THE UNIVERSITY OF MANITOBA

THE TERNARY SYSTEM BERYLLIUM SULPHATE - SULPHURIC ACID - WATER

BEING A THESIS SUBMITTED TO THE COMMITTEE
ON POST-GRADUATE STUDIES IN PARTIAL
FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF
SCIENCE

By
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To Dr. A. N. Campbell

In sincere appreciation of his constant guidance and many helpful suggestions.

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INTRODUCTION

The existing literature on beryllium sulphate and its hydrates is to some extent uncertain and largely contradictory. In addition to the anhydrous form of this salt and the hemihydrate, other hydrates having a water content ranging through all integral values from one to seven moles of water per mole of the salt have been reported. While many of the reports appear to be based on somewhat superficial evidence the results of more exhaustive investigations indicate the existence of those hydrates only with one, two, four and five moles of water, besides the anhydrous salt. The tetrahydrate is known to be the stable hydrate under ordinary room conditions. At a higher temperature, according to the most general opinion, the tetrahydrate is transformed to the dihydrate. According to one report a tetrahydrate-monohydrate transition point exists below that of the tetrahydrate and dihydrate, from which it follows that the dihydrate is always metastable with respect to the monohydrate. The pentahydrate has been found to exist at a temperature in the vicinity of -18 degrees.

The object of the present study is an accurate determination of the upper temperature limit of stable existence of beryllium sulphate tetrahydrate and a determination of the nature of the stable hydrate existing above this limit.

REVIEW OF THE LITERATURE

Introduction

Most of the more important investigations concerning beryllium sulphate and its hydrates have been conducted since 1900. With further experimental evidence some of the results of these and earlier studies have been deemed unsound. The following resume of the literature discusses the more important aspects of the subject in order to reveal the controversial nature of various published opinions.

Anhydrous Beryllium Sulphate

Preparation - Anhydrous beryllium sulphate may be prepared in three ways. These are 1 - direct dehydration by heating of the salt hydrates, 2 - dehydration of the hydrates by contact with concentrated sulphuric acid, and 3 - treating the oxide or hydroxide with concentrated sulphuric acid.

With regard to the method of dehydration by heating the hydrates, different authors have disagreed concerning the minimum temperature necessary in order to produce the anhydrous salt. The temperatures suggested are given in the following table:

G. Kruss and H. Morath (15) - - - - -	250-60 degrees
M. Levi-Malvano (17) - - - - - - - -	218-20
F. Krauss and H. Gerlach (14) - - - -	300
L. Hackspill and A.P. Kieffer (11) -	320

The other two methods mentioned have achieved somewhat less prominence in the literature. F. Taboury (27) dehydrated the hydrates of beryllium sulphate to the anhydrous form by contact with concentrated sulphuric acid, while F. Lebeau (16) prepared the anhydrous salt by treating the oxide or hydroxide with this concentrated acid. These authors suggest no means for the subsequent removal of the excess acid. Similar methods were employed by Krauss and Gerlach (14) who removed the excess acid by washing the crystalline salt with absolute alcohol. This was followed by filtration and drying the salt over sulphuric acid in an evacuated desiccator.

Properties - The possibility of obtaining pure anhydrous beryllium sulphate by heating the hydrates has been disputed by C. L. Parsons (19), claiming that the sulphate begins to decompose with the evolution of sulphuric anhydride even before all the water of hydration is removed. According to Parsons this simultaneous loss of anhydride and water takes place at temperatures between 300 and 400 degrees. The same author has raised a similar objection to the methods of preparation involving the use of sulphuric acid, stating that the free acid could not be removed by heating without decomposing some of the salt. As evidence he cited the presence of a small amount of insoluble residue, presumably beryllium oxide arising from the decomposition of the sulphate, whenever he prepared the anhydrous salt in this way.

Experiments performed by Taboury (27) on the thermal dehydration of beryllium sulphate hydrates showed that a temperature of 530-40 degrees is required in order to produce decomposition of the anhydrous salt. Taboury showed that the sulphuric anhydride obtained by Parsons was not due to the decomposition of the salt but rather to the presence of traces of free sulphuric acid retained by the hydrate even after several crystallizations.

Krauss and Gerlach obtained experimental evidence similar to the results obtained by Taboury. They show diagrams representing the progressive dehydration of beryllium sulphate tetrahydrate to the anhydrous form, followed by heating the product to its decomposition temperature. In reasonable agreement with Taboury they regard the decomposition temperature of the anhydrous salt as lying somewhat above 580 degrees. Their disagreement with Parsons is explained on the same basis as that of Taboury.

A more recent study of the progressive dehydration of beryllium sulphate tetrahydrate by T. N. Hladun (12) shows that the decomposition of the anhydrous salt begins at 650 degrees, becoming measurable only at temperatures above 700 degrees. In Hladun's investigations the degree of dehydration of the hydrate and dissociation of the anhydrous salt was measured by means of Guichard's hydrostatic balance.

Beryllium Sulphate Hemihydrate

On the basis of experiments on the progressive dehydration of beryllium sulphate tetrahydrate the possibility of existence of the hemihydrate was claimed by Taboury (27). No other investigators have given support to this belief. According to Krauss and Gerlach (14) valid evidence for the existence of the hemihydrate does not exist.

Beryllium Sulphate Monohydrate

According to Krauss and Gerlach (14) the existence of beryllium sulphate monohydrate was claimed as early as 1873 by A. Atterberg, and again in 1891 by G. Klatzo. These investigators had reported that the monohydrate may be prepared by heating the tetrahydrate to 150 degrees. A number of other studies have given support to this belief, mainly on the basis of experiments on the dehydration of the tetrahydrate. Taboury (27) claimed that the monohydrate can be prepared by heating the tetrahydrate to 100 degrees, while Levi-Malvano (17) suggested that a temperature of 145-50 degrees is required. In a more recent report Hladun (12) has stated that the monohydrate can be prepared by rapid dehydration of the tetrahydrate at 220 degrees. Another report of recent date by R. Rohmer (22) indicates again the existence of this hydrate. Rohmer's arguments are based on his study of the ternary system, beryllium sulphate - sulphuric acid -

water, at 100 degrees. By means of Schreinemakers' method of "wet residues" Rohmer determined the nature of the solid phase in equilibrium with the saturated solution of varying acid content, from zero to about 90 per cent acid. The monohydrate was met with as the only stable solid phase.

In opposition to these opinions exhaustive studies conducted by Krauss and Gerlach produced no definite evidence to indicate the existence of the monohydrate. Their measurements, using Huttig's tensi-eudiometer, gave no conclusive evidence of its chemical individuality.

Beryllium Sulphate Dihydrate

Preparation - The preparation of beryllium sulphate dihydrate by dehydration of the tetrahydrate has been reported by a number of investigators, most of whom seem to be in close agreement with regard to the temperature required. This is shown in the following table, giving the temperatures suggested by different authors:

Kruss and Morath (15)	105 degrees
Parsons (19)	100
Levi-Malvano (17)	100
Krauss and Gerlach (14)	120
Hladun (12)	160

Taboury (27) prepared the dihydrate by heating the tetrahydrate to 50-60 degrees in a current of dry air.

Properties - From a study of the properties of the dihydrate Parsons has found that it is quite stable in a dry atmosphere at ordinary temperatures but slowly loses water if kept in dry air at about 100 degrees. Experiments conducted by Levi-Malvano seemed to indicate that the dihydrate suffers no hysteresis on rehydration when moistened with two moles of water per mole of the salt. A thermometer immersed in the moist salt indicated a temperature rise to above 113 degrees during the hydration process. By means of such experiments Levi-Malvano concluded that the tetrahydrate-dihydrate transition point lies at 111.5 degrees.

As a result of a more recent study of beryllium sulphate and its hydrates Rohmer (22) has presented an argument to show that the dihydrate is metastable throughout its range of existence. Despite its metastability Rohmer states that the duration of existence of the dihydrate may exceed six months at about 90 degrees. For this reason, according to him, one might easily regard it as a stable hydrate.

Beryllium Sulphate Trihydrate

Krauss and Gerlach (14) have stated that a hydrate of beryllium sulphate with water content corresponding to the trihydrate can be produced by heating the tetrahydrate at 55 degrees. They maintain, however, that this is not sufficient evidence for regarding the trihydrate as a definite chemical individual. Their tensi-eudiometer measurements showed that only the tetrahydrate, dihydrate and possibly the monohydrate, in addition to the anhydrous salt, can be considered as separate chemical compounds. The only investigators who have actually claimed the existence of the trihydrate are Y. A. Fialkov and S. D. Shargorodskii (7). These workers based their opinions on their interpretation of certain endothermal effects observed on heating the tetrahydrate.

Gmelin (10), reviewing the work of Krauss and Gerlach, considers the existence of beryllium sulphate trihydrate established as a certainty.

Beryllium Sulphate Tetrahydrate

Preparation - According to J. W. Mellor (18) the tetrahydrate of beryllium sulphate was first prepared and studied by J. J. Berzelius in 1815. Berzelius prepared it by dissolving the oxide, hydroxide or carbonate in an excess of sulphuric acid. The excess acid was removed by evaporation and the crystalline salt washed with alcohol. This same method of preparation has since been used by many other investigators, with only slight modifications in some cases. Preparation methods have been discussed by Kruss and Morath (15), Parsons (19), Levi-Malvano (17), Taboury (27), H.T.S. Britton (3), F. Wirth (28), Krauss and Gerlach (14) and L. Schreiner and A. Sieverts (25).

In preparing beryllium sulphate tetrahydrate from beryllium oxide and sulphuric acid Parsons found that a slight excess of the oxide in the resulting solution produced a non-crystallizable syrup on evaporation. As an alternative method of preparation Parsons dissolved beryllium oxide in concentrated sulphuric acid, driving off the excess acid by heating over a Bunsen flame, taking care to heat but little higher than necessary to remove the free acid. The resulting residue of anhydrous sulphate was dissolved in water, the solution filtered from undissolved oxide and then evaporated to produce the tetrahydrate crystals.

The method of preparation of the tetrahydrate employed by Krauss and Gerlach involved the treatment of beryllium hydroxide with excess dilute sulphuric acid. The resulting solution was concentrated on a water bath and cooled to produce crystallization. The crystals were washed with absolute alcohol and dried.

Schreiner and Sieverts prepared the tetrahydrate from beryllium nitrate by evaporating twice to fuming with sulphuric acid. This was followed by re-crystallizing the beryllium sulphate twice from dilute sulphuric acid. The final product they regarded as pure.

<u>Properties</u> - According to Parsons beryllium sulphate tetrahydrate is stable under ordinary atmospheric conditions but dehydrates readily with a rise in temperature. He states also that it undergoes a slow and continuous loss of water over desiccating agents, particularly phosphorus pentoxide.

On the other hand, Taboury has found that the tetrahydrate may be kept over sulphuric acid in an evacuated desiccator without dehydration.

Crystal Structure - R. Fricke and L. Havestadt (8) and P. Schonefeld (24) have reported the crystalline structure of beryllium sulphate tetrahydrate as tetragonal body-centered. Fricke and Havestadt give the unit-cell dimensions as $a = 8.03$ and $c = 10.75$ angstroms. In good agreement Schonefeld gives these as $a = 8.02$ (± 0.02) and $c = 10.75$ (± 0.014) angstroms.

Beryllium Sulphate Pentahydrate

The only evidence for the existence of beryllium sulphate pentahydrate is that presented by Rohmer (22). He concludes from thermal analysis experiments and a study of the ternary system, beryllium sulphate - sulphuric acid - water, that the pentahydrate is the stable hydrate through the short temperature range from -16.4 to -18.5 degrees.

Beryllium Sulphate Hexahydrate

The preparation of beryllium sulphate hexahydrate by treating beryllium carbonate or hydroxide with a small excess of sulphuric acid was first claimed by Levi-Malvano (17), stating that he obtained it in the form of octahedral crystals. A study of the hexahydrate crystals by F. Zambonini (29) showed them to be cubic, predominantly octahedral. A further claim by Levi-Malvano, stating that he obtained the hexahydrate by evaporating a solution containing equivalent quantities of beryllium sulphate and potassium sulphate, was proved unsound by H. T. S. Britton and A. J. Allmand (4). The latter obtained the double salt $BeSO_4 \cdot K_2SO_4 \cdot 2H_2O$ under the conditions described by Levi-Malvano.

Further evidence for the existence of the hexahydrate was provided by F. Wirth (28), who determined its solubility in water and in aqueous sulphuric acid. According to Wirth, if the acid solution has a concentration greater than about 45 per cent the large, almost transparent, hexahydrate crystals become transformed into a finely divided white powder which settles slowly in the body of the solution. This latter form he regarded as the tetrahydrate.

Experiments performed by Britton (3) in his determinations of the solubility of beryllium sulphate in water and in aqueous sulphuric acid produced no results to correspond to the hexahydrate solubility curve of Wirth. Unsuccessful attempts at the preparation of the hexahydrate by Britton, C. L. Parsons and C. T. Fuller (20) and Krauss and Gerlach (14) have indicated that the methods suggested for its preparation are questionable and that conclusive evidence for its existence has not been produced.

It is of interest to note that Wirth's description of the change in appearance of the solid phase in equilibrium with its saturated solution, on increasing the sulphuric acid content, corresponds exactly to that found by other investigators, namely Schreiner and Sieverts (25), for the transformation of the tetrahydrate to a lower hydrate.

Beryllium Sulphate Heptahydrate

Parsons (19), Levi-Malvano (17) and Krauss and Gerlach (14) have discussed reports by earlier workers, notably G. Klatzo, C. Marignac and A. Atterberg, who have claimed the existence and preparation of beryllium sulphate heptahydrate. Following their own unsuccessful attempts to prepare the heptahydrate these authorities have all agreed that this hydrate of beryllium sulphate does not exist.

According to a recent report B. Ghosh (9) investigated certain transient (unstable) hydrates of beryllium sulphate by means of a thermal dehydration method involving the use of differential thermocouples. In opposition to the opinions expressed by Parsons, Levi-Malvano and Krauss and Gerlach, Ghosh has indicated that his starting material was the heptahydrate. He offers no information regarding the source of this substance or methods for its preparation.

