THE UNIVERSITY OF MANITOBA

A STUDY OF THE HYDRATES
OF BERYLLIUM SULFATE

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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WINNIPEG, MANITOBA
SEPTEMBER, 1950

To Dr. A. N. Campbell

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

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ACKNOWLEDGMENTS

The author would like to express his indebtedness to Miss P. Clark for her instruction and guidance in the techniques of X-ray powder photography and to Mr. G. Trider for his helpfulness in the construction of various pieces of apparatus.

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INTRODUCTION

The study of beryllium sulfate and its hydrates has occupied the attention of a large number of investigators during the past half-century. Their findings to date have been largely contradictory and considerable confusion still exists in this field. The existence of hydrates of beryllium sulfate with water contents ranging from one to seven moles of water per mole of salt, in addition to the hemihydrate and the anhydrous form, has been reported. The evidence for the existence of several of these hydrates appears to be somewhat superficial and has been disputed by several workers in this field. More exhaustive investigations appear to indicate the existence of only those hydrates with zero, one, two, four, and five moles of water per mole of salt. The tetrahydrate is known to be the stable hydrate under ordinary room conditions. At a higher temperature the tetrahydrate is transformed to the dihydrate. The presumed metastability of the latter with respect to the monohydrate (18) has been conclusively disproved by A. J. Sukava (22) and the chief uncertainty at the present time seems to centre on the existence or non-existence of the monohydrate of beryllium sulfate. The present study is largely concerned with this problem.

The system, beryllium sulfate - sulfuric acid - water has been investigated by Sukava over an extended range of acid concentrations at 25, 50, and 75 degrees and for low acid concentrations only at 85 and 95 degrees. The Schreinemaker method of "wet residues" was employed in each case and the phase diagrams were represented by the familiar Gibbs equilateral triangle method. The transition temperature for the transformation of the tetrahydrate to the next lower hydrate was accurately determined and was further checked by a dilatometric study. The solid phase which appeared, that is, the next lower hydrate, was found to be the dihydrate and this was confirmed by X-ray studies. An approximate determination of the transition temperature for a presumed dihydrate - anhydrous transformation was also made.

The present study is a sequel to the above investigation and is chiefly concerned with the transition from the dihydrate to a lower hydrate or from the dihydrate to the anhydrous form. An attempt has been made to extend the 95 degree isotherm for the system, beryllium sulfate - sulfuric acid - water, to higher acid concentrations. The isothermal phase diagram for the system, beryllium sulfate - ethyl alcohol - water, has been determined at 25 degrees and the system, beryllium sulfate - propyl alcohol - water, has been investigated at 90 degrres. The two latter investigations were undertaken in order to determine the usefulness of these two alcohols as dehydrating agents. Further detailed X-ray studies have been made using carefully dehydrated samples of beryllium sulfate corresponding to water contents of zero to two moles of water per mole of salt. Vapor pressure measurements have been made on samples of known water content at temperatures from 30 to 300 degrees.

There has been of necessity a considerable amount of repetition of the work of Sukava. Due acknowledgement of this fact has been made wherever possible. The sections dealing with a review of the preceding literature and with some of the initial experimental procedure are practically identical with the corresponding sections in Sukava's thesis.

REVIEW OF THE LITERATURE

Anhydrous Beryllium Sulfate - $BeSO_4$

The existence of anhydrous beryllium sulfate has been conclusively established. The only dispute seems to be concerned with its method of preparation. There are in general three methods of preparing the anhydrous salt: 1 - direct dehydration of the salt hydrates by heating, 2 - dehydration of the hydrates by contact with concentrated sulfuric acid, and 3 - reaction of concentrated sulfuric acid on the oxide or hydroxide of beryllium. The latter two methods have been used by F. Taboury (23) and F. Lebeau (13) respectively but neither author has suggested any means for subsequent removal of the excess acid. Krauss and Gerlach (11) employed similar methods and removed the excess acid by washing with absolute alcohol, Most authors are agreed that direct heating of the salt hydrates will produce the anhydrous form. The minimum temperatures they have suggested as necessary in order to produce the anhydrous salt range from 220 to 320 degrees (9) (11) (12) (14).

C. L. Parsons (16) has disputed the possibility of obtaining pure anhydrous beryllium sulfate by any of these three methods and has claimed that between 300 and 400 degrees the hydrate will start to lose water and sulfuric anhydride simultaneously. He has based this claim on the fact that whenever he prepared the anhydrous salt in any of these ways, he always obtained a small amount of insoluble residue. This residue he assumed to be beryllium oxide arising from the partial decomposition of the sulfate. Further experiments by Taboury (23) and Krauss and Gerlach (11) on the progressive thermal dehydration of beryllium sulfate tetrahydrate to the anhydrous form, followed by heating the product to its decomposition temperature, have indicated, however, that a temperature of at least 540 degrees is required for the decomposition of the anhydrous salt. Hence they have reasoned that the sulfuric anhydride observed by Parsons between 300 and 400 degrees must have been due to the presence of traces of free sulfuric acid retained by the hydrate even after several crystallizations from absolute alcohol. A later study by T. N. Hladun (10) has shown a still higher decomposition temperature for the anhydrous salt, the decomposition beginning at 650 degrees and becoming measurable only at 700 degrees. As far as can be determined, none of these authors has suggested any explanation for the small amount of insoluble residue present whenever anhydrous beryllium sulfate is prepared by any method involving concentrated sulfuric acid.

Beryllium Sulfate Hemihydrate - $BeSO_4 \cdot \frac{1}{2} H_2O$

The existence of the hemihydrate of beryllium sulfate has been claimed by Taboury (23) but no other investigator has verified this claim. In fact Krauss and Gerlach (11) consider that valid evidence for the existence of the hemihydrate does not exist.

Beryllium Sulfate Monohydrate - $BeSO_4 \cdot H_2O$

The preparation of the monohydrate of beryllium sulfate by heating the tetrahydrate salt to approximately 150 degrees.has been claimed as early as 1873 by A. Atterberg and again in 1891 by G. Klatzo (11). Later investigators have verified the existence of the monohydrate chiefly on the basis of experiments on the progressive dehydration of the tetrahydrate. The temperatures they have suggested as necessary in order to produce the monohydrate are as follows:

F. Taboury (23)-------------	100 degrees
M. Levi-Malvano (14)--------	145-150 "
T. N. Hladun (10)-----------	220 "

R. Rohmer (18) has made an extensive study of the system, beryllium sulfate - sulfuric acid - water, at 100 degrees, using Schreinemaker's method of "wet residues" to determine the nature of the solid phase in equilibrium with the various saturated solutions. The resulting isothermal phase diagram indicates that the monohydrate is the only stable solid phase at that temperature at all acid concentrations from zero to about 90 per cent.

In direct contradiction to the above report, Krauss and Gerlach (11), using measurements based on Hüttig's tensieudiometer, have found no evidence for the existence of the monohydrate as a chemical individual. Their data and diagrams for a progressive dehydration of beryllium sulfate tetrahydrate show an abrupt transformation at about

120 degrees when the tetrahydrate changes to the dihydrate. Krauss and Gerlach have suggested that the monohydrate may still exist but that its range of existence is probably restricted by its tendency to form solid solutions with both the dihydrate and the anhydrous salt. The observations of Hackspill and Kieffer (9) differ only slightly from those of Krauss and Gerlach. They indicate a fairly abrupt transition from the tetrahydrate to the dihydrate but further dehydration seems to be continuous except for a slight departure from continuity when the composition of the material corresponds to the monohydrate. The X-ray powder experiments of Sukava on progressively dehydrated samples of beryllium sulfate tetrahydrate reveal no evidence for the existence of the monohydrate but appear to indicate that a series of solid solutions exists between the dihydrate and the anhydrous salt.

Beryllium Sulfate Dihydrate - $BeSO_4 \cdot 2H_2O$

The dihydrate of beryllium sulfate may be prepared by dehydration of the tetrahydrate at approximately 100 degrees (12) (14) (16). Taboury (23) has accomplished the tetrahydrate - dihydrate transformation by heating the tetrahydrate in a current of dry air at 50 to 60 degrees. The experiments of Krauss and Gerlach (11) as well as those of Hackspill and Kieffer (9) indicate a more or less abrupt transformation at 120 degrees while Hladun (10) considers 160 degrees to be the transition temperature. Levi-Malvano (14) has obtained a tetrahydrate - dihydrate transition point of 111.5 degrees by moistening the dihydrate salt with the requisite amount of water, immersing a thermometer in the moist salt, and observing the temperature rise. Previous experiments of a similar nature had indicated that the dihydrate suffered no appreciable hysteresis on rehydration.

Rohmer's study of the system, beryllium sulfate - sulfuric acid - water, and his experiments on boiling saturated solutions of beryllium sulfate in water have led him to conclude that the dihydrate is metastable throughout its range of existence. According to Rohmer the boiling point of such a saturated solution passes through three successive values: 117, 112, and 109 degrees, corresponding to the presence of tetrahydrate, dihydrate, and monohydrate respectively as solid phases. His investigations show that the saturated solution in contact with excess solid boils at 117 degrees for the first ten minutes of the experiment, decreases to constancy at 112 degrees, and finally decreases to 109 degrees after about ninety minutes have elapsed. He concludes that the monohydrate is the stable form above 76 degrees and that the dihydrate is metastable with respect to the monohydrate throughout its range of existence. In a rather arbitrary manner he fixes the limits of this metastable range of existence as from 88.4 to 111.6 degrees. He admits, however, that the equilibria involving the dihydrate can last for more than a month despite continuous stirring and therefore might easily be regarded as stable.

A recent experiment by Sukava is in direct contradiction to the observations of Rohmer. Using an equilibrium still maintained at exactly 760 millimetres of mercury by means of an electronically controlled barostat, he has found no change in the boiling point of saturated solutions of beryllium sulfate even after several hours of continuous operation. He maintains therefore that Rohmer's conclusions as to the metastability of the dihydrate are probably not well founded. Further dilatometric experiments by Sukava, as well as isothermal studies of the system, beryllium sulfate - sulfuric acid - water, indicate a tetrahydrate - dihydrate transition temperature of 89.0 degrees and a stable range of dihydrate existence from 89.0 to at least 200 degrees.

Beryllium Sulfate Trihydrate - $BeSO_4 \cdot 3H_2O$

Only two investigators, Y. A. Fialkov and S. D. Shargorodski (5), have actually claimed the existence of the trihydrate of beryllium sulfate. They base their opinions on the interpretation of certain endothermal effects observed on heating the tetrahydrate. Krauss and Gerlach (11) have reported the preparation of a hydrate of beryllium sulfate whose water content corresponds to the trihydrate but they do not consider this as sufficient evidence for regarding the trihydrate as a definite chemical individual.

