

THE TERNARY SYSTEM LITHIUM  
SULPHATE - AMMONIUM  
SULPHATE - WATER

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A THESIS SUBMITTED TO  
THE COMMITTEE ON POST-GRADUATE STUDIES  
THE UNIVERSITY OF MANITOBA

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IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE  
MASTER OF SCIENCE

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By  
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MAY, 1952.



To Dr. A. N. Campbell

In sincere appreciation of his continual guidance and many helpful suggestions in this, my first venture, into the field of research.

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ACKNOWLEDGMENTS

The author is indebted to Mr. Gordon Trider and Mr. Jack Atkinson of the University of Manitoba Instrument Shop, whose accurate and skillful workmanship contributed immeasurably to the success of this research.

The author is also indebted to Pearl McCulloch for valuable assistance in the preparation of the final work.

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## INTRODUCTION

The existing literature on the ternary system lithium sulphate - ammonium sulphate - water is, to a certain extent, incomplete. Certain isotherms have been studied and only two of these would appear to have been investigated with any degree of accuracy. It was felt, therefore, that two more isotherms should be studied. The investigation of these two isotherms would indicate the accuracy of the previous researches, as well as indicating the regions of stability of any and all double salts formed in the temperature range over which the investigation was carried out.

Further perusal of the literature revealed the possibility of the existence of higher hydrates than the monohydrate of lithium sulphate. The evidence was contradictory and unsubstantial. The present research would remove the confusion that existed in connection with this point.

Whereas, the temperature and composition of the two binary eutectic points have been established with a rather large degree of certainty, the temperature and composition of the ternary eutectic points has not been established. The determination of this temperature and composition represents another phase of the present research.

The object of the present study, therefore, is the investigation of isotherms at zero and seventy degrees, a determination of the number of stable hydrates of lithium

sulphate that exist over the temperature range under investigation, a check of the binary eutectic temperatures and compositions, and finally, a determination of the ternary eutectic temperatures and compositions.

## REVIEW OF THE LITERATURE

### Introduction

The investigations that have been carried out on the system lithium sulphate - ammonium sulphate - water were carried out by Schreinemakers and Spielrein working independently at the beginning of the twentieth century. Investigations into the solubilities of the two salts and into the equilibria of the binary systems were carried out at a later date. As a result of further experimental research, a certain degree of uncertainty was cast upon the results of both of these investigations. The following resumé of the literature discusses the more important aspects of the subject in order to indicate the information that must be corrected, the information that must be verified, and finally, the new information that must be obtained.

### The Binary System, Lithium Sulphate - Water

The univariant binary equilibria, at constant pressure, for the system lithium sulphate - water have been studied by Campbell (1). Using the method of Davison, van Klooster, and Bauer (2) he checked Dreyer's (3) measurements, which had been made for concentrations up to 4.55% lithium sulphate, and continued his measurements down to the eutectic composition. This final determination was verified by the method of thermal analysis using a copper - constantan thermocouple and a sensitive galvanometer. Table I represents Campbell's results.

TABLE I  
 FREEZING POINTS OF SOLUTIONS OF  $\text{Li}_2\text{SO}_4$

Concentration Grams $\text{Li}_2\text{SO}_4$ / 100 grams $\text{H}_2\text{O}$	Freezing Point °C
4.07	- 1.735
7.79	- 3.30
11.30	- 5.11
14.33	- 7.04
17.67	- 9.67
21.95	-14.65
24.85	-18.45
27.1	-21.4
eutectic	-23.0

All the ice points fell on a smooth curve and, when this curve was extrapolated to intersect Friend's (4) solubility curve, intersection was found to occur at -23.0 degrees and 27.9% anhydrous lithium sulphate. Campbell states that there is no doubt as to the eutectic temperature, but that the eutectic composition rests upon two uncertain extrapolations. He further states that it is virtually impossible to determine the eutectic directly because of the impossibility of preparing a solution of 27.9% concentration at any other temperature than the eutectic temperature itself.

A controversial point has been brought out by Friend's (4) solubility data as given in Table II. His measurements indicate that the solubility decreases progressively as the temperature increases. Etard (5) had previously indicated that the solubility increases rapidly from the eutectic temperature, passes through a maximum below zero degrees, and subsequently decreases.

Another point to be verified in the present research is the nature of the equilibrium solid phase at low temperatures. Friend (4) has stated that the dihydrate  $\text{Li}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  exists at low temperatures. Indeed, he indicates the possible existence of higher hydrates in this region. His method of analysis and subsequent lack of agreement of check results indicated his interpretation might prove incorrect. Campbell (1), in testing this point, carried out dilatometric experiments on the system lithium sulphate - water at  $-12^\circ\text{C}$  and did not detect any discontinuity. He also investigated the equilibrium diagram lithium sulphate - lithium chloride - water at  $-12.25^\circ$  to test this matter further. His evidence points to the existence of the monohydrate as the stable phase.