General Considerations

The determinations by Wirth (28) of the solubility at 25 degrees of beryllium sulphate in aqueous solutions of sulphuric acid showed that the hexahydrate is the stable solid phase up to an acid concentration of about 45 per cent. His data show a minimum solubility of the hexahydrate for an acid concentration of about 34 per cent, and a maximum for about 5 per cent. For concentrations above 45 per cent he obtained the tetrahydrate as the solid phase. Subsequent work by Britton (3) produced results in complete disagreement with those of Wirth. The smooth character of Britton's curve for 25.0 degrees shows a gradual decrease in the solubility of the beryllium sulphate with an increase in sulphuric acid concentration, the equilibrium solid phase always being the tetrahydrate throughout the range investigated, which was zero to about 65 per cent acid. Britton found that at 25.0 degrees the solubility of beryllium sulphate in pure water is 29.94 grams per 100 grams of solution, as compared to Wirth's value of 8.212 grams. A later determination of the solubility by N. V. Sidgwick and N. B. Lewis (26) gave the solubility as 29.74 per cent beryllium sulphate.

Progressive dehydration of the tetrahydrate by Krauss and Gerlach (14), using Huttig's tensi-eudiometer, appeared to indicate that of the hydrates of beryllium sulphate having from zero to four moles of water only the tetrahydrate, dihydrate and anhydrous form are definite chemical individuals. The results of their experiments do not indicate conclusively the existence of the monohydrate.

The authors do not, however, dispute this possibility, but suggest that the range of existence of the monohydrate is perhaps lessened by its tendency to form solid solutions with both the dihydrate and the anhydrous salt. They also suggest that since the water content of beryllium sulphate, when heated to above 150 degrees, seems to be continuously variable it might be assumed that the water in this case is zeolitically bound. Their data and diagrams show an abrupt transformation at about 120 degrees, when the tetrahydrate changes to the dihydrate.

In somewhat close agreement with the results of Krauss and Gerlach are those of Hackspill and Kieffer (11). The results obtained by these investigators also indicate that the transition from the tetrahydrate to the dihydrate is more or less abrupt, but the dehydration of the dihydrate seems to be continuous except for a slight departure from continuity when the composition of the material corresponds to the monohydrate.

Schreiner and Sieverts (25) have determined the solubility of beryllium sulphate in water up to a temperature of 100 degrees. According to their results the equilibrium solid phase is the tetrahydrate throughout the range from the tetrahydrate-ice eutectic at -18.0 degrees to this temperature.

In their investigation of the ternary system, beryllium sulphate - sulphuric acid - water, Schreiner and Sieverts found no transition points for any of the four isotherms deduced, that is, at 0, 25, 50 and 75 degrees. Despite this absence of discontinuities in their solubility curves these investigators observed that, while the tetrahydrate is the equilibrium solid phase for solutions of low acid content, above acid concentrations of about 65 per cent the solid was finely divided, unlike the semi-transparent tetrahydrate crystals. This finely divided form they regarded as probably being the anhydrous salt. They were unable to determine the solid phase composition by Schreinemakers' method of "wet residues." Their 25-degree isotherm for the ternary system agrees well with that obtained by Britton.

A recent study of an isotherm at -17.5 degrees for this same system by Rohmer (22) indicates that the equilibrium solid phase at this temperature is the pentahydrate up to an acid concentration of 8.9 per cent. From thermal analytical data Rohmer concludes that from -16.4 to -18.5 degrees the pentahydrate is the stable solid phase in equilibrium with its saturated solution in water. The solubility curve is presented, including also the ice curve. According to his results a eutectic point exists for ice-pentahydrate at -18.5 degrees while a metastable ice-tetrahydrate eutectic lies at -21.5 degrees. Comparing his results with those of Schreiner and Sieverts, Rohmer also states that the solubility curve, with tetrahydrate as the equilibrium solid phase, can be readily investigated up to the boiling point of the saturated solution.

Rohmer's investigations have shown that the boiling point of the saturated solution of beryllium sulphate in water varies appreciably with time. According to him the boiling point passes through three successive values, each of which corresponds to the presence of a different solid phase. His diagram indicates that the three boiling points lie at about 117, 112 and 109 degrees. These correspond to the presence of the tetrahydrate, dihydrate and monohydrate respectively. According to Rohmer's results the saturated solution in contact with solid boils at 117 degrees for the initial ten minutes of the experiment, gradually decreases to constancy at 112 degrees, and finally to 109 degrees when a total time of about 90 minutes has elapsed. Full detail of the experimental procedure is not presented.

Rohmer obtained corresponding results from a study of solubility variations between the boiling point of the saturated solution and 88.4 degrees, the temperature at which, according to his thermal analysis experiments, the tetrahydrate changes to the dihydrate. In this case also no experimental detail is given.

On the basis of these results Rohmer concludes that beryllium sulphate tetrahydrate is metastable above 76 degrees and that above this temperature the monohydrate is the stable hydrate. Without further explanation he states that the metastable dihydrate exists between 88.4 and 111.6 degrees. Rohmer obtained further evidence from his study of the 100-degree isotherm for the ternary system. This has been discussed in a previous section dealing with the monohydrate. According to him the labile equilibria of the tetrahydrate with solutions containing sulphuric acid at 100 degrees are not very lasting, the dehydration to the dihydrate taking place rapidly. On the other hand, he finds that the labile equilibria involving the dihydrate can last for more than a month, despite continuous stirring, and therefore might easily be regarded as stable. Boiling the solution is believed to bring about the transformation from dihydrate to monohydrate in less than an hour.

EXPERIMENTAL PROCEDURE

Introduction

The determination of the transition temperature of beryllium sulphate tetrahydrate to the next lower hydrate has been accomplished in this study by an investigation of the ternary system, beryllium sulphate - sulphuric acid - water. This system has been treated as a condensed system, the phase diagrams being represented by the familiar Gibbs equilateral triangle method. The composition of the saturated solution of beryllium sulphate in aqueous sulphuric acid of varying concentration has been determined under different isothermal conditions, together with the nature of the equilibrium solid phase. At each temperature a determination has been made of the exact liquid phase composition which indicates by a break in the solubility curve the transformation of the tetrahydrate to the next lower hydrate. From a knowledge of these compositions the transition temperature of the pure tetrahydrate has been obtained by methods of extrapolation.

In addition to the determination of this transition temperature the composition of the lower hydrate has been conclusively established. Experiments involving thermal analysis, dilatometry and X-ray powder photography have been performed in order to supplement and clarify the results obtained.

The principles and theory underlying the experimental methods employed are not discussed in this work. These can be found in the standard text-books.

Preparation and Purification of Starting Material

The tetrahydrate of beryllium sulphate used in this study was prepared from the carbonate (glucinum carbonate obtained from British Drug Houses Limited) by treating with excess sulphuric acid. The procedure was similar to that employed by Parsons (19) and Krauss and Gerlach (14).

The beryllium carbonate, stirred into a thin paste with distilled water, was treated with an excess of slightly diluted sulphuric acid. The acid was added slowly with constant stirring. The resulting solution was boiled to expel carbon dioxide, filtered from a usual brown solid impurity, and then concentrated by boiling to almost the point of crystallization. This syrupy solution was poured while hot into strong alcohol from which the solid was allowed to crystallize out by cooling. The crystals were filtered under suction. In order to ensure proper removal of the free sulphuric acid the crystalline solid was dissolved in water, boiled down, and a second crystallization from alcohol performed. After a few hours of drying subsequent to the alcohol treatment the salt was re-crystallized three times from water, filtered under suction, and finally allowed to stand open to the atmosphere for about a day.

Analysis of the product always showed good agreement when the beryllium sulphate content was calculated from separate estimations of both sulphate and beryllium ion. This indicates that the prepared tetrahydrate was reasonably free from occluded sulphuric acid. Determination of the beryllium sulphate content of the salt usually indicated the possibility of a slight degree of dehydration in the process of preparation. The amount of beryllium sulphate in the tetrahydrate calculated from the formula is 59.32 per cent. The value obtained from the analysis of the prepared tetrahydrate was usually between 60 and 61 per cent. This is attributed to the fact that, as the results of this study will show, the dihydrate crystallizes out from the solution when above 89 degrees. Since the re-crystallization from water was always carried out by concentrating the solution by boiling it is possible that some of the solid would have appeared as the dihydrate on crystallization.

In his preparation of beryllium sulphate tetrahydrate by this method Parsons (19) found that an excess of the carbonate in the solution yielded a non-crystallizable syrup on evaporation. This observation was confirmed also in connection with this study. A full investigation of this phenomenon, the solubility of beryllium oxide, hydroxide or carbonate in solutions of beryllium sulphate, has been carried out by Parsons and Robinson (21) and later by Sidgwick and Lewis (26).

Analytical Procedure--System: $BeSO_4$ - H_2SO_4 - H_2O

For the determination of the isothermal solubility curves of beryllium sulphate in aqueous sulphuric acid the solutions were saturated by stirring in contact with solid phase in tubes suspended in a water thermostat. To prevent undue evaporation at the higher temperatures a mercury-seal stirrer was used. The stirring time varied from one day for solutions of low acid content to about two weeks for the high acid concentrations. The solubility isotherms were determined for 25, 50, 75, 85 and 95 degrees, employing Schreinemakers' method of "wet residues" for the determination of the composition of the equilibrium solid phase. For the first three temperatures an attempt was made to determine the complete isotherm. The data obtained in the region of high acid concentration may be somewhat uncertain as the resulting diagrams will show. This uncertainty is attributed to the practical difficulty in the proper separation of the viscous liquid phase from the solid, which in this region was always finely divided. At 85 and 95 degrees no attempt was made to investigate the region of high acid content.

At 25, 50 and 75 degrees the thermostat was regulated by means of a mercury thermoregulator with a precision of about ± 0.05 degree. At 85 and 95 degrees a toluene-mercury thermoregulator was employed. The precision in this case cannot be considered better than about ± 0.1 degree since an exposed stem correction was necessary for the thermometer. The thermometer in all cases was mercury-in-glass, calibrated against a certified standard.

After sufficient stirring to ensure equilibrium the liquid phase was drawn off by suction into a weighed receiver for analysis. For this purpose fritted-glass filter sticks were used. The apparatus employed was an all-glass assembly

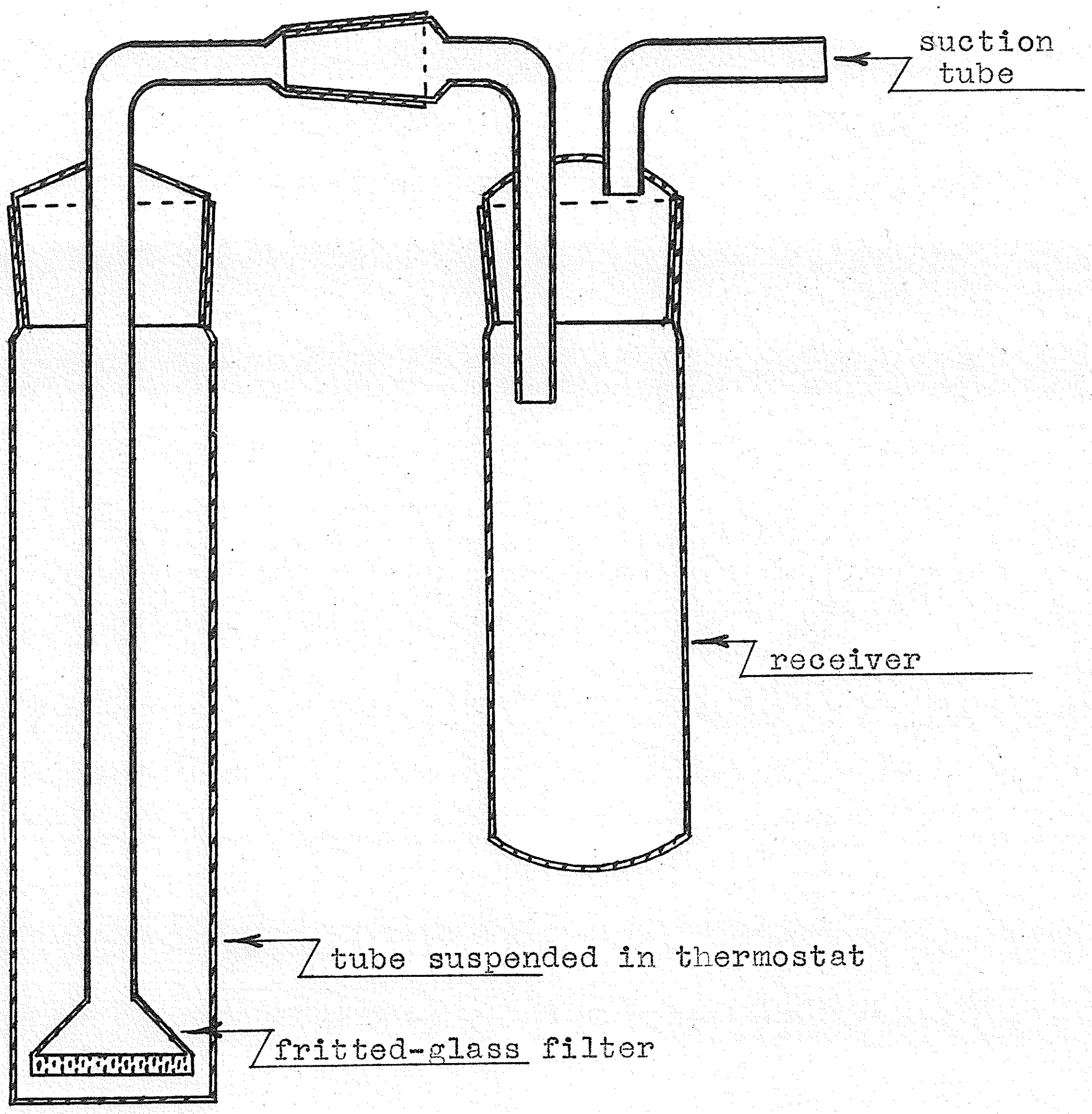


Figure 1. Filter Assembly for the Separation of Liquid and Wet Solid Phases.

of the filter stick, suction tube, and liquid receiver fitted together with ground-glass joints as shown in figure 1. The equilibrium liquid phase was drawn away from the solid as completely as possible without allowing the risk of appreciable dehydration due to the passage of air through the solid mass. A sample of the moist solid was removed and weighed in a stoppered weighing bottle. Both the liquid phase and wet solid samples taken were dissolved in water to give 250 milliliters of solution, the amount of liquid sample varying from about 20 to 80 grams and the wet solid varying from about 5 to 10 grams. Separate aliquot portions of these solutions were analyzed for total sulphate and for beryllium. The sulphate was precipitated with barium chloride in the presence of hydrochloric acid, the barium sulphate filtered under suction by means of fritted-glass filters and dried in these by heating overnight at not more than 150 degrees. For the estimation of beryllium a method suggested by Bleyer and Boshard (1) was employed. The beryllium ion was precipitated as the hydroxide with ammonia in the presence of ammonium chloride, filtered by ordinary means, and ignited to the oxide in platinum crucibles. From the weight of barium sulphate and beryllium oxide obtained the beryllium sulphate and free sulphuric acid content of the liquid and wet solid phases were calculated. These are expressed in terms of weight per cent and are given in tables 1 to 5. The corresponding isothermal phase diagrams are given in figures 2 to 6, the end of the tie-line in each case indicating the composition of the pure equilibrium solid phase. These diagrams show that the break in the solubility curve represents the tetrahydrate-dihydrate transition. All five liquidus curves are shown in figure 7.