Beryllium Sulfate Tetrahydrate - $BeSO_4 \cdot 4H_2O$

Under ordinary room conditions the tetrahydrate of beryllium sulfate is the stable hydrate. As indicated before it may be readily dehydrated with a rise in temperature. Parsons (16) states that the presence of a dehydrating agent such as phosphorus pentoxide is sufficient to produce a slow but continuous loss of water. Taboury (23), however, has found that no dehydration will occur when the tetrahydrate is kept over concentrated sulfuric acid in an evacuated desiccator.

According to J. W. Mellor (15) Berzelius first prepared and studied the tetrahydrate of beryllium sulfate. His method of preparation, still used by most investigators, consisted of heating the oxide, hydroxide, or carbonate of beryllium with an excess of sulfuric acid and then removing the excess acid by evaporation and by washing with strong alcohol. Discussions of this method with slight modifications have been given by such authors as Parsons (16), Levi-Malvano (14), Taboury (23), Krauss and Gerlach (11), and L. Schreiner and A. Sieverts (20). In addition to the above method, Schreiner and Sieverts prepared the tetrahydrate from beryllium nitrate by evaporating twice to fuming with sulfuric acid and recrystallizing the beryllium sulfate twice from dilute sulfuric acid.

The crystalline structure of beryllium sulfate tetrahydrate has been reported as tetragonal body-centred by R. Fricke and L. Havestadt (6). The unit cell dimensions are given as a = 8.03 angstroms and c = 10.75 angstroms. A similar investigation by P. Schonefeld (19) agrees very well with these results.

Beryllium Sulfate Pentahydrate - $BeSO_4 \cdot 5H_2O$

A recent study of the system, beryllium sulfate - sulfuric acid - water, has been made by Rohmer (18. His isothermal phase diagram for this system at 17.5 degrees indicates that the equilibrium solid phase at this temperature up to an acid concentration of 8.9 per cent is the pentahydrate. From the data on this system and from thermal analysis experiments, he concludes that from -16.4 to -18.5 degrees the pentahydrate is the stable solid phase in equilibrium with a saturated solution of beryllium sulfate in water. 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. Schreiner and Sieverts, on the other hand, claim that a stable ice-tetrahydrate eutectic exists at 18.0 degrees and that the tetrahydrate is the equilibrium solid phase from -18.0 to 100 degrees.

Beryllium Sulfate Hexahydrate - $BeSO_4 \cdot 6H_2O$

The evidence for the existence of this hydrate of beryllium sulfate appears to be largely contradictory. Two methods of preparation of the hexahydrate have been claimed by Levi-Malvano (14). These are: 1 - treating the carbonate or hydroxide of beryllium with a small excess in pure water at 25 degrees is 29.94 grams of salt per 100 grams of solution. This agrees very well with later solubility determinations by N. V. Sidgwick and N. B. Lewis (21).

According to Wirth large, transparent hexahydrate crystals persist in sulfuric acid solution until the acid concentration becomes greater than 45 per cent. Then the hexahydrate crystals become transformed into a finely divided white powder which settles slowly in the body of the solution. This white powder he regards as the tetrahydrate. The change in appearance of the solid phase on increasing the sulfuric acid content of the solution corresponds exactly to that found by other investigators for the transformation of the tetrahydrate to a lower hydrate.

Numerous investigators (1), (11), (17), have attempted to prepare the hexahydrate, but to date none has been successful. They have concluded that the suggested methods of preparation are questionable and that conclusive evidence for the existence of the hexahydrate of beryllium sulfate has not been produced.

Beryllium Sulfate Heptahydrate - $BeSO_4 \cdot 7H_2O$

The existence and preparation of beryllium sulfate heptahydrate has been claimed by such early workers as G. Klatzo, C. Marignac, and A. Atterberg(8). More recent attempts by Parsons (16), Levi-Malvano (14), and Krauss and Gerlach (11) to prepare the heptahydrate have all been unsuccessful and these authors are agreed that this hydrate does not exist.

A report published in 1943 by B. Ghosh (7) describes an investigation of certain transient hydrates of beryllium sulfate and indicates that the starting material was the heptahydrate. No information is given, however, as to the source of this substance or the methods for its preparation.

EXPERIMENTAL PROCEDURE

The System $BeSO_4$ - H_2SO_4 - H_2O at 95.00°C.

It was decided to attempt a more complete isothermal study of the system, $BeSO_4$ - H_2SO_4 - H_2O at 95 degrees, because the region of high acid concentration had not been investigated by Sukava at 85 and 95 degrees. For this purpose pure beryllium sulfate tetrahydrate was prepared using a procedure similar to that employed by Parsons (16) and Krauss and Gerlach (11). This procedure has been adequately described by Sukava (22). As a check on the purity of the preparation, quantitative analyses of the resulting product were made for both beryllium and sulfate ion. The agreement was invariably good although the possibility of a slight degree of dehydration in the process of preparation was always indicated. The calculated weight per cent of beryllium sulfate in the pure tetrahydrate is 59.32 per cent. The observed weight per cent of beryllium sulfate in the prepared tetrahydrate was always one to two per cent higher. As pointed out by Sukava this may be attributed to the fact that the dihydrate crystallizes out of solution above 89 degrees. Since the recrystallization from water was always carried out by concentrating the solution by boiling, it is possible that some of the solid would appear as the dihydrate on crystallization.

For the determination of the isothermal solubility curve of beryllium sulfate in aqueous sulfuric acid at 95 degrees, the solutions were saturated with excess solid phase by intermittent stirring in an all-glass assembly fitted with a removable ground-glass plug, a sintered-glass filter, and a receiving vessel as shown in Figure 1. It was found impossible to have the receiving vessel immersed in the thermostat liquid, since on removal of the assembly from the bath the contraction of the glass effectively sealed the receiving vessel to the rest of the assembly. To prevent undue evaporation at this high temperature, a mercury-seal stirrer was used. The stirring time for each trial was usually three or four days. The thermostat liquid -- paraffinol -- was controlled at 95.00 degrees by means of a mercury thermoregulator with a gravity "make-break" relay. To minimize the heating lag on either side of the "make-break" the thermostat vessel was surrounded by felt. A precision of ± 0.05 degrees was obtained in this way. Beryllium sulfate tetrahydrate was used as the solid phase initially. At the very high acid concentrations samples of the salt were carefully dehydrated to correspond to the water content of the dihydrate.

After stirring the solution intermittently for three or four days to ensure proper equilibrium, the mercury-seal stirrer was removed and the glass plug quickly withdrawn, allowing the saturated solution and the solid phase to settle on the sintered-glass filter. Suction was then applied to the receiving vessel and the liquid phase withdrawn into the weighed container. The separation was made as rapidly as possible, the remaining solid being tamped continuously

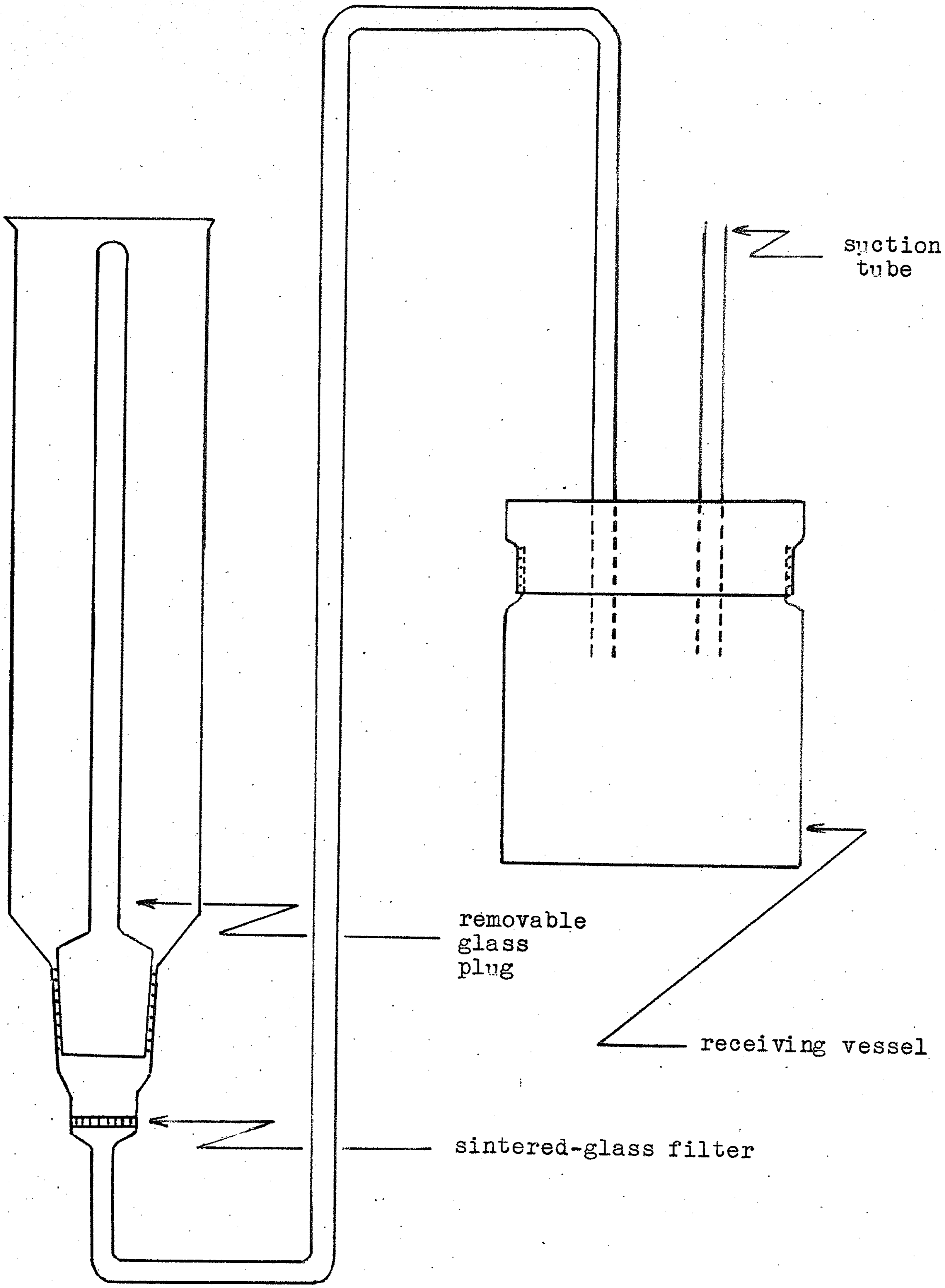

Figure 1

Filter Assembly for Separation of Liquid and Wet Solid Phases during this time. The equilibrium liquid phase was then withdrawn from the solid as completely as possible, without allowing the passage of an undue amount of air through the solid mass. A sample of the wet solid was removed and weighed in a stoppered weighing bottle. A vessel containing the liquid phase was detached from the remainder of the glass assembly by gentle tapping, stoppered and weighed.

