Small amount disilicate in glass	K1603
				985	2 hr.	All glass	
1.503	38.4	4.0	57.6	965	3 hr.	Very rare disilicate in glass	K1604
				970	2 hr.	All glass	
1.507	41.6	1.0	57.4	1025	2 hr.	Small amount disilicate in glass	K1701
				1030	2 hr.	All glass	
1.503	38.0	5.0	57.0	945	2 hr.	Moderate amount disilicate in glass	K1605
				950	2 hr.	All glass	
1.506	41.2	2.0	56.8	1010	3 hr.	Moderate amount disilicate in glass	K1702
				1015	3 hr.	All glass	
1.503	37.6	6.0	56.4	935	3 hr.	Moderate amount disilicate in glass	K1606
				940	3 hr.	All glass	
1.505	40.7	3.0	56.3	995	2 hr.	Moderate amount disilicate in glass	K1703
				1000	2 hr.	All glass	
1.503	37.2	7.0	55.8	915	24 hr.	Lots disilicate and leucite with very little glass	K1607
				920	6 days	Moderate amount disilicate in glass	
				925	24 hr.	All glass	
1.505	40.3	4.0	55.7	985	3 hr.	Small amount disilicate in glass	K1704
				990	2 hr.	All glass	
1.505	39.9	5.0	55.1	975	3 hr.	Very rare disilicate in glass	K1705
				980	2 hr.	All glass	
1.508	43.1	2.0	54.9	1015	1 hr.	Moderate amount disilicate in glass	K202
				1020	1 hr.	All glass	
1.505	39.5	6.0	54.5	945	3 hr.	Small amount disilicate in glass	K1706
				950	2 hr.	All glass	
1.504	39.1	7.0	53.9	930	3 hr.	Small amount disilicate in glass	K1707
				935	2 hr.	All glass	
1.507	42.2	4.0	53.8	990	1 hr.	Very rare disilicate in glass	K204
				995	1 hr.	All glass	
1.507	41.4	6.0	52.6	945	2 hr.	Rare disilicate in glass	K206
				950	2 hr.	All glass	
1.507	40.9	7.0	52.1	930	3 hr.	Small amount disilicate in glass	K207
				935	4 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
			Points in Potash Feldspar Field				
1.478	12.7	9.5	77.8	945	14 days	Rare feldspar in glass	K809-1/2
				950	14 days	All glass	
1.478	12.6	10.0	77.4	980	14 days	Very rare feldspar in glass	K810
				985	7 days	All glass	
1.481	14.1	9.0	76.9	935	7 days	Very rare feldspar in glass	K1509
				940	10 days	All glass	
1.478	12.5	11.0	76.5	1010	14 days	Rare feldspar in glass	K811
				1015	10 days	All glass	
1.482	15.6	8.0	76.4	900	7 days	Rare feldspar in glass	K1208
				905	11 days	All glass	
1.481	14.0	10.0	76.0	975	10 days	Rare feldspar in glass	K1510
				980	8 days	All glass	
1.482	15.5	9.0	75.5	935	7 days	Rare feldspar in glass	K1209
				940	10 days	All glass	
1.481	13.8	11.0	75.2	1010	14 days	Rare feldspar in glass	K1511
				1015	10 days	All glass	
1.482	15.3	10.0	74.7	975	10 days	Rare feldspar in glass	K1210
				980	8 days	All glass	
1.487	19.5	6.0	74.5	840	10 days	Rare feldspar in glass	K706
				845	10 days	All glass	
1.481	13.6	12.0	74.4	1050	8 days	Rare feldspar in glass	K1512
				1055	8 days	All glass	
1.482	15.1	11.0	73.9	1010	14 days	Rare feldspar in glass	K1211
				1015	14 days	All glass	
1.481	13.6	12.5	73.9	1065	10 days	Rare feldspar in glass	K1512-1/2
				1070	14 days	All glass	
1.487	19.3	7.0	73.7	875	7 days	Very rare feldspar in glass	K707
				880	10 days	All glass	
1.488	21.8	5.0	73.2	810	14 days	Rare feldspar in glass	K2605
				815	14 days	All glass	
1.482	15.0	12.0	73.0	1045	11 days	Rare feldspar in glass	K1212
				1050	8 days	All glass	
1.487	19.1	8.0	72.9	915	14 days	Rare feldspar in glass	K708
				920	10 days	All glass	
1.488	21.6	6.0	72.4	850	10 days	Rare feldspar in glass	K2606
				855	9 days	All glass	
1.487	18.9	9.0	72.1	955	14 days	Rare feldspar in glass	K709
				960	14 days	All glass	
1.490	24.0	4.0	72.0	770	14 days	Very rare feldspar in glass	K1104
				775	14 days	All glass	
1.488	21.4	7.0	71.6	895	11 days	Very rare feldspar in glass	K2607
				900	7 days	All glass	
1.490	23.7	5.0	71.3	820	14 days	Rare feldspar in glass	K1105
				825	14 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.487	18.7	10.0	71.3	985 990	7 days 7 days	Rare feldspar in glass All glass	K710
1.488	21.2	8.0	70.8	930 935	7 days 7 days	Rare feldspar in glass All glass	K2608
1.492	25.4	4.0	70.6	790 795	21 days 14 days	Rare feldspar in glass All glass	K3104
1.487	18.4	11.0	70.6	1015 1020	10 days 5 days	Rare feldspar in glass All glass	K711
1.496	23.5	6.0	70.5	870 875	7 days 7 days	Rare feldspar in glass All glass	K1106
1.488	20.9	9.0	70.1	965 970	7 days 7 days	Rare feldspar in glass All glass	K2609
1.491	23.2	7.0	69.8	900 905	7 days 11 days	Rare feldspar in glass All glass	K1107
1.488	20.7	10.0	69.3	990 995	7 days 10 days	Rare feldspar in glass All glass	K2610
1.493	27.0	4.0	69.0	790 795	21 days 14 days	Rare feldspar in glass All glass	K604
1.491	23.0	8.0	69.0	940 945	10 days 11 days	Very rare feldspar in glass All glass	K1108
1.491	22.7	9.0	68.3	965 970	7 days 7 days	Rare feldspar in glass All glass	K1109
1.493	26.8	5.0	68.2	835 840	7 days 7 days	Very rare feldspar in glass All glass	K605
1.493	26.5	6.0	67.5	875 880	7 days 2 days	Very rare feldspar in glass All glass	K606
495	28.8	4.0	67.2	790 795	21 days 14 days	Rare feldspar in glass All glass	K1404
493	26.2	7.0	66.8	905 910	11 days 7 days	Rare feldspar in glass All glass	K607
496	29.9	3.5	66.6	690 695 715 720	14 days 21 days 28 days 27 days	Only a little glass present Lots feldspar, small amount potassium tetrasilicate and very rare potassium disilicate in glass Rare feldspar in glass All glass	K3503-1/2
1.494	28.5	5.0	66.5	840 845	10 days 14 days	Rare feldspar in glass All glass	K1405
1.496	29.8	4.0	66.2	790 795	26 days 21 days	Rare feldspar in glass All glass	K3504
1.493	25.9	8.0	66.1	935 940	10 days 2 days	Very rare feldspar in glass All glass	K608
1.493	28.2	6.0	65.8	875 880	7 days 7 days	Rare feldspar in glass All glass	K1406

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.497	29.4	5.0	65.6	835	21 days	Rare feldspar in glass	K3505
				840	10 days	All glass	
1.498	30.7	4.0	65.3	790	26 days	Rare feldspar in glass	K1804
				795	21 days	All glass	
1.493	27.9	7.0	65.1	905	11 days	Rare feldspar in glass	K1407
				910	7 days	All glass	
1.498	30.6	4.5	64.9	810	14 days	Rare feldspar in glass	K1804-1/2
				815	14 days	All glass	
1.498	29.1	6.0	64.9	875	7 days	Rare feldspar in glass	K3506
				880	10 days	All glass	
1.498	30.4	5.0	64.6	825	14 days	Rare feldspar in glass	K1805
				830	10 days	All glass	
1.499	30.2	5.5	64.3	845	10 days	Rare feldspar in glass	K1805-1/2
				850	10 days	All glass	
1.498	31.5	4.5	64.0	785	7 days	Feldspar and very rare sodium disilicate in glass	K3404-1/2
				790	14 days	Feldspar in glass	
				805	14 days	Very rare feldspar in glass	
				810	14 days	All glass	
1.498	31.3	5.0	63.7	815	14 days	Small amount feldspar in glass	K3405
				820	7 days	All glass	
1.500	31.2	5.5	63.3	830	10 days	Rare feldspar in glass	K3405-1/2
				835	11 days	All glass	
				Points in Leucite Field			
1.481	13.5	13.0	73.5	1120	21 days	Leucite and rare potash feldspar in glass	K1513
				1125	28 days	Leucite in glass	
				1140	28 days	Small amount leucite in glass	
				1145	14 days	All glass	
1.482	13.4	13.5	73.1	1195	10 days	Very rare leucite in glass	K1513-1/2
1.482	14.9	12.5	72.6	1060	14 days	Leucite and rare potash feldspar in glass	K1212-1/2
				1065	10 days	Leucite in glass	
				1085	9 days	Rare leucite in glass	
				1090	10 days	All glass	
1.482	14.8	13.0	72.2	1155	2 days	Rare leucite in glass	K1213
				1160	2 days	All glass	
1.481	13.4	14.5	72.1	1245	14 days	Very rare leucite in glass	133
1.482	14.6	14.0	71.4	1270	4 days	Very rare leucite in glass	K1214
1.482	13.0	16.0	71.0	1200	10 days	Small amount leucite in glass	K1516
				1205	11 days	All glass	
1.483	14.4	15.0	70.6	1340	4 days	Rare leucite in glass	K1215
				1345	4 days	All glass	
1.482	14.2	15.3	70.5	1320	4 days	Rare leucite in glass	175
				1325	7 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.487	18.3	11.5	70.2	1065	7 days	Rare leucite in glass	K711-1/2
				1070	7 days	All glass	
1.487	18.2	12.0	69.8	1120	24 hr.	Rare leucite in glass	K712
				1125	10 hr.	All glass	
1.481	14.9	16.1	69.0	1390	2 days	Rare leucite in glass	121
				1395	2 days	All glass	
1.482	14.1	17.0	68.9	1345	4 days	Rare leucite in glass	K1217
				1350	4 days	All glass	
1.488	20.5	11.0	68.5	1055	6 days	Small amount leucite in glass	K2611
				1060	6 days	All glass	
1.487	17.8	14.0	68.2	1320	3 hr.	Rare leucite in glass	K714
				1325	3 hr.	All glass	
1.482	13.9	18.0	68.1	1330	3 days	Small amount leucite in glass	K1218
				1335	3 days	All glass	
1.488	20.2	12.0	67.8	1160	3 days	Rare leucite in glass	K2612
				1165	3 days	All glass	
1.492	22.5	10.0	67.5	1055	4 hr.	Rare leucite in glass	K1110
				1060	7 hr.	All glass	
1.484	15.6	16.9	67.5	1450	2 days	Very rare leucite in glass	176
				1455	2 days	All glass	
1.493	24.1	9.0	66.9	960	7 days	Potash feldspar and rare leucite in glass	K3109
				970	7 days	Moderate amount leucite in glass	
				980	7 days	Rare leucite in glass	
				985	7 days	All glass	
1.492	22.2	11.0	66.8	1150	4 hr.	Rare leucite in glass	K1111
				1155	5 hr.	All glass	
1.486	17.4	16.0	66.6	1460	3 hr.	Very rare leucite in glass	K716
1.488	19.8	14.0	66.2	1305	4 hr.	Rare leucite in glass	K2614
				1310	4 hr.	All glass	
1.493	25.6	9.0	65.4	1015	10 days	Small amount leucite in glass	K609
				1010	7 days	All glass	
1.492	21.7	13.0	65.3	1275	2 hr.	Rare leucite in glass	K1113
				1280	2 hr.	All glass	
1.487	16.9	18.3	64.8	1530	8 hr.	Rare leucite in glass	Potash feldspar comp'n
				1535	8 hr.	All glass	
1.488	19.3	16.0	64.7	1455	3 hr.	Rare leucite in glass	K2616
				1460	3 hr.	All glass	
1.493	25.4	10.0	64.6	1155	18 hr.	Very rare leucite in glass	K610
				1160	17 hr.	All glass	
1.493	27.6	8.0	64.4	975	2 days	Rare leucite in glass	K1408
				980	2 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.498	28.8	7.0	64.2	895	11 days	Lots feldspar in glass	K3507
				900	7 days	Rare leucite in glass	
				905	7 days	All glass	
1.492	21.2	15.0	63.8	1405	2 hr.	Very rare leucite in glass	K1115
				1410	3 hr.	All glass	
1.493	27.3	9.0	63.7	1075	2 hr.	Rare leucite in glass	K1409
				1080	2 hr.	All glass	
1.498	29.9	6.5	63.6	885	10 days	Rare leucite in glass	K1806-1/2
				890	10 days	All glass	
1.489	16.6	20.0	63.4	1540	8 hr.	Very rare leucite in glass	K720
1.498	29.8	7.0	63.2	950	24 hr.	Rare leucite in glass	K1807
				955	2 days	All glass	
1.494	24.8	12.0	63.2	1290	2 hr.	Very rare leucite in glass	K612
				1295	2 hr.	All glass	
1.488	18.9	18.0	63.1	1570	1-1/2 hr.	Rare leucite in glass	K2618
				1575	1 hr.	All glass	
1.498	31.0	6.0	63.0	855	7 days	Rare leucite in glass	K3406
				860	6 days	All glass	
1.493	27.0	10.0	63.0	1165	24 hr.	Very rare leucite in glass	K1410
1.488	17.9	19.3	62.8	1570	7 hr.	Rare leucite in glass	177
				1575	7 hr.	All glass	
1.498	29.4	8.0	62.6	1035	2 days	Rare leucite in glass	K1808
				1040	24 hr.	All glass	
1.500	32.1	5.5	62.4	805	14 days	Lots feldspar, small amount leucite and rare disilicate in glass	K1905-1/2
				810	14 days	Lots leucite, lots feldspar and very rare disilicate in glass	
				830	10 days	Small amount leucite in glass	
				835	10 days	All glass	
1.495	26.7	11.0	62.3	1235	24 hr.	Rare leucite in glass	K1411
				1240	24 hr.	All glass	
1.492	20.7	17.0	62.3	1520	1-1/2 hr.	Rare leucite in glass	K1117
				1525	1-1/2 hr.	All glass	
1.499	32.0	6.0	62.0	880	7 days	Small amount leucite in glass	K1906
				885	7 days	All glass	
1.497	29.1	9.0	61.9	1130	5 hr.	Rare leucite in glass	K1809
				1135	5 hr.	All glass	
1.494	24.2	14.0	61.8	1385	2 hr.	Rare leucite in glass	K614
				1390	2 hr.	All glass	
1.492	16.2	22.0	61.8	1460	3 days	Rare leucite in glass	K722
				1463	3 days	All glass	
1.490	18.4	20.0	61.6	1594	7 hr.	Rare leucite in glass	K2620
				1599	7 hr.	All glass	
1.498	31.6	7.0	61.4	985	24 hr.	Very rare leucite in glass	K1907