In the filtration of beryllium hydroxide precipitated in the cold it was always found that some of the gelatinous precipitate adhered strongly to the sides of the beaker and could not be removed by ordinary washing. In order to remove this last trace of the hydroxide it was found convenient to dissolve it by washing with a small quantity of dilute hydrochloric acid. This was followed by washing down the walls of the beaker with water and then re-precipitating the beryllium ion with ammonia. The small amount of precipitate obtained in the form of a light suspension could then be removed from the beaker without further difficulty.

The ordinary ignition of beryllium hydroxide to the oxide presented difficulty in that traces of carbon arising from the filter paper seemed to remain even after prolonged heating. The evidence for this lay in the usual bluish grey appearance of the residue and the fact that test analyses gave results which were too high with respect to the beryllium oxide. This same difficulty was met with by Britton (3). In connection with this study it was found possible to obtain a reasonably white carbon-free residue by treating it with concentrated nitric acid. After preliminary ignition to burn off all the filter paper the bluish grey residue in the platinum crucible was well covered with strong nitric acid. The crucible and contents were then carefully heated over an electric hot-plate until all the solid had dissolved, adding more acid if necessary. This solution was then evaporated to dryness by cautious heating to avoid loss of material by spattering. Ten hours ignition of the final residue was found necessary to produce a reasonably white product of constant weight.

Method for Obtaining Invariant Solutions.-- It was always found that when the solid phase in equilibrium with the solution was tetrahydrate it appeared as transparent crystals up to about 2 millimeters in length. The dihydrate on the other hand always appeared as a finely divided white solid which settled but slowly. This definite difference in the appearance of the two solid phases suggested a convenient method for obtaining the liquid phases of invariant composition. The method adopted was to add small amounts of sulphuric acid to the solution in equilibrium with tetrahydrate until all the solid was barely transformed to the finely divided state. The acid was added at intervals of a few hours to allow the system sufficient time to reach an approximate equilibrium. When the concentration of the acid was just sufficient to cause the solid phase transformation the supernatant liquid was decanted and poured over fresh tetrahydrate. Stirring this final mixture for one or two days revealed the presence of both solid phases.

TABLE 1

ISOTHERM FOR 25.00° (± 0.05)

	Solution		Wet Residue		Nature of Solid Phase
	% $BeSO_4$	% H_2SO_4	% $BeSO_4$	% H_2SO_4	
1	29.32	0.00	52.35	0.00	$BeSO_4 \cdot 4H_2O$
2	12.64	23.88	51.68	3.99	"
3	4.39	43.23	51.38	6.31	"
4	3.10	51.42	37.37	20.17	"
5	3.05	54.29	55.07	7.78	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
6	3.08	54.27	51.32	12.41	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
7	1.43	60.15	45.83	23.84	$BeSO_4 \cdot 2H_2O$
8	1.28	62.08	42.62	27.01	"
9	0.90	66.65	58.03	15.17	"
10	0.64	74.65	49.18	26.80	"
11	1.55	80.60	43.71	35.68	"
12	2.14	81.47	24.20	58.55	?
13	2.14	85.63	36.51	54.59	$BeSO_4$
14	0.37	93.81	12.98	82.20	"

Mean of #5 and 6 (invariant solution composition)

% $BeSO_4$	% H_2SO_4
3.06	54.28

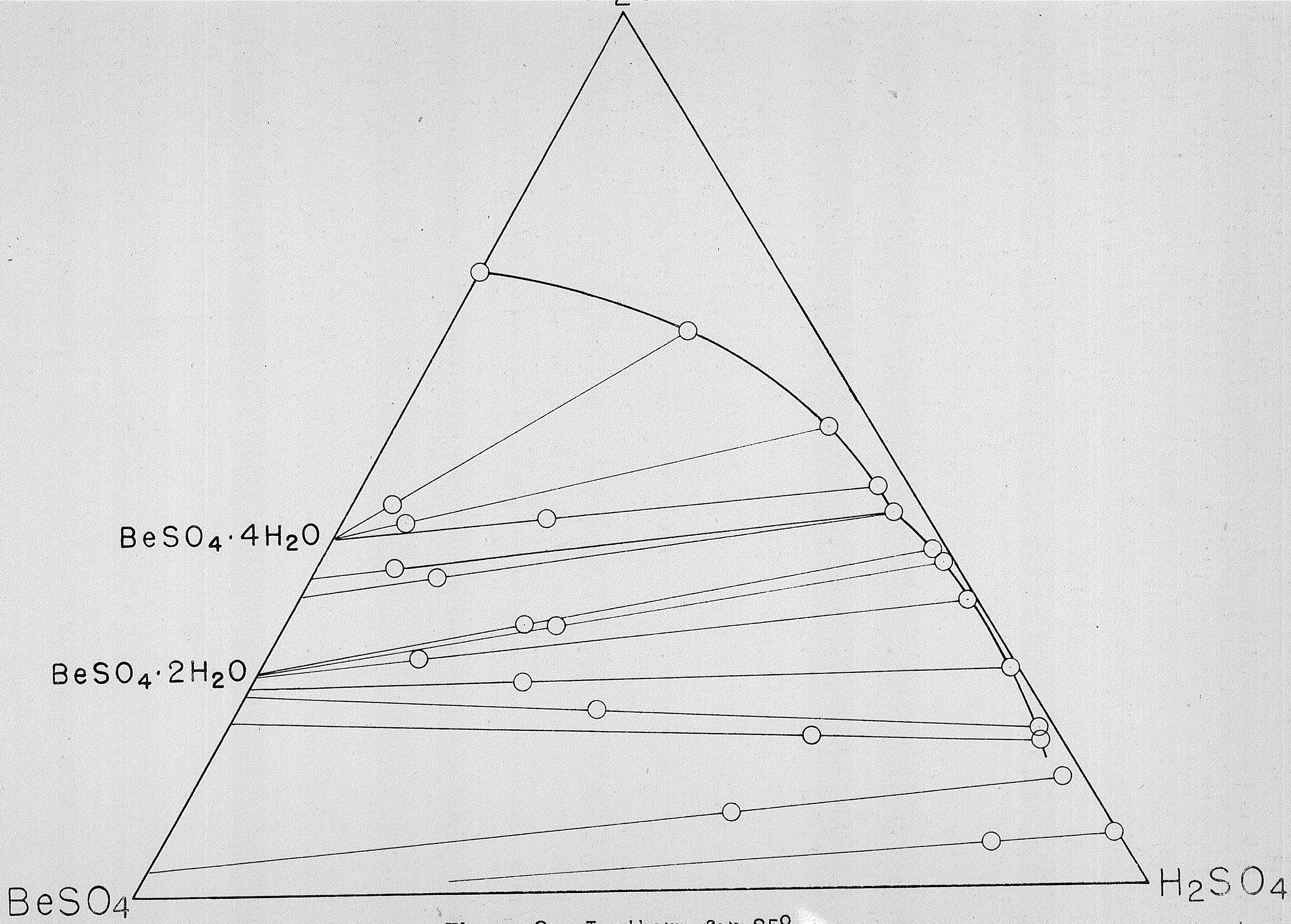


Figure 2. Isotherm for 25°

TABLE 2

ISOTHERM FOR 50.00° (± 0.05)

	Solution		Wet Residue		Nature of Solid Phase
	% $BeSO_4$	% H_2SO_4	% $BeSO_4$	% H_2SO_4	
1	32.93	0.00	56.68	0.00	$BeSO_4 \cdot 4H_2O$
2	21.02	16.01	52.01	3.23	"
3	13.38	29.83	48.64	7.02	"
4	9.45	39.67	53.07	5.15	"
5	8.64	42.77	56.10	7.39	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
6	8.91	42.75	49.64	13.19	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
7	8.03	43.34	50.72	15.33	$BeSO_4 \cdot 2H_2O$
8	4.89	49.98	52.37	15.91	"
9	2.37	58.54	55.57	15.26	"
10	1.54	64.49	45.81	25.88	"
11	1.61	71.12	45.27	28.98	"
12	2.71	78.03	43.35	34.69	"
13	3.01	78.00	54.16	29.65	?
14	3.17	77.99	58.95	24.48	?
15	2.79	80.03	45.66	39.76	?
16	0.36	93.30	39.89	54.32	$BeSO_4$

Mean of #5 and 6 (invariant solution composition)

% $BeSO_4$	% H_2SO_4
8.78	42.76

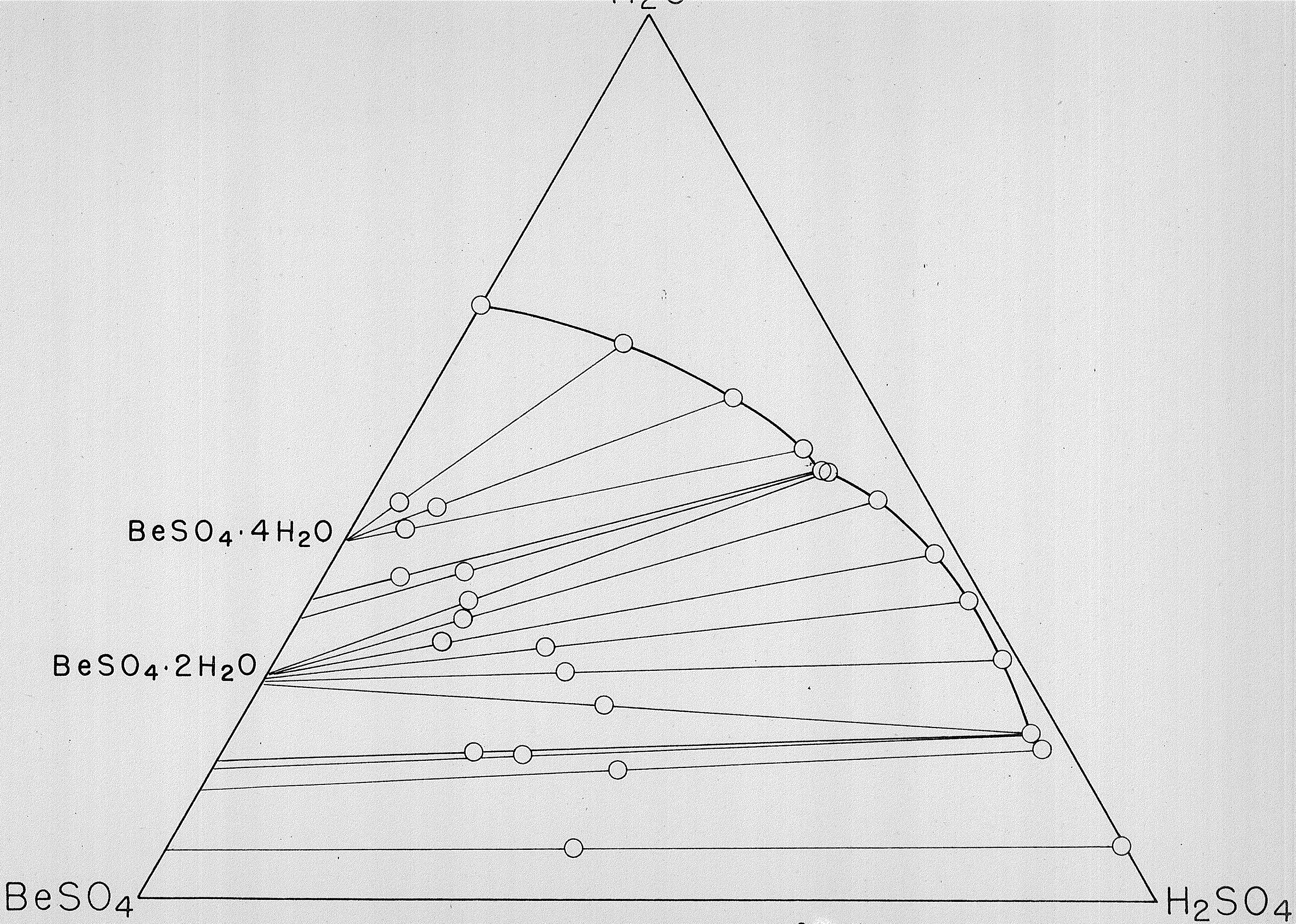


Figure 3. Isotherm for 50°

TABLE 3

ISOTHERM FOR 75.00° (± 0.05)

	Solution		Wet Residue		Nature of Solid Phase
	% $BeSO_4$	% H_2SO_4	% $BeSO_4$	% H_2SO_4	
1	37.98	0.00	--	--	$BeSO_4 \cdot 4H_2O$
2	35.77	2.14	53.81	0.40	"
3	26.45	16.14	57.30	0.98	"
4	23.68	21.01	56.91	1.36	"
5	23.52	21.90	58.70	4.01	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
6	23.12	22.00	58.94	4.42	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
7	23.64	21.68	54.03	7.65	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
8	19.76	26.55	59.98	7.01	$BeSO_4 \cdot 2H_2O$
9	14.61	34.02	55.98	10.51	"
10	7.18	48.04	45.60	20.64	"
11	4.14	56.03	45.49	23.19	"
12	2.42	66.30	47.98	24.72	"
13	2.40	69.29	44.40	29.40	"
14	4.28	75.29	51.94	25.01	"
15	4.35	79.54	51.83	32.40	?
16	4.08	80.43	52.95	37.53	$BeSO_4$