Both the liquid and wet solid samples were then dissolved in water and diluted to exactly 250 millilitres. Separate aliquot portions of these solutions were analyzed for total sulfate and for beryllium. The sulfate ion was precipitated with barium chloride in the presence of hydrochloric acid, filtered under suction in sintered-glass filters, and dried overnight at approximately 120 degrees. For the estimation of beryllium the beryllium ion was precipitated as the hydroxide with strong ammonia in the presence of ammonium chloride and filtered by ordinary means. After standing overnight to allow for thorough drying, the precipitate was ignited in a platinum crucible. The filter paper was first charred off and the residue reduced to a greyish-yellow ash. The ash was then covered with concentrated nitric acid and heated very gently until all the solid had dissolved. More acid was added if necessary. It was then evaporated to dryness by cautious heating to avoid spattering. A minimum of eight hours ignition of the final residue was found necessary to produce a reasonably white product -- beryllium oxide -- of constant weight. From the weights of barium sulfate and beryllium oxide obtained, the beryllium sulfate and sulfuric acid contents of the liquid and wet solid phases could be readily calculated. These were expressed in terms of weight per cent and the results are given in Table 1. The corresponding phase diagram is given in Figure 2. In each case the end of the tie line indicates the composition of the pure equilibrium solid phase.

Discussion -- The separation of liquid and wet solid phases using the above assembly was found to be increasingly difficult as the sulfuric acid content of the solution increased. Even with direct aspirator suction on the receiving vessel and continued tamping of the solid phase, ten to twenty minutes of continuous suction were normally required, before the solid phase appeared to be reasonably free of sulfuric acid. The direction of the tie lines obtained in this way almost invariably indicated a considerable dehydration of the wet solid and yet in every case the percentage of occluded sulfuric acid was still unduly high. The "filter-stick" technique described by Sukava was also attempted but with no greater success. Hence the results of all these trials are somewhat uncertain and probably not very reliable. They do verify the fact that in solution at 95 degrees the dihydrate is the stable form and they seem to indicate that in solutions whose sulfuric acid contents are below 76 per cent there is no transition to a lower hydrate at 95 degrees. In all probability the estimations by Sukava of the approximate compositions of the ternary solutions corresponding to a dihydrate - anhydrous salt transformation at 25, 50, and 75 degrees are far too low. From the present study it seems likely that at 25 degrees, at least, there would be no such transformation. Accordingly the estimated transition temperature of 200 degrees based on the above approximate compositions will in all likelihood be well below the true transition temperature.

(6)

TABLE ~~1~~

$BeSO_4$ - H_2SO_4 - H_2O at 95.00°C. (± 0.05)

	Solution		Wet Residue		Nature of Solid
	%$BeSO_4$	%H_2SO_4	%$BeSO_4$	%H_2SO_4	Phase
1.	23.10	22.85	53.36	9.52	$BeSO_4 \cdot 2H_2O$
2.	16.04	33.89	52.20	12.96	"
3.	9.16	46.40	44.39	20.98	"
4.	4.65	61.24	42.50	28.21	"
5.	4.89	68.36	26.86	46.30	"
6.	6.04	70.95	38.80	37.35	"
7.	6.90	75.42	34.75	45.20	?
8.	7.45	76.80	39.20	43.25	?

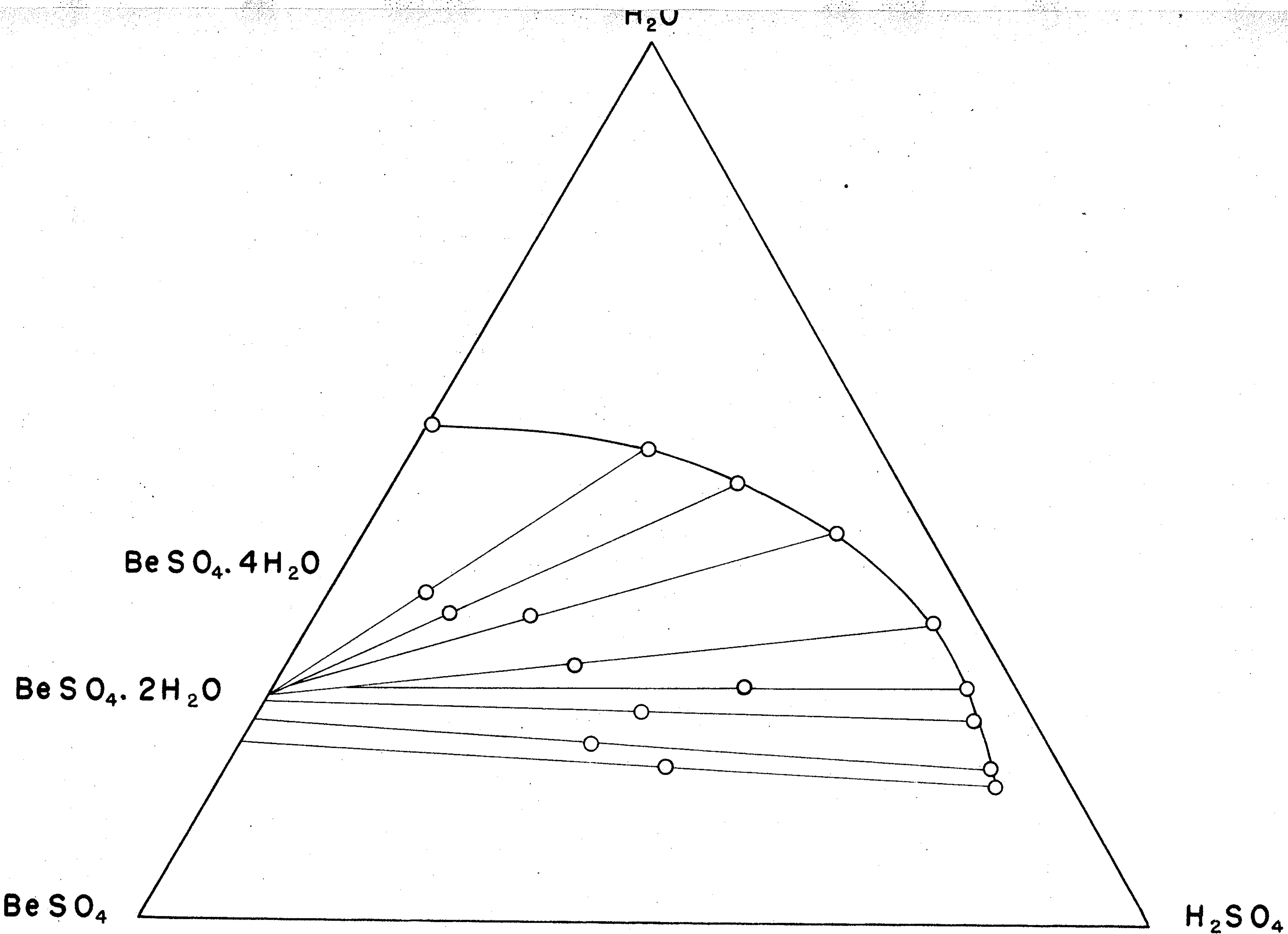

Figure 2. System $BeSO_4$ - $H SO_4$ - H_2O at 95°C.

The System $BeSO_4$ - EtOH - H_2O at 25.00°C.

The possibility of using an alcohol as a dehydrating agent was considered and a study of the system, beryllium sulfate - ethyl alcohol - water, was made at 25.00degrees. As before the saturated solutions with excess solid phase were stirred vigorously for one to three days to ensure proper equilibrium and the liquid and wet solid phases separated and diluted to 250 millilitres in the proper volumetric flasks. Aliquot portions were then analyzed for sulfate in the normal manner. To determine the alcohol contents of the two phases, aliquot portions were withdrawn from the volumetric flasks and the solutions distilled through an efficient condenser into a weighed receiving vessel. The distillation was prolonged until the remaining solution contained virtually no alcohol, as shown by the temperature of the distillate. The receiving vessel was then filled by dilution with water and weighed again. Using a small pyknometer and a water bath controlled at 25.00 degrees, the relative density of the aqueous alcohol in the receiving vessel was determined, that is, the density of the aqueous alcohol at 25 degrees relative to the density of pure water at the same temperature. From tables in the Handbook of Chemistry and Physics the corresponding weight per cent of alcohol was found(26) Since the total weight of the aqueous alcohol was known, the amount of alcohol present in the aliquot portion and hence the alcohol content of the original liquid or wet solid sample could be readily calculated.

The solubility curve for beryllium sulfate in aqueous alcohol at 25 degrees was determined by the above method and the results plotted as before on triangular coordinate paper. The results are given in Table 2 and the corresponding isothermal phase diagram is given in Figure 3.

Discussion -- The slight discontinuity in the solubility curve corresponds to the tetrahydrate - dihydrate transition. At all higher alcohol concentrations the stable solid phase, as indicated by the ends of the tie lines, is seen to be the dihydrate. The possibility of a partial miscibility phenomenon occurring in this system was considered but was not observed in any of the trials. This may be explained by the fact that a range of alcohol concentrations from 12 to 65 per cent was not investigated. From this investigation it was concluded that ethyl alcohol would not have sufficient dehydrating power to cause any transformation beyond the tetrahydrate - dihydrate transition.

TABLE ~~2~~ 7.