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.492	20.2	19.0	60.8	1610	1 hr.	Rare leucite in glass	K1119
				1615	1 hr.	All glass	
1.498	31.3	8.0	60.7	1080	3 hr.	Rare leucite in glass	K1908
				1085	3 hr.	All glass	
1.497	28.5	11.0	60.5	1250	3 hr.	Rare leucite in glass	K1811
				1255	2 hr.	All glass	
1.494	23.7	16.0	60.3	1480	2 hr.	Rare leucite in glass	K616
				1485	1 hr.	All glass	
1.501	33.8	6.0	60.2	885	3 hr.	Very rare leucite in glass	K506
1.495	25.8	14.0	60.2	1380	2 hr.	Rare leucite in glass	K1414
				1385	2 hr.	All glass	
1.498	30.9	9.0	60.1	1150	3 hr.	Rare leucite in glass	K1909
				1155	3 hr.	All glass	
1.500	33.5	7.0	59.5	990	3 hr.	Rare leucite in glass	K507
				995	3 hr.	All glass	
1.493	17.7	23.0	59.3	1545	3 days	Small amount leucite in glass	K2623
				1550	3 days	All glass	
1.497	27.8	13.0	59.2	1340	2 hr.	Very rare leucite in glass	K1813
1.500	33.1	8.0	58.9	1055	3 hr.	Rare leucite in glass	K508
				1060	3 hr.	All glass	
1.494	23.1	18.0	58.9	1570	2 hr.	Small amount leucite in glass	K618
				1575	2 hr.	All glass	
1.498	30.3	11.0	58.7	1250	3 hr.	Rare leucite in glass	K1911
				1255	2 hr.	All glass	
1.496	24.9	17.0	58.1	1515	1 hr.	Rare leucite in glass	K1417
				1520	1 hr.	All glass	
1.497	27.2	15.0	57.8	1430	2 hr.	Rare leucite in glass	K1815
				1435	2 hr.	All glass	
1.495	17.2	25.0	57.8	1530	4 days	Rare leucite in glass	K2625
				1535	4 days	All glass	
1.502	35.3	7.0	57.7	970	4 hr.	Rare leucite in glass	K2107
				975	5 hr.	All glass	
1.500	32.4	10.0	57.6	1180	3 hr.	Very rare leucite in glass	K510
1.494	22.5	20.0	57.5	1640	1/2 hr.	Small amount leucite in glass	K620
				1645	1/2 hr.	All glass	
1.498	29.6	13.0	57.4	1340	2 hr.	Very rare leucite in glass	K1913
1.502	35.0	8.0	57.0	1055	3 hr.	Rare leucite in glass	K2108
				1060	3 hr.	All glass	
1.502	34.6	9.0	56.4	1105	3 hr.	Rare leucite in glass	K2109
				1110	3 hr.	All glass	
1.497	26.6	17.0	56.4	1515	1 hr.	Very rare leucite in glass	K1817
				1520	1 hr.	All glass	
1.500	31.7	12.0	56.3	1260	3 hr.	Very rare leucite in glass	K512
				1265	3 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.498	28.9	15.0	56.1	1405	2 hr.	Rare leucite in glass	K1915
				1410	2 hr.	All glass	
1.496	24.0	20.0	56.0	1620	1 hr.	Small amount leucite in glass	K1420
				1625	1 hr.	All glass	
1.497	18.5	26.0	55.5	1560	7 hr.	Small amount leucite in glass	K1126
				1565	7 hr.	All glass	
1.503	36.8	8.0	55.2	990	3 hr.	Very rare leucite in glass	K1608
1.502	33.8	11.0	55.2	1180	2 hr.	Very rare leucite in glass	K2111
1.497	25.9	19.0	55.1	1575	1 hr.	Rare leucite in glass	K1819
				1580	1 hr.	All glass	
1.500	31.0	14.0	55.0	1330	2 hr.	Rare leucite in glass	K514
				1335	2 hr.	All glass	
1.498	28.2	17.0	54.8	1465	2 hr.	Rare leucite in glass	K1917
				1470	2 hr.	All glass	
1.503	36.4	9.0	54.6	1045	3 hr.	Rare leucite in glass	K1609
				1050	3 hr.	All glass	
1.504	36.0	10.0	54.0	1080	3 hr.	Rare leucite in glass	K1610
				1085	3 hr.	All glass	
1.502	33.1	13.0	53.9	1245	2 hr.	Rare leucite in glass	K2113
				1250	2 hr.	All glass	
1.500	30.2	16.0	53.8	1390	2 hr.	Rare leucite in glass	K516
				1395	2 hr.	All glass	
1.497	25.3	21.0	53.7	1625	3/4 hr.	Rare leucite in glass	K1821
				1630	3/4 hr.	All glass	
1.498	27.5	19.0	53.5	1525	1 hr.	Rare leucite in glass	K1919
				1530	1 hr.	All glass	
1.504	38.6	8.0	53.4	965	2 hr.	Very rare leucite in glass	K1708
				970	2 hr.	All glass	
1.503	35.6	11.0	53.4	1120	3 hr.	Rare leucite in glass	K1611
				1125	3 hr.	All glass	
1.504	38.2	9.0	52.8	1025	3 hr.	Very rare leucite in glass	K1709
				1030	3 hr.	All glass	
1.502	32.3	15.0	52.7	1300	2 hr.	Rare leucite in glass	K2115
				1305	2 hr.	All glass	
1.500	29.5	18.0	52.5	1445	2 hr.	Rare leucite in glass	K518
				1450	2 hr.	All glass	
1.502	31.9	16.0	52.1	1335	2 hr.	Rare leucite in glass	K2116
				1340	1 hr.	All glass	
1.499	26.9	21.0	52.1	1580	1 hr.	Rare leucite in glass	K1921
				1585	1 hr.	All glass	
1.500	20.3	28.0	51.7	1615	4 hr.	Very rare leucite in glass	K628
1.503	34.4	14.0	51.6	1255	3 hr.	Rare leucite in glass	K1614
				1260	3 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.502	31.5	17.0	51.5	1355	3 hr.	Rare leucite in glass	K2117
				1360	2 hr.	All glass	
1.501	28.8	20.0	51.2	1485	1 hr.	Rare leucite in glass	K520
				1490	1 hr.	All glass	
1.502	20.0	29.0	51.0	1585	7 hr.	Leucite and corundum with very little glass	K629
				1590	7 hr.	Rare leucite in glass	
				1594	7 hr.	All glass	
1.502	31.2	18.0	50.8	1390	2 hr.	Rare leucite in glass	K2118
				1395	2 hr.	All glass	
1.500	26.2	23.0	50.8	1630	1 hr.	Very rare leucite in glass	K1923
				1635	1 hr.	All glass	
1.502	28.1	22.0	49.9	1545	2 hr.	Rare leucite in glass	K522
				1550	1 hr.	All glass	
1.502	21.3	29.0	49.7	1611	8 hr.	Very rare leucite in glass	K1429
				1615	8 hr.	All glass	
1.501	25.5	25.0	49.5	1635	3/4 hr.	Very rare leucite in glass	K1925
				1640	3/4 hr.	All glass	
1.503	21.1	29.5	49.4	1594	7 hr.	Rare leucite in glass	K1429-1/2
				1600	6 hr.	All glass	
1.503	21.0	30.0	49.0	1570	8 hr.	Small amount leucite and rare corundum in glass	K1430
				1575	8 hr.	Rare leucite in glass	
				1580	8 hr.	Very rare leucite in glass	
				1585	8 hr.	All glass	
1.503	22.7	29.0	48.3	1615	8 hr.	Very rare leucite in glass	K1829
				1620	1 hr.	All glass	
1.503	22.4	30.0	47.6	1590	7 hr.	Rare leucite in glass	K1830
				1595	8 hr.	All glass	
1.504	22.1	31.0	46.9	1550	24 hr.	Almost all crystalline	K1831
				1555	24 hr.	Lots leucite, moderate amount corundum, rare corroded orthorhombic $KAlSiO_4$ with a little glass	
				1560	24 hr.	Small amount leucite and very rare corundum in glass	
				1565	24 hr.	Rare leucite in glass	
				1570	24 hr.	All glass	
Points in Corundum Field							
1.488	13.4	21.0	65.6	1465	7 days	Rare corundum and rare mullite in glass	K1221
				1470	7 days	Rare corundum in glass	
				1475	5 days	Rare corundum in glass	
				1480	4 days	All glass	
1.489	13.3	22.0	64.7	1495	3 days	Rare corundum and very rare mullite in glass	K1222
				1500	3 days	Rare corundum in glass	
				1505	3 days	Rare corundum in glass	
				1510	3 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.491	13.1	23.0	63.9	1525	3 days	Small amount corundum and rare mullite in glass	K1223
				1530	3 days	Rare corundum in glass	
				1535	4 days	Rare corundum in glass	
				1540	4 days	All glass	
1.493	12.9	24.0	63.1	1555	4 days	Small amount corundum and very rare mullite in glass	K1224
				1565	4 days	Rare corundum in glass	
				1570	3 days	All glass	
1.495	12.7	25.0	62.3	1596	8 hr.	Very rare corundum in glass	K1225
				1601	8 hr.	All glass	
1.493	16.0	23.0	61.0	1460	4 days	Rare corundum and rare leucite in glass	K723
				1465	4 days	Rare corundum in glass	
				1470	6 days	Rare corundum in glass	
				1475	5 days	All glass	
1.494	15.8	24.0	60.2	1505	3 days	Very rare corundum in glass	K724
				1510	3 days	All glass	
1.496	15.3	26.0	58.7	1570	3 days	Rare corundum in glass	K726
				1575	3 days	All glass	
1.499	14.9	28.0	57.1	1625	8 hr.	Rare corundum in glass	K728
				1632	7 hr.	All glass	
1.497	17.0	26.0	57.0	1530	4 days	Rare corundum in glass	K2626
				1535	4 days	All glass	
1.497	16.8	27.0	56.2	1570	3 days	Rare corundum in glass	K2627
				1575	24 hr.	All glass	
1.498	16.6	28.0	55.4	1596	8 hr.	Rare corundum in glass	K2628
				1601	8 hr.	All glass	
1.499	16.3	29.0	54.7	1625	1 hr.	Rare corundum in glass	K2629
				1630	1 hr.	All glass	
1.500	18.0	28.0	54.0	1550	3 days	Rare corundum and very rare leucite in glass	K1128
				1565	3 days	Rare corundum in glass	
				1570	3 days	Rare corundum in glass	
				1575	24 hr.	All glass	
1.501	17.7	29.0	53.3	1588	8 hr.	Rare corundum in glass	K1129
				1595	8 hr.	All glass	
1.502	17.5	30.0	52.5	1625	8 hr.	Rare corundum in glass	K1130
				1632	7 hr.	All glass	
1.502	19.9	29.5	50.6	1585	7 hr.	Lots leucite and corundum with very little glass	K629-1/2
				1590	7 hr.	Very rare corundum in glass	
				1594	7 hr.	All glass	
1.503	19.7	30.0	50.3	1596	7 hr.	Very rare corundum in glass	K630
				1602	7 hr.	All glass	
1.503	19.4	31.0	49.6	1605	8 hr.	Rare corundum in glass	K631
				1612	6 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.504	20.7	31.0	48.3	1570	8 hr.	Small amount corundum and rare leucite in glass	K1431
				1575	8 hr.	Small amount corundum in glass	
				1586	8 hr.	Rare corundum in glass	
				1590	8 hr.	All glass	
1.504	20.4	32.0	47.6	1607	8 hr.	Rare corundum in glass	K1432
				1611	8 hr.	All glass	
1.505	21.8	32.0	46.2	1550	24 hr.	Almost all crystalline	K1832
				1555	24 hr.	Lots corundum, lots leucite and corroded crystals orthorhombic $KAlSiO_4$ with a little glass	
				1560	24 hr.	Small amount corundum and very rare leucite in glass	
				1575	24 hr.	Very rare corundum in glass	
				1580	6 hr.	All glass	
1.506	21.4	33.0	45.6	1596	8 hr.	Small amount corundum in glass	K1833
				1600	7 hr.	All glass	
1.507	21.1	34.0	44.9	1624	7 hr.	Very rare corundum in glass	K1834
1.507	22.8	33.0	44.2	1570	8 hr.	Rare corundum and very rare orthorhombic $KAlSiO_4$ in glass	K1933
				1575	7 hr.	Rare corundum in glass	
				1580	8 hr.	All glass	
1.509	20.8	35.0	44.2	1650	3/4 hr.	Rare corundum in glass	K1835
				1655	3/4 hr.	All glass	
1.509	22.4	34.0	43.6	1600	1 hr.	Rare corundum in glass	K1934
				1605	1 hr.	All glass	
1.510	23.8	34.0	42.2	1595	8 hr.	Rare corundum and very rare orthorhombic $KAlSiO_4$ in glass	K534
				1605	8 hr.	Very rare corundum in glass	
				1613	8 hr.	All glass	
1.511	23.4	35.0	41.6	1621	8 hr.	Very rare corundum in glass	K535
(no index determined)	26.8	39.0	34.2	1670	1 hr.	Corundum and orthorhombic $KAlSiO_4$ (all crystalline)	K239
				1675	1 hr.	Corundum and orthorhombic $KAlSiO_4$ in glass	
				1680	1/2 hr.	Corundum in glass	
				1685	2 hr.	Small amount corundum in glass	
				1693	1 hr.	All glass	
Points in Mullite Field							
1.472	6.3	9.5	84.2	1310	10 days	Small amount mullite in glass	K1309-1/2
				1315	10 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.473	6.3	10.0	83.7	1335	6 days	Rare mullite in glass	K1310
				1340	7 days	All glass	
1.474	6.2	11.0	82.8	1405	7 days	Rare mullite in glass	K1311
				1410	7 days	All glass	
1.473	7.6	10.0	82.4	1205	14 days	Very rare mullite in glass	K2910
				1210	14 days	All glass	
1.474	7.6	10.5	81.9	1270	14 days	Very rare mullite in glass	K2910-1/2
				1275	14 days	All glass	
1.475	6.2	12.0	81.8	1460	4 days	Rare mullite in glass	K1312
				1465	24 hr.	All glass	
1.477	6.1	13.0	80.9	1500	3 days	Rare mullite in glass	K1313
				1505	3 days	All glass	
1.478	6.0	14.0	80.0	1530	3 days	Small amount mullite in glass	K1314
				1535	4 days	All glass	
1.476	8.8	11.5	79.7	1215	14 days	Rare mullite in glass	K911-1/2
				1220	14 days	All glass	
1.477	8.8	12.0	79.2	1255	10 days	Very rare mullite in glass	K912
				1260	10 days	All glass	
1.479	5.9	15.0	79.1	1560	8 hr.	Rare mullite in glass	K1315
				1565	2 hr.	All glass	
1.478	8.7	13.0	78.3	1340	7 days	Very rare mullite in glass	K913
				1345	7 hr.	All glass	
1.481	5.9	16.0	78.1	1580	3 hr.	Rare mullite in glass	K1316
				1585	1 hr.	All glass	
1.478	8.6	14.0	77.4	1430	2 days	Very rare mullite in glass	K914
				1435	3 hr.	All glass	
1.478	10.4	13.0	76.6	1185	14 days	Rare mullite in glass	K2513
				1190	14 days	All glass	
1.478	10.4	13.5	76.1	1250	14 days	Very rare mullite in glass	K2513-1/2
				1255	14 days	All glass	
1.479	10.3	14.0	75.7	1290	3 days	Very rare mullite in glass	K2514
				1295	7 days	All glass	
1.482	8.4	16.0	75.6	1500	3 days	Small amount mullite in glass	K916
				1505	3 hr.	All glass	
1.480	10.2	15.0	74.8	1365	7 days	Rare mullite in glass	K2515
				1370	7 days	All glass	
1.481	10.1	16.0	73.9	1435	6 days	Very rare mullite in glass	K2516
				1440	7 days	All glass	
1.484	8.2	18.0	73.8	1560	8 hr.	Small amount mullite in glass	K918
				1565	8 hr.	All glass	
1.481	11.9	15.0	73.1	1220	14 days	Rare mullite in glass	K815
				1225	14 days	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.482	10.0	17.0	73.0	1475	5 days	Rare mullite in glass	K2517
				1480	4 days	All glass	
1.482	11.8	16.0	72.2	1310	4 days	Very rare mullite in glass	K816
				1315	4 days	All glass	
1.484	9.8	18.0	72.2	1510	3 days	Very rare mullite in glass	K2518
				1515	3 days	All glass	
1.485	8.0	20.0	72.0	1610	1 hr.	Very rare mullite in glass	K920
				1615	1 hr.	All glass	
1.483	11.6	17.0	71.4	1380	2 days	Rare mullite in glass	K817
				1385	3 days	All glass	
1.486	9.7	19.0	71.3	1540	3 days	Rare mullite in glass	K2519
				1545	3 days	All glass	
1.483	12.9	16.5	70.6	1250	14 days	Rare mullite in glass	K1516-1/2
				1255	10 days	All glass	
1.484	11.5	18.0	70.5	1435	6 days	Rare mullite in glass	K818
				1440	7 days	All glass	
1.486	9.6	20.0	70.4	1570	7 hr.	Rare mullite in glass	K2520
				1575	7 hr.	All glass	
1.483	12.9	17.0	70.1	1295	7 days	Very rare mullite in glass	K1517
				1300	2 days	All glass	
1.487	9.5	21.0	69.5	1596	8 hr.	Rare mullite in glass	K2521
				1600	1 hr.	All glass	
1.484	12.7	18.0	69.3	1365	7 days	Very rare mullite in glass	K1518
				1370	6 days	All glass	
1.486	11.2	20.0	68.8	1520	4 days	Rare mullite in glass	K820
				1525	3 days	All glass	
1.485	12.6	19.0	68.4	1420	24 hr.	Rare mullite in glass	K1519
				1425	2 days	All glass	
1.487	12.4	20.0	67.6	1470	6 days	Rare mullite in glass	K1520
				1475	2 hr.	All glass	
1.490	10.9	22.0	67.1	1584	3 days	Rare mullite in glass	K822
				1588	8 hr.	All glass	
1.488	12.2	21.0	66.8	1505	3 days	Rare mullite in glass	K1521
				1510	2 hr.	All glass	
1.489	12.1	22.0	65.9	1535	8 hr.	Rare mullite in glass	K1522
				1540	8 hr.	All glass	
1.491	11.9	23.0	65.1	1575	3 days	Rare mullite in glass	K1523
				1580	8 hr.	All glass	
1.493	11.8	24.0	64.2	1596	8 hr.	Small amount mullite in glass	K1524
				1603	8 hr.	All glass	
1.495	11.6	25.0	63.4	1617	8 hr.	Rare mullite in glass	K1525
				1620	1 hr.	All glass	