Mean of #5, 6 and 7 (invariant solution composition)

% $BeSO_4$	% H_2SO_4
23.43	21.86

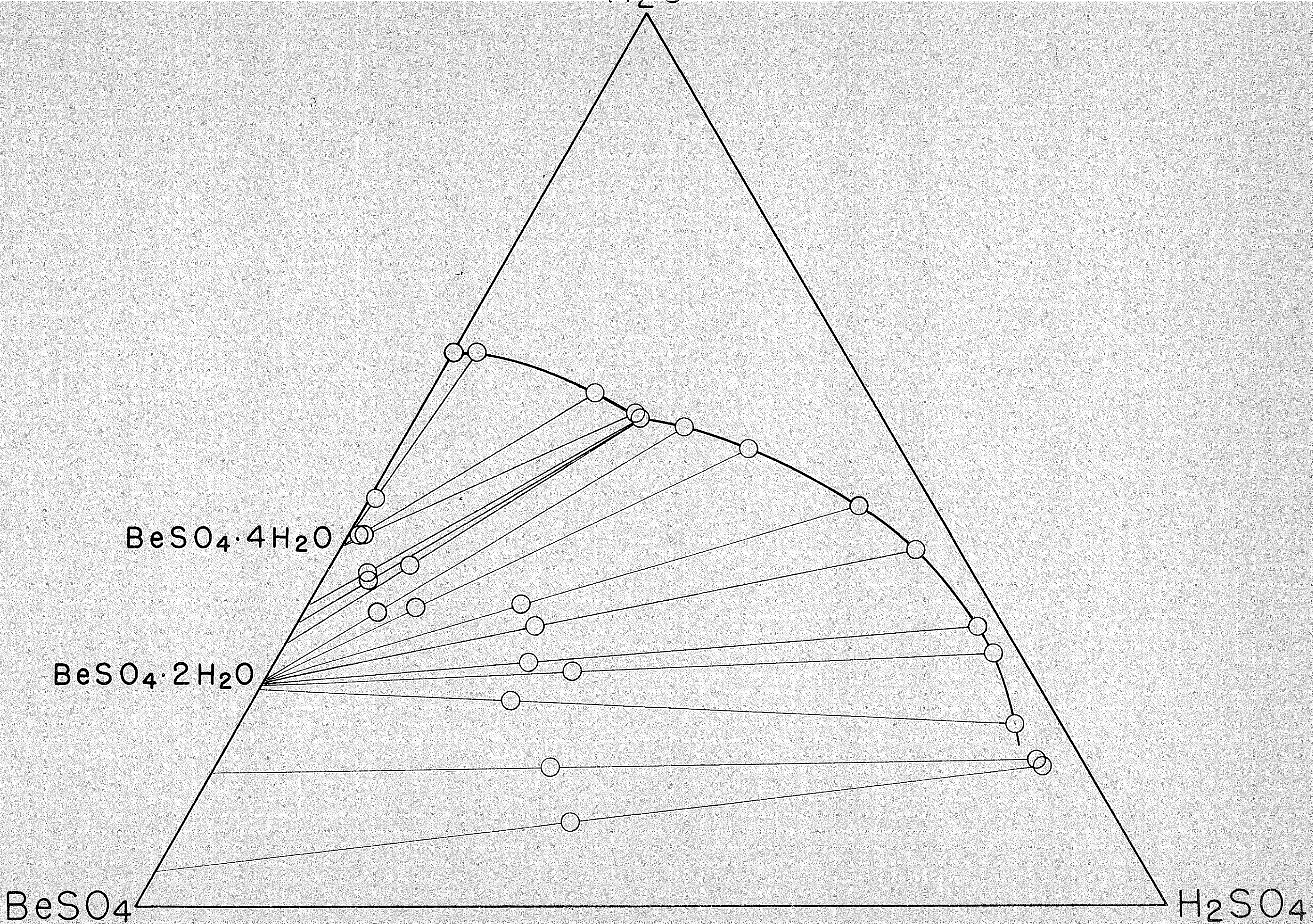


Figure 4. Isotherm for 75°

TABLE 4

ISOTHERM FOR 85.0° (± 0.1)

	Solution		Wet Residue		Nature of Solid Phase
	% $BeSO_4$	% H_2SO_4	% $BeSO_4$	% H_2SO_4	
1	41.33	0.00	--	--	$BeSO_4 \cdot 4H_2O$
2	36.42	4.14	57.56	0.48	"
3	33.82	9.54	56.69	2.83	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
4	33.63	9.00	68.34	0.89	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
5	31.21	12.05	57.72	4.80	$BeSO_4 \cdot 2H_2O$

Mean of #3 and 4 (invariant solution composition)

% $BeSO_4$	% H_2SO_4
33.72	9.27

TABLE 5

ISOTHERM FOR 95.0° (± 0.1)

	Solution		Wet Residue		Nature of Solid Phase
	% $BeSO_4$	% H_2SO_4	% $BeSO_4$	% H_2SO_4	
1	43.45	0.00	--	--	$BeSO_4 \cdot 2H_2O$
2	41.80	1.20	65.84	0.43	"
3	35.41	7.34	56.90	3.41	"
4	26.86	17.50	57.25	6.50	"
5	25.34	19.98	57.11	7.43	"
6	6.36	53.50	42.86	25.85	"