$BeSO_4$ - EtOH - H_2O AT 25.00°C.(± 0.05)

	Solution		Wet Residue		Nature of Solid Phase
	%$BeSO_4$	%EtOH	%$BeSO_4$	%EtOH	
1.	20.51	12.14	47.05	4.23	$BeSO_4 \cdot 4H_2O$
2.	2.10	64.81	49.50	11.87	"
3.	0.31	89.50	41.03	27.88	$BeSO_4 \cdot 4H_2O$ and $BeSO_4 \cdot 2H_2O$
4.	0.50	89.00	38.04	37.11	" "
5.	0.29	89.20	42.70	29.95	" "
6.	1.01	97.43	49.85	31.70	$BeSO_4 \cdot 2H_2O$
7.	1.05	98.95	48.10	36.27	"

Invariant Solution Composition (mean of No.3,4, and 5)

0.38% $BeSO_4$

89.25% EtOH

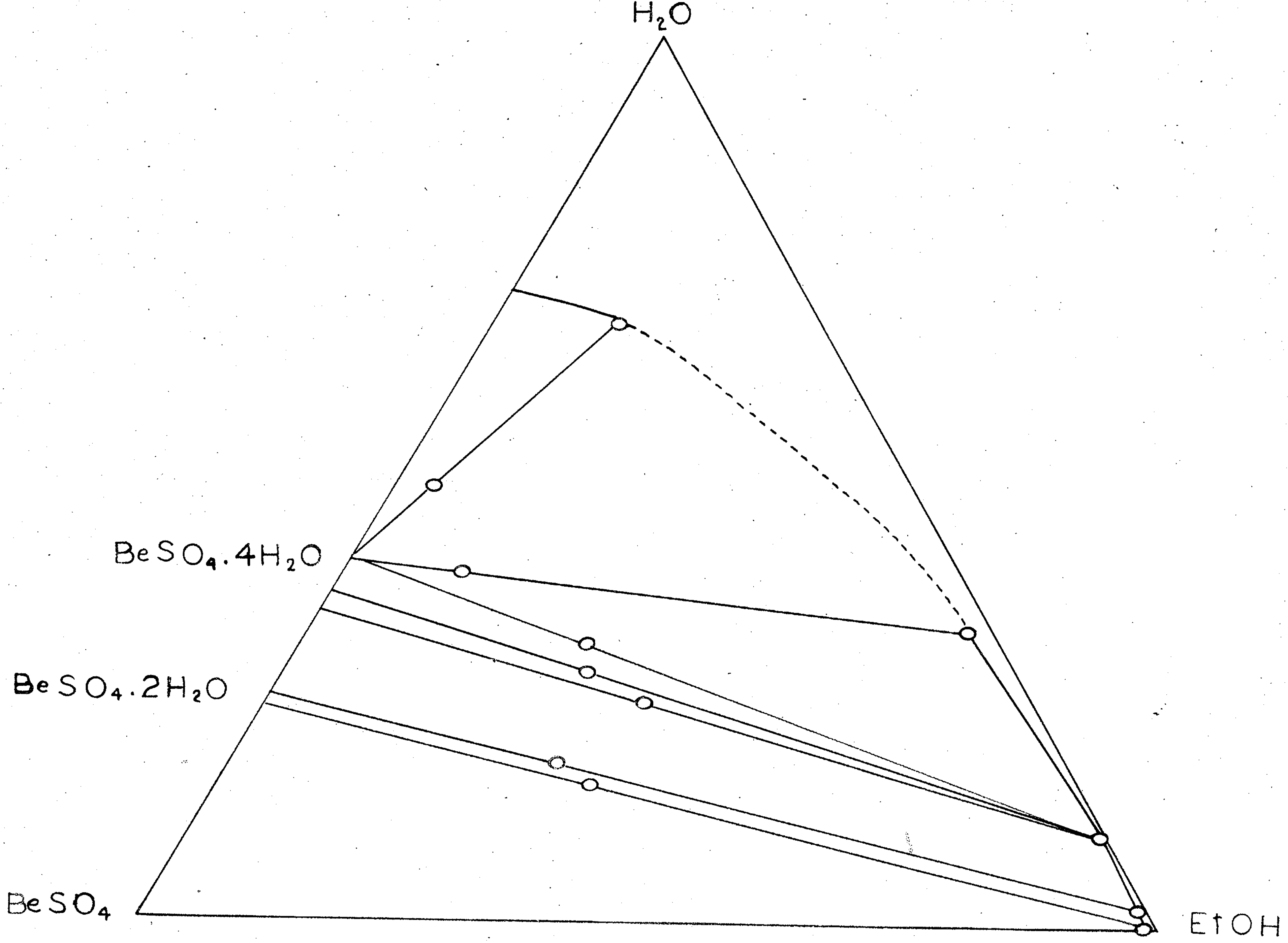

Figure 3. System $BeSO_4$ - EtOH - H_2O at 25°C

The System $BeSO_4$ - PrOH - H_2O at 90.0°C.

To investigate the dehydrating action of propyl alcohol on the hydrates of beryllium sulfate, the isothermal phase diagram for the system, beryllium sulfate - propyl alcohol - water, was determined at 90.0 degrees. The procedure was similar to that used for the system beryllium sulfate - ethyl alcohol - water. The only literature values relating relative densities of aqueous propyl alcohol solutions to weight percentages are given for 15 degrees (4). Because of the practical difficulty of keeping a thermostat at 15 degrees, a series of relative density determinations were made at 25 degrees on accurately weighed propyl alcohol solutions corresponding to weight percentages of zero to ten. The extrapolated results for the integral weight per cent values from zero to ten are shown in Table 3 and are compared with the literature values for 15 degrees.

TABLE ~~3~~ 8

RELATIVE DENSITIES OF PROPYL ALCOHOL - WATER Solutions

%PrOH	Experimental Relative Density 25/25	Literature Relative Density (4) 15/15
0 0	1.0000	1.0000
1	0.9984	0.9983
2	0.9966	0.9966
3	0.9951	0.9952
4	0.9937	0.9937
5	0.9922	0.9923
6	0.9907	0.9909
7	0.9893	0.9896
8	0.9878	0.9883
9	0.9864	0.9871
10	0.9850	0.9859

An extensive miscibility gap was found in this system at 90.0 degrees and the limits of partial miscibility were carefully determined. The remainder of the phase diagram was also investigated. The results are given in Tables 4 and 5, and the corresponding phase diagram is shown in Figure 4.

No transition was observed in this isothermal study and it was concluded that propyl alcohol does not have sufficient dehydrating power to cause any further transformations.

Table 4

LIMITS OF PARTIAL MISCIBILITY IN SYSTEM

$BeSO_4$ - PrOH - H_2O at 90.0°C

Top Layer		Bottom Layer	
%$BeSO_4$	%PrOH	%$BeSO_4$	%PrOH
1.01	80.88	41.81	1.33
1.30	80.70	42.18	1.28
Mean		Mean	
1.15	80.80	42.00	1.30

Table 5

$BeSO_4$ - PrOH - H_2O at 90.0°C. (± 0.1)

Solution		Wet Residue		Nature of Solid Phase
%$BeSO_4$	%PrOH	%$BeSO_4$	%PrOH	
0.34	89.60	50.01	29.26	$BeSO_4.2H_2O$
0.08	99.15	47.75	35.14	"

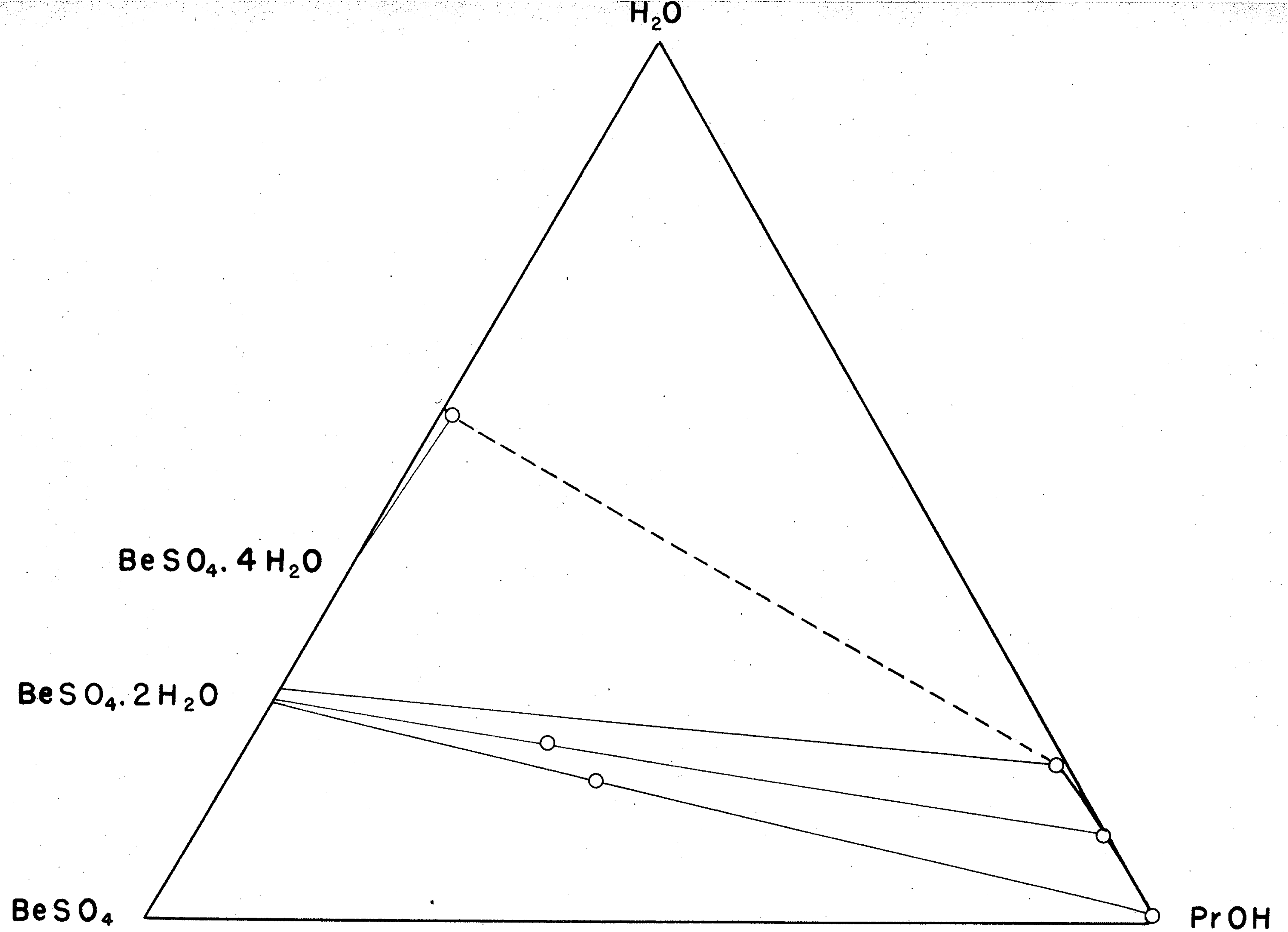

Figure 4. $BeSO_4$ - PrOH - H_2O at 90°C.