The latest work on the solubility of lithium sulphate in water has been carried out by Appleby, Crawford, and Gordon (6). Their results are tabulated in Table III. On comparison with Friend's data, one notices rather good agreement over the temperature range common to both investigators.

TABLE II  
SOLUBILITY OF LITHIUM SULPHATE IN WATER

Solubility Grams anhydrous salt/100 grams solution	Temperature °C
27.32	-16.0
27.24	-13.0
27.18	-11.5
26.73	- 6.5
26.51	0.6
26.07	14.0
25.96	16.5
25.96	16.7
25.85	19.6
25.47	31.8
25.28	38.0
25.12	42.2
25.00	43.7
24.82	51.6
24.71	52.4
24.34	65.7
24.05	77.0
23.76	94.8
23.72	103.0
23.72	103.0

TABLE III  
SOLUBILITY OF LITHIUM SULPHATE IN WATER

Solubility Grams anhydrous salt/100 grams solution	Temperature °C
23.4	94.9
23.5	100.5
23.56	102.5
23.55	104.0

The Binary System, Ammonium Sulphate - Water.

The solubility curve of ammonium sulphate has been determined by Mülder (7) in 1864. De Coppet (8), Rudorff (9), and Guthrie (10) have successively studied the branch of the curve corresponding to the ice phase.

The eutectic point, according to De Coppet, is at  $-19^{\circ}$  and according to Guthrie is at  $-17^{\circ}$ . Because of this disagreement, Matignon and Meyer (11) made a new determination of this temperature, and measured the solubility of the salt at  $-16^{\circ}$ .

The results of all these experiments are given in Table IV (11).



TABLE IV  
SYSTEM, AMMONIUM SULPHATE - WATER

Temperature °C	Mülder Grams Anhydrous	De Coppet Salt/100 grams	Rüdorff	Guthrie	Matignon & Meyer water
-19.05		62.2			
-17				71.5	
-18		60.0			
-16				66.7	64.8
-11		40.0			
-10.8				40.1	
- 7.9			30		
- 6				25.0	
- 5.45		20.0			
- 5.20			20		
- 2.8			10		
- 2.6				11.1	
- 2.3			8		
- 1.10			4		
0	70.6			72.2	
10	73				
19				76.1	
20	75.4				

Cont.

Matignon and Meyer found that at  $-16^{\circ}$ , 100 grams of solution contained 39.36 grams of ammonium sulphate. This value is higher than that obtained by interpolation from the experiments of De Coppet, and gives a more regular form to the solubility curve.

Table V lists representative values of experimental results of the solubility of ammonium sulphate in water over the temperature range  $-16.3$  to  $100$  degrees as compiled in Gmelin (12). Original references are given opposite each result.

Table VI represents the data which yields the ice line for a solution of ammonium sulphate and ice.

Table VII is a compilation of various experimental determinations of the eutectic temperature and composition for ammonium sulphate and ice.

#### The Double Salt, Lithium Ammonium Sulphate

F. A. K. Schreinemakers (27) has investigated the solubility of the above double salt in water at various temperatures. His results are recorded in Table VIII. These results indicate that the solubility of the double salt is nearly independent of temperature.

Further investigation by the same worker (27) is recorded in Table IX which represents the freezing point of aqueous solutions of lithium ammonium sulphate.

By determining the point of intersection of the curves of Tables VIII and IX Schreinemakers has shown that

TABLE V  
SOLUBILITY OF AMMONIUM SULPHATE IN WATER

Temperature °C	Weight % $(\text{NH}_4)_2\text{SO}_4$	Reference
-16.32	40.1*	(13)
-16.0	40.1*	(13)
-13.0	40.4*	(13)
-11.02	40.5*	(13)
-10.5	40.6*	(14)
-10.0	40.6*	(14)
0.0	41.5	(15)
10.0	42.2	(16)
20.0	42.99	(16)
25.0	43.46	(15)
30.0	43.60	(17)
40.0	44.8	(18)
50.0	45.77	(16)
60.0	46.80	(17)
70.0	47.80	(19)
80.0	48.8	(18)
90.0	49.88	(20)
100.0	50.45	(15)

\*Concentrations were originally expressed in equivalents ammonium sulphate per 1000 moles of water.

TABLE VI  
THE ICE LINE. SYSTEM, AMMONIUM SULPHATE - WATER

Temperature °C	Weight % $(\text{NH}_4)_2\text{SO}_4$	Reference
- 1.05	3.246	(21)
- 1.99	6.516	(21)
- 3.70	12.23	(21)
- 5.28	17.10	(21)
- 7.10	22.40	(22)
- 7.94	24.26	(22)
-10.15	28.97	(22)
-10.43	29.14	(22)
-12.00	31.87	(22)
-13.99	34.47	(22)
-15.99	37.20	(22)
-17.49	38.86	(22)