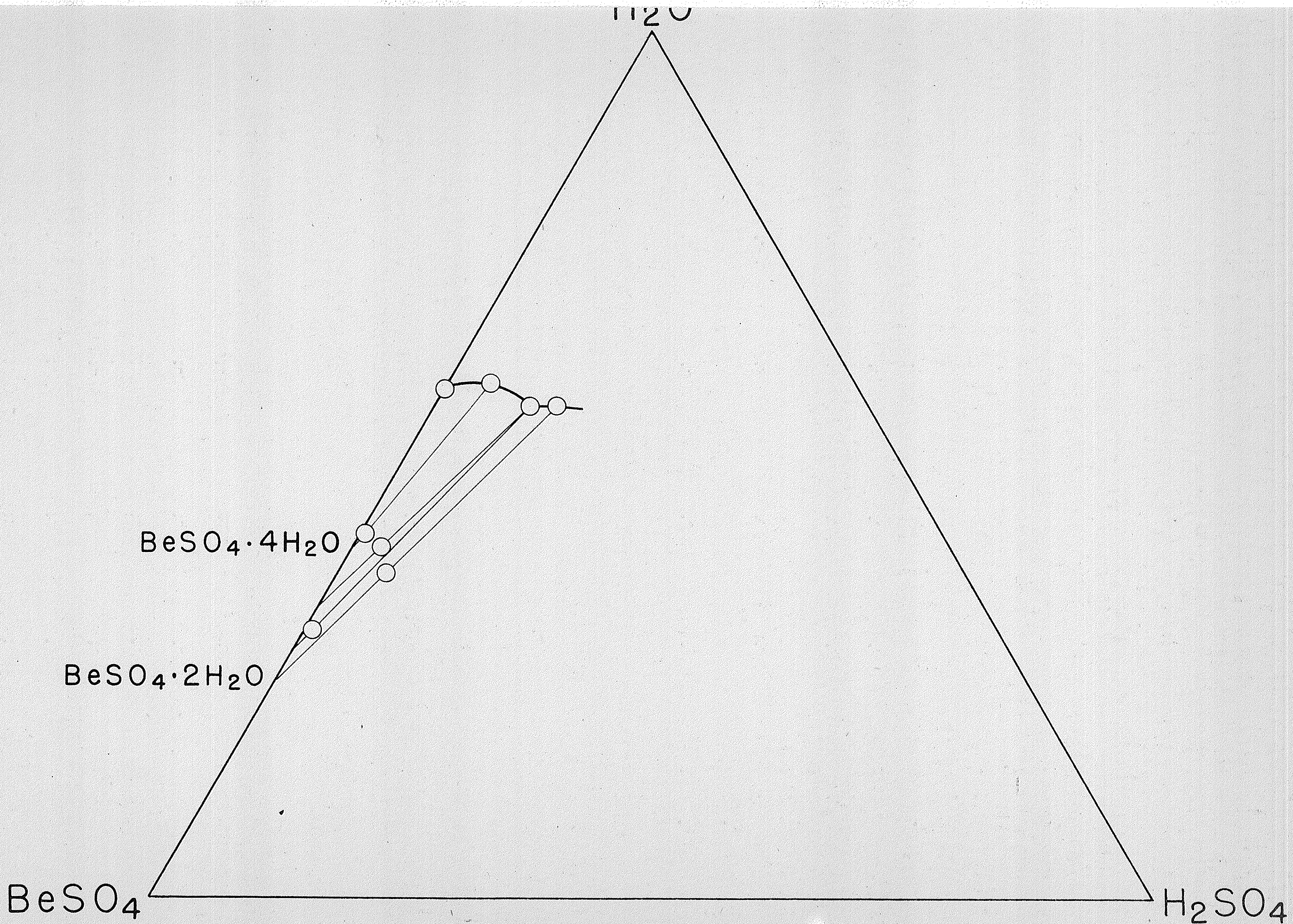


Figure 5. Isotherm for 85°

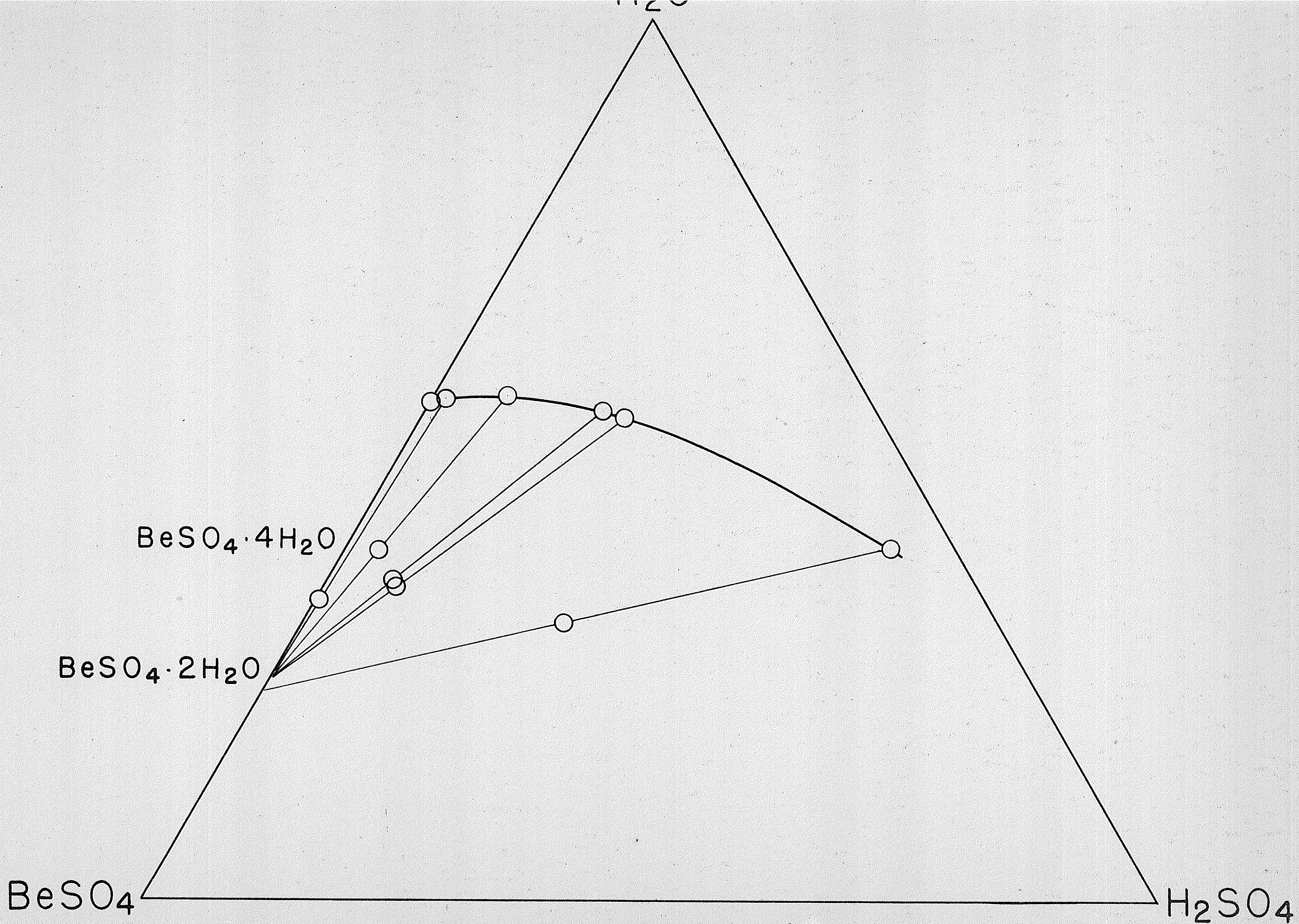


Figure 6. Isotherm for 95°

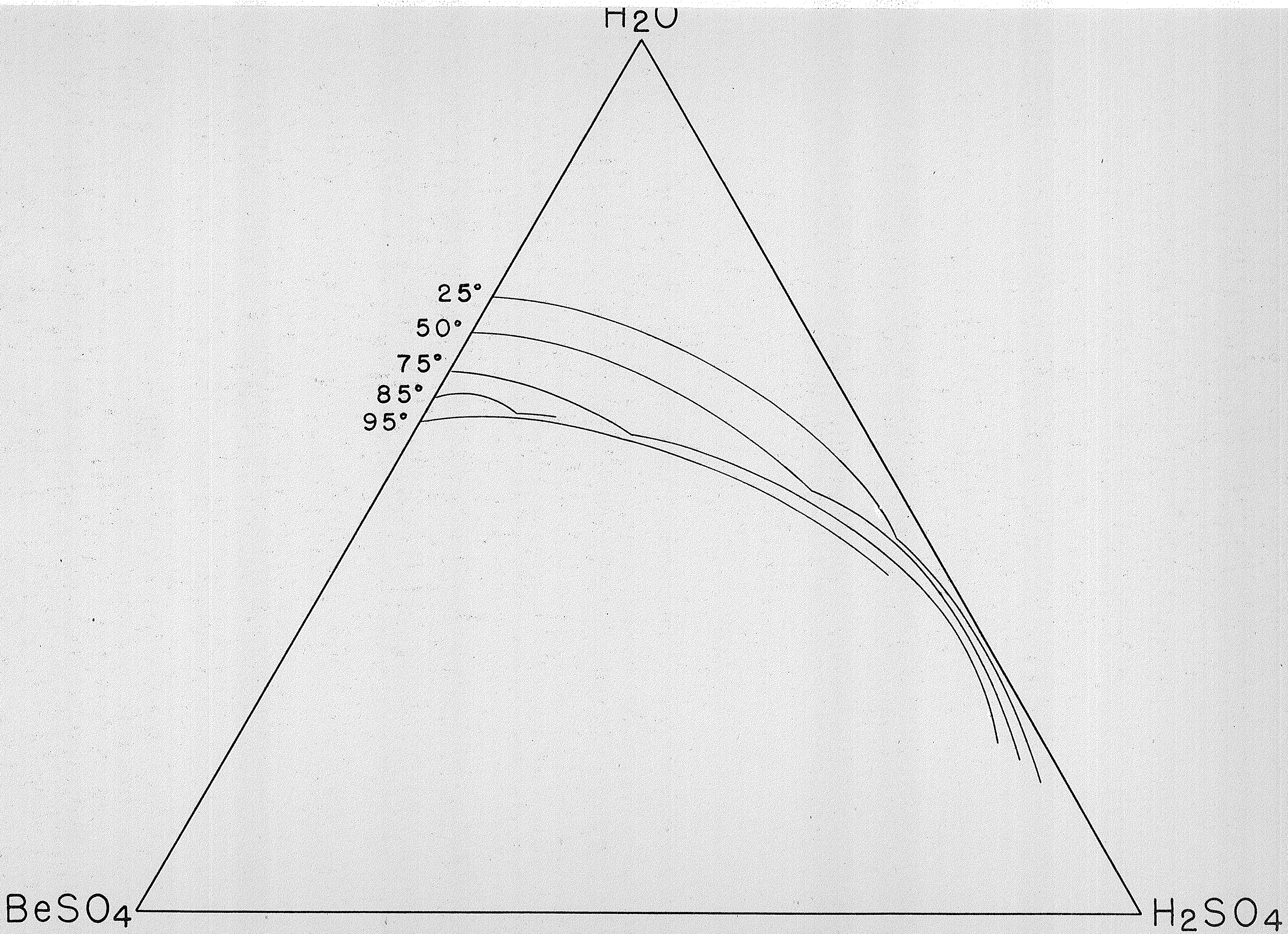


Figure 7. $BeSO_4$ - H_2SO_4 - H_2O Isotherms

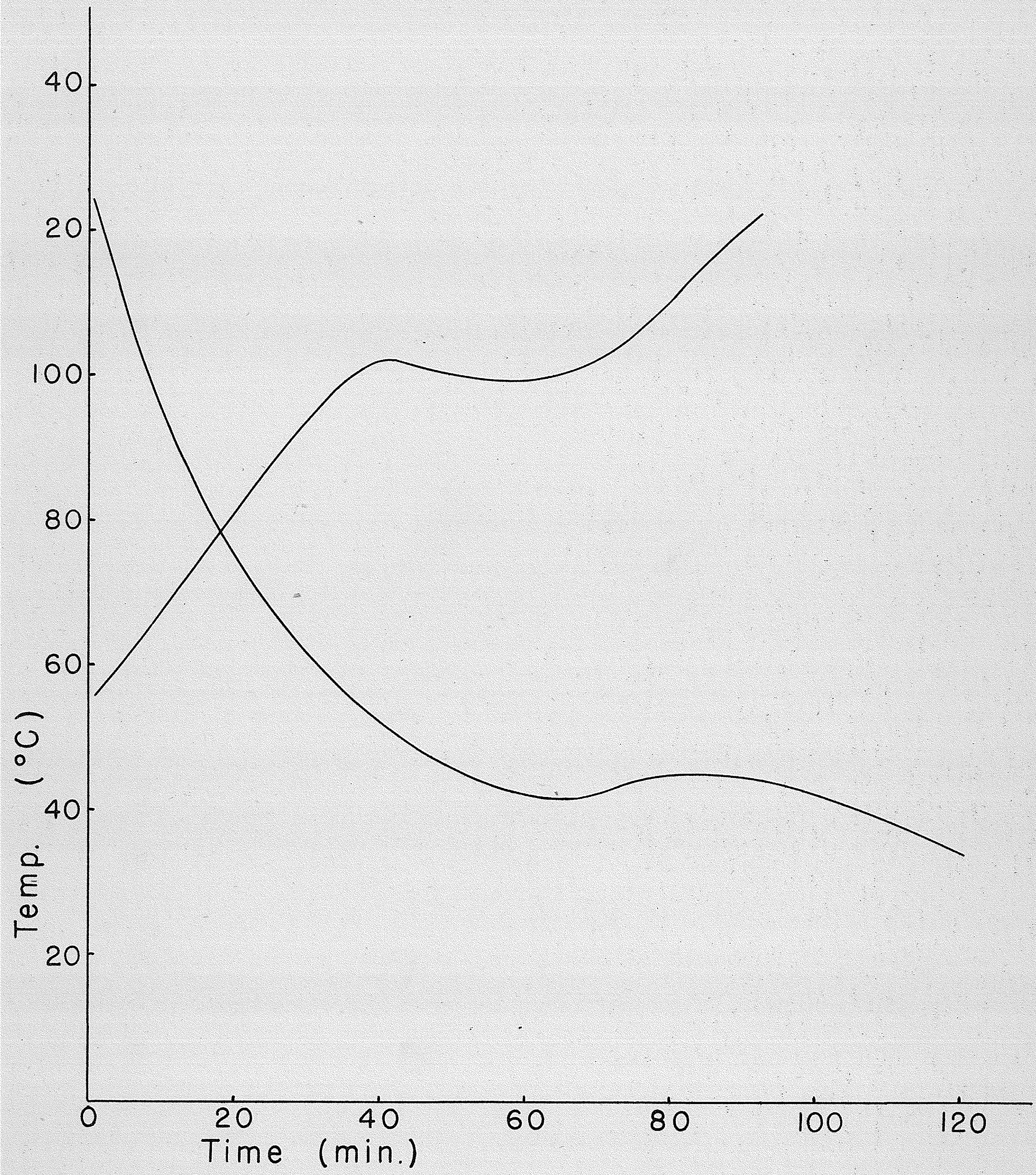
Thermal Analysis

For the determination of the transition temperature of beryllium sulphate tetrahydrate by thermal analysis the powdered material was enclosed in a sealed glass tube of about 25 milliliter capacity and incorporating a thermometer well. This tube was placed inside a larger one, which served as an air jacket, and then heated in a mineral-oil bath. A pool of mercury in the thermometer well served to establish proper thermal contact between the contents of the tube and the thermometer. The temperature of the bath was about 17 degrees higher than that of the salt up to the point of transformation, the heating rate being about one degree per minute. After superheating to 100.7 degrees the temperature of the salt dropped to constancy at 99.0 degrees for a few minutes, becoming quite moist.

Subsequent cooling of the moist dihydrate was brought about by raising the tube and air jacket out of the bath and allowing to cool at room temperature. The cooling rate was rapid at first, about three degrees per minute, slowing down to less than one degree per minute on approaching the transformation point. After supercooling to 41.1 degrees the temperature of the salt rose to 44.9 degrees, remaining constant for a short while.

Throughout the heating and cooling procedure temperature readings were taken at one-minute intervals. The heating

Figure 8. Heating and Cooling Curves--
$BeSO_4 \cdot 4H_2O$ - $BeSO_4 \cdot 2H_2O$



and cooling curves of figure 8 were plotted from the data obtained.

Dilatometry

The dilatometers first used in this study were constructed in the ordinary manner, a long capillary tube attached to a bulb containing the beryllium sulphate tetrahydrate. The dilatometer scale consisted of two meter-sticks on end attached to the capillary stem. Amylic alcohol (fusel oil) was used as the indicator liquid. The thermostat was a mineral-oil bath regulated by means of a toluene-mercury thermoregulator. An ordinary thermometer, calibrated against a certified standard, was used for the temperature readings.

In the course of this work involving both dilatometer and sealed tubes used in thermal analysis it was invariably found that after the tetrahydrate-dihydrate transformations had occurred cooling the instrument to room temperature caused the bulb or tube to crack. An examination of the solid contents showed that the powdered material had been transformed into a hard porous mass with sufficient expansion to cause the breakage. This change never occurred at temperatures immediately below the transition point, even after prolonged standing. Cooling to room temperature for one day was required. Although this phenomenon has not been further investigated it may indicate the possible existence of dimorphous tetrahydrate, the allotropic change occurring approximately at room temperature.

In the construction of the dilatometer finally used it was considered necessary, therefore, to use a double bulb. A diagram of this dilatometer is shown in figure 9. The bulb consisted of an inner tube of about 40 milliliter capacity, containing the powdered salt, and resting loosely in an outer tube attached to the capillary stem. A brass cylinder was placed around the inner tube to protect the outer one in the event of breakage on cooling. The outer tube, with the bottom end open, was first attached to the capillary. The inner tube, containing the powdered tetrahydrate and surrounded by the brass cylinder, was then introduced and closed in by sealing the bottom of the outer.

Prior to the introduction of the indicator liquid the dilatometer was evacuated for ten hours by means of a hyvac-oil pump. The amylic alcohol was introduced under the low pressure by means of apparatus designed for the purpose. Despite these precautions in the removal of adsorbed air from the powder a considerable amount remained, becoming released only with the hydrate transformations. Further evacuation was therefore necessary until no more air remained when the final transformation cycle was performed. This evacuation was always carried out at room temperature to prevent undue dehydration of the salt.