Vapor Pressure Measurements

To investigate further the possibility of a transition from the dihydrate to a lower hydrate or from the dihydrate to the anhydrous salt, it was decided to do vapor pressure measurements on samples of beryllium sulfate of known water content. For pressures up to one atmosphere an all-glass system including an ordinary closed mercury manometer was used, as shown in Figure 5. The mercury used in the manometer was thoroughly cleaned by "scrubbing" with nitric acid and by distillation. The right-hand side of the manometer was evacuated by means of a hyvac oil pump and the mercury heated to expel all vapors and gases. The evacuation was continued for about three hours and the manometer was then sealed off. After placing a salt sample of known water content in the bulb of the apparatus, the remainder of the system was evacuated and eventually sealed off. The apparatus was immersed in a bath of water - white "Wyrol J" oil with only the upper half of the closed end of the manometer protruding above the surface. A cathetometer was used to read the difference in the mercury levels. The initial level of the mercury in the capillary tubing was 4.8 millimetres below the level of the mercury in the reservoir. This was in fair agreement with the calculated capillary depression effect. The oil bath was controlled at a series of temperatures from 50 degrees to 180 degrees by means of a mercury thermo - regulator and the corresponding

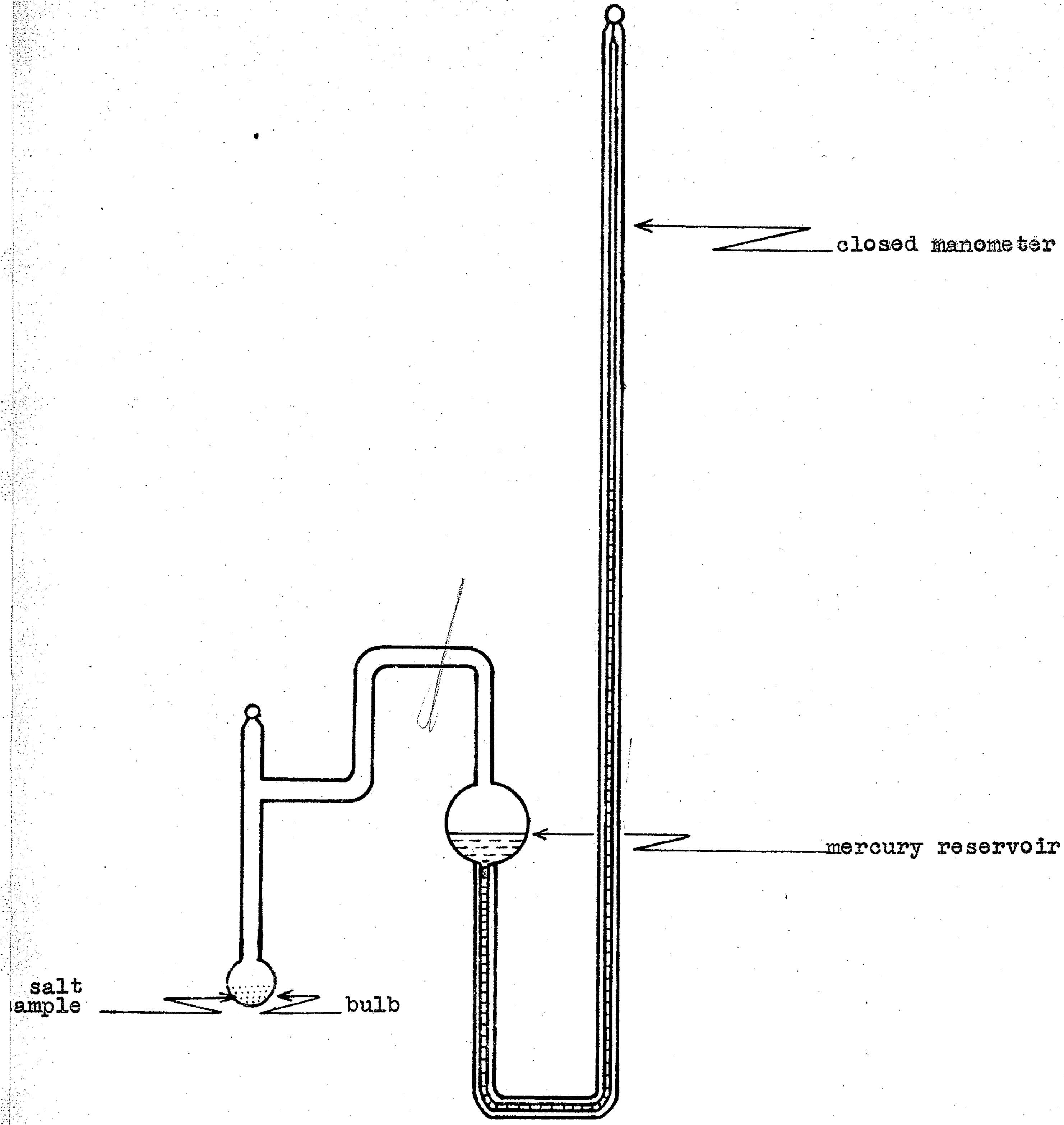

Figure 5. Assembly for Vapor Pressure Measurements.

vapor pressure readings were determined by means of the cathetometer. Two samples of beryllium sulfate were analyzed as to water content and were then carefully dehydrated by heating in an oven. The extent of dehydration was checked at frequent intervals by cooling in a dessicator and weighing, until the water contents of the salt samples corresponded to approximately 19 per cent. The data of Table 6 represents the mean vapor pressures obtained for these two samples at the various controlled temperatures.

For vapor pressures above one atmosphere it was found necessary to use a manometer sealed off at atmospheric pressure. The apparatus, similar in design to that used before, was constructed entirely of capillary glass tubing. An air bath was constructed of wide glass tubing and alternate layers of asbestos and Nichrome resistance wiring. The glass furnace was made large enough to allow the whole vapor pressure apparatus to be suspended entirely inside it and slits were cut through the asbestos layers front and back to permit proper observation. After introduction of a salt sample of known water content, both sides of the apparatus were sealed off at atmospheric pressure and the assembly was suspended inside the glass furnace. Two thermometers were suspended inside the furnace in such a way that their bulbs were respectively three inches above and below the salt sample. The temperature gradient was relatively small, never exceeding five degrees. A variable resistance in series with the heating coils was used to give an approximate temperature control for various temperatures from 180 degrees to 350 degrees. The corresponding vapor pressures were calculated by applying Boyle's Law to the compressed volume of air above the mercury in the right-hand arm of the manometer. Throughout the investigation the initial volume V_1 was the difference in height between the sealed end of the capillary and the mercury level at the time of sealing, while the initial pressure P_1 was the atmospheric pressure at the time of sealing. For each subsequent temperature setting the new volume V_2 was obtained from the appropriate cathometer readings and the corresponding pressure P_2 for that temperature could then be readily calculated by applying the Boyle's Law relationship, $P_1 V_1 = P_2 V_2$. In order to determine the actual vapor pressure of the salt sample, it was necessary to add to P_2 the difference in height between the two mercury levels and subtract from this sum the observed atmospheric pressure at the time of sealing. A sample of beryllium sulfate whose water content corresponded to approximately 19 per cent was investigated in this way. Vapor pressure readings were taken for both increasing and decreasing temperatures. The agreement throughout was very good. Mean vapor pressure values obtained at the various controlled temperatures are given in Table 7.

Individual graphical plots of log P versus 1/T, where

P was the vapor pressure of the salt sample at the absolute temperature T, were made for pressures above and below one atmosphere but it was not considered necessary to reproduce them here. Instead a combined plot of log P versus 1/T for the complete temperature range investigated is given in Figure 6.

TABLE ~~6~~ 11

VAPOR PRESSURE MEASUREMENTS: $P < 1$ ATMOSPHERE

	Temperature (T° K.)	Vapor Pressure (P mm.)	Log P	$1/T \times 10^3$
1.	324	1.3	0.115	3.086
2.	337	3.1	0.492	2.967
3.	351	6.8	0.835	2.849
4.	368	17.1	1.234	2.717
5.	381	33.5	1.525	2.625
6.	395	64.9	1.812	2.532
7.	408	112	2.050	2.451
8.	420	182	2.261	2.381
9.	437	344	2.536	2.288
10.	440	383	2.583	2.273
11.	449	510	2.708	2.227
12.	453	577	2.761	2.208
13.	457	684	2.835	2.188

273

184

TABLE ~~X~~ 12

VAPOR PRESSURE MEASUREMENTS: P > 1 ATMOSPHERE

	Temperature (T^o K.) T	Vapor Pressure (P mm.)	Log P	$1/T \times 10^3$
1	467	955	2.980	2.141
2	483	1556	3.192	2.070
3	492	1968	3.294	2.033
4	497	2296	3.361	2.012
5	508	3034	3.482	1.969
6	513	3451	3.538	1.949
7	521	4345	3.638	1.919
8	528	5082	3.706	1.894
9	535	5932	3.773	1.869
10	540	6918	3.840	1.852
11	543	7295	3.863	1.842
12	545	7447	3.872	1.835
13	553	7889	3.897	1.808
14	563	8979	3.953	1.776
15	573	9530	3.979	1.745
16	578	10100	4.004	1.730
17	585	10870	4.036	1.709
18	593	11860	4.070	1.686
19	603	12420	4.094	1.658
20	611	13300	4.124	1.637
21	622	14520	4.160	1.608
22	625	14860	4.172	1.600