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
			Points in Hexagonal $KAlSiO_4$ Field				
1.504	37.8	10.0	52.2	1075	3 hr.	Very rare $KAlSiO_4$ in glass	K1710
1.504	37.4	11.0	51.6	1140	3 hr.	Rare $KAlSiO_4$ in glass	K1711
				1145	4 hr.	All glass	
1.507	40.5	8.0	51.5	915	24 hr.	$KAlSiO_4$ and disilicate with a little glass	K208
				920	24 hr.	$KAlSiO_4$ and rare disilicate in glass	
				925	24 hr.	$KAlSiO_4$ in glass	
				935	16 hr.	Rare $KAlSiO_4$ in glass	
				940	17 hr.	All glass	
1.505	37.0	12.0	51.0	1195	3 hr.	Very rare $KAlSiO_4$ in glass	K1712
1.503	34.0	15.0	51.0	1270	3 hr.	Moderate amount $KAlSiO_4$ and small amount leucite in glass	K1615
				1275	3 hr.	Rare $KAlSiO_4$ in glass	
				1280	3 hr.	All glass	
1.505	36.5	13.0	50.5	1245	3 hr.	Very rare $KAlSiO_4$ in glass	K1713
1.507	39.6	10.0	50.4	1090	4 hr.	Small amount $KAlSiO_4$ in glass	K210
				1095	3 hr.	All glass	
1.503	33.6	16.0	50.4	1340	2 hr.	Rare $KAlSiO_4$ in glass	K1616
				1345	2 hr.	All glass	
1.502	30.8	19.0	50.2	1430	2 hr.	Rare $KAlSiO_4$ in glass	K2119
				1435	2 hr.	All glass	
1.505	36.1	14.0	49.9	1295	3 hr.	Small amount $KAlSiO_4$ in glass	K1714
				1300	2 hr.	All glass	
1.504	33.2	17.0	49.8	1390	3 hr.	Rare $KAlSiO_4$ in glass	K1617
				1395	3 hr.	All glass	
1.507	38.7	12.0	49.3	1195	3 hr.	Very rare $KAlSiO_4$ in glass	K212
				1200	3 hr.	All glass	
1.506	35.7	15.0	49.3	1345	2 hr.	Small amount $KAlSiO_4$ in glass	K1715
				1350	2 hr.	All glass	
1.504	32.8	18.0	49.2	1445	2 hr.	Very rare $KAlSiO_4$ in glass	K1618
				1450	2 hr.	All glass	
1.502	30.0	21.0	49.0	1525	1 hr.	Rare $KAlSiO_4$ in glass	K2121
				1530	1 hr.	All glass	
1.507	37.8	14.0	48.2	1325	2 hr.	Small amount $KAlSiO_4$ in glass	K214
				1330	2 hr.	All glass	
1.506	34.9	17.0	48.1	1435	2 hr.	Rare $KAlSiO_4$ in glass	K1717
				1440	1 hr.	All glass	
1.504	32.0	20.0	48.0	1530	1 hr.	Very rare $KAlSiO_4$ in glass	K1620
1.507	37.0	16.0	47.0	1430	1 hr.	Very rare $KAlSiO_4$ in glass	K216

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.506	34.0	19.0	47.0	1520	1 hr.	Rare $KAlSiO_4$ in glass	K1719
				1525	1 hr.	All glass	
1.507	36.1	18.0	45.9	1505	1 hr.	Rare $KAlSiO_4$ in glass	K218
				1510	1 hr.	All glass	
						Points in Field of Orthorhombic $KAlSiO_4$	
1.503	27.4	24.0	48.6	1610	1 hr.	Small amount $KAlSiO_4$ in glass	K524
				1615	1 hr.	All glass	
1.503	29.3	23.0	47.7	1600	1 hr.	Rare $KAlSiO_4$ in glass	K2123
				1605	1 hr.	All glass	
1.502	24.5	28.0	47.5	1630	1 hr.	Rare $KAlSiO_4$ in glass	K1928
				1635	3/4 hr.	All glass	
1.503	24.1	29.0	46.9	1625	1 hr.	Rare $KAlSiO_4$ in glass	K1929
				1630	1 hr.	All glass	
1.505	31.2	22.0	46.8	1590	1 hr.	Rare $KAlSiO_4$ in glass	K1622
				1595	1 hr.	All glass	
1.504	23.8	30.0	46.2	1620	3/4 hr.	Rare $KAlSiO_4$ in glass	K1930
				1625	3/4 hr.	All glass	
1.506	33.2	21.0	45.8	1590	1 hr.	Rare $KAlSiO_4$ in glass	K1721
				1595	1 hr.	All glass	
1.505	23.5	31.0	45.5	1615	3/4 hr.	Very rare $KAlSiO_4$ in glass	K1931
1.506	23.1	32.0	44.9	1595	1 hr.	Rare $KAlSiO_4$ in glass	K1932
				1600	1 hr.	All glass	
1.508	35.2	20.0	44.8	1570	1 hr.	Small amount $KAlSiO_4$ in glass	K220
				1575	1 hr.	All glass	
1.509	34.3	22.0	43.7	1620	1 hr.	Very rare $KAlSiO_4$ in glass	K222
1.509	24.1	33.0	42.9	1625	1 hr.	Very rare $KAlSiO_4$ in glass	K533
1.509	33.0	25.0	42.0	1670	1 hr.	Rare $KAlSiO_4$ in glass	K225
				1680	1 hr.	All glass	
(not determined)	27.7	37.0	35.3	1670	1 hr.	$KAlSiO_4$ and corundum (all crystalline)	K237
				1680	2 hr.	$KAlSiO_4$ in glass	
				1695	2 hr.	Small amount $KAlSiO_4$ in glass	
				1710	2 hr.	All glass	
						Points on or very near Boundary Curves	
1.470	3.5	8.0	88.5	1435	6 days	Rare tridymite and rare mullite in glass	x6
				1440	7 days	All glass	
1.481	14.2	8.5	77.3	915	14 days	Very rare tridymite and very rare potash feldspar in glass	K1508-1/2
1.488	22.1	4.0	73.9	720	14 days	Very rare potassium tetrasilicate, rare tridymite and rare orthoclase in glass	K2604
				740	14 days	Very rare tridymite* and very rare potash feldspar in glass	
				745	14 days	All glass	

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* Metastable solid phase (see text).

TABLE 1 (Continued)

Refractive index of glass ±0.003	Composition (wt. %)			Temp. (°C.)	Time	Phases	Preparation No.
	K_2O	Al_2O_3	SiO_2				
1.485	13.9	18.5	67.6	1310	10 days	Moderate amount leucite and moderate amount mullite in glass	K1218-1/2
				1315	10 days	Very rare leucite, small amount mullite, and rare corundum in glass	
				1320	10 days	Very rare corundum in glass	
1.487	13.8	19.0	67.2	1375	7 days	Rare mullite and rare corundum in glass	K1219
				1380	7 days	Very rare mullite and very rare corundum in glass	
1.488	13.6	20.0	66.4	1430	7 days	Rare mullite and rare corundum in glass	K1220
				1435	6 days	Very rare mullite and very rare corundum in glass	
				1440	7 days	All glass	
1.487	13.5	20.5	66.0	1445	6 days	Rare mullite and rare corundum in glass	K1220-1/2
				1450	7 days	Very rare mullite and very rare corundum in glass	
				1455	7 days	All glass	
1.499	30.1	6.0	63.9	855	9 days	Very rare leucite and very rare potash feldspar in glass	K1806
				860	10 days	All glass	
1.498	18.2	27.0	54.8	1550	3 days	Very rare leucite and very rare corundum in glass	K1127
				1555	3 days	All glass	
1.502	24.8	27.0	48.2	1615	8 hr.	Leucite and orthorhombic $KAlSiO_4$ in glass (nearly all crystalline)	K1927
				1620	8 hr.	All glass	

Figure 3 shows the ternary compositions studied (shown as black dots; note that most of these lie in 22 joins between a particular K_2O—SiO_2 composition and the Al_2O_3 apex) and the fields of the primary crystalline phases. Figure 4 is the equilibrium diagram for the system with isotherms. In figures 3 and 4 the compositions of compounds are shown as double open circles. In these two figures the fields of the several crystalline phases (labelled Cristobalite, Tridymite, Potash Feldspar, etc.) which appear on the liquidus surface are separated by boundary curves—heavy curves or heavy dashed curves where experimental data are not sufficiently complete to give their location accurately. Arrows on boundary curves indicate the direction of falling temperature. They show the positions of temperature maxima on these curves at I, O, D′, B′, F′, V, T and Q (figs. 3 and 4). When no arrow is shown on a boundary curve, this curve is also an isotherm (AJL, BH and probably H′I′

of figs. 3 and 4). All tie lines[3] (straight lines which join the compositions of pairs of solid phases which may coexist at equilibrium within the temperature range under investigation) within the ternary system are shown as light lines. The tie lines mullite—corundum, mullite—silica (cristobalite, tridymite), potassium tetrasilicate—silica (quartz), potassium disilicate—potassium tetrasilicate and potassium disilicate—potassium metasilicate lie on the sides Al_2O_3—SiO_2 or K_2O—SiO_2 of the triangle K_2O—Al_2O_3—SiO_2. The tie lines divide the system K_2O—Al_2O_3—SiO_2 into triangular areas whose significance will be seen later.

In addition to the compositions recorded in table 1, many additional compositions were prepared, but no suitable crystals were obtained for quenching experiments on these preparations, even after considerable effort. For completeness of the record their compositions are given here: K909 and K911 (K_2O 10, SiO_2 90, with 9 and 11 percent Al_2O_3, respectively), K2510 and K2510-1/2 (K_2O 12, SiO_2 88, with 10 and 10.5 percent Al_2O_3, respectively), K812, K814 and K814-1/2 (K_2O 14, SiO_2 86, with 12, 14 and 14.5 percent

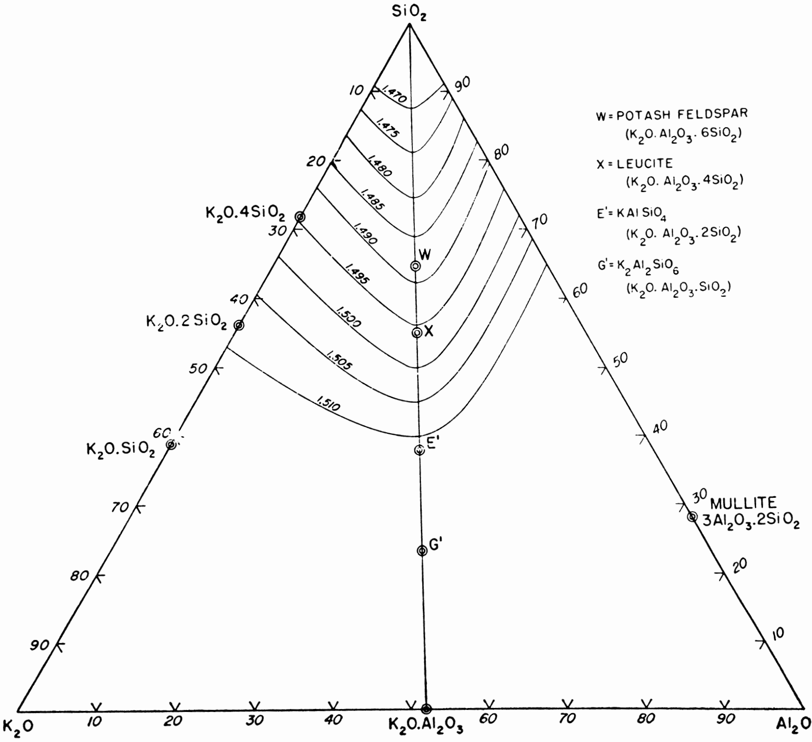

Fig. 5. Refractive indices of glasses at 25°C.

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[3] In figures 3 (p. 199) and 4 (p. 201) of the previous summary paper on K_2O—Al_2O_3—SiO_2 (Schairer and Bowen, 1947a) not all the tie lines were shown. Only those tie lines which are binary or partially binary systems within the ternary system were shown. For completeness the tie lines leucite—mullite, potash feldspar—mullite and potassium disilicate—potash feldspar should have been shown.

Al_2O_3, respectively) and many compositions which lie in the line leucite—silica, containing between 72 and 84 percent total SiO_2.

A preliminary equilibrium diagram of the system $K_2O—Al_2O_3—SiO_2$ (after Schairer and Bowen) and a discussion of its petrologic and technologic significance were given by Bowen (1943, fig. 11, p. 295-298).

REFRACTIVE INDICES OF THE GLASSES

Homogeneous glasses were prepared for the many ternary compositions which were studied, and the index of refraction of each glass was measured at 25°C. with the petrographic microscope by comparison with standardized immersion liquids. Only two compositions which lie near F′ of figures 3 and 4 failed to quench to a clear glass, and no index data are given for these two compositions (K237 and K239). The measured values for index of refraction of the glasses are given in column 1 of table 1. No attempt was made to obtain great accuracy, the glasses were not annealed after quenching, and the measurements were made in white light. The values are accurate to ± 0.003.

Figure 5 is a plot of the isofracts from the index-of-refraction measurements. The values for indices of the $K_2O—SiO_2$ glasses are from Morey and Merwin (Morey, 1954, table XVI.22, p. 403) and those for $Al_2O_3—SiO_2$ glasses are from Morey and Merwin (Morey, 1954, table XVI.18, p. 397) and several other investigators whose results are compared by Yoder and Eugster (1955, in press).

An examination of figure 5 shows the marked symmetry of the isofracts about the line $K_2O{\cdot}Al_2O_3—SiO_2$ in which lie the compositions of the ternary compounds.

BINARY SYSTEMS WITHIN THE TERNARY SYSTEM $K_2O—Al_2O_3—SiO_2$

Six of the tie lines shown in figures 3 and 4 define binary systems within the ternary system $K_2O—Al_2O_3—SiO_2$, and one tie line is partially binary. They are as follows: (1) leucite—silica, (2) leucite—corundum, (3) potassium disilicate—leucite, (4) $KAlSiO_4$—leucite, (5) potassium disilicate—$KAlSiO_4$, (6) $KAlSiO_4$—corundum and (7) potassium tetrasilicate—potash feldspar (only partially binary owing to the incongruent melting of potash feldspar to leucite and liquid). Data for the binary invariant points within the ternary system $K_2O—Al_2O_3—SiO_2$ are summarized in table 2.