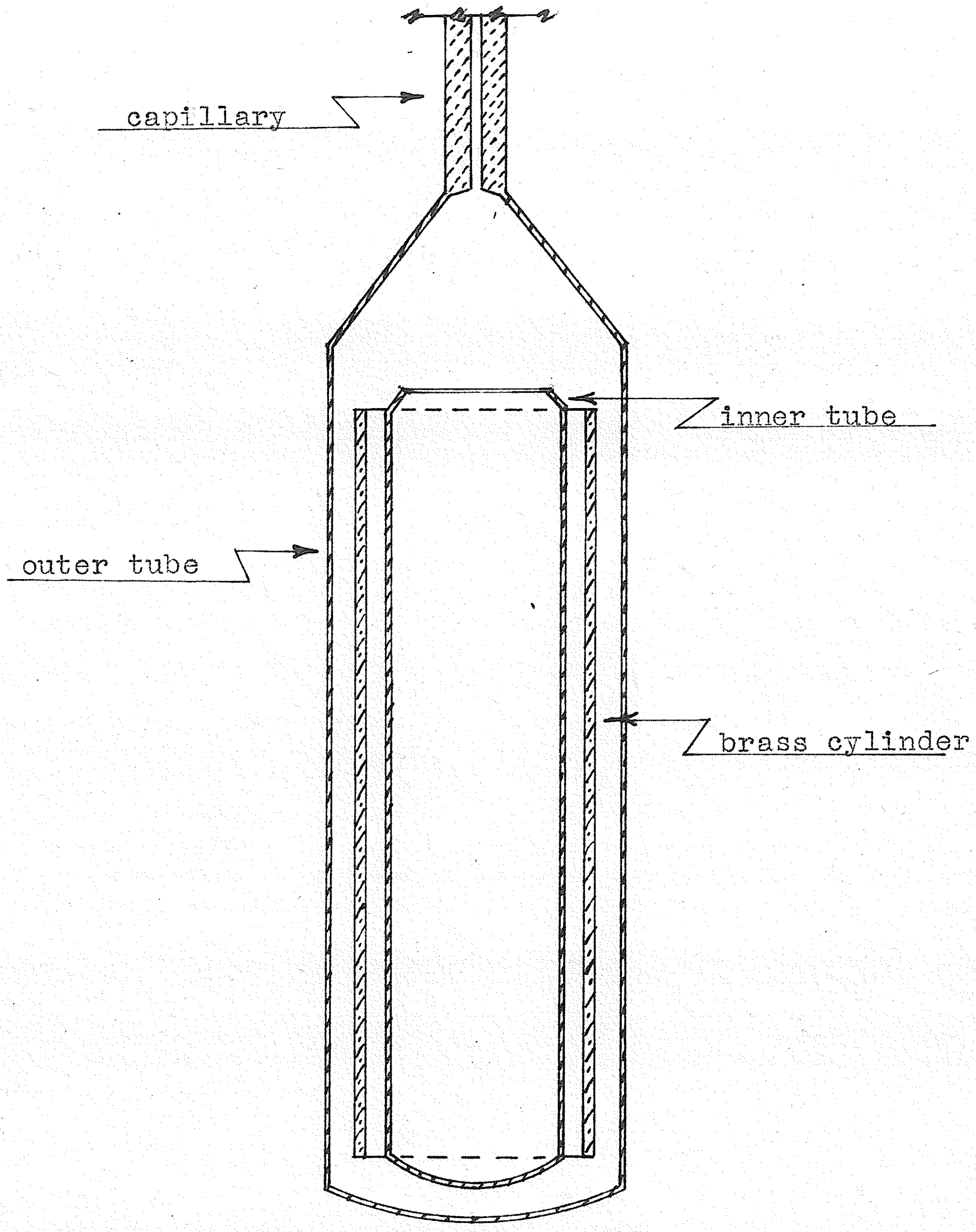


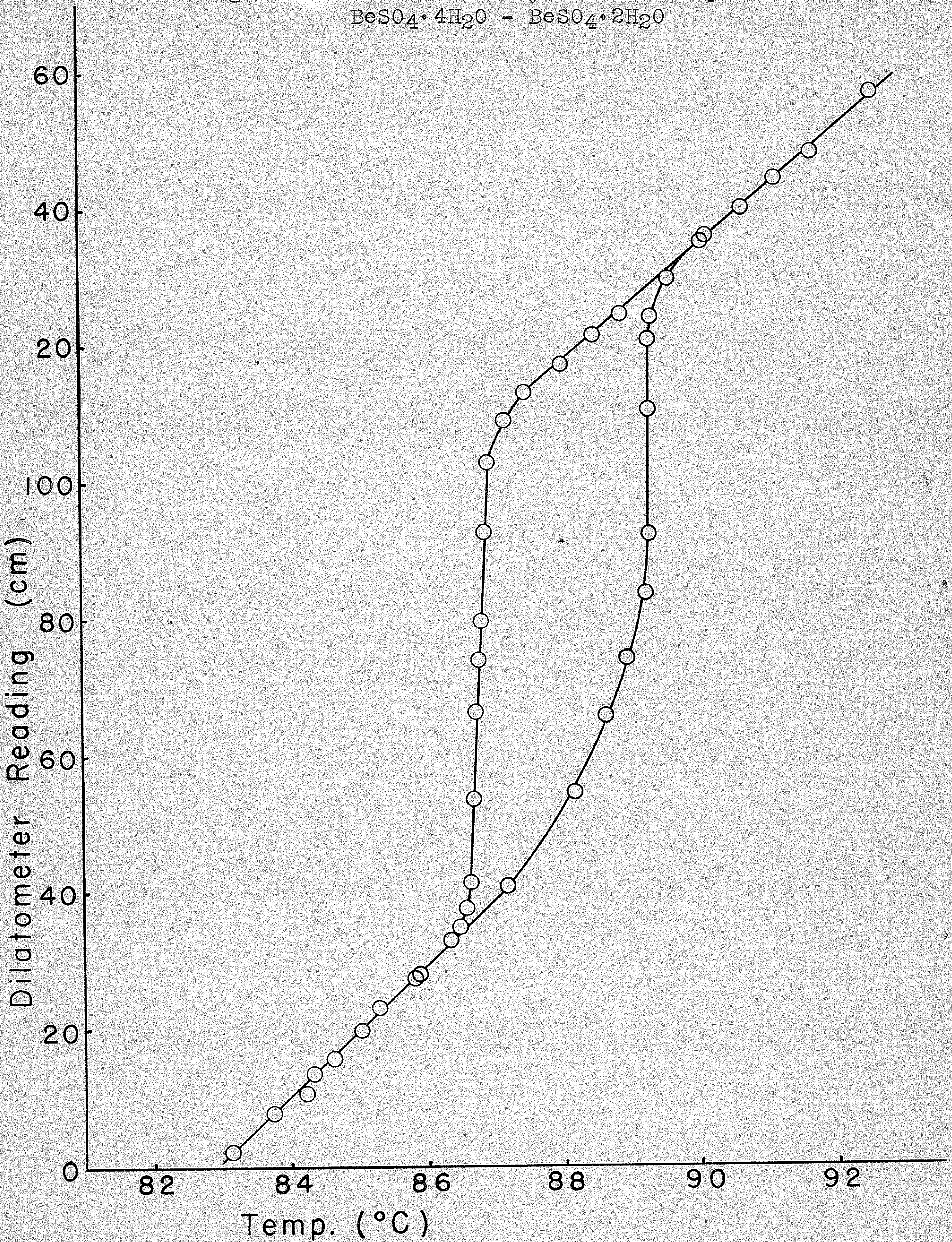
Figure 9. Dilatometer Bulb.

TABLE 6

DILATOMETER DATA

Temperature (°C)	Dilatometer Reading (cm)	Temperature (°C)	Dilatometer Reading (cm)
83.15	2.1	91.15	144.0
84.25	10.8	90.15	135.8
84.65	15.6	88.90	124.0
85.90	27.8	88.50	121.2
86.35	32.7	88.15	117.0
87.20	40.8	87.50	113.0
88.20	54.5	87.20	108.9
88.65	65.5	86.95	102.7
88.95	74.0	86.90	92.4
89.25	83.4	86.85	79.5
89.30	91.9	86.80	73.8
89.30	110.2	86.75	66.1
89.30	120.4	86.70	53.5
89.35	123.7	86.65	41.1
89.60	129.2	86.60	37.5
90.10	134.9	86.50	34.8
90.72	139.8	86.35	33.0
91.70	147.9	85.85	27.3
92.60	156.6	85.30	23.3
		85.05	19.8
		84.35	13.5
		83.75	8.0

Figure 10. Dilatometer Hysteresis Loop--
$BeSO_4 \cdot 4H_2O$ - $BeSO_4 \cdot 2H_2O$



Repetition of the transformation cycle for the removal of air also served to reduce the amount of hysteresis in the final cycle. Small changes in temperature were used, one day being allowed between each change to ensure approximate equilibrium. The data for the final cycle are given in table 6 and the corresponding hysteresis loop represented in figure 10.

X-Ray Powder Photography

X-ray diffraction photographs serve as a means for the positive identification of different crystalline substances. A given pure substance will give rise to its own unique diffraction pattern, considering both the positions and intensities of the lines or spots in the photograph. Such a unique pattern is therefore sufficient evidence for the identification of the substance as a separate crystalline individual. In the case of a mixture of two or more substances the resulting pattern will consist of the separate patterns superimposed. Solid solutions, on the other hand, will produce patterns which are intermediate between the unique patterns of the two end members.

For the identification of the separate hydrates of beryllium sulphate, X-ray powder photographs were taken for various degrees of hydration from the tetrahydrate down to the anhydrous salt. Unique diffraction patterns were obtained only for the tetrahydrate, dihydrate and anhydrous salt. Although considerable care was exercised in the dehydration of the tetrahydrate to a water content corresponding exactly to the monohydrate, X-ray photographs of the product revealed a combination of the dihydrate and anhydrous salt patterns. Slight but apparent displacement of the lines of the individual patterns in the combination indicates the possibility of solid solution existing between these two compounds.

An X-ray powder diffraction pattern can be represented in tabular form by indicating the spacing of each set of lattice planes which gives rise to a line in the pattern, along with the relative intensity of the line. This procedure has been followed here, the diffraction patterns obtained for the tetrahydrate, dihydrate and anhydrous salt being represented in tables 7 to 9. The actual photographs are shown in figures 11 to 13.

The position of each line in the powder photographs was first measured, the spacing $\underline{d}$ of the corresponding set of lattice planes being obtained from tables provided for use with the cameras employed. The relative intensity $\underline{I}$ of each line was estimated visually. For the purpose of these tables, and in accordance with standard procedure, this intensity estimation was done by assigning to the strongest line in each pattern the value 10. The intensities of all other lines were compared to this and are assigned values as given. For example, a line one-half as intense as the strongest is assigned the value 5, etc. The lattice spacings given in the tables are expressed in kX units (2), one kX unit being equal to 1.002 angstroms.

The powder specimen of the tetrahydrate was prepared directly from the material obtained as described on page 19. The dihydrate was obtained by heating a weighed amount of tetrahydrate at 100 degrees until the weight of the product indicated pure dihydrate. The anhydrous salt was obtained similarly by heating the tetrahydrate for about five hours at 400 degrees.

In order to investigate the X-ray patterns for the degree of hydration corresponding to the formula $BeSO_4 \cdot H_2O$, for which the water content would be 14.64 per cent by weight, powder specimens were prepared from dehydration products obtained by heating the tetrahydrate overnight at temperatures of 160 to 180 degrees. Photographs taken of samples with a water content of 16.16, 14.34, 9.56, and 7.46 per cent all revealed a combination of the dihydrate and anhydrous salt patterns. These are shown in figures 14 to 17.

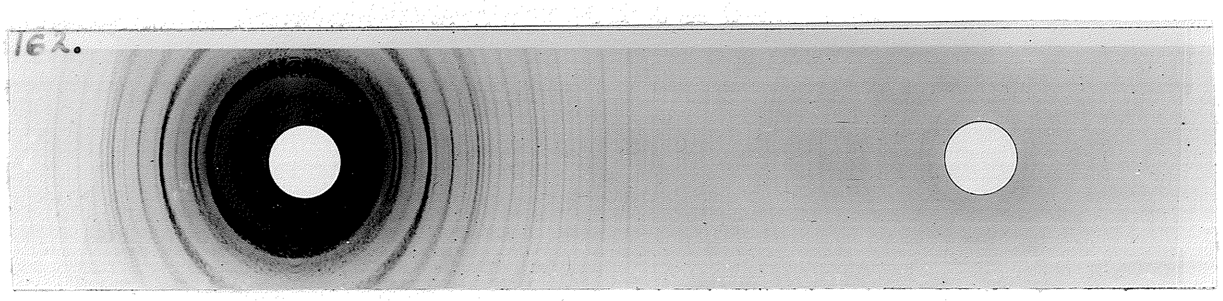


Figure 11. X-Ray Powder Photograph, $BeSO_4 \cdot 4H_2O$

Figure 12. X-Ray Powder Photograph, $BeSO_4 \cdot 2H_2O$

Figure 13. X-Ray Powder Photograph, Anhydrous $BeSO_4$

TABLE 7

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4 \cdot 4H_2O$

I	d	I	d
5	5.719	1	1.485
2	5.325	5	1.455
10	3.897	4	1.411
5	3.392	0.5	1.368
5	3.194	0.5	1.349
2	2.819	4	1.326
8	2.515	0.5	1.297
1	2.416	2	1.263
0.5	2.213	0.5	1.231
5	2.165	1	1.218
2	1.996	4	1.176
1	1.939	0.5	1.142
5	1.879	0.5	1.127
4	1.836	4	1.107
4	1.772	0.5	1.086
2	1.697	0.5	1.069
4	1.599	0.5	1.048
0.5	1.540	0.5	1.039

TABLE 8

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4 \cdot 2H_2O$

I	d	I	d
10	4.874	8	1.932
5	4.102	0.5	1.834
1	3.906	3	1.771
10	3.559	0.5	1.706
4	3.329	1	1.663
8	2.886	1	1.645
8	2.785	4	1.506
4	2.618	0.5	1.447
0.5	2.461	0.5	1.420
5	2.379	0.5	1.397
5	2.165	1	1.361
0.5	2.123	1	1.329
0.5	2.054	0.5	1.306

TABLE 9

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4$

I	d	I	d
5	4.969	0.5	1.442
5	4.218	1	1.368
10	3.751	0.5	1.317
0.5	3.450	0.5	1.258
2	3.183	1	1.224
7	2.385	0.5	1.169
2	1.934	0.5	1.130
1	1.877		
0.5	1.588		
2	1.507		

Additional Experiments

Boiling Point of the Saturated Aqueous Solution -- In order to determine the validity of Rohmer's arguments (22) concerning the metastability of beryllium sulphate dihydrate it was decided in this study to carry out determinations of the boiling point of the saturated aqueous solution, claimed by him as evidence for his opinions. Preliminary tests performed by boiling the saturated solution in contact with solid in an open flask showed wide fluctuations in temperature due to superheating. Use was therefore made of a special type of apparatus described by Scatchard, Raymond and Gilmann

Figure 14. X-Ray Powder Photograph, $BeSO_4$, 16.16% H_2O

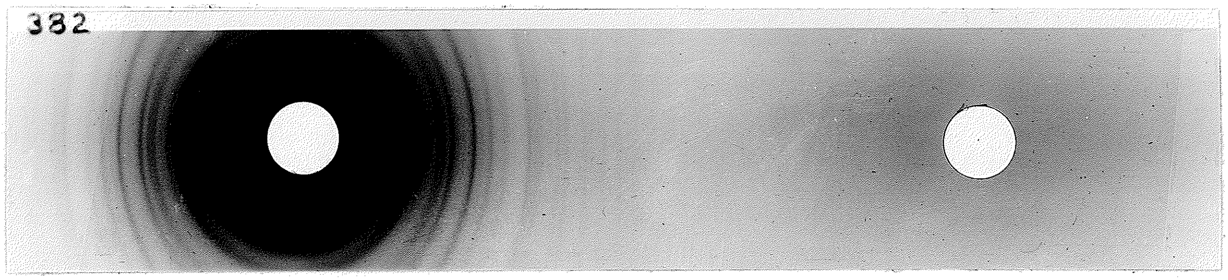


Figure 15. X-Ray Powder Photograph, $BeSO_4$, 14.34% H_2O

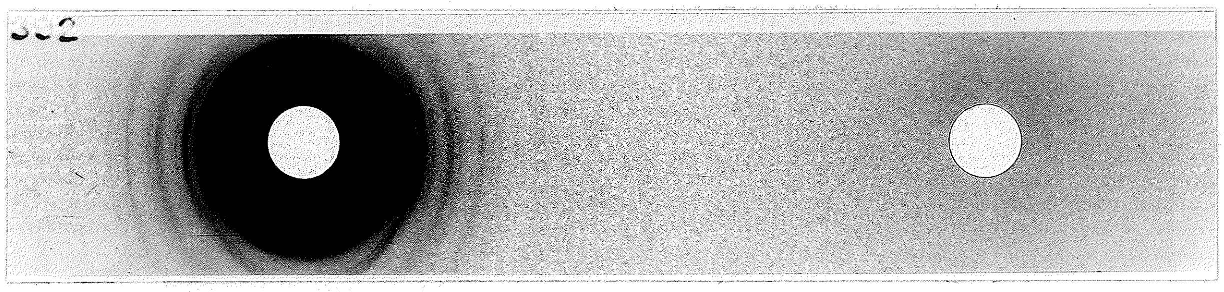


Figure 16. X-Ray Powder Photograph, $BeSO_4$, 9.56% H_2O

Figure 17. X-Ray Powder Photograph, $BeSO_4$, 7.46% H_2O

(23), consisting principally of an inner and outer boiler and operating on the principle of the Cottrell pump (6). By means of this equilibrium still the test liquid or solution in the inner boiler can be maintained at its boiling point without superheating, being heated only through the medium of its equilibrium vapor.

A quantity of pure crystalline tetrahydrate was first placed in the inner boiler and saturated solution at a temperature of about 75 degrees was added. Saturated solution at a somewhat higher temperature was poured into the outer boiler and heating was commenced immediately. The temperature within the inner boiler rose to 108.2 degrees, remaining unchanged even after several hours of continuous operation, solid being present throughout the entire period. No other boiling point was found, as claimed by Rohmer.

The pressure inside the equilibrium still was maintained at exactly 760 mm of mercury by means of a barostat controlled by a sensitive electronic-switch relay, fully described by Campbell and Dulmage (5). The boiling point found is therefore the normal boiling point of the saturated solution.