272

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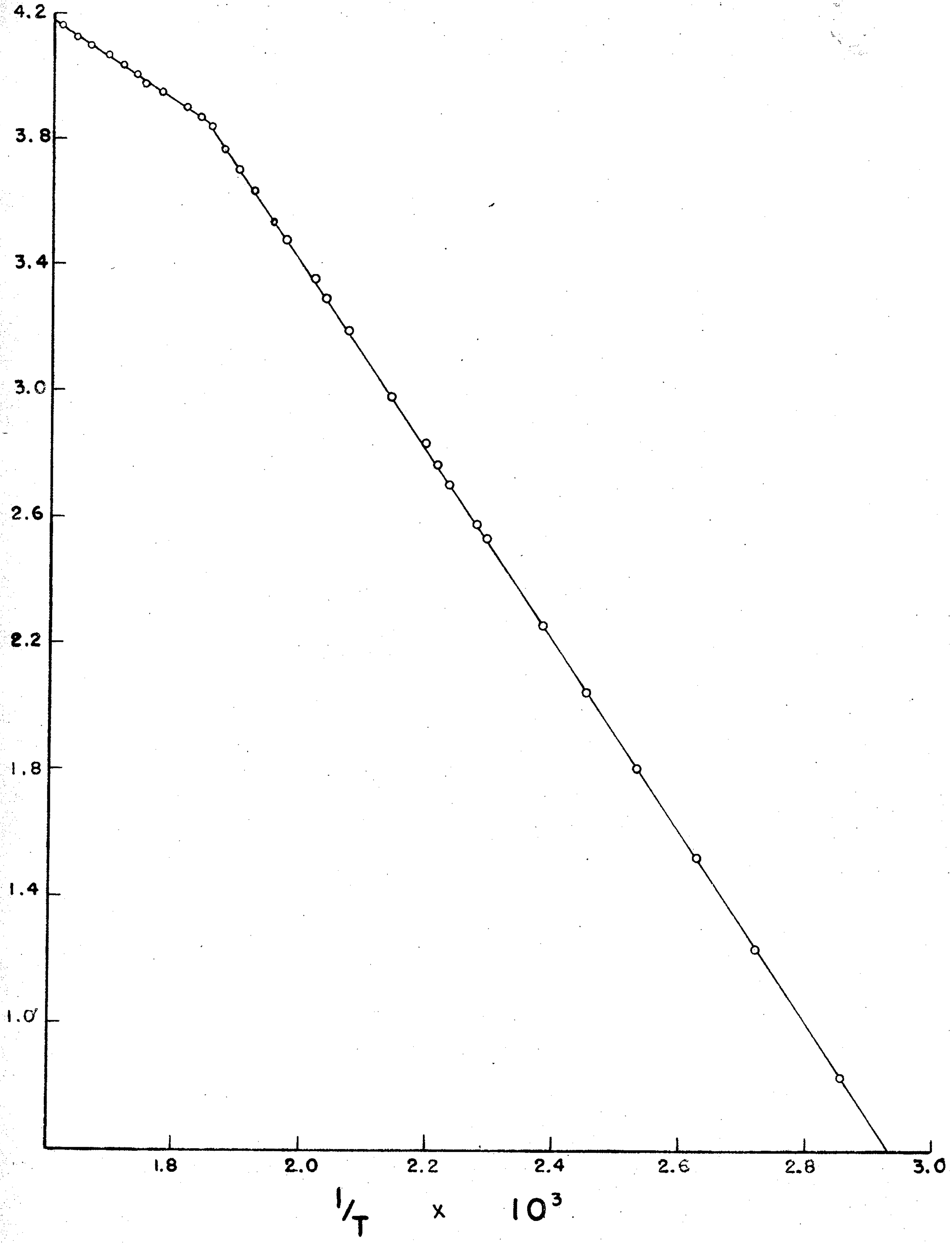
Figure 6. Log P versus 1/T Plot.



A Visual Study of the Behavior of Beryllium Sulfate Dihydrate on Heating

An approximate determination of the upper limit for the stable existence of beryllium sulfate dihydrate was made. A small furnace was constructed of wide glass tubing and alternate layers of asbestos and Nichrome resistance wiring. A freshly prepared sample of slightly dehydrated beryllium sulfate dihydrate was put into a short capillary tube, sealed off, and suspended inside the furnace. A small window was cut into the asbestos layers to permit visual observation of the salt sample. To permit a slow uniform rise in temperature several variable resistances were included in the heating circuit. A sharply-defined transition was observed at 269 to 270 degrees, with a considerable portion of the solid sample appearing to go into solution. Several similar determinations gave identical results with the transition occurring sharply at 270 degrees.

X - Ray Powder Diffraction Measurements

X-ray diffraction patterns serve as a means of identifying crystalline substances. Each crystalline species produces its own characteristic pattern which is different from the patterns given by other species (3). Thus a unique diffraction pattern is sufficient evidence for the existence of a chemical individual. A mixture of two or more substances gives a pattern consisting of the superimposed patterns of the individual components. Solid solutions, on the other hand, give diffraction patterns which are, in general, intermediate with respect to both the positions and the intensities of the arcs between those of the pure constituents. Two cases must, however, be distinguished here. If two solid substances are miscible in all proportions, they will form a continuous series of solid solutions with one another and the diffraction patterns of all such solid solutions will be in actual fact intermediate between those of the two pure constituents. It is often possible to estimate the percentage of each constituent in such a solution by a visual comparison of the solid solution pattern with those of the two pure constituents. If, however, two solid substances (A and B) are miscible to a limited extent only, they will form a discontinuous series of solid solutions. Pure A will dissolve increasing amounts of B, forming a series of homogeneous solid solutions, until A becomes saturated with B. Similarly pure B will dissolve increasing amounts of A, forming another series of homogeneous solid solutions, until B becomes saturated with A. Between these two saturation limits there will be a so-called miscibility gap or range of heterogeneity in which the two saturated end-members co-exist in varying proportions. An X-ray investigation of the whole range of composition between pure A and pure B will reveal three types or series of diffraction patterns. The patterns corresponding to the range of composition from pure A to a saturated solution of B in A will be essentially the pattern of pure A with only a slight displacement of lines with changing composition. Similarly the patterns corresponding to the range of composition from pure B to a saturated solution of A in B will be essentially the pattern of pure B with only a slight displacement of lines with changing composition. Since the miscibility gap contains a mixture of the two saturated end-members , the patterns corresponding to its range of composition will consist of the superimposed patterns of the two end-members.

The theory underlying the various aspects of X-ray powder photography can be found in any textbook on crystallography. In practice a narrow monochromatic beam of X-rays is passed through a small specimen of the powdered crystalline solid. Numerous cones of diffracted beams emerge from the specimen and these are recorded as arcs on a strip of film encircling the specimen. Each arc on the strip of film represents the combined diffracted beams from all the crystals in the powder specimen which happen to be suitably oriented for reflecting the primary X-ray beam with one particular set of planes. The fundamental equation of X-ray diffraction by crystalline solids is known as Bragg's Law and is of the form

$$\frac{d}{n} = \frac{\lambda}{2 \sin\theta} \qquad (3)$$

where λ is the wave-length of the X-rays,

$\underline{d}$ is the distance between successive identical planes of atoms in the crystal,

θ is the angle between the primary X-ray beam and these atomic planes,

and $\underline{n}$ is any whole number. A measurement of the linear distances between corresponding arcs on either side of the primary-beam direction permits an evaluation of the angles of diffraction $\underline{\theta}$. Since the value of λ is known and constant for all the lines in any one photograph, it is then possible to calculate the lattice spacings $\underline{d}$ of the powder specimen under investigation.

The X-ray photographs taken in this study were obtained from powder rollings of samples of beryllium sulfate whose water contents had been adjusted to the desired values by proper dehydration. In every case the starting material was the dihydrate and the dehydration was accomplished by heating. To prepare samples of the anhydrous salt it was necessary to heat the dihydrate at 300 degrees for several hours. The powder rollings were made as quickly as possible to minimize the possibility of rehydration and the rolled specimens were kept over concentrated sulfuric acid while drying. After drying over concentrated sulfuric acid for a day, the specimens were mounted in the cameras in the appropriate manner and exposed to copper K-alpha radiation for the required length of time. In accordance with standard procedure, the lines or arcs on each negative were "read" and tabulations of relative intensities $\underline{I}$ and lattice spacings $\underline{d}$ were made (22). Tables 8 to 12, inclusive, represent data obtained in this way for beryllium sulfate samples of varying degrees of hydration. No attempt was made to determine the unit cell dimensions of the dihydrate and the anhydrous forms. A prerequisite for such a determination is a knowledge of the crystal structure of the solid and it was not found possible to do a crystallographic structure determination in this work.

TABLE ~~8~~ 15

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

I	d	I	d
8	4.887	1	1.883
4	3.975	1	1.854
10	3.594	2	1.773
2	3.392	0.5	1.705
6	2.841	1	1.656
2	2.614	0.5	1.601
2	2.535	0.5	1.554
3	2.398	1	1.508
5	2.185	1	1.449
0.5	2.056	0.5	1.398
0.5	1.996	0.5	1.359
5	1.936	1	1.327

TABLE ~~9~~ 16

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4$, 19.13% H_2O

I	d	I	d
8	4.860	1	1.894
4	3.923	1	1.847
10	3.580	3	1.786
2	3.379	0.5	1.705
6	2.832	1	1.656
2	2.629	0.5	1.608
2	2.549	0.5	1.559
3	2.391	2	1.515
5	2.195	1	1.461
0.5	2.061	0.5	1.404
0.5	1.992	1	1.366
5	1.943	1.5	1.334

TABLE ~~10~~ 17

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4$, 14.55% H_2O

I	d	I	d
6	5.293	0.5	2.061
8	4.834	0.5	1.996
0.5	4.471	4	1.951
9	3.906	4	1.894
10	3.580	2	1.843
2	3.392	3	1.789
3	3.200	1	1.708
1	3.030	1	1.656
5	2.867	2	1.603
0.5	2.723	0.5	1.559
2	2.644	1	1.504
5	2.549	2	1.461
2	2.398	1	1.404
3	2.314	1	1.361
4	2.200	2	1.330
1	2.121		

TABLE ~~11~~ 18

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4$, 10.80% H_2O

I	d	I	d
7	5.293	2	2.116
0.5	4.449	1	2.043
10	3.923	0.5	1.988
8	3.566	2	1.883
1	3.392	0.5	1.840
2	3.223	3	1.773
1	3.039	1	1.726
3	2.850	2	1.603
0.5	2.715	2	1.492
3	2.637	2	1.469
3	2.542	1.5	1.402
7	2.367	1	1.355
3	2.200	1	1.325

TABLE 12

X-RAY POWDER DIFFRACTION PATTERN FOR $BeSO_4$

I	d	I	d
7	5.325	2	2.107
0.5	4.427	0.5	1.984
10	3.889	1	1.879
7	3.552	2	1.773
0.5	3.366	0.5	1.720
1	3.200	2	1.601
0.5	3.029	1	1.488
2	2.832	2	1.469
2	2.629	1	1.404
2	2.522	0.5	1.352
7	2.355	0.5	1.324
3	2.195		

Experiments on the Nature of the Solid Phase in Equilibrium with Saturated Solutions of Beryllium Sulfate in Sulfuric Acid

In order to gain additional information on the nature of the solid phase in equilibrium with aqueous sulfuric acid at various temperatures, it was decided to apply a simple technique previously used by Sukava for a somewhat similar purpose (22). Aqueous solutions of varying sulfuric acid content were made up and saturated with beryllium sulfate dihydrate at their respective boiling points. In every case the solution in contact with at least two or three grams of excess solid phase was refluxed for three to four hours. The hot liquid and solid phases were then rapidly separated by filtering under suction and a portion of the hot liquid was immediately transferred to a stoppered weighing bottle for analysis. The wet solid was washed with acetone to remove water and sulfuric acid and was then transferred to a flask and refluxed with acetone for a few minutes to complete the removal of occluded sulfuric acid. After washing with acetone under suction once more, the solid was transferred to a porous plate and exposed to a current of dry air for a few minutes to remove any adhering acetone. Both solid and liquid phases were then analyzed for beryllium and for sulfate ion in the usual manner. The results of these analyses were used to calculate the sulfuric acid content of the original solution and the composition of the solid phase in equilibrium with the solution at its boiling point. It was found in every case that only negligible amounts of sulfuric acid still adhered to the solid phase after the vigorous treatment with acetone.