Leucite—silica.—When leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) and silica are chosen as components, potash feldspar ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) becomes a binary compound between these components. Morey and Bowen (1922) showed the incongruent nature of the melting of potash feldspar to leucite and a viscous, more siliceous, complementary liquid and presented a largely hypothetical diagram for the system leucite—silica. They were not able to determine the composition of this siliceous complementary liquid. In the present studies glasses of many intermediate compositions between potash feldspar and silica were prepared. Those compositions with a liquidus temperature below about 1250°C. were extremely viscous and it was not possible to crystallize them dry even during periods as long as five years. The viscosity of these liquids is so great that even at temperatures near the liquidus the powdered glasses fail to flow together and barely frit in periods of several days or weeks. When these

TABLE 2

Binary Invariant Points within the Ternary System K_2O—Al_2O_3—SiO_2

Letters (Figures 3 and 4)	Temperature °C.	Solid and Liquid Phases
I	990 ± 20	Potash feldspar, tridymite and liquid (K_2O 9.8 Al_2O_3 10.7 SiO_2 79.5 or leucite 45.6 silica 54.4)
J	1470 ± 10	Tridymite, cristobalite and liquid (K_2O 4.3 Al_2O_3 4.7 SiO_2 91.0 or leucite 20.0 silica 80.0)
O	1150 ± 20	Leucite, potash feldspar and liquid (K_2O 12.5 Al_2O_3 13.5 SiO_2 74.0 or leucite 57.8 silica 42.2)
Q	725 ± 5	Potassium tetrasilicate, potash feldspar and liquid (K_2O 26.1 Al_2O_3 3.3 SiO_2 70.6 or potassium tetrasilicate 82 potash feldspar 18)
T	918 ± 5	Potassium disilicate, leucite and liquid (K_2O 36.9 Al_2O_3 7.4 SiO_2 55.7 or potassium disilicate 68.3 leucite 31.7)
V	923 ± 5	Potassium disilicate, hexagonal $KAlSiO_4$ and liquid (K_2O 40.6 Al_2O_3 7.7 SiO_2 51.7 or potassium disilicate 76.1 $KAlSiO_4$ 23.9)
I′	about 1540	Hexagonal $KAlSiO_4$, orthorhombic $KAlSiO_4$ and liquid (approximately K_2O 35.6 Al_2O_3 19.0 SiO_2 45.4 or potassium disilicate 41 $KAlSiO_4$ 59)
B′	1588 ± 5	Leucite, corundum and liquid (K_2O 19.9 Al_2O_3 29.3 SiO_2 50.8 or leucite 92.2 corundum 7.8)
F′	1680 ± 10	Orthorhombic $KAlSiO_4$, corundum and liquid (K_2O 27.4 Al_2O_3 37.7 SiO_2 34.9 or $KAlSiO_4$ 92 corundum 8)
D′	1615 ± 10	Leucite, orthorhombic $KAlSiO_4$ and liquid (K_2O 24.8 Al_2O_3 27.0 SiO_2 48.2 or leucite 58.9 $KAlSiO_4$ 41.1)

glasses were crystallized hydrothermally in sealed tubes (for method see Greig and Barth, 1938, p. 98-100) equilibrium between crystals and viscous liquids could not be attained in any reasonable period of time.

Small, well distributed leucite crystals were grown in seven of the leucite—silica glasses (preparations nos. K2620, 177, potash feldspar composition, 176, 121, 175 and 133 of table 1) by holding the powdered glasses about 50° to 75°C. below their respective liquidus temperatures. When the temperatures of crystallization were above approximately 1500°C. crystals grew in a few hours or days. Longer periods, with intermediate crushing and examination of the glasses under the microscope, were necessary at lower temperatures, and nearly two years were required to obtain very small, well distributed crystals of leucite in preparation no. 133. In silicate glasses that are difficult to crystallize, crystals appear first on the surface of the glass grains. Frequent crushing is a great help in promoting crystallization. From quenching runs on the seven compositions the liquidus curve of leucite was followed from pure leucite at 1686°C. as far as the composition leucite 62.1, silica 37.9 at 1245°C.

In a similar way small, well distributed cristobalite crystals were grown in four of the leucite—silica glasses (preparations nos. 152, 154, 153 and 167 of table 1), and the liquidus curve of cristobalite was followed from pure silica at 1713° (Greig, 1927) as far as the composition leucite 65.5, silica

34.5, at 1218°C. In the last three of these viscous leucite—silica glasses no tridymite crystals appeared and only cristobalite crystallized below 1470° even though temperatures were in the stability range of tridymite (Fenner, 1912, 1913), and that portion of the cristobalite liquidus curve below 1470° ± 10° is metastable. Fortunately, it was possible to obtain reliable information on the liquidus curves for tridymite, potash feldspar and leucite for these highly viscous intermediate compositions of the binary system leucite—silica indirectly by a short extrapolation from data on the very numerous compositions studied in that portion of the ternary system K_2O—Al_2O_3—SiO_2 between leucite—silica and the side line $K_2O \cdot 2SiO_2$—SiO_2.

There was a notable and marked decrease in viscosity of the melts and a marked increase in the ease of crystallization on both sides of the line leucite—silica (see figs. 3 and 4)—that is, toward the side line $K_2O \cdot 2SiO_2$—SiO_2 and toward the side line Al_2O_3—SiO_2. This may be seen from an examination of some of the quenching data in table 1. An examination of the data on preparation no. 153, which lies in the line leucite—silica; and on K1306, which lies only a very small distance in composition away from this line toward the side line $K_2O \cdot 2SiO_2$—SiO_2, shows that their liquidus temperatures are nearly the same, but that tridymite crystallized in K1306 and a point on the stable tridymite liquidus surface was obtained. These data also show that there can be only a small temperature difference between the stable tridymite liquidus surface and the metastable cristobalite surface. Similarly, an examination of the data on preparation K1308, which lies close to the line leucite—silica but on the side toward the side line Al_2O_3—SiO_2, shows a metastable cristobalite liquidus temperature at 1282°; while preparation K1309, which lies a little farther away from the line leucite—silica, gave a stable tridymite liquidus at 1272°. Although, as was mentioned previously, considerable difficulty was experienced in growing cristobalite crystals in preparation no. 167 and in determining the metastable cristobalite liquidus at 1218°, it was possible to grow small sharp crystals of tridymite in K2907 and K908, both of which lie near the line leucite—silica but on the side toward the side line $K_2O \cdot 2SiO_2$—SiO_2, and to determine the tridymite liquidus at 1258° and at 1158°, respectively. The preparation K908 lies in the join (K_2O 10, SiO_2 90)—Al_2O_3 with 8 percent Al_2O_3. Preparation K909 was made in the same join but with 9 percent Al_2O_3. It also should have a tridymite liquidus temperature, but it lies closer to the line leucite—silica. Even after seven years it was not possible to crystallize this composition and no data for it are recorded in table 1.

Schairer and Bowen (1938, fig. 3, p. 293) presented a preliminary diagram for the binary system leucite—silica. Now, on the basis of a few new data on the system K_2O—Al_2O_3—SiO_2, particularly on compositions closer to the binary system leucite—silica, a final diagram is available and is given here as figure 6. The portions of the liquidus curves of figure 6 given as dashed lines indicate the part of the diagram based on extrapolated data. This diagram, but not the data on which it is based, was given by Schairer and Bowen (1947b, fig. 3, p. 74). The incongruent melting temperature of potash feldspar is placed at 1150° ± 20°C., and the composition of the liquid formed is leucite

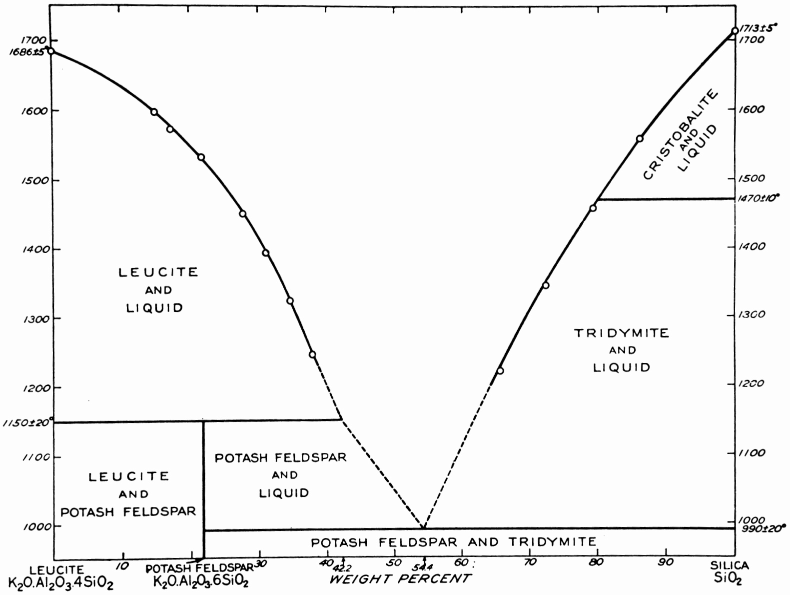

Fig. 6. Equilibrium diagram of the binary system leucite—silica.

57.8, silica 42.2 percent (or potash feldspar 73.7, silica 26.3 percent). The eutectic temperature between potash feldspar and tridymite is placed at 990° ± 20°C. at the composition leucite 45.6, silica 54.4 percent (or potash feldspar 58.2, silica 41.8 percent). The inversion temperature between cristobalite and tridymite in the binary system leucite—silica lies at 1470° ± 10° at the composition leucite 20.0, silica 80.0 percent. An examination of figures 3 and 4 shows that temperatures along the boundary curves HIM and RON fall in both directions from the binary eutectic I and the binary reaction point O, respectively, in the system leucite—silica and that I and O are temperature maxima on these boundary curves.

Leucite—corundum.—Five of the compositions (K628, K629, K629-1/2, K630 and K631) whose quenching data are given in table 1 lie in the join $K_2O \cdot 4SiO_2$—Al_2O_3 and in the binary system leucite—corundum. The data for leucite—corundum are presented graphically in figure 7. In two of these compositions (K630 and K631) some crystals of "β-Al_2O_3" were present in addition to corundum (α-Al_2O_3) and leucite in the crystallized material used for the quenching experiments. The phase "β-Al_2O_3," whatever may be its composition, must be metastable. It dissolved and corundum crystals grew as the liquidus temperatures were approached from below, and the length of time of the quenching runs was increased. Only corundum crystals were present at the liquidus. The presence of a very small amount of glass in K629 and K629-1/2 just below the eutectic temperature may indicate that compositions in the system leucite—corundum are very slightly off composition owing to a small loss of K_2O during their preparation because of the high temperatures necessary to melt them completely and obtain a homogeneous glass.

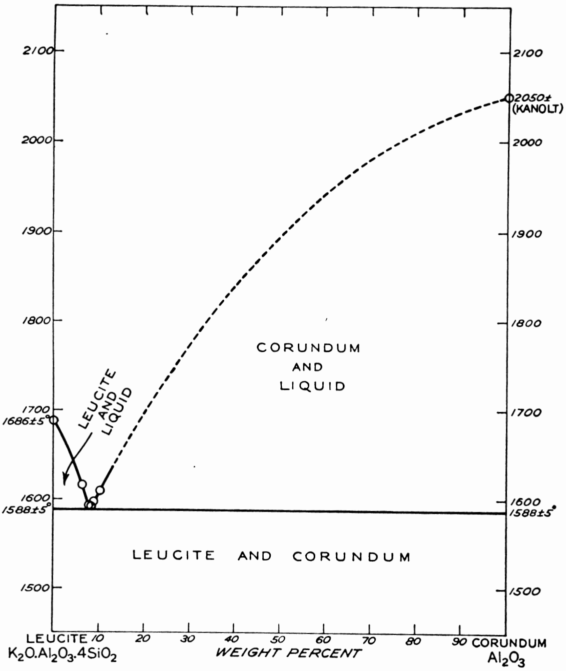

Fig. 7. Equilibrium diagram of the binary system leucite—corundum.

The eutectic between leucite and corundum in the binary system leucite—corundum lies at 1588° ± 5°C. at the composition leucite 92.2, corundum 7.8 or K_2O 19.9, Al_2O_3 29.3, SiO_2 50.8 weight percent. An examination of figures 3 and 4 shows that temperatures along the boundary curve C′B′A′ fall in both directions from the binary eutectic B′ in the system leucite—corundum and that B′ is a temperature maximum on this boundary curve.

Potassium disilicate—leucite.—Only one of the compositions (K1607) whose quenching data are given in table 1 lies in this binary system. But many compositions given in table 1 lie close to this system. The equilibrium diagram for the binary system potassium disilicate—leucite is given here as figure 8 and is based on short interpolations from data on these ternary compositions. The binary eutectic between potassium disilicate and leucite is placed at 918° ± 5° at the composition potassium disilicate 68.3, leucite 31.7 weight percent, or K_2O 36.9, Al_2O_3 7.4, SiO_2 55.7. An examination of figures 3 and 4 shows that the temperature along the boundary curve UTR falls in both directions from the binary eutectic T in the system potassium disilicate—leucite and that T is a temperature maximum on this boundary curve.

$KAlSiO_4$—leucite.—Only one of the compositions (K1927) whose quenching data are given in table 1 lies in the binary system $KAlSiO_4$—leucite. The quenching data place this composition at the binary eutectic between orthorhombic $KAlSiO_4$ and leucite at 1615° ± 10°C. at the composition $KAlSiO_4$ 41.1, leucite 58.9, or K_2O 24.8, Al_2O_3 27.0, SiO_2 48.2 weight percent.

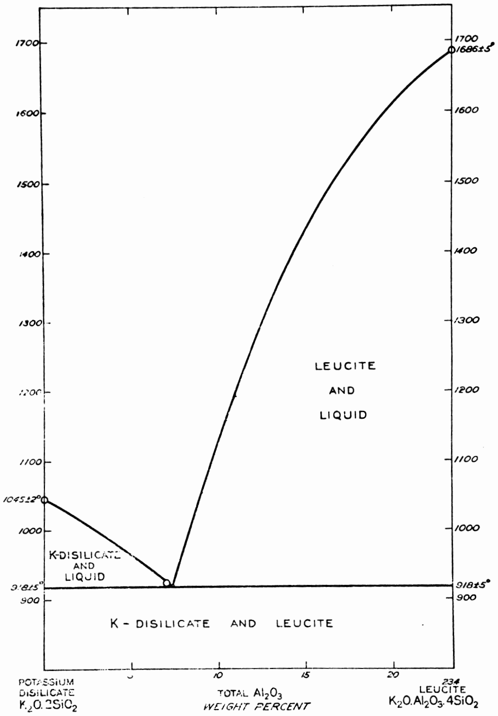

Fig. 8. Equilibrium diagram of the binary system potassium disilicate—leucite.

The presence of a small amount of glass in K1927 just below the eutectic temperature indicates that this mixture may be slightly off composition owing to a small loss of K_2O during its preparation. For this reason the eutectic temperature is placed ± 10°C. instead of more precisely. The binary system $KAlSiO_4$—leucite is presented graphically in figure 9. Since the melting point of orthorhombic $KAlSiO_4$ is known to be above 1700°C. and probably near or above 1750°, but is not known precisely, the liquidus curve of this phase in figure 9 is not accurately located.

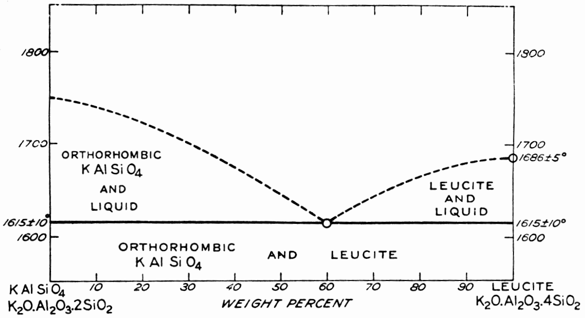

Fig. 9. Equilibrium diagram of the binary system $KAlSiO_4$—leucite.

An examination of figures 3 and 4 shows that temperatures along the boundary curve H′D′C′ fall in both directions from the binary eutectic D′ in the system $KAlSiO_4$—leucite and that D′ is a temperature maximum on this boundary curve.

Potassium disilicate—$KAlSiO_4$.—Thirteen of the compositions (K202, K204, K206, K207, K208, K210, K212, K214, K216, K218, K220, K222 and K225) whose quenching data are given in table 1 lie in the join $K_2O \cdot 2SiO_2$—Al_2O_3 and in the binary system potassium disilicate—$KAlSiO_4$. The data are presented graphically in figure 10. An examination of the liquidus data presented in this figure shows that the measured liquidus temperatures do not lie on smooth curves. All the glasses are hygroscopic, and the data indicate that some or all of them may be slightly off composition owing to loss of K_2O during their preparation. The presence of a small amount of glass at a temperature 8°C. below the eutectic temperature also indicates departure from the desired composition.

The crystals obtained from the melts were small, rounded and sometimes intergrown with fine-grained crystalline material formed during the quenching. Only in K220, K222 and K225 were euhedral crystals obtained near liquidus temperatures. These were crystals of the orthorhombic form of $KAlSiO_4$. Be-

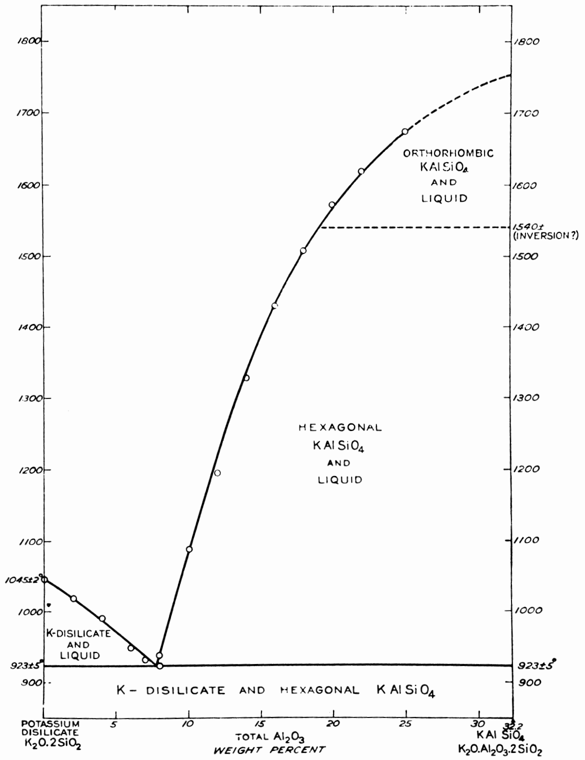

Fig. 10. Equilibrium diagram of the binary system potassium disilicate—$KAlSiO_4$.

cause of experimental difficulties with hygroscopic melts and with fine-grained products formed during the quenching, no attempt was made to study the exact relations between hexagonal and orthorhombic $KAlSiO_4$ in these melts or to ascertain whether this inversion was affected by solid solution. We have accepted the enantiotropic inversion (Bowen, 1917) at 1540° and assumed no solid solution in figure 10.