In order to determine the composition of the solid phase in equilibrium with saturated solution at its boiling point, the solution, in contact with solid, was boiled under a reflux condenser for four hours. At the end of this time the hot liquid and solid phases were rapidly separated by filtering under suction. The wet solid, immediately washed with acetone to remove the free water, was dried further on a porous plate for about one-half hour. A weighed sample was analyzed by direct ignition to the oxide, accomplished by heating overnight at 950 degrees. The results obtained indicated that the solid in equilibrium with the boiling solution was the dihydrate. The lines in an X-ray photograph of this material, shown in figure 18, belong to the dihydrate pattern.

Rehydration of Beryllium Sulphate "Monohydrate" at 100 Degrees -- Another experiment, perhaps unnecessary in view of X-ray evidence obtained, involved the rehydration at 100 degrees of a dehydration product with water content corresponding to the formula $BeSO_4 \cdot H_2O$, assumed in this case to be the monohydrate. If, according to Rohmer, the dihydrate is always metastable with respect to the monohydrate then the latter would not spontaneously rehydrate when placed in contact with water vapor above the temperature of stable existence of the tetrahydrate. Such a transformation would mean a thermodynamically impossible spontaneous increase in the free energy of the substance.

A quantity of tetrahydrate was dehydrated to correspond to the formula $BeSO_4 \cdot H_2O$. A weighed sample of the product, kept at 100 degrees, was placed in a small open bottle

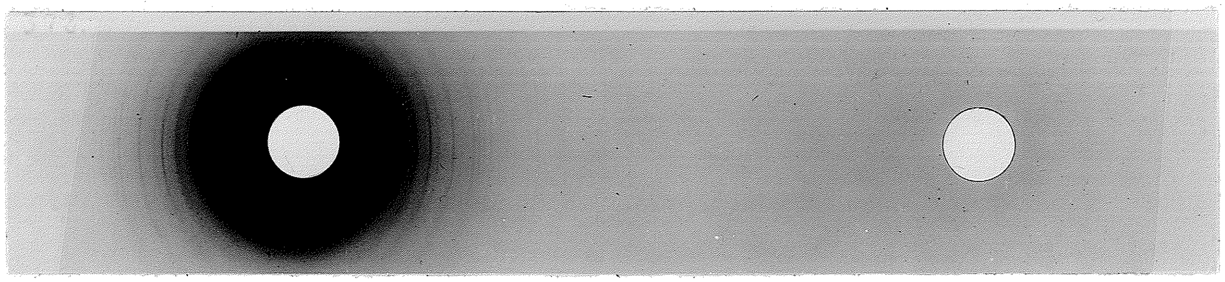


Figure 18. X-Ray Powder Photograph, Solid Phase in Equilibrium with Saturated Aqueous $BeSO_4$ Solution at its Boiling Point.

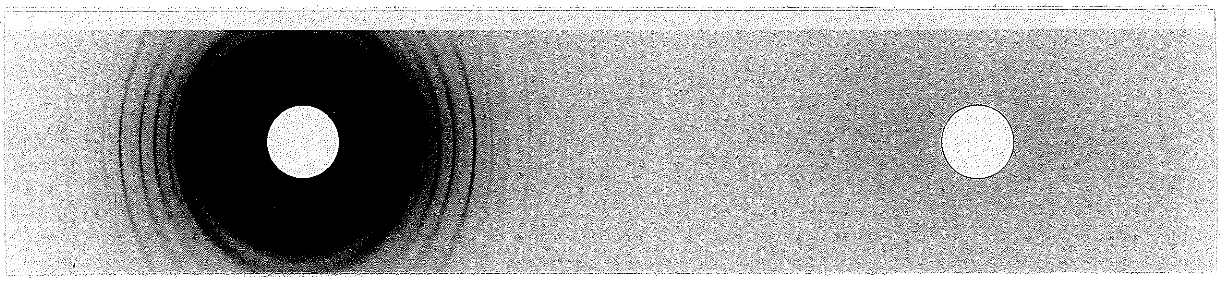


Figure 19. X-Ray Powder Photograph, $BeSO_4$ "Monohydrate" Rehydrated at 100°.

suspended in a stoppered flask. Sufficient tetrahydrate was placed in the bottom of the flask to produce, on transformation to dihydrate, the necessary water for the complete rehydration to dihydrate of the substance in the bottle. In order to allow free vapor contact between the two solids the flask was evacuated through a stop-cock tube fitted into the stopper.

After heating the flask and contents overnight at 100 degrees the material in the bottle had gained weight to correspond exactly to the dihydrate. In view of the result this material did not therefore consist, either wholly or in part, of any substance more stable at 100 degrees than the dihydrate itself. An X-ray photograph of the final product, figure 19, showed nothing but the dihydrate pattern.

Determination of the Density of Beryllium Sulphate Dihydrate -- The density of beryllium sulphate dihydrate was determined at 25.0 degrees, employing the familiar powder method. A small pyknometer was used, xylene being used as the liquid medium. The dihydrate was obtained by heating the tetrahydrate overnight at 100 degrees.

This experiment involved nothing other than the standard procedure in such density measurements. The experimental detail need not therefore be discussed, except to mention that considerable care was exercised in removing adsorbed air from the dihydrate powder. This was done by careful evacuation with a hyvac-oil pump, both before and after the introduction of the xylene.

The value obtained for the density of the dihydrate at 25.0 degrees was 1.865 grams per cubic centimeter.

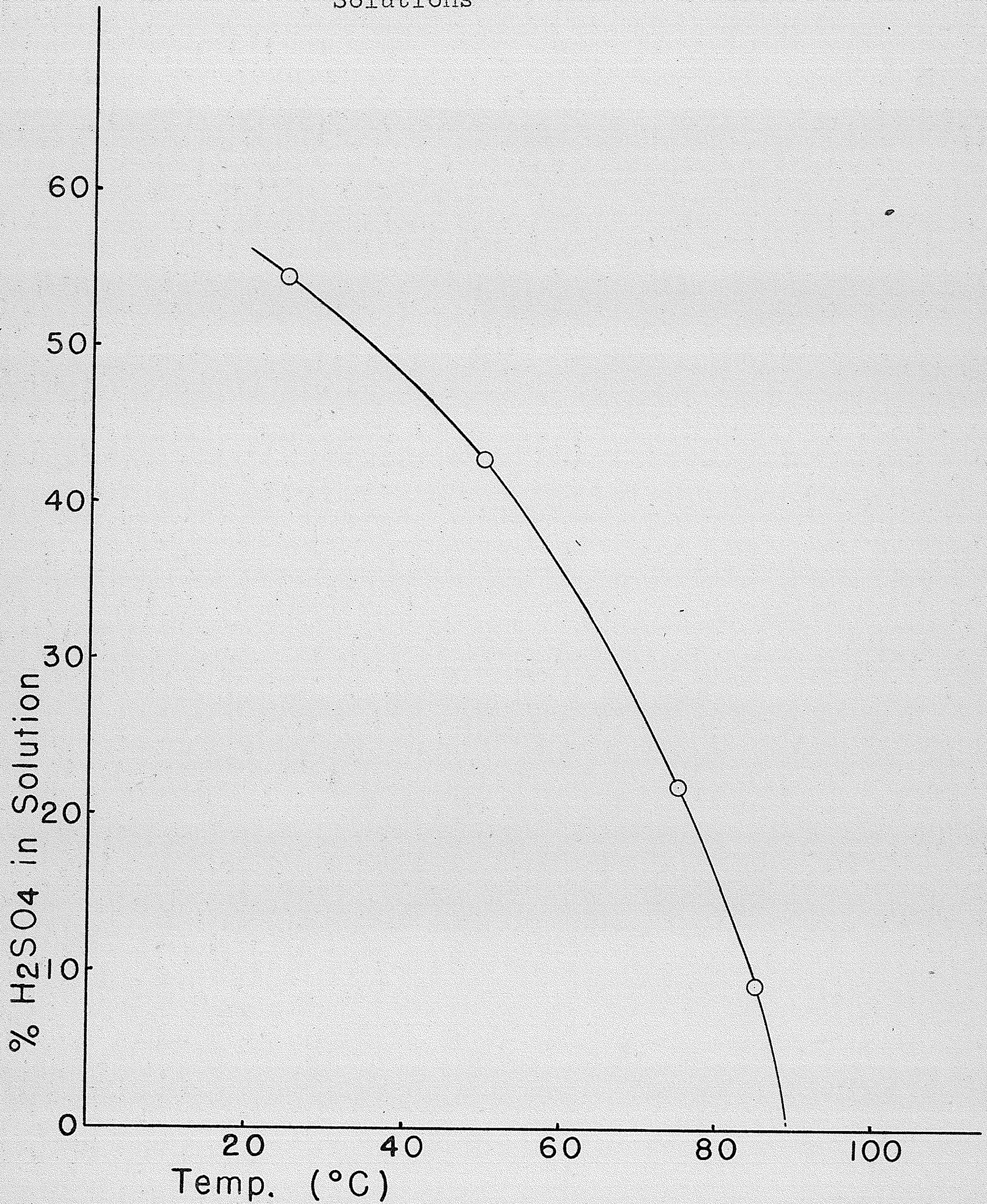
DISCUSSION OF RESULTS

The Tetrahydrate-Dihydrate Transition

The isothermal ternary system phase diagrams of figures 2 to 4 show that at all temperatures at which the tetrahydrate of beryllium sulphate is the equilibrium solid for low sulphuric acid concentrations it passes to the dihydrate when the acid concentration is increased. Figure 5 shows that at 95 degrees the tetrahydrate does not exist. The solubility of the salt is shown to decrease considerably with an increase in concentration of the acid, reaching a first minimum when the acid content is about 65 per cent.

As shown at the end of tables 1 to 4 the composition of the invariant solution in equilibrium with the tetrahydrate-dihydrate mixture has been obtained for each isotherm by taking the mean of at least two separate determinations. From these compositions the transition temperature of pure tetrahydrate can be determined by extrapolating to zero concentration of the acid. This has been done as shown in figure 20, the sulphuric acid content of the isothermally

Figure 20. Sulphuric Acid Content-Temperature Relationship--Invariant Ternary Solutions



invariant solution being plotted against temperature. The transition temperature is shown by this method to be somewhere between 89 and 90 degrees.

A consideration of the dilatometer hysteresis loop of figure 10 shows that a mean value between the almost vertical sides of the loop would place the transition point at about 88 degrees. However, this conclusion is perhaps not well justified since it is reasonably correct to assume that the dehydration of the tetrahydrate would suffer less hysteresis than the reverse transformation, where intimate contact between the dihydrate and aqueous solution may have been lost to some extent due to the force of gravity. The obvious truth of this in the case of the thermal analysis experiment is borne out by the results obtained. These show a wide hysteresis gap of 54 degrees, from 10 degrees above the true transition point to about 44 degrees below it. In any case, due to its slight solubility in water, the use of amylic alcohol as the indicator liquid in the dilatometer had undoubtedly caused the lowering of the transition point.

Calculation of the Tetrahydrate-Dihydrate Transition Temperature from Isothermally Invariant Ternary Solution Data.

With reference to figure 21, representing the equilibria in the binary system, beryllium sulphate - water, in the region of the tetrahydrate-dihydrate transition temperature, it is seen that the addition of sulphuric acid to the system affects only those univariant equilibria which involve solution. Adding sulphuric acid lowers the transition point, that is, the quadruple point, along curve 1 as shown by the dotted curves.

In the ternary system the vapor pressure of the solution of beryllium sulphate and sulphuric acid in water in equilibrium with the co-existing solid tetrahydrate and dihydrate must be equal to the vapor pressure of this hydrate mixture. For the varying amounts of the solutes present in the solution at different temperatures the corresponding vapor pressure could therefore be given by the pressure co-ordinate along curve 1 of figure 21.

Since the curves of this figure represent univariant equilibria according to the phase rule, $F = C - P + 2$, then the log P - 1/T relationships are linear in accordance with the Clausius-Clapeyron equation (see any standard text). It would therefore be possible to determine the tetrahydrate-dihydrate transition temperature if the vapor pressures of the ternary solutions in equilibrium with the hydrate mixture were known for the different temperatures--same as the vapor pressure of the hydrate mixture along curve 1--together with the vapor pressures of the saturated solutions of pure tetrahydrate along curve 3. These could be plotted as the log P - 1/T relationships, the point of intersection of the two straight

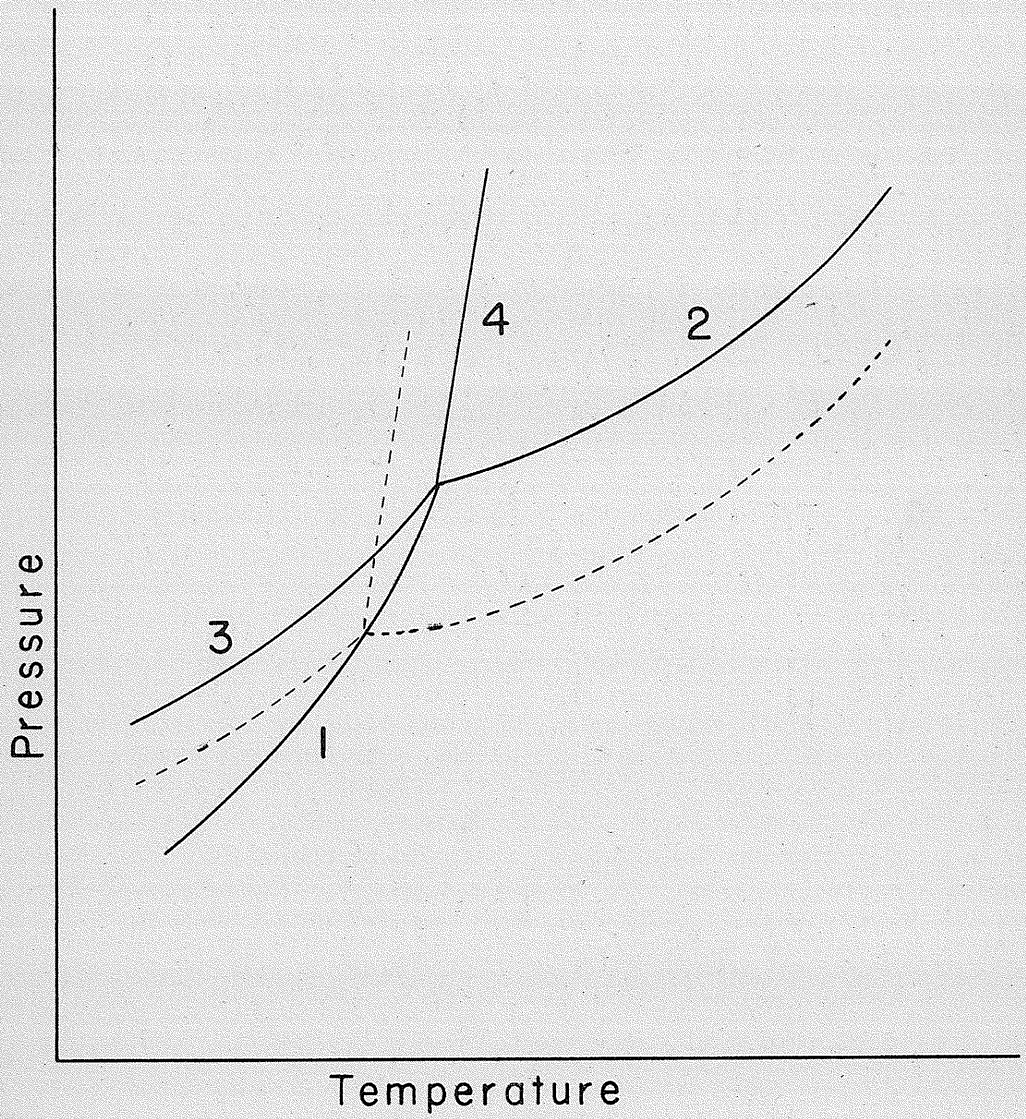


Figure 21. Pressure-Temperature Relationships--
The Binary System: $BeSO_4$ - H_2O
1--tetrahydrate - dihydrate - vapor
2--dihydrate - solution - vapor
3--tetrahydrate - solution - vapor
4--tetrahydrate - dihydrate - solution

lines giving the transition temperature.