Table 13 gives a tabular summary of the experimental results, including the observed boiling points of the various solutions. A graphical plot of the sulfuric acid contents of the solutions versus the water contents of the equilibrium solid phase is given in Figure 7. A distinct break in the curve is evident at a water content of approximately 19 per cent. Since this experiment was performed well in advance of the vapor pressure and the X-ray work, the significance of the discontinuity at 19 per cent was not fully realized until later. It did, however, result in the use of beryllium sulfate samples of approximately 19 per cent water content for the vapor pressure measurements.

TABLE 13

Composition of Solid Phase in Equilibrium with Boiling Aqueous Sulfuric Acid

Observed Boiling Point (°C.)	H_2SO_4 Content of Solution (%H_2SO_4)	H_2O Content of Solid Phase (%H_2O)
115	38.3	25.2
128	52.5	22.2
139	59.1	21.4
146	63.0	21.0
165	70.0	20.4
194	78.2	19.6
229	86.0	16.0
241	88.0	14.6

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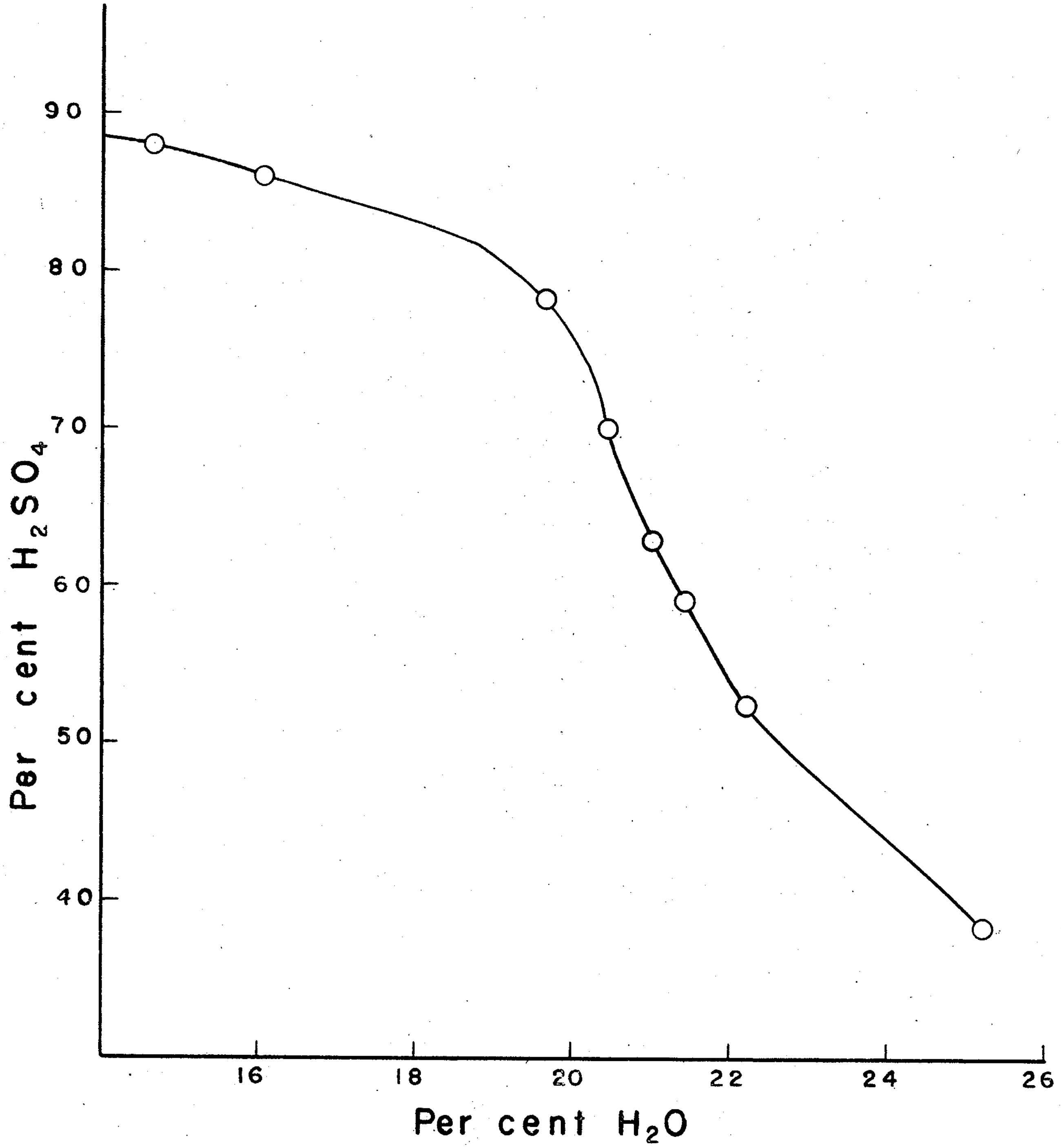

Figure 7. Plot of H_2SO_4 Content of Solution versus Water Content of Solid Phase.

DISCUSSION OF RESULTS

The Ternary Investigations

The evidence obtained from the three ternary investigations undertaken in this work has served mainly to confirm the previous observations of Sukava (20). The investigation of the system, beryllium sulfate - sulfuric acid - water, at 95.0 degrees has confirmed that at that temperature the tetrahydrate no longer exists and that up to a minimum acid concentration of 76 per cent the dihydrate is the only stable solid phase encountered . With increasing acid concentration there is a tendency for the tie lines, notably numbers 7 and 8 to "wander". According to elementary phase rule theory this indicates the formation of solid solutions between the dihydrate and a form of lower water content. The isothermal phase diagram for the system, beryllium sulfate - propyl alcohol - water, provides a further indication of the fact that the dihydrate of beryllium sulfate forms solid solutions with a form of lower water content.

X-Ray Evidence

A careful and extensive study of the patterns of the numerous X-ray photographs taken reveals only two unique diffraction patterns in the range of composition investigated, namely, those of the dihydrate and of the anhydrous salt. The data for these two unique patterns are given in Tables 8 and 12. There is, however, conclusive evidence of the formation of a discontinuous series of solid solutions between these two chemical individuals. With decreasing water content of the powder samples, the dihydrate pattern persists, except for a very slight but definite displacement of the lines, until a water content of approximately 19 per cent is reached. On further dehydration the X-ray diffraction patterns become suddenly more complex. All the lines of the dihydrate pattern can still be readily recognized but there are a considerable number of additional lines which coincide exactly with the lines of the anhydrous pattern. The pattern complexity persists down to a water content of approximately 11 per cent. On further dehydration the lines corresponding to the dihydrate pattern disappear entirely and the anhydrous pattern, with only a slight displacement of lines, characterizes all powder photographs of samples of lower water content. The data for the patterns of the two so-called end-members of the above range of heterogeneity are given in Tables 9 and 11, and a tabular summary of the observed pattern changes is given in Table 14.

There was no indication of any unique monohydrate diffraction pattern. A number of X-ray photographs were taken of samples of beryllium sulfate whose water contents corresponded to that of the monohydrate. Table 10 gives the data obtained from one of these photographs. A comparison of only the first few lines of Table 10 with those of Tables 9 and 11 indicates clearly that the monohydrate pattern is in actual fact a composite of the 19 per cent and the 11 per cent patterns. The possibility of the existence of the monohydrate as a chemical individual is thus conclusively eliminated.

The numerous X-ray diffraction photographs, which were taken in the course of this investigation, indicate clearly that there is no abrupt transition from the dihydrate to a form of lower water content, such as was found for the tetrahydrate - dihydrate transformation. With progressive dehydration of the dihydrate, homogeneous solid solutions (of the alpha series, say), are formed, consisting of the dihydrate plus increasing amounts of the anhydrous salt. The solid system remains homogeneous until a water content of approximately 19 per cent is reached. At that point the dihydrate is saturated with anhydrous salt and further dehydration causes the appearance of the other saturated end-member (of the beta series, say,) that is, a saturated solution of dihydrate in the anhydrous salt. The system remains heterogeneous, forming more and more of the beta end-member at the expense of the alpha, until an overall water content of approximately 11 per cent is reached. The alpha end-member then disappears entirely and homogeneous solid solutions of the beta series, containing decreasing amounts of dihydrate, persist until the salt is completely dehydrated to the anhydrous form.

TABLE ~~14~~ ~~20~~ 21

TABULAR SUMMARY OF PATTERN CHANGES WITH DECREASING WATER CONTENT

Water Content of Powder Sample	Type of X-Ray Pattern
25.50 per cent	dihydrate only
19.13 " "	" "
18.00 " "	dihydrate and anhydrous
17.00 " "	" " "
16.00 " "	" " "
14.55 " "	" " "
12.76 " "	" " "
10.80 " "	anhydrous only
8.83 " "	" "
5.10 " "	" "
0.00 " "	" "

Vapor Pressure Data and Visual Evidence

The two linear portions of the log P versus 1/T plot given in Figure 6 are in excellent agreement with the Clausius - Clapeyron relation for univariant equilibria. Their point of intersection at 270 degrees must accordingly correspond to a point of invariance. Applying the basic relationship of Phase Rule to a univariant, two-component system, it is seen that the number of phases must be three to justify the experimental linearity above and below 270 degrees. Consequently the systems under investigation both above and below 270 degrees must consist of two condensed phases and a vapor phase. On the basis of X-ray evidence the 19 per cent water content of the salt samples investigated, corresponds approximately to the upper limit of the miscibility gap in the discontinuous series of solid solutions formed between the dihydrate and the anhydrous salt. The two condensed phases of the univariant system below 270 degrees must therefore be the two end-members of the alpha and beta series (α_0 and β_0, say), forming the three-phase system

$$\alpha_0 + \beta_0 + \text{vapor}.$$

At 270 degrees liquid solution makes its appearance and the system becomes invariant under an observed equilibrium pressure of 7130 millimetres of mercury or 9.38 atmospheres. With the application of more heat the alpha end-member α_0 eventually disappears and the three-phase system

$$\beta_0 + \text{liquid solution} + \text{vapor}$$

is formed. As the temperature rises above 270 degrees and the solution begins to evaporate, the beta end-member β_0 undergoes progressive dehydration forming solid solutions of the beta series with decreasing water contents. The linear portion of the log P versus 1/T plot above 270 degrees therefore corresponds to the univariant, three-phase system

$$\beta + \text{liquid solution} + \text{vapor}$$

The phase change at 270 degrees involving the disappearance of the alpha end-member α_0 and the appearance of liquid solution is borne out in a striking manner by the visual experiment in which a slightly dehydrated sample of beryllium sulfate dihydrate was carefully heated in a sealed capsule.