The binary eutectic between potassium disilicate and hexagonal $KAlSiO_4$ is placed at 923° ± 5° at the composition $K_2Si_2O_5$ 76.1, $KAlSiO_4$ 23.9, or K_2O 40.6, Al_2O_3 7.7, SiO_2 51.7 weight percent. The binary inversion temperature is placed at about 1540°C. and the liquid in equilibrium with the two forms has the approximate composition $K_2Si_2O_5$ 41, $KAlSiO_4$ 59, or K_2O 35.6, Al_2O_3 19.0, SiO_2 45.4 weight percent. In figures 3 and 4 the boundary curve between potassium disilicate and hexagonal $KAlSiO_4$ is UV and a temperature maximum on this curve is shown at V. The boundary curve H′I′ (figs. 3 and 4) is the isotherm for 1540°C. and has been shown as a dashed curve.

$KAlSiO_4$—corundum.—Two of the compositions (K237 and K239) whose quenching data are given in table 1 lie in the join $K_2O{\cdot}2SiO_2$—Al_2O_3 and in the binary system $KAlSiO_4$—corundum. The data are presented graphically in figure 11. The preparation of the compositions K237 and K239 was very difficult because of their high melting temperatures, which severely taxed the upper practical temperature limit of platinum-wound furnaces. The data obtained on these two compositions are not as accurate as those obtained on other mixtures studied in the ternary system K_2O—Al_2O_3—SiO_2 for three reasons: (1) difficulty in completely melting these compositions to obtain homogeneous liquids, (2) probable loss of at least small amounts of K_2O by

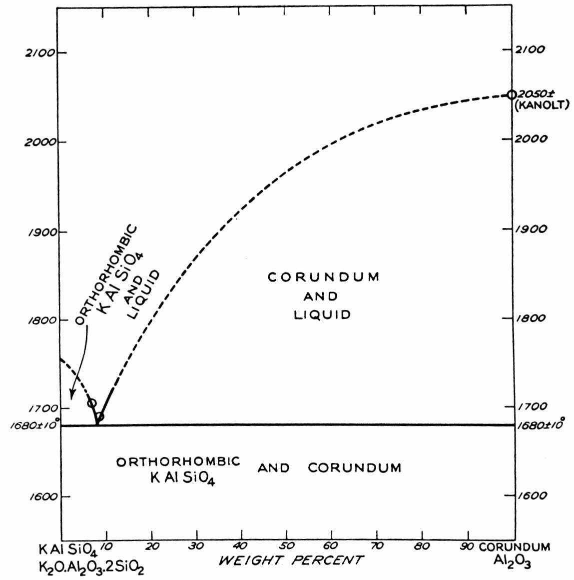

Fig. 11. Equilibrium diagram of the binary system $KAlSiO_4$—corundum.

volatilization during preparation of the melts and (3) difficulty in quenching rapidly enough to obtain clear glasses free from crystals formed during the short quenching period. For this last reason the indices of refraction of these two glasses were not obtained.

From the quenching data on these two compositions recorded in table 1 we place the binary eutectic between orthorhombic $KAlSiO_4$ and corundum at 1680° ± 10°C. at the composition $KAlSiO_4$ 92, corundum 8, or K_2O 27.4, Al_2O_3 37.7, SiO_2 34.9 weight percent. The melting point of orthorhombic $KAlSiO_4$ is above 1700°, but was not accurately located. In figures 3 and 4 the boundary curve between orthorhombic $KAlSiO_4$ and corundum is C′F′ and a temperature maximum on this boundary curve is shown at F′.

Potassium tetrasilicate—potash feldspar (partially binary).—Two of the compositions (K1109 and K2614) whose quenching data are given in table 1 lie almost exactly in the tie line between potassium tetrasilicate and potash feldspar, and many compositions in table 1 lie close to this tie line. Figure 12

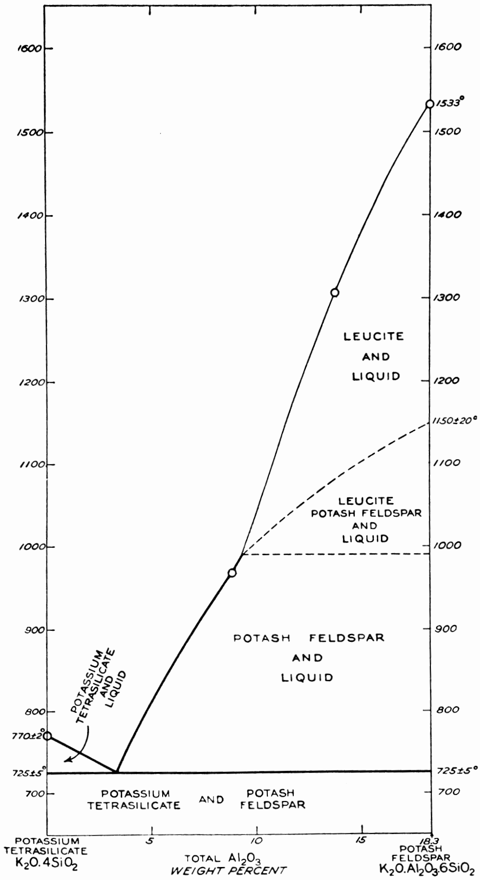

Fig. 12. Equilibrium diagram of the join $K_2O \cdot 4SiO_2$—$K_2O \cdot Al_2O_3 \cdot 6SiO_2$. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium.

presents graphically the relations in the tie line potassium tetrasilicate—potash feldspar. It is binary only in part because of the appearance of leucite crystals whose composition does not lie in this line. There is a consequent departure of the composition of liquids from this line when leucite is present as a solid phase. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium. Below about 980° behavior of all compositions in the tie line is binary. and final complete consolidation occurs at the binary eutectic between potassium tetrasilicate and potash feldspar, which is placed at 725° ± 5°C. at the composition potassium tetrasilicate 82, potash feldspar 18, or K_2O 26.1, Al_2O_3 3.3, SiO_2 70.6 weight percent. An examination of figures 3 and 4 shows that the temperature along the boundary curve PQS falls in both directions from the binary eutectic Q in the tie line potassium tetrasilicate—potash feldspar and that Q is a temperature maximum on this boundary curve.

With perfect equilibrium between crystals and liquid all compositions in the tie line potassium tetrasilicate—potash feldspar (figs. 3 and 4) which have leucite as the primary phase, on cooling first crystallize leucite and then reach the boundary curve OR at some temperature between O and the point where this boundary curve cuts the tie line. The liquid composition follows the boundary curve with potash feldspar separating and leucite crystals dissolving until the leucite is completely resorbed at the point where the boundary curve cuts the tie line. At temperatures below this point (about 980°) their behavior is binary. In figure 12 they follow the heavy liquidus curve of potash feldspar with potash feldspar crystals separating to the binary eutectic at 725° ± 5° where complete consolidation to crystals of potash feldspar and potassium tetrasilicate occurs.

TERNARY SYSTEMS WITHIN THE TERNARY SYSTEM K_2O—Al_2O_3—SiO_2

Six of the tie lines (figs. 3 and 4) are binary systems within the ternary system K_2O—Al_2O_3—SiO_2. They divide that portion of the ternary system K_2O—Al_2O_3—SiO_2 for which data are available into four smaller ternary systems, which are subsystems within the larger ternary system K_2O—Al_2O_3—SiO_2. Since all the crystalline phases are of fixed composition (little or no solid solution) crystallization behavior in these systems is quite simple. The data for the ternary invariant points within the system K_2O—Al_2O_3—SiO_2 are given in table 3.

The ternary system $KAlSiO_4$—leucite—corundum.—The three binary systems $KAlSiO_4$—corundum (fig. 11), $KAlSiO_4$—leucite (fig. 9) and leucite—corundum (fig. 7) limit the ternary system $KAlSiO_4$—leucite—corundum. From the three binary eutectics F′, D′ and B′ (figs. 3 and 4), the boundary curves F′C′, D′C′ and B′C′ proceed, respectively, to the ternary eutectic C′ (figs. 3 and 4). Crystallization is very simple, and all compositions in the triangle $KAlSiO_4$—leucite—corundum complete their crystallization at the ternary eutectic C′ at 1553° ± 5° and at that temperature consist of orthorhombic $KAlSiO_4$, leucite and corundum. The last liquid has the composition C′.

The ternary system $KAlSiO_4$—leucite—potassium disilicate.—The three binary systems $KAlSiO_4$—$K_2O{\cdot}2SiO_2$ (fig. 10), $KAlSiO_4$—leucite (fig. 9),

TABLE 3

Ternary Invariant Points in the System K_2O—Al_2O_3—SiO_2

Letters (Figures 3 and 4)	Temperature °C.	Solid and Liquid Phases
P	710 ± 20	Potash feldspar, quartz, potassium tetrasilicate and liquid (K_2O 22.8 Al_2O_3 3.7 SiO_2 73.5)
H	867 ± 3	Quartz, tridymite, potash feldspar and liquid (K_2O 17.0 Al_2O_3 6.8 SiO_2 76.2)
M	985 ± 20	Potash feldspar, tridymite, mullite and liquid (K_2O 9.5 Al_2O_3 10.9 SiO_2 79.6)
L	1470 ± 10	Tridymite, cristobalite, mullite and liquid (K_2O 2.4 Al_2O_3 7.3 SiO_2 90.3)
N	1140 ± 20	Potash feldspar, leucite, mullite and liquid (K_2O 12.2 Al_2O_3 13.7 SiO_2 74.1)
A′	1315 ± 10	Leucite, mullite, corundum and liquid (K_2O 13.9 Al_2O_3 18.5 SiO_2 67.6)
R	810 ± 5	Potash feldspar, leucite, potassium disilicate and liquid (K_2O 32.1 Al_2O_3 5.3 SiO_2 62.6)
S	695 ± 5	Potash feldspar, potassium tetrasilicate, potassium disilicate and liquid (K_2O 30.4 Al_2O_3 3.2 SiO_2 66.4)
U	905 ± 10	Leucite, hexagonal $KAlSiO_4$, potassium disilicate and liquid (K_2O 39.3 Al_2O_3 7.8 SiO_2 52.9)
H′	about 1540	Hexagonal $KAlSiO_4$, orthorhombic $KAlSiO_4$, leucite and liquid (approximately K_2O 28.5 Al_2O_3 22.0 SiO_2 49.5)
C′	1553 ± 5	Leucite, orthorhombic $KAlSiO_4$, corundum and liquid (K_2O 22.1 Al_2O_3 31.3 SiO_2 46.6)

and leucite—$K_2O \cdot 2SiO_2$ (fig. 8) limit the ternary system $KAlSiO_4$—leucite—potassium disilicate. There are two ternary invariant points in this ternary system—the point H′ (figs. 3 and 4) and the ternary eutectic U (figs. 3 and 4). The boundary curve I′H′ (figs. 3 and 4) is an isotherm at about 1540°C., the inversion temperature between hexagonal and orthorhombic $KAlSiO_4$. Temperatures fall from the eutectics in the limiting binary systems to the ternary eutectic U (figs. 3 and 4) at 905° ± 10°. Crystallization is very simple, and all compositions in the triangle $KAlSiO_4$—leucite—potassium disilicate complete their crystallization at the ternary eutectic U and consist of crystals of hexagonal $KAlSiO_4$, leucite and potassium disilicate, the last liquid having the composition U.

The ternary system leucite—corundum—silica.—The three binary systems leucite—silica (fig. 6), leucite—corundum (fig. 7) and Al_2O_3—SiO_2 (fig. 2) limit the ternary system leucite—corundum—silica. This system is divided into three triangular portions by the tie lines leucite—mullite and potash feldspar—mullite (figs. 3 and 4). With perfect equilibrium between crystals and liquid all compositions lying in the triangle leucite—corundum—mullite become completely crystalline at 1315° ± 10°, the temperature of the ternary reaction point A′ (figs. 3 and 4), and consist of crystals of leucite, corundum and mullite, the last liquid having the composition A′. With perfect equilibrium all compositions lying in the triangle leucite—mullite—potash feldspar become completely crystalline only at 1140° ± 20°, the temperature of the ternary reaction point N (figs. 3 and 4), and consist of crystals of leucite, mullite and potash feldspar, the last liquid having the composition N. With perfect equilibrium all compositions lying in the triangle potash feldspar —mullite—silica become completely crystalline only at 985° ± 20°, the temperature of the ternary eutectic M (figs. 3 and 4), and consist of tridymite (from the viscous dry liquids actually cristobalite metastably), mullite and potash feldspar, the last liquid having the composition M.

In leucite—corundum—silica, only those compositions lying exactly in the line leucite—mullite should consist of the two solid phases leucite and mullite when completely crystallized from a melt with perfect equilibrium. Let us examine the crystallization paths on cooling of compositions lying in the line leucite—mullite to see how they crystallize so that we may evaluate the chances of attaining perfect equilibrium during crystallization. Those compositions in the line leucite—mullite lying to the right of a line that may be drawn between Al_2O_3 and A′ (figs. 3 and 4) first crystallize corundum and then at appropriate temperatures the crystallization path reaches the boundary curve YA′, which it follows to A′ with mullite separating and corundum resorbing. The temperature should remain constant at 1315° ± 10°, the temperature of A′, while any remaining corundum reacts with liquid to form mullite, and leucite separates and the liquid is completely used up. The liquid A′ is viscous and the complete resorption of all corundum and the simultaneous disappearance of the last bit of liquid to yield a mixture of only mullite and leucite demanded by perfect equilibrium would be very improbable in practice. Those compositions lying in the line leucite—mullite, between the point where a line that may be drawn between Al_2O_3 and A′ cuts the line leucite—mullite and where the boundary curve B′A′ cuts the line leucite—mullite, first crystallize corundum, then at appropriate temperatures the crystallization path reaches some point on the boundary curve B′A′, which it follows to A′ with both corundum and leucite separating. The temperature should remain constant at 1315° ± 10° until all the corundum has been resorbed by reaction with the liquid A′ and converted to mullite. With perfect equilibrium corundum and liquid should both disappear completely to yield a mixture of only leucite and mullite. With the viscous liquid A′ it would be very improbable that all corundum would be resorbed and all liquid used up quantitatively and simultaneously in practice. The rest of the compositions in the line leucite—mullite (those between leucite and the point where the boundary curve B′A′ cuts the line leucite—mullite) behave very similarly to those just discussed, except that leucite would appear as the primary phase before the crystallization path reached the boundary curve B′A′. Perfect equilibrium to yield only leucite and mullite in the final product of complete crystallization would be improbable in practice.

If a series of glasses whose compositions lie in the line leucite—mullite was crystallized at a temperature just below 1315°C. and any corundum crystallized metastably, it would be almost impossible to convert it to mullite by reaction with the viscous complementary liquid and to obtain a product consisting only of crystals of leucite and mullite.

In leucite—corundum—silica, only compositions lying exactly on the line potash feldspar—mullite should consist of the two solid phases potash feldspar and mullite when completely crystallized from a melt with perfect equilibrium. Nearly all compositions lying in the line potash feldspar—mullite must pass through the point A′ (figs. 3 and 4) in their crystallization path, with the possibility of some corundum not being resorbed at 1315°. (Only that restricted range of compositions in the line potash feldspar—mullite between pure potash feldspar, W, and the point where the line that may be drawn between leucite and A′ crosses the line potash feldspar—mullite do not pass through the point A′ but proceed toward either A′N or ON with primary separation of leucite crystals.) When perfect equilibrium is attained and all corundum is resorbed at 1315°, the liquid composition then follows the boundary curve A′N with leucite and mullite separating along A′N until the point N is reached. At this ternary reaction point the temperature should remain constant at 1140° ± 20° until all the leucite has been resorbed and transformed by reaction with liquid N to potash feldspar. We previously noted that liquid A′ is extremely viscous at 1315°C. We now note that the liquid N at 1140° with a higher SiO_2 content and at the considerably lower temperature is considerably more viscous than A′. The possibility of converting all the leucite crystals present to potash feldspar by reaction with liquid at N and the simultaneous completion of this conversion and disappearance of the liquid to yield only potash feldspar and mullite is very remote indeed in practice.