However, empirical methods employed in the present study have shown that if the beryllium sulphate component is disregarded in both of these cases, and the vapor pressures of the resulting aqueous sulphuric acid and pure water are considered, then the log P - 1/T relationships are again linear. This linearity is obvious in the case of the pure water since the system water - vapor constitutes a familiar univariant equilibrium. Moreover, the two straight lines obtained are found to intersect at the tetrahydrate-dihydrate transition temperature, this too being obvious since the sulphuric acid content of the ternary solution, and therefore of the binary aqueous sulphuric acid, reduces to zero at this temperature. This would be true whether the log P - 1/T relationships are linear or not.

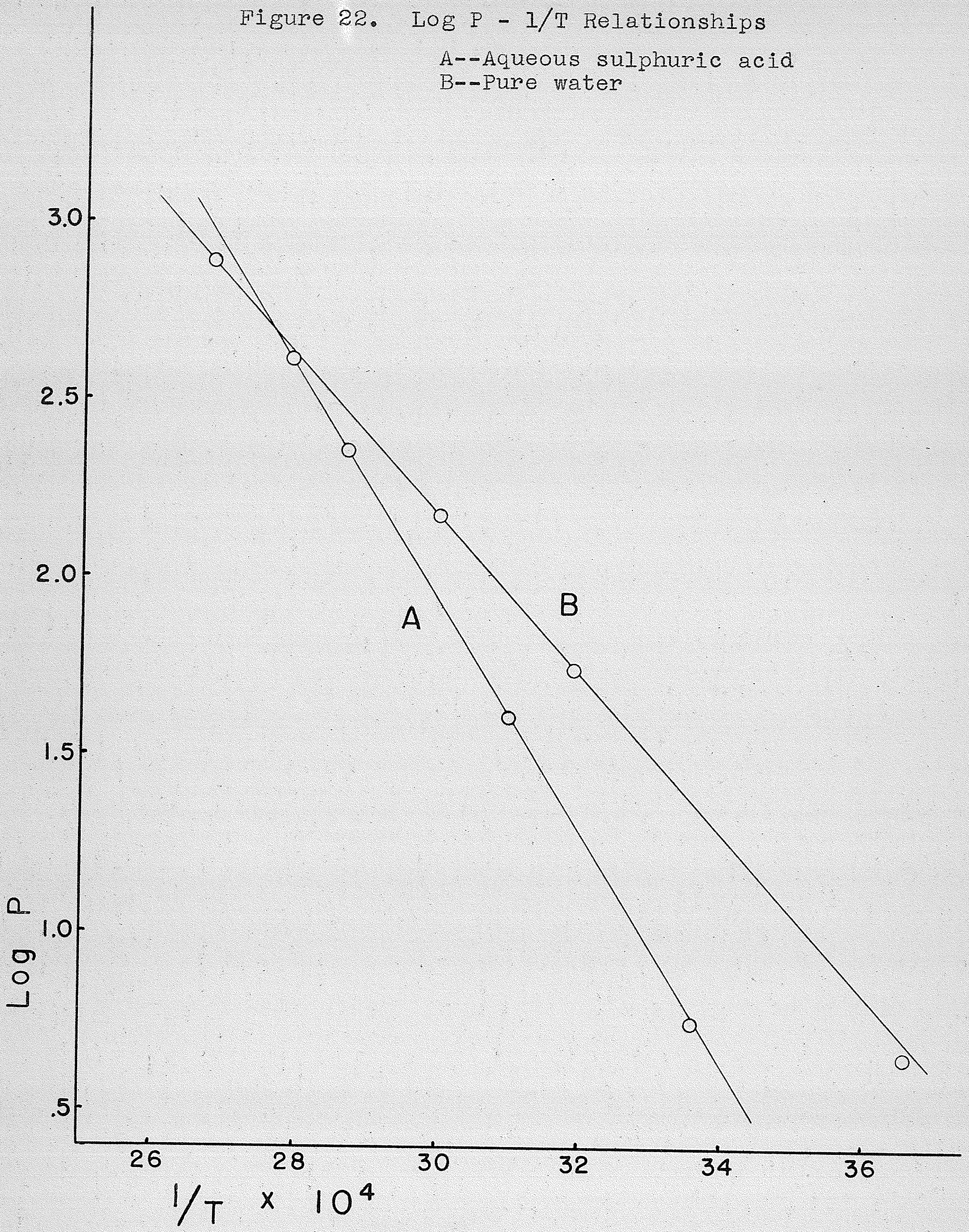
Suggested Explanation of the Linearity of the Log P - 1/T Relationship for the Aqueous Sulphuric Acid -- In disregarding the beryllium sulphate component of the univariant ternary system, tetrahydrate - dihydrate - solution - vapor, the resulting system consists only of aqueous sulphuric acid in equilibrium with vapor. Ordinarily, such a binary system constitutes a bivariant equilibrium since, for example, both concentration and temperature must be specified in order to define the vapor pressure. However, the linearity of the log P - 1/T relationship indicates that the equilibrium in this case is actually univariant.

From a consideration of the circumstances involved here it is seen that the concentration of the aqueous sulphuric acid is not independent of the temperature for a given vapor pressure. The amount of sulphuric acid relative to a given amount of water in the ternary solution is directly dependent on the pressure-temperature conditions necessary for the co-existence of the two hydrates. In other words, these pressure-temperature conditions determine not only the exact composition of the ternary solution but also the exact concentration of aqueous sulphuric acid which, if saturated with beryllium sulphate, would produce this ternary solution. That is, if the temperature alone is specified then the composition and vapor pressure of both the ternary solution and the aqueous sulphuric acid are defined. The aqueous sulphuric acid in equilibrium with its own vapor at the different temperatures will therefore constitute in every sense a univariant equilibrium. The log P - 1/T relationship will be linear, P being the actual vapor pressure of the aqueous sulphuric acid alone.

<u>Calculation of the Transition Temperature</u> -- In accordance with these arguments an accurate value of the tetrahydrate-dihydrate transition temperature has been determined as represented graphically in figure 22. It is known that, due to the slight variation with temperature of the heat effect

Figure 22. Log P - 1/T Relationships

A--Aqueous sulphuric acid
B--Pure water



involved in the liquid-vapor transformations, the linearity of the log P - 1/T relationships for such univariant equilibria cannot be considered accurate except for short ranges of temperature. Therefore, for the purposes of this determination, the method adopted was to choose two points on each line in the vicinity of the transition temperature, calculating the 1/T coordinate of the point of intersection by a familiar principle of elementary geometry. The points chosen on the line for pure water were at 70 and 100 degrees, while the points on the aqueous sulphuric acid line were at the experimental temperatures of 75 and 85 degrees. The vapor pressure values for pure water were obtained directly from the International Critical Tables (13). In order to obtain the vapor pressures of the sulphuric acid solutions of specified concentration it was necessary to interpolate graphically from data given in the same source. The data for this calculation of the transition point are given in table 10, together with other data necessary for plotting the log P - 1/T curve for the aqueous sulphuric acid. Complete data for the corresponding plot for pure water are not included. The concentration of the aqueous sulphuric acid solution given in this table was calculated for each temperature from the composition of the corresponding ternary solution given at the end of tables 1 to 4.

The calculation, carried out as described, gave the value 89.0 degrees for the tetrahydrate-dihydrate transition temperature.

TABLE 10

DATA FOR CALCULATION OF TETRAHYDRATE-DIHYDRATE TRANSITION TEMPERATURE

A--Aqueous Sulphuric Acid

t(°C)	% H_2SO_4 in Aqueous Solution	Vapor Pressure P(mm)	log P	1/T x 10^4
25	56.00	5.66	.7528	33.56
50	46.88	40.6	1.6085	30.96
75	28.55	227.5	2.3570	28.73
85	13.99	404.5	2.6069	27.93

B--Pure Water

t(°C)	Vapor Pressure P(mm)	log P	1/T x 10^4
70	233.7	2.3687	29.15
100	760.0	2.8808	26.81

The Dihydrate-Anhydrous Salt Transition

Although the results obtained in the analyses for the ternary system in the region of high acid concentration may be somewhat uncertain, due to the difficulty experienced in separating the equilibrium liquid from the solid beryllium sulphate, the trend of the tie-lines that have been obtained indicates that a definite transition exists between the dihydrate and a lower hydrate. As X-ray evidence has shown, this transition is undoubtedly that between the dihydrate and the anhydrous salt. An estimation of the approximate composition of the invariant solution for this transition can be made for each of the first three isotherms given in figures 2 to 4. These estimated values are given in table 11.

TABLE 11

APPROXIMATE COMPOSITION OF THE TERNARY SOLUTION FOR THE $BeSO_4 \cdot 2H_2O - BeSO_4$ TRANSITION

	Solution	
t(°C)	% $BeSO_4$	% H_2SO_4
25	2	82
50	3	78
75	5	76

A determination of the dihydrate-anhydrous salt transition temperature from the approximate data in this table, by the same procedure as that used for the case of tetrahydrate and dihydrate, was found to give a value of about 200 degrees. This was shown merely by the point of intersection in a graphical plot of the log P - 1/T lines for pure water and the aqueous sulphuric acid. Due to the obvious inaccuracy of the method in this case, the experimental temperatures being far removed from the transition point, the actual data and diagrams for this determination are not presented.

Further Conclusions

The ternary system phase diagrams, figures 2 to 6, indicate that Rohmer's arguments (22) concerning the existence of the monohydrate as the stable solid phase at 100 degrees are probably not well founded. It was noticed in the present work that prolonged suction in separating the liquid and wet solid phases appeared to dehydrate the solid, particularly at the higher temperatures. This might therefore suggest a possible reason for Rohmer's results. The solid samples obtained by him could not have consisted of the true equilibrium hydrate wet with solution, but would have been deficient in water content.

The dilatometer used in this work was operated for a period of over four months, through several transformation cycles. Considering this length of time, and the repeated reversibility of the phase change at 89 degrees, it seems doubtful that this could represent a metastable transition, which it would be if the monohydrate were the stable hydrate at this temperature.

The determination of the boiling point of the saturated aqueous beryllium sulphate solution has produced evidence in complete disagreement with Rohmer's results. His conclusions concerning the three different boiling points can only be regarded as the result of superheating.

In the rehydration experiment discussed on page 40 the result obtained was to be expected, since X-ray evidence had previously shown that the starting material consisted only of the dihydrate and anhydrous salt.

GENERAL DISCUSSION

The results of this work indicate that of the hydrates of beryllium sulphate with four moles or less of water per mole of the salt only the tetrahydrate, dihydrate and anhydrous salt are definite chemical individuals. The deductions regarding the monohydrate, based on X-ray analysis, are almost in accord with those of Krauss and Gerlach (21) who based their arguments on the results of their tensi-eudiometer measurements. Assuming without proof the existence of the monohydrate, Krauss and Gerlach suggested the possibility of solid solutions existing between the monohydrate and anhydrous salt and between the monohydrate and dihydrate. The X-ray powder photographs obtained in this study reveal no evidence of the existence of the monohydrate but appear to indicate that a series of solid solutions exist between the dihydrate and anhydrous salt.

Accepting Rohmer's result with regard to the pentahydrate (29), and that of Krauss and Gerlach (21) for the decomposition temperature of the anhydrous salt, the temperature ranges for the stable existence of the separate hydrates of beryllium sulphate will be as shown in the following table:

Temperature Range (°C)	Stable Hydrate
-18.5 to -16.4	$BeSO_4 \cdot 5H_2O$
-16.4 to 89.0	$BeSO_4 \cdot 4H_2O$
89.0 to 200	$BeSO_4 \cdot 2H_2O$
200 to 580	$BeSO_4$

No great accuracy is claimed for the dihydrate-anhydrous salt transition temperature, as explained in the section dealing with its determination.

SUMMARY

1. The transition temperature for

$$BeSO_4 \cdot 4H_2O \rightleftharpoons BeSO_4 \cdot 2H_2O + \text{solution}$$

has been found to be 89.0 degrees.

2. Below this temperature the tetrahydrate is stable, above it the dihydrate is the stable hydrate.

3. The normal boiling point of the saturated aqueous beryllium sulphate solution is 108.2 degrees, the equilibrium solid phase being the dihydrate.

4. The non-existence of beryllium sulphate monohydrate has been indicated by X-ray powder diffraction methods.

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