The excellent linearity of the two portions of the log P versus 1/T plot given in Figure 6 permits a calculation of the enthalpy changes involved in the corresponding phase reactions. The Clausius-Clapeyron relation for univariant equilibria may be readily integrated over a finite temperature and pressure change, if the enthalpy change H is assumed to be constant within the integration limits. An expression of the form

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

is obtained where

P_1 and T_1 are the initial pressure and temperature,

P_2 and T_2 are the final pressure and temperature,

ΔH is the enthalpy change for the reaction considered,

and R is the molar gas constant: 2 calories per degree per mole.

The phase reaction for the linear portion of the log P versus 1/T plot below 270 degrees is

$$\alpha_0(s) = \beta_0(s) + H_2O\ (g) \quad . . . \quad (1)$$

Applying the integrated form of the Clausius-Clapeyron relation to this portion of the plot, the enthalpy change is found to be 13630 calories, that is, $\Delta H_1 = -13630$ calories.

The phase reaction for the linear portion of the log P versus 1/T plot above 270 degrees is

$$\text{solution}\ (\ell) = \beta\ (s) + H_2O\ (g) \quad . . . \quad (2)$$

where solution (ℓ) refers to an aqueous solution saturated with respect to the beta series of solid solutions. The calculated enthalpy change for this reaction is found to be 6160 calories,

that is, $\Delta H_2 = -6160$ calories.

The phase reaction at the transition point and the enthalpy change involved in this transition reaction are obtained by applying the Hess Law of Constant Heat Summation to the above two reactions, that is, subtracting (2) from (1), to get

$$\begin{array}{ll}
\alpha_0(s) = \beta_0(s) + H_2O\ (g) & \Delta H_1 = -13630 \text{ calories} \\
\text{solution } (\ell) = \beta(s) + H_2O(g) & \Delta H_2 = -6160 \text{ calories} \\ \hline
\alpha_0(s) = \text{solution } (\ell) & \Delta H_3 = -7470 \text{ calories}
\end{array}$$

The cancellation of $\beta_0(s)$ and $\beta(s)$ in the above subtraction is justified since at the transition point $\beta_0(s)$ is identical with $\beta(s)$. The net reaction at the transition point is thus seen to be a transformation of the solid alpha end-member to a saturated solution of the beta series of solid solutions. The solid beta end-member is, of course, present before the transition point and is unchanged at 270 degrees. With a rise in temperature, however, the beta end-member immediately begins to dehydrate forming the beta series of solid solutions.

The Dihydrate - Anhydrous Salt Transition

The tetrahydrate - dihydrate transition has been shown by Sukava (22) to occur at 89.0 degrees under atmospheric pressure. The quadruple point corresponding to this transition must of necessity be somewhat different from

89.0 degrees since it represents the temperature at which the transition would occur if the system were under its own equilibrium vapor pressure. A complete investigation of the binary system, beryllium sulfate - water, in the region of the tetrahydrate - dihydrate transition temperature would result in a diagram similar to that represented by Figure 8. Four pressure - temperature curves, representing the equilibrium pressures of four univariant three-phase systems at various temperatures, intersect at the quadruple point. The four curves might possibly be labelled as follows:

1 -- tetrahydrate - dihydrate - vapor
2 -- dihydrate - solution - vapor
3 -- tetrahydrate - solution - vapor
4 -- tetrahydrate - dihydrate - solution.

As has been shown by the present study, the dihydrate and the anhydrous salt form a discontinuous series of solid solutions. The dihydrate - anhydrous salt transition is therefore not a transition between two chemical individuals but it is a transition between two series of solid solutions. The temperature of the quadruple point corresponding to this transition has been shown to be 270 degrees. In order to describe accurately the pressure-temperature relationships of the four univariant three-phase systems in the region of the dihydrate - anhydrous salt transition temperature, the four univariant curves of Figure 8 should be labelled as follows:

1 -- alpha end-member - beta end-member - vapor
2 -- beta solid solutions - solution - vapor
3 -- alpha solid solutions - solution - vapor
4 -- alpha end-member - beta end-member - solution.

The pressure - temperature coordinates of the quadruple point are 9.38 atmospheres and 270 degrees.

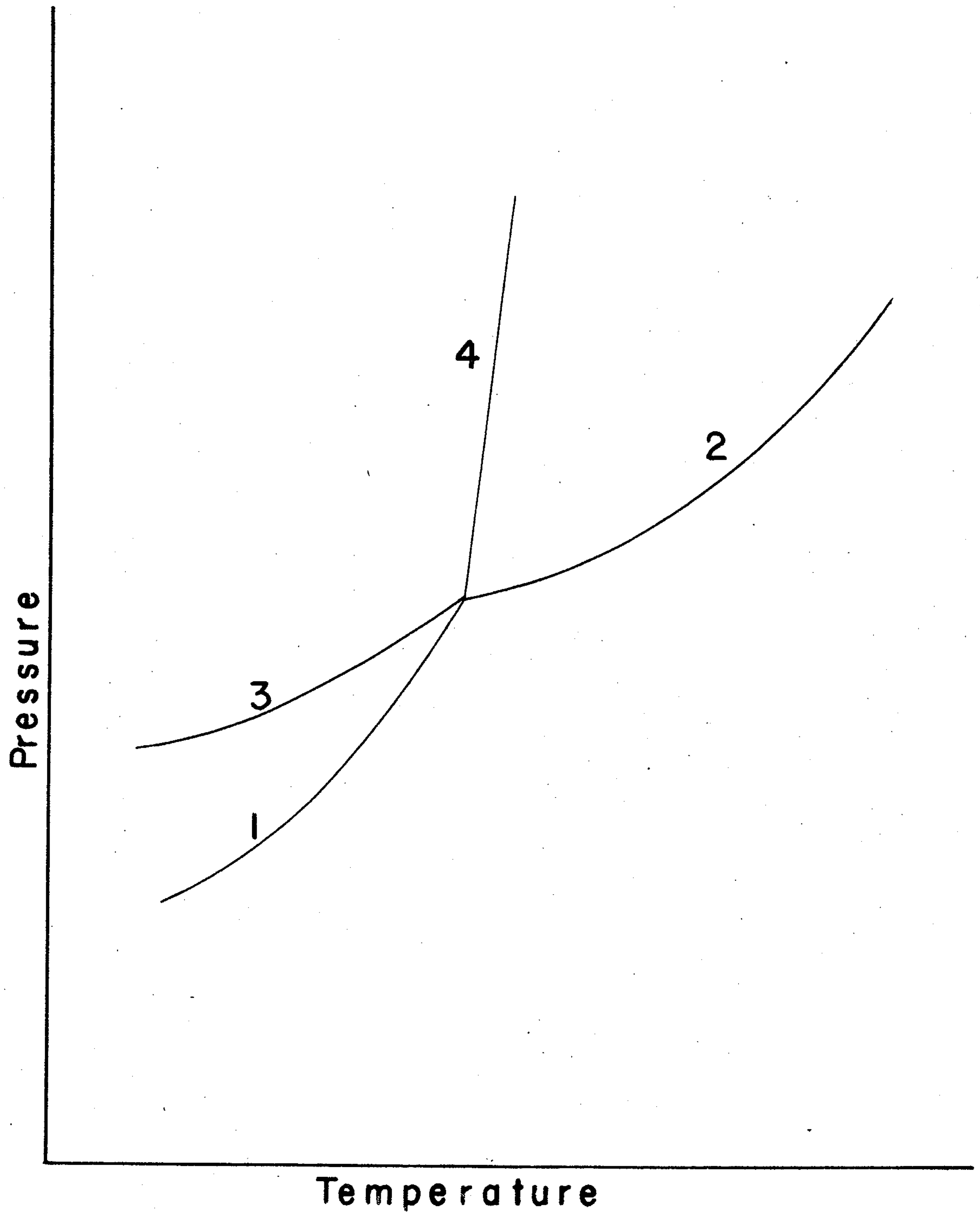

Figure 8. Pressure - Temperature Relationships.

GENERAL DISCUSSION

The results of this investigation have shown that of the hydrates of beryllium sulfate with two moles or less of water per mole of salt only the dihydrate and the anhydrous salt can be considered as chemical individuals. The conclusions regarding the non-existence of the monohydrate are in close agreement with the findings of most recent investigators. Using measurements based on Hüttig's tensi-eudiometer, Krauss and Gerlach (11) found no conclusive evidence for the existence of the monohydrate as a chemical individual. They suggested, however, that the lack of evidence regarding the existence of the monohydrate might be due to a tendency of the monohydrate to form solid solutions with both the dihydrate and the anhydrous salt. This possibility has been conclusively disproved by a careful study of the large number of X-ray diffraction photographs taken in the course of the present investigation. Hackspill and Kieffer (9) also found no conclusive evidence for the existence of the monohydrate. The progressive dehydration of the dihydrate seemed to be continuous except for a very slight departure from continuity when the composition of the material corresponded approximately to that of the monohydrate. On the basis of the present evidence the discontinuity observed by Hackspill and Kieffer probably corresponded to the miscibility gap in the discontinuous series of solid solutions formed between the dihydrate and the anhydrous salt.

SUMMARY

1. The existence of the monohydrate of beryllium sulfate has been conclusively disproved by exhaustive X-ray diffraction studies.
2. The range of composition between the dihydrate of beryllium sulfate and the anhydrous salt has been found to correspond to a discontinuous series of solid solutions.
3. The miscibility gap in this discontinuous series of solid solutions has been found to be bounded by two saturated end-members, a saturated solid solution of anhydrous salt in dihydrate and a saturated solid solution of dihydrate in anhydrous salt, with respective water contents of 19 per cent and 11 per cent.
4. The dihydrate - anhydrous salt transition occurring at 270 degrees under an equilibrium pressure of 9.38 atmospheres has been found to be a transition from the dihydrate (or alpha) end-member of the miscibility gap to the anhydrous (or beta) end-member of the miscibility gap, and hence, essentially a transition from one series of solid solutions to the other series of solid solutions.

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