If a series of glasses whose compositions lie in the line potash feldspar—mullite was crystallized at a temperature just below 1140° (such a crystallization dry may be nearly impossible or would take years) and any leucite or corundum crystallized metastably, it would be almost impossible to convert such crystals to potash feldspar or mullite by reaction with the viscous liquid phase and to obtain a product consisting only of potash feldspar and mullite.

Great caution should be exercised in evaluating mineral compatibilities from an examination of the products of crystallized silicate glasses which are extremely viscous. Although it is possible to attain equilibrium in appropriate compositions between crystals of corundum, mullite and leucite, this is only possible when these crystals are present as very small crystals and in small amounts with a large amount of liquid phase—in other words with small crystals at temperatures near liquidus temperatures.

We have seen that it is possible to find corundum, mullite, leucite, potash feldspar and a small amount of liquid present simultaneously in compositions in the line potash feldspar—mullite at a temperature where only crystals of potash feldspar and mullite with no liquid should be present. This is a consequence of failure to attain equilibrium. We are sure that if certain glasses, whose compositions lie in the triangle potash feldspar—mullite—silica and whose liquidus lies in the field of corundum (for example, a mixture slightly more alumina rich than A′), were crystallized dry for several years at 950°C. we might even find crystals of corundum, mullite, leucite, cristobalite and tridymite all present in metastable association in a partly crystallized glass.

In the present studies it has been noted that crystals of corundum and leucite once formed metastably are very difficult to convert to mullite and potash feldspar, respectively, when these latter two should be the stable solid phases. In extremely viscous glasses cristobalite once formed may persist for many months or years metastably in the temperature stability range of tridymite.

The ternary system leucite—potassium disilicate—silica.—The three binary systems leucite—$K_2O \cdot 2SiO_2$ (fig. 8), leucite—silica (fig. 6), and $K_2O \cdot 2SiO_2$—SiO_2 (fig. 1) limit the ternary system leucite—potassium disilicate—silica. In figures 3 and 4 the tie line $K_2O \cdot 4SiO_2$—W (potash feldspar) divides this ternary system into two portions, the triangle $K_2O \cdot 4SiO_2$—W (potash feldspar)—SiO_2 and the quadrilateral $K_2O \cdot 4SiO_2$—W (potash feldspar)—X (leucite)—$K_2O \cdot 2SiO_2$. This quadrilateral portion is still further divided into the two triangular portions $K_2O \cdot 2SiO_2$—X (leucite)—W (potash feldspar) and $K_2O \cdot 4SiO_2$—W (potash feldspar)—$K_2O \cdot 2SiO_2$ by the tie line $K_2O \cdot 2SiO_2$—W (potash feldspar). With perfect equilibrium all compositions in the triangle $K_2O \cdot 4SiO_2$—W—SiO_2 (figs. 3 and 4) become completely crystalline at 710° ± 20°, the temperature of the ternary eutectic P, and consist of crystals of potassium tetrasilicate, quartz and potash feldspar, the last liquid having the composition P. With perfect equilibrium all compositions in the triangle $K_2O \cdot 2SiO_2$—X (leucite)—W (potash feldspar) of figures 3 and 4 become completely crystalline at 810° ± 5°, the temperature of the ternary reaction point R, and consist of crystals of potassium disilicate, leucite and potash feldspar, the last liquid having the composition R. With perfect equilibrium all compositions in the triangle $K_2O \cdot 4SiO_2$—W (potash feldspar)—$K_2O \cdot 2SiO_2$ become crystalline only at 695° ± 5°, the temperature of the ternary eutectic S, and consist of crystals of potassium tetrasilicate, potash feldspar and potassium disilicate, the last liquid having the composition S.

In the quadrilateral $K_2O \cdot 4SiO_2$—W (potash feldspar)—X (leucite)—$K_2O \cdot 2SiO_2$, only those compositions which lie exactly in the line $K_2O \cdot 2SiO_2$—W (potash feldspar) should consist of the two solid phases potassium disilicate and potash feldspar when completely crystallized from a melt with perfect equilibrium. Let us examine the crystallization paths on cooling of compositions which lie in the line $K_2O \cdot 2SiO_2$—W (potash feldspar) to see how they crystallize so that we may evaluate the chances of attaining perfect equilibrium during crystallization. Those compositions in the line $K_2O \cdot 2SiO_2$—W (potash feldspar) lying to the right of a line that may be drawn between X (leucite) and R first crystallize leucite, then at appropriate temperatures the crystallization path reaches the boundary curve OR, which it follows to R with potash feldspar separating and leucite resorbing. The temperature should remain constant at 810° ± 5°, the temperature of R, while any remaining leucite is converted to potash feldspar, potassium disilicate crystals separate and the liquid is completely used up. At this low temperature the liquid R is quite viscous; the complete resorbtion of all leucite and the simultaneous disappearance of the last bit of liquid to yield a mixture of only potash feldspar and potassium disilicate demanded by perfect equilibrium would be improbable in practice. Those compositions lying in the line $K_2O \cdot 2SiO_2$—W (potash feldspar), between the point where a line that may be drawn between X (leucite) and R cuts $K_2O \cdot 2SiO_2$—W and where the boundary curve TR cuts $K_2O \cdot 2SiO$—W, first crystallize leucite and then at appropriate temperatures the crystallization path reaches some point on the boundary curve TR, which it follows to R with both leucite and potassium disilicate crystals separating. The temperature should remain constant at 810° ± 5° until all the leucite has been resorbed by reaction with the liquid R and converted to potash feldspar. With perfect equilibrium leucite and liquid should both disappear completely and simultaneously to yield a mixture of potash feldspar and potassium disilicate crystals. With the viscous liquid R it would be improbable that all leucite would be resorbed and all liquid used up quantitatively and simultaneously in practice. The rest of the compositions in the line $K_2O \cdot 2SiO_2$—W (potash feldspar)—those between $K_2O \cdot 2SiO_2$ and the point where the boundary curve TR cuts this line—behave very similarly to those just discussed, except that potassium disilicate crystals appear as the primary phase before the crystallization path reaches the boundary curve TR. Perfect equilibrium to yield a completely crystalline product with only potash feldspar and potassium disilicate crystals would be improbable in practice.

In a previous section of this paper we discussed crystallization with perfect equilibrium in the tie line $K_2O \cdot 4SiO_2$—W (potash feldspar) to yield a completely crystalline product with only crystals of potassium tetrasilicate and potash feldspar. The relations in this tie line, which is a partially binary system, were shown in figure 12. During the crystallization of any of those compositions in this tie line which have leucite as the primary phase, if cooling was too rapid to permit equilibrium between leucite crystals and liquid after the boundary curve OR (figs. 3 and 4) was reached, some of the leucite crystals might be left undissolved and the final product might consist of the metastable assemblage leucite, potash feldspar, quartz (and/or tridymite, and/or cristobalite) and potassium tetrasilicate.

With perfect equilibrium between crystals and liquid all compositions in the triangle $K_2O \cdot 4SiO_2$—W (potash feldspar)—SiO_2 complete their crystallization at 710° ± 20° and consist of quartz, potassium tetrasilicate and potash feldspar, and the last liquid has the composition of the ternary eutectic P (figs. 3 and 4). Crystallization of most compositions in this triangle is so simple as to require no comment. Let us examine the crystallization behavior of those mixtures in this triangle which also lie in the field of leucite. From those melts leucite appears as the primary phase and separates until at appropriate temperatures the crystallization path (a straight line between the initial composition and the composition of the solid phase which is separating) reaches a point on the boundary curve OR at some point between O and the point (not lettered in figs. 3 and 4) where the tie line $K_2O \cdot 4SiO_2$—W (potash feldspar) cuts the boundary curve OR. As soon as the boundary curve OR is reached, potash feldspar appears as the second solid phase; as the temperature falls the liquid moves along OR with potash feldspar separating and leucite being resorbed. At the point in OR where a straight line that may be drawn through W (potash feldspar) and the initial composition cuts OR all the leucite has been resorbed; then the crystallization path leaves OR and crosses the field of potash feldspar to reach IH, HP or QP (depending on the initial composition of the particular mixture selected) and from thence to the ternary eutectic P. For those mixtures in the leucite field just discussed, if cooling was too rapid to permit equilibrium between leucite crystals and liquid after the boundary curve OR was reached. some of the leucite crystals might be left undissolved and the final product might consist of a metastable assemblage of leucite, potash feldspar. quartz (and/or tridymite, and/or cristobalite) and potassium tetrasilicate.

FIELDS OF THE PRIMARY CRYSTALLINE PHASES

The fields of the primary crystalline phases which appear on the liquidus surface within the ternary system K_2O—Al_2O_3—SiO_2 are shown in figures 3 and 4. Isotherms within the fields and the boundaries of the several fields have been located by the data in table 1. The optical properties of the several crystalline phases have already been recorded in previous papers from the Geophysical Laboratory.

Cristobalite.—The field of cristobalite. ASiO_2KLJA of figure 4, extends from 1470° ± 10°, the temperature of the boundary curve and isotherm AJL, to the melting point of cristobalite at 1713° ± 5° (Greig, 1927, p. 5-12). The crystals obtained in our melts were very small octahedra, usually much rounded so as to resemble fish eggs, and were easily identified by their shape. isotropic character and index of refraction.

Tridymite and quartz.—An examination of figure 4 shows a field of tridymite, BAJLMIHB, and a small field of quartz, CBHPC. Except in the very viscous melts whose compositions lie on or very near the line leucite—silica, it was possible to crystallize tridymite from appropriate melts in its stability range. It appeared as very small and very thin plates with a perfect hexagonal outline that appear as needles when viewed on edge and could be identified by the shape and optical properties.

It was relatively easy to obtain crystals of tridymite but very difficult to obtain quartz crystals in melts at appropriate temperatures in K_2O—Al_2O_3—SiO_2. On the other hand, in Na_2O—Al_2O_3—SiO_2 melts it was possible to obtain tridymite only with considerable difficulty, but quartz crystallized without particular trouble. Fenner (1913) placed the inversion temperature between quartz and tridymite at 870° ± 10° for pure silica. Kracek (1939), from studies of melts of very low viscosity in the system Na_2SiO_3—Li_2SiO_3—SiO_2, was able to locate the inversion temperature between quartz and tridymite at 867° ± 3°. Buerger (1935) indicated that tridymite and cristobalite have open crystal structures capable of enclosing foreign ions which may prevent them from repacking at lower temperatures to go over to quartz, and that solid solution in the quartz structure is restricted to a very small range and to small ions. It is difficult to reconcile all the above observations.

In the system K_2O—Al_2O_3—SiO_2 the field of quartz is small and only three of the compositions studied (K1101, K2603 and K705 of table 1) lie in this field, with one other (K2604 of table 1) on the boundary curve between quartz and potash feldspar (PH of fig. 4). Tridymite crystals grew in these compositions, and the metastable tridymite liquidus was obtained. Kracek, Bowen and Morey (1937) showed that in the system $K_2O \cdot 2SiO_2$—SiO_2 there was only 2°C. difference in temperature between the stable quartz—potassium tetrasilicate eutectic and the metastable eutectic with tridymite. Accordingly, the boundary curve BH has been placed at the isotherm for 867° and the stable field CBHP of quartz has been indicated.

Potassium tetrasilicate.—The field EDCPQSE of potassium tetrasilicate is shown in figure 4. This compound, whose composition lies at D, has a congruent melting point at 770° ± 2°. In the boundary curve SQP there is a temperature maximum at Q at 725° ± 5°. In the region of this boundary curve particular care was taken to have both potassium tetrasilicate and potash feldspar crystals present in the glasses before making the quenching experiments. When no potash feldspar crystals were present it was possible to follow the metastable extension of the potassium tetrasilicate liquidus surface beneath the stable potash feldspar field. Crystals of potassium tetrasilicate grew readily and appeared as thin blades and needles easily identified by their low indices and low birefringence.

Potassium disilicate.—This field is shown in figure 4 between the boundary curves ES, SR, RTU and UV and the part J′FE of the side line $K_2O—SiO_2$. Potassium disilicate, whose composition lies at F, has a congruent melting point at 1045° ± 2°. There is a temperature maximum at T on the boundary curve UTR. On the boundary curve between hexagonal $KAlSiO_4$ and potassium disilicate a temperature maximum is shown at V, although no compositions were studied below the line $K_2O\cdot 2SiO_2$—E′. Potassium disilicate crystallizes very readily to orthorhombic blades, often in radiating aggregates. It is readily distinguished from potassium tetrasilicate by its higher indices and micaceous cleavage.

In the region near the boundary curve SR particular care was taken to have both potassium disilicate and potash feldspar crystals present in the glasses before the quenching experiments were carried out. When no potash feldspar crystals were present it was possible to follow the metastable extension of the potassium disilicate liquidus surface beneath the stable potash feldspar field.

Mullite.—The field of mullite is shown as KLMNA′YK in figure 4. It has an incongruent melting point at 1810° ± 10° and its composition lies at Z outside the field of mullite. For those compositions in the field of mullite with liquidus temperatures below about 1400°, considerable difficulty in crystallization was encountered, and for those with liquidus temperatures around 1200° many months were required at temperatures about 75° below estimated liquidus temperatures in order to obtain sharp mullite needles in the glasses before the quenching experiments were begun. Mullite grew in the melts as very small needles or rods easily distinguished by their shape from corundum and by their shape and high indices from feldspar. M and N and the boundary curve MN were accurately located by the steep liquidus surface of mullite at temperatures below 1400°.

Corundum.—A large field of corundum lies between the boundary curves F′C′, C′B′A′, A′Y and the Al_2O_3 apex of the triangle (fig. 4). It extends from A′ (fig. 4) at 1315° to the melting point of corundum (α-Al_2O_3). A temperature maximum was found at B′ in the boundary curve C′B′A′ and a maximum is shown at F′, although no compositions were studied below the line

E′F′Al_2O_3. From most of the compositions in the field of corundum both corundum and the so-called "β-Al_2O_3" crystallized from the glasses when they were held about 100° below liquidus temperatures. There has been considerable discussion in the literature concerning the composition of "β-Al_2O_3," with some evidence that it is not a polymorph of Al_2O_3 but a compound of Al_2O_3 with an alkali or an alkaline earth oxide. This evidence will be presented later in this paper.

In the quenching experiments it was found that when both corundum and "β-Al_2O_3" crystals were present in any of the glasses corundum grew and "β-Al_2O_3" crystals became corroded and dissolved when the length of time of the quenching runs was increased and that only corundum was present at the liquidus. The phase "β-Al_2O_3," whatever may be its composition, was metastable with respect to corundum at and near liquidus temperature. In the melts corundum grew as equant, faceted hexagonal crystals easily distinguished from "β-Al_2O_3" by the habit and low birefringence of corundum. "β-Al_2O_3" always appeared as very thin plates with a perfect hexagonal outline and a much higher birefringence than that of corundum.

Potash feldspar.—The field of potash feldspar is shown as RSQPHIMNOR in figure 4. This ternary compound has an incongruent melting point at 1150° ± 20°, the temperature of O, and its composition $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ at W lies outside the field of potash feldspar. The temperature maximum at Q at 725° ± 5° on the boundary curve SQP was measured. Temperature maxima have been placed at I and O in the boundary curves HIM and RON, respectively. The temperature drop between I and M and between O and N must be small.

Considerable difficulty was experienced in obtaining crystals of potash feldspar in all compositions which lie in its field. In those extremely viscous melts that also lie on and very near the line leucite—SiO_2 it was never possible to obtain feldspar crystals. By determining liquidus temperatures in a few melts from which feldspar or both leucite and feldspar were crystallized it was finally possible to follow the feldspar field down to the binary eutectic Q and the ternary eutectics P and S and to locate the boundary curve RON from R to a point near O. Even after several months of crystallization at temperatures about 50° to 75° below liquidus temperatures only a few percent of very small feldspar laths were present in the glasses. These very small crystals were ideal for quenching runs to determine liquidus temperatures but quite unsuitable for exact optical or X-ray determination of the crystals. The term potash feldspar is used because it could not be ascertained whether the crystals might be sanidine, orthoclase or microcline. The small rectangular laths of feldspar could readily be distinguished under the microscope from tridymite, mullite, potassium tetrasilicate, potassium disilicate and leucite by their shape and mean index of refraction as compared with the glass.

Leucite.—There is a large field UTRONA′B′C′D′H′U of leucite in figure 4. The lowest temperature in this field is near R at 810° ± 5° and temperatures rise to a maximum at X, the composition $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ of leucite with a congruent melting point at 1686° ± 5° (Bowen and Schairer, 1929). Crystals of leucite were readily obtained from melts in this field except for those compositions near R and except for those on and very near that portion of the line leucite—silica which lies in the leucite field with liquidus temperatures below about 1400°, particularly those compositions near O.

Leucite appeared as very small crystals with a low index of refraction. They look like tiny fish eggs and are usually twinned and surrounded by a rim of highly strained glass because of the volume change during the rapid inversion (Bowen and Schairer, 1929, p. 311; Wyart, 1937) that occurs during quenching. In some cases, particularly with very small crystals quenched from temperatures below about 900°, the leucite crystals failed to invert during the rapid quenching and remained completely isotropic. Leucite was very easy to distinguish from all other crystals by the shape and low index. At high temperatures (around 1600°) the leucite crystals grew large and were not rounded but sharp isometric crystals with many facets. The crystals, however, showed twinning under crossed nicols because of the inversion that occurred during the quenching.

Hexagonal and orthorhombic $KAlSiO_4$.—In figures 3 and 4 a field of hexagonal $KAlSiO_4$, VUH′I′V, and also a field of orthorhombic $KAlSiO_4$, I′H′D′C′F′E′I′, are shown. The orthorhombic form of $KAlSiO_4$ or $K_2O \cdot Al_2O_3 \cdot 2SiO_2$, whose composition lies at E′, has a congruent melting point at an unknown high temperature which must lie above 1700°, the liquidus of composition K237, a point in the field of orthorhombic $KAlSiO_4$ in the binary system $KAlSiO_4$—Al_2O_3 (fig. 11).

No euhedral crystals of hexagonal $KAlSiO_4$ were found in the preparations. At high temperatures in a few of the preparations euhedral crystals of orthorhombic $KAlSiO_4$ were obtained, usually showing the characteristic interpenetration twins giving a hexagonal section divided into sextants that extinguish together in opposite pairs, but occasionally showing polysynthetic twinning. The confusing data on the polymorphs of $KAlSiO_4$ will now be discussed.

THE COMPOUND $K_2O \cdot Al_2O_3 \cdot 2SiO_2$

Our knowledge of the polymorphs of $KAlSiO_4$ and their stability relations is still in a very unsatisfactory state. This compound was first described as the mineral kaliophilite, a hexagonal mineral from Mte. Somma, by Mierisch (1887). One of us (Bowen, 1917) made the first systematic synthetic study of pure $KAlSiO_4$ and of its relations to $NaAlSiO_4$ at high temperatures in the system $KAlSiO_4$—$NaAlSiO_4$. In that study a melt of pure synthetic $KAlSiO_4$ was prepared with considerable difficulty from $KHCO_3$, Al_2O_3 and SiO_2 in an iridium furnace. The glass was easily crystallized at 1300°C. to hexagonal crystals. Particularly at higher temperatures, crystals of a twinned orthorhombic form were encountered. Crystals of the hexagonal form were converted to the orthorhombic form at about 1540°C., but it was not possible to convert the orthorhombic crystals back to the hexagonal form. The possibility of an enantiotropic inversion at 1540°C., or perhaps a little lower, was indicated.

Bannister and Hey (1942) described the hexagonal mineral kalsilite from Mafuru, Uganda, as a polymorphous form of $KAlSiO_4$ which is not isomorphous with nepheline, $NaAlSiO_4$, and has a different X-ray structure from hexagonal kaliophilite from Mte. Somma (Gossner and Mussgnug, 1930;

Bannister, 1931; Lukesh and Buerger, 1942). Rigsby and Richardson (1947), from a study of artificial kalsilite and orthorhombic $KAlSiO_4$ in blast-furnace linings and from synthetic studies of potassium aluminum silicates in the laboratory, indicate the existence of three forms of $KAlSiO_4$: (1) a low-temperature hexagonal modification, probably similar to natural kaliophilite and formed below 900°C.; (2) a high-temperature orthorhombic modification, sometimes twinned and sometimes free from twinning, formed at temperatures above 1000°C.; (3) the hexagonal mineral kalsilite, which can be formed only in the presence of some Na_2O, formed at temperatures between 650° and 1200°C., and which is converted to orthorhombic $KAlSiO_4$ at temperatures below 1300° or above 1500°C., depending on the soda content. Kunze (1954) made a complete review of the literature on $KAlSiO_4$, including mineralogy, X-ray data and synthetic studies with and without fluxes, and he reported on the crystallography and crystal structure of orthorhombic $KAlSiO_4$.

Recently, Tuttle and Smith (1953, p. 53-56) made a new study of the system $KAlSiO_4$—$NaAlSiO_4$ by both dry and hydrothermal methods. They reported only their preliminary results, which showed that hexagonal kalsilite was the stable form of pure $KAlSiO_4$ up to 840°C. at atmospheric pressure and above this temperature an orthorhombic form was stable. They also found a different "high-orthorhombic" form in some of the melts with moderate amounts of $NaAlSiO_4$ present. Kalsilite takes up limited amounts of $NaAlSiO_4$ in solid solution and there is a miscibility gap between kalsilite with limited $NaAlSiO_4$ and low-nepheline with limited but larger amounts of $KAlSiO_4$. Schairer and Bowen in their liquidus studies of $NaAlSiO_4$—$KAlSiO_4$—SiO_2 (quoted by Schairer, 1950, fig. 1, p. 514) found a ternary invariant point with leucite, an orthorhombic (K,Na)$AlSiO_4$ solid solution and a hexagonal Na,K nepheline in equilibrium with a liquid at about 1460°C.

In the studies of the system K_2O—Al_2O_3—SiO_2 the join $K_2O \cdot 2SiO_2$—Al_2O_3 and that portion of the ternary system that includes the fields labelled Hexagonal $KAlSiO_4$ and Orthorhombic $KAlSiO_4$ in figures 3 and 4 were investigated in the years between 1931 and 1935. The crystals obtained from the melts were small and rounded, sometimes intergrown with fine-grained material formed during the quenching. Only at temperatures above about 1500° were euhedral crystals obtained. These were always the orthorhombic form of $KAlSiO_4$. No special effort was made to study the exact relations between hexagonal and orthorhombic $KAlSiO_4$ and no X-ray studies of the crystals were made. This area of the diagram requires further careful study in the light of the confusing results on the polymorphs of $KAlSiO_4$ described above.

Temporarily the writers have accepted the evidence of Bowen (1917) of an enantiotropic inversion between hexagonal and orthorhombic $KAlSiO_4$ at about 1540°C., have assumed no solid solution in the system $K_2O \cdot 2SiO_2$—$KAlSiO_4$ and have placed the binary and ternary inversion points I′ and H′, respectively, at this temperature, but have shown the boundary curve I′H′ as a heavy dashed curve instead of a heavy curve in figures 3 and 4.

THE COMPOUND $K_2O \cdot Al_2O_3 \cdot SiO_2$

Weyberg (1908) described the compound $K_2Al_2SiO_6$, which he prepared from melts with the aid of a flux (kaolin with K_2CrO_4). It consisted of octahedra with an index of refraction close to that of balsam. A chemical analysis definitely fixed the composition. One of us (Bowen, 1917, p. 118) obtained this same compound while preparing the orthorhombic form of $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ with the aid of fluxes. It was present in the product in small amounts as octahedra with an index of refraction of about 1.540.

In our studies on the system $K_2O—Al_2O_3—SiO_2$ an attempt was made to prepare the compound $K_2O \cdot Al_2O_3 \cdot SiO_2$ (G′ of figs. 3 and 4) from appropriate amounts of $K_2O \cdot SiO_2$ and Al_2O_3. After preliminary heatings at 1400°, with intermediate crushing of the charge, it was heated for two-hour periods at 1665°, 1685° and 1712°. Even above 1700° the powdered charge did not sinter. The charge was still inhomogeneous with some undissolved Al_2O_3 present. The compound $K_2O \cdot Al_2O_3 \cdot SiO_2$ must have a very high melting point.

Because of the experimental difficulties and lack of geological interest in such compositions, the study of compositions below the join $K_2O \cdot 2SiO_2$—Al_2O_3 was not pursued.

SO-CALLED "β-Al_2O_3"

β-Al_2O_3 was first reported and described as an allotropic modification of alumina, monotropic with respect to corundum (α-Al_2O_3), by Rankin and Merwin (1916), who obtained β-Al_2O_3 crystals in melts in the system CaO—MgO—Al_2O_3. Hendricks and Pauling (1926) were the first to investigate its structure by X-rays and found that it was hexagonal with 12 Al_2O_3 in the unit cell. This was confirmed by Gottfried (1928). In later studies Bragg, Gottfried and West (1931) considered Na_2O as an essential constituent of the so-called "β-Al_2O_3" and suggested the formula $NaAl_{23}O_{35}$, which, however, would violate space group considerations. They pointed out that $Na_2O \cdot 11Al_2O_3$ would satisfy space group conditions.

Gallup (1935) showed that "β-Al_2O_3" is converted to α-Al_2O_3 on heating under different furnace atmospheres, and at temperatures as low as 1300°C. in a vacuum. Ridgeway, Klein and O'Leary (1936) reviewed the literature on so-called "β-Al_2O_3" and produced evidence to show that it is not an allotropic modification of Al_2O_3 but an alkali aluminate and they tentatively assigned the formula $R_2O \cdot 12Al_2O_3$ (R = alkali metal). They prepared and described $Na_2O \cdot 12Al_2O_3$ and $K_2O \cdot 12Al_2O_3$ and prepared mixed soda- and potash-bearing "β-Al_2O_3."

Beevers and Brohult (1936) in a short note and Beevers and Ross (1937) in a longer communication discussed various proposed compositions on the basis of X-ray and density data, and suggested that the formulae $Na_2O \cdot 11Al_2O_3$ and $K_2O \cdot 11Al_2O_3$ best fitted the data. Lagerqvist, Hallmark and Westgren (1937) gave X-ray data on two "β-Al_2O_3"-like materials to which they assigned the tentative formulae $3CaO \cdot 16Al_2O_3$ and $3SrO \cdot 16Al_2O_3$ and suggested that there exists an analogous BaO compound. Austin (1938), in an attempt to determine the linear thermal expansion of "β-Al_2O_3" containing 4.47 percent K_2O and 1.03 percent Na_2O, found that the expansion was irregular and not reproducible. On successive heatings the sample lost alkalies which corroded parts of the apparatus, and the expansion approached more and more closely that of corundum.

Toropov and Stukalova (1939) indicate that aluminates of the formula $RO \cdot Al_2O_3$ (R = Ca, Sr or Ba) can be converted into aluminates with the formula $R_2O \cdot 6Al_2O_3$ (R = Na, K or Rb). All these aluminates have the "β-Al_2O_3" structure. These same authors (1940) converted Na_2O-bearing "β-Al_2O_3" to $CaO \cdot 6Al_2O_3$, to $BaO \cdot 6Al_2O_3$ and to $SrO \cdot 6Al_2O_3$ by repeated fusions with the respective alkali earth chlorides and determined the X-ray parameters of these hexa-aluminates.

Kato and Yamauchi (1943) studied the formation of "β-Al_2O_3" in melts of varying alkali content in the systems Na_2O—Al_2O_3 and K_2O—Al_2O_3 and determined its presence in ignited alumina made by the Bayer process. They determined the optical constants, densities and X-ray properties and assigned the formulae $Na_2O \cdot 12Al_2O_3$ and $K_2O \cdot 12Al_2O_3$ for the so-called "β-Al_2O_3."

Filonenko (1945) ascribed the poor abrasive properties of a fused alumina product to the presence of a compound $CaO \cdot 6Al_2O_3$ and gave a chemical analysis and optical data for this compound. Belyankin, Lapin and Simanov (1946, 1947) described "β-Al_2O_3" from two high-alumina slags. In one of the slags there were two types of "β-Al_2O_3," one an alkali type and the other a titanium-bearing calcareous type, and crystals of the former were surrounded by a reaction rim of the latter.

Filonenko (1949) studied the phase-equilibrium relations in the high-alumina portion of the system CaO—Al_2O_3. The compound $CaO \cdot 2Al_2O_3$ melts congruently at 1750° ± 10°, and the compound $CaO \cdot 6Al_2O_3$ melts incongruently at 1850° ± 10° to corundum and liquid, becoming completely liquid only at about 1910°. There is a eutectic between $CaO \cdot 2Al_2O_3$, $CaO \cdot 6Al_2O_3$ and liquid at 1730° ± 10° at the composition CaO 19.5 ± 1.0 percent, Al_2O_3 80.5 ± 1.0 percent. Filonenko and Lavrov (1949, 1950) determined the relations in the Al_2O_3 corner of the system CaO—Al_2O_3—SiO_2 and located the ternary reaction point $CaO \cdot 6Al_2O_3$ + anorthite + corundum + liquid at 1495° ± 5°C. at the composition CaO 23.0, Al_2O_3 41.0, SiO_2 36.0, all ± 0.5 percent. The reaction $CaO \cdot 6Al_2O_3 \rightleftarrows \alpha\text{-}Al_2O_3$ + liquid takes place along the boundary curve $CaO \cdot 6Al_2O_3$—corundum at temperatures between 1495° and 1850°.

Foster and Stumpf (1951) described the gallia-analogs ($K_2O \cdot 11Ga_2O_3$ and $Na_2O \cdot 11Ga_2O_3$) of "β-Al_2O_3." Cirilli and Brisi (1951) found that "β-Fe_2O_3" ($K_2O \cdot 11Fe_2O_3$) has an X-ray powder pattern strikingly like that of "β-Al_2O_3" ($K_2O \cdot 11Al_2O_3$) and prepared mixed crystals with up to 40 percent of the former in the latter. Toropov and Galakhov (1952) determined the complete phase-equilibrium relations in the system BaO—Al_2O_3. The "β-Al_2O_3"-like compound $BaO \cdot 6Al_2O_3$ has a congruent melting point at 1900° and a eutectic with corundum at 1890°.

In our studies of compositions in the system K_2O—Al_2O_3—SiO_2 which lie in the field where Al_2O_3 is the primary phase only corundum was present at liquidus temperatures. Although all these melts are viscous it was found that some crystallization occurred when samples of the powdered glasses were held about 100° below the estimated liquidus temperatures. For those compositions with a liquidus temperature of 1500° or higher, small, thin hexagonal plates were obtained in a few hours. At the lower temperatures in the more siliceous compositions it was necessary to hold the glasses about 100° below liquidus temperatures for several days to obtain suitable small, well-distributed crystals for the quenching experiments. They were cooled, crushed, and examined with the petrographic microscope every 24 hours. All the glasses showed small crystals of both "β-Al_2O_3" and corundum. They were easily distinguished because of the high birefringence of "β-Al_2O_3" and very low birefringence of corundum. The former always occurred as very thin plates with a perfect hexagonal outline that look like needles when on edge and showed high interference colors under crossed nicols. The latter was present as equant crystals with so low a birefringence as to appear almost isotropic. In those compositions near the boundary curves A′Y, A′B′C′ and C′F′ (fig. 4) crystals of mullite, leucite and orthorhombic $KAlSiO_4$, respectively, appeared with "β-Al_2O_3" and corundum.

In the quenching experiments near liquidus temperatures, as the time at a given temperature was increased it was found that the "β-Al_2O_3" crystals became "wormy looking" and corroded. They were obviously dissolving while the corundum crystals were growing larger and became beautifully sharp and faceted. At the liquidus only corundum was present. No information could be obtained on the exact chemical composition of the "β-Al_2O_3" crystals, since it was not possible to separate these tiny crystals from the glass. The phase "β-Al_2O_3," whatever may be its composition, was metastable with respect to corundum at all temperatures from 1315° ± 10°, the temperature of A′ (fig. 4), to 1690°, the highest liquidus temperature determined in the corundum field.

THE "ANHYDROUS MUSCOVITE" COMPOSITION

The composition of muscovite approximates $K[Al_2](AlSi_3)O_{10}(OH,F)_2$ (Hendricks and Jefferson, 1939). The ideal formula for a hydroxyl muscovite is $K[Al_2](Al,Si_3)O_{10}(OH)_2$ or, in terms of oxides, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$. The composition of the anhydrous equivalent ($K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$) lies in the triangle leucite (X)—potash feldspar (W)—mullite (Z) of figures 3 and 4; it also lies in the join potash feldspar—corundum and the join leucite—$Al_2O_3 \cdot SiO_2$ (sillimanite, andalusite, kyanite), which are not shown in these figures, and it lies at the intersection of these two joins. Since these two joins are not tie lines in the system K_2O—Al_2O_3—SiO_2 at temperatures between the liquidus temperature and temperatures at and somewhat below that of complete solidification, the two solid phases potash feldspar and corundum or leucite and one of the polymorphs of $Al_2O_3 \cdot SiO_2$ cannot coexist at equilibrium at these temperatures.

Greig (1926) has shown that cyanite, andalusite and sillimanite are unstable at elevated temperatures and are converted to mullite and cristobalite or mullite and liquid.

Because many petrologists have been interested in the decomposition products of muscovite on heating, let us examine the system K_2O—Al_2O_3—SiO_2 to see what it indicates for the crystallization behavior of the "anhydrous muscovite" composition. Since it lies in the triangle leucite—potash feldspar—mullite, at equilibrium it must consist of these three solid phases when completely crystalline and in the proportions by weight given by the position of this composition in the triangle. It has been shown earlier in this paper that all compositions in this triangle complete their crystallization at 1140° ± 20° and the final liquid has the composition N.

An examination of figure 4 shows that a melt with the composition of "anhydrous muscovite" lies in the field of corundum and has a liquidus temperature estimated at 1730° ± 10° or 15°. On cooling this melt crystals of corundum appear at this temperature, and the composition of the liquid phase follows the extension of the straight line which may be drawn between the initial composition of the melt and Al_2O_3 until it reaches the boundary curve B′A′ at 1462°C.[4] when crystals of leucite appear as the second solid phase. The composition of the liquid then follows B′A′ toward A′ with both corundum and leucite separating until the liquid reaches the ternary reaction point A′ at 1315° ± 10°. At this point, with perfect equilibrium, the temperature remains constant until all corundum crystals have reacted with liquid and have been converted to mullite, at which time with falling temperature the composition of the liquid follows the boundary curve A′N to N with leucite and mullite crystals separating. At the point N, with perfect equilibrium, the temperature remains constant at 1140° ± 20° until all the remaining liquid has been exhausted by the reaction between leucite crystals and liquid to give potash feldspar crystals. The last bit of liquid has the composition N and some leucite still remains after the requisite portion of the leucite has been converted by reaction with liquid to potash feldspar.

As was noted previously in this paper, the liquid A′ at 1315° is extremely viscous and the liquid N at the lower temperature 1140° and higher silica content is even more viscous, and "β-Al_2O_3" also may appear as a metastable phase in some of the melts with corundum as the stable primary phase. In the thermal decomposition of pure muscovite it would not be surprising to find that potash feldspar had not crystallized below 1140° and that metastable assemblages of leucite, mullite, corundum, "β-Al_2O_3" and liquid might be found in the neighborhood of 1315°.

Yoder and Eugster (1955) have summarized previous studies of the thermal decomposition of muscovite on heating and have determined the P-T curve for the decomposition of muscovite in the system muscovite—water. Above this curve high-sanidine, corundum and vapor were the stable solid phases in the hydrous system.

TIE LINES AND COMPATIBILITY OF CRYSTALLINE PHASES

The region $KAlSiO_4$—Al_2O_3—SiO_2 of figure 4 embraces the two ternary systems $KAlSiO_4$—leucite—corundum and leucite—corundum—silica, whose crystallization relations have already been described. The following pairs of crystalline phases are compatible or incompatible at equilibrium:

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[4] This is the temperature where the join ($K_2O \cdot 6SiO_2$)—Al_2O_3 cuts the boundary curve B′A′ (see data on preparations nos. K722 and K723 in table 1).

Compatible	Incompatible
$KAlSiO_4$ (orthorhombic) + corundum	$KAlSiO_4$ + feldspar
Leucite + $KAlSiO_4$ (orthorhombic)	$KAlSiO_4$ + mullite
Leucite + corundum	$KAlSiO_4$ + tridymite
Leucite + mullite	$KAlSiO_4$ + cristobalite
Leucite + feldspar	Leucite + tridymite
Mullite + corundum	Leucite + cristobalite
Mullite + feldspar	Corundum + feldspar
Mullite + tridymite	Corundum + tridymite
Mullite + cristobalite	Corundum + cristobalite
Feldspar + tridymite	Feldspar + cristobalite
Tridymite + cristobalite	

Similarly, the region $KAlSiO_4$—$K_2O\cdot 2SiO_2$—SiO_2 of figure 4 embraces the two ternary systems $KAlSiO_4$—leucite—potassium disilicate and leucite—potassium disilicate—silica, whose crystallization relations have already been described. The following pairs of crystalline phases are compatible or incompatible at equilibrium:

Compatible	Incompatible
$KAlSiO_4$ (hexagonal) + $K_2O\cdot 2SiO_2$	$K_2O\cdot 2SiO_2$ + $KAlSiO_4$ (orthorhombic)
$KAlSiO_4$ (orthorhombic) + leucite	$K_2O\cdot 2SiO_2$ + quartz
$KAlSiO_4$ (hexagonal) + $KAlSiO_4$ (orthorhombic)	$K_2O\cdot 2SiO_2$ + tridymite
Leucite + $K_2O\cdot 2SiO_2$	$K_2O\cdot 2SiO_2$ + cristobalite
Leucite + $KAlSiO_4$ (hexagonal)	$K_2O\cdot 4SiO_2$ + $KAlSiO_4$ (orthorhombic)
Leucite + feldspar	$K_2O\cdot 4SiO_2$ + $KAlSiO_4$ (hexagonal)
Feldspar + $K_2O\cdot 2SiO_2$	$K_2O\cdot 4SiO_2$ + leucite
Feldspar + $K_2O\cdot 4SiO_2$	$K_2O\cdot 4SiO_2$ + tridymite
Feldspar + quartz	$K_2O\cdot 4SiO_2$ + cristobalite
Feldspar + tridymite	Feldspar + $KAlSiO_4$ (orthorhombic)
$K_2O\cdot 4SiO_2$ + $K_2O\cdot 2SiO_2$	Feldspar + $KAlSiO_4$ (hexagonal)
$K_2O\cdot 4SiO_2$ + quartz	Feldspar + cristobalite
Quartz + tridymite	Leucite + quartz
Tridymite + cristobalite	Leucite + tridymite
	Leucite + cristobalite
	Quartz + cristobalite
	$KAlSiO_4$ (orthorhombic or hexagonal) + SiO_2 (quartz or tridymite or cristobalite)

These compatibilities or lack thereof apply only to the temperature range studied, i.e., between the liquidus and just below the temperature of complete consolidation. Two or more crystalline phases incompatible at equilibrium in the temperature range studied might become compatible at equilibrium at some lower temperature. In anhydrous silicate systems the rate of reaction between two or more crystalline phases below the solidus is usually so small as to discourage investigation of equilibrium relations. The problem becomes one of rates of solid diffusion. However, the outlook is much more encouraging in hydrous systems. There is, for example, good evidence from studies of a portion of the system K_2O—Al_2O_3—SiO_2—H_2O that one pair of the incompatible minerals listed above, namely potash feldspar + corundum, becomes compatible at lower temperatures and at high pressures. These studies were made by Yoder and Eugster (1953, 1955), who determined the P-T curve for the decomposition of muscovite in the system muscovite—water. Above this curve potash feldspar (high sanidine), corundum and vapor were the stable phases. The temperature and pressure region in which the tie line feldspar—corundum is replaced by the tie line leucite—mullite is now under investigation at the Geophysical Laboratory.

Some data are available on the solid and liquid phases that coexist in the system K_2O—Al_2O_3—SiO_2—H_2O. Goranson (1938, fig. 5 and p. 87-89) has shown that in the system potash feldspar—water the stability field of leucite vanishes at about 2500 bars water pressure at 950°C. and potash feldspar melts congruently above this pressure. These results were confirmed by Bowen and Tuttle (1950), who found that the field of leucite in the system $NaAlSi_3O_8$—$KAlSi_3O_8$—H_2O decreased in size and disappeared as the water pressure was increased. Tuttle (1948, p. 632-635) has given data for two joins, $K_2O \cdot 4SiO_2$—leucite and ($K_2O \cdot 6SiO_2$)—potash feldspar, in K_2O—Al_2O_3—SiO_2—H_2O. Goranson and Kracek (1932) determined the effect of pressure in the absence of water on that portion of the system K_2O—SiO_2 with between 60 and 80 weight percent of silica.

PETROLOGIC AND TECHNOLOGIC IMPORTANCE

The data presented here for the system K_2O—Al_2O_3—SiO_2 have considerable geological interest and should be very useful in many ways in the chemical, metallurgical and ceramic industries. One of us (Bowen, 1943) has already discussed some aspects of their petrologic and technologic significance. They are of fundamental importance in depicting the crystallization behavior of the important ternary compounds with all possible excesses of the component oxides.

Three of the ternary compounds occur as rock-forming minerals in igneous rocks. Leucite, kaliophilite, kalsilite and potash-rich alkali feldspar occur in the alkaline rocks. The most acid igneous rocks, the granites, are an important rock type and of widespread occurrence. They consist principally of feldspar and quartz, with minor amounts of micas and/or ferromagnesian minerals. The feldspar is not exclusively the potash variety; there may be important amounts of soda feldspar or a lime feldspar (plagioclase) very rich in soda. The soda feldspar melts congruently, and no compound corresponding to leucite appears (Greig and Barth, 1938). There is a similar low melting eutectic between soda feldspar and silica (Schairer, 1950, fig. 1, p. 514; Schairer and Bowen, 1947a), and in the system Na_2O—Al_2O_3—SiO_2 the mullite field crowds the feldspar field (Schairer and Bowen, 1947a) in exactly the same manner as in K_2O—Al_2O_3—SiO_2. The general relations in a granite or granitic liquid with both potash and soda present should be as in the portion $NaAlSi_3O_8$—$KAlSi_3O_8$—SiO_2 of the system $NaAlSiO_4$—$KAlSiO_4$—SiO_2 (Schairer and Bowen, 1935; Schairer, 1950, fig. 1, p. 514). It is not surprising that the geologic evidence points strongly to granitic magmas as the lowest temperature magmas. Phase-equilibrium relations in the system $NaAlSi_3O_8$—$KAlSi_3O_8$—SiO_2—H_2O, which even more closely approximates granitic liquids, have been worked out by Tuttle and Bowen (1955), and the results should appear soon.

One of us (Bowen, 1937, 1954) has emphasized the importance of the system $NaAlSiO_4$—$KAlSiO_4$—SiO_2 as petrogeny's "residua" system. The system leucite—silica (fig. 6), a binary system within the ternary system K_2O—Al_2O_3—SiO_2, is a portion of the limiting binary system, $KAlSiO_4$—SiO_2, of the "residua" system. An examination of figure 4 shows the close proximity both in temperature and composition of the binary eutectic potash feldspar + tridymite + liquid (I of fig. 4) and the ternary eutectic potash feldspar + tridymite + mullite + liquid (M of fig. 4). A series of ternary systems which combine one of the early-forming minerals olivine (forsterite or fayalite), pyroxene (diopside or enstatite), or anorthite with late-forming alkali aluminosilicates in the system leucite—silica have been studied. The results on leucite—forsterite—silica (Schairer, 1954), leucite—fayalite—silica (Roedder, 1951), leucite—diopside—silica (Schairer and Bowen, 1938) and leucite—anorthite—silica (Schairer and Bowen, 1947b) show that the residual liquids from crystallization in these systems closely approach the binary eutectic between potash feldspar and silica, with only small amounts of olivine, pyroxene or lime feldspar in the several ternary eutectics. The studies by Schairer (1954) on a portion of the dry quaternary system K_2O—MgO—Al_2O_3—SiO_2 show in a detailed and convincing manner that residual liquids from crystallization (particularly fractional crystallization) in a large portion of this quaternary system are granitic in composition and very close to the composition of the potash feldspar—silica eutectic. This system has only potash present with soda lacking, only magnesia present with ferrous oxide lacking, and only alumina present with ferric oxide lacking; there is no lime. The system is anhydrous instead of having at least a small water content like most magmas. In spite of these deficiencies, it can be seen that a large range of rock-forming compositions would give a common end product of crystallization, a granite, if differentiation proceeded by fractional crystallization.

We have just seen that phase-equilibrium studies indicate that granitic liquids are to be expected as the residual liquids from crystallization. Conversely, if assemblages of appropriate minerals in igneous, metamorphic or sedimentary rocks were reheated to a sufficiently high temperature in any manner, for example by very deep burial and subsequent thermal metamorphism, the first liquid to form should have this same granitic composition. A discussion of this subject should be reserved until more data on hydrous systems, particularly the systems K_2O—Al_2O_3—SiO_2—H_2O and K_2O—MgO—Al_2O_3—SiO_2—H_2O, are available. These studies should give much information on sericitization, rock alteration and many metamorphic processes.

Attention is called again to the close proximity in composition and temperature of the ternary eutectic (M of fig. 4) between potash feldspar, tridymite and mullite and the binary eutectic (I of fig. 4) between potash feldspar and tridymite. From this ternary eutectic, and indeed from all points on the mullite—feldspar boundary curve (MN of fig. 4), the temperature of the mullite liquidus surface rises very abruptly. In figure 4 the 1100°, 1200° and 1300° isotherms in the mullite field are so close together that it is almost impossible to show them clearly on the scale of this diagram. From these relations it is easy to see why granitic magmas do not acquire more than an insignificant excess of Al_2O_3 over the feldspar ratio even when they have abundant inclusions of argillaceous rocks. Even if heated some 200° to 300° above their fusion temperatures granitic magmas could still dissolve no more than a small amount of alumina, and such a degree of superheat is not to be expected in natural magmas, more especially in granitic types. In these melts the rate of conversion of argillaceous xenoliths to mineral assemblages stable in equilibrium with such melts might be very slow.

The extreme viscosity of dry liquids that approach granitic compositions and the difficulties encountered in attempts to crystallize such glasses have been noted. It is not surprising that geologic evidence indicates that the rhyolites and obsidians which are the extrusive equivalents of granitic rock types were extruded as viscous flows or ejected as tuffs and pumices and that many of them are largely glass which failed to crystallize during cooling and have only small phenocrysts or microlites of quartz and feldspar present.

The results presented here on the system K_2O—Al_2O_3—SiO_2 should be widely useful in technology. The effect of the addition of potash on the refractoriness of Al_2O_3—SiO_2 compositions (mullite or pure silica refractories or some types of firebrick) can be seen from figure 4. All compositions in the area corundum—mullite—leucite are completely solid at temperatures below that of A′, 1315° ± 10°; those in the area mullite—potash feldspar—leucite, at temperatures below that of N, 1140° ± 20°; those in the area mullite—potash feldspar—silica, only at temperatures below that of M, the ternary eutectic at 985° ± 20°.

Many porcelains are mixtures of clays and flint with feldspar to form a vitreous binder. On firing, vitrification should begin at the temperature of the ternary eutectic M (fig. 4). For small additions of feldspar, the point representing the total composition will lie close to the Al_2O_3—SiO_2 side of the triangle, and only a small amount of liquid will be formed at this temperature. The crystalline phases will be mullite and silica. The amount of liquid will increase only moderately if firing is conducted at higher temperatures, as normally it would be, and silica will persist. Not until the temperature is raised to a very high point in such material will the silica be completely dissolved, and only mullite will remain as crystals. With increased amounts of feldspar, the temperature at which the silica disappears on firing is lowered; with a certain proportion of feldspar and adequately prolonged firing at the eutectic, both silica and feldspar would disappear and mullite crystals alone would survive in the liquid. Further increase in feldspar will result in survival of feldspar with mullite at temperatures immediately above the eutectic. The exact proportion of feldspar necessary to produce these effects may be worked out graphically on the diagram for any assumed mixture of metakaolin and flint. The behavior of feldspar or even potassium silicates when used as glazes is apparent from the diagram.

In addition to the technologic applications just noted, the data presented here give a wide variety of useful information in connection with the corrosion of blast furnace linings or glass-tank linings, the effects of alkali in slags or furnace atmospheres on refractories, the manufacture of refractories, whiteware, glass, etc., and their stability or deterioration in service, and the extraction of potash from silicate minerals. In many industrial processes rate of the reaction is an important consideration. The petrologist or ceramist with adequate microscopic control soon discovers how slow may be the attainment of equilibrium in viscous silicate compositions even at moderately high temperatures. Equilibrium, however, is the goal toward which the changes trend. Even though it may not often be completely attained, the equilibrium relations must be understood in order to know the nature of the changes and the direction toward which they are proceeding.

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