TABLE VII  
EUTECTIC: AMMONIUM SULPHATE - WATER

Temperature °C	Weight % $(\text{NH}_4)_2\text{SO}_4$	Reference
-18.34	39.90	(22)
-18.50	39.75	(21)
-19.05	39.40	(23)
-19.05	39.86	(24)
-19.05	38.40	(25)
-19.5	38.48	(26)

TABLE VIII  
SOLUBILITY OF LITHIUM AMMONIUM SULPHATE IN WATER

Temperature °C	Weight % Salt
-10.0	35.25
0.0	35.36
10.0	35.53
20.0	35.80
30.0	35.87
40.0	35.89
50.0	36.00
60.0	36.05
70.0	36.18

TABLE IX  
FREEZING POINT OF AQUEOUS SOLUTIONS OF  $\text{LiNH}_4\text{SO}_4$

Temperature °C	Weight % Salt
- 0.58	1.372
- 0.97	2.496
- 1.35	3.560
- 2.05	5.435
- 3.20	9.101
- 4.40	12.017
- 5.12	13.524
- 6.60	15.83
- 7.63	19.52
- 8.56	21.025
- 9.58	22.79
-10.52	24.23
-12.44	26.79
-13.11	27.54
-14.96	29.75
-15.22	29.84
-16.23	31.14
-18.23	32.84
-19.23	33.98
-20.15	35.02



the cryohydric solution will contain 35.15% double salt and that the cryohydric temperature is  $-20.7^{\circ}$ . He secured a cryohydric temperature of  $-20.7^{\circ}\text{C}$  by direct determination.

The Ternary System, Lithium Sulphate -

Ammonium Sulphate - Water

Two workers have carried out investigations upon the equilibrium existing in the above ternary system. Schreinemakers and his co-workers carried out isothermal investigations of the equilibrium existing among the three components, lithium sulphate, ammonium sulphate and water at 30 and 50 degrees while Mlle. Cecile Spielrein (28) conducted a rather doubtful and sketchy investigation into the equilibria existing at temperatures of 20, 57, and 97 degrees. Qualitative agreement has been obtained by the two researchers.

Schreinemakers, assisted by Mr. D. H. Cocheret, (27) found that when  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  was added to a saturated  $(\text{NH}_4)_2\text{SO}_4$  solution successive separations of the following salts occur: ammonium sulphate, ammonium sulphate and double salt, double salt, anhydrous lithium sulphate and double salt, anhydrous lithium sulphate, and the monohydrate of lithium sulphate. Their results are compiled in Table X. The graphical representation of these results is given in Figure 1, the system being treated as a condensed system, and the phase diagram being represented by the familiar Roozeboom equilateral triangle method.

TABLE X

THE TERNARY SYSTEM,  $\text{Li}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ 

Temperature = 30°C

Number	Solution		Wet Residue		Nature Of Solid Phase
	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	
1	0.0	25.1	-	-	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
2	4.89	24.07	1.58	67.23	"
3	6.66	23.67	2.67	62.78	"
4	8.44	23.09	3.68	62.12	"
5	9.42	23.03	4.80	58.43	"
6	10.67	22.49	5.85	58.85	"
7	10.93	22.51	6.97	55.21	"
8	12.46	21.88	19.38	48.53	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} +$ $\text{LiNH}_4\text{SO}_4$
9	12.28	21.71	26.26	37.96	"
10	12.54	21.99	24.09	45.66	"
11	14.30	20.35	19.40	23.30	$\text{LiNH}_4\text{SO}_4$
12	14.27	19.94	38.32	34.94	"
13	19.29	16.58	40.50	33.65	"
14	25.27	12.68	43.56	34.17	"
15	28.75	10.78	41.68	28.56	"
16	32.15	9.31	42.82	27.23	"
17	35.56	7.84	45.28	28.65	"
18	36.37	7.69	47.34	30.54	"

Cont.



TABLE X CONTINUED

THE TERNARY SYSTEM,  $\text{Li}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ 

Temperature = 30°C

Number	Solution		Wet Residue		Nature Of Solid Phase
	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	
19	39.55	6.59	71.94	7.23	$\text{LiNH}_4\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$
20	39.38	6.42	48.38	26.99	"
21	39.55	6.37	77.71	2.65	$(\text{NH}_4)_2\text{SO}_4$
22	39.56	6.26	70.66	2.91	"
23	40.95	2.93	71.39	1.63	"
24	44.1	0.0	-	-	"

Temperature = 50°C

1	0.0	24.3	-	-	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
2	7.56	22.86	5.13	63.80	"
3	8.58	23.09	7.58	57.87	"
4	9.63	22.79	6.58	60.35	"
5	11.45	21.75	8.96	61.50	"
6	13.97	21.23	18.9	30.8	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{LiNH}_4\text{SO}_4$
7	13.90	21.20	22.7	29.2	"
8	19.65	16.35	-	-	$\text{LiNH}_4\text{SO}_4$
9	43.05	5.86	51.9	9.4	$\text{LiNH}_4\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$
10	45.7	0.0	-	-	$(\text{NH}_4)_2\text{SO}_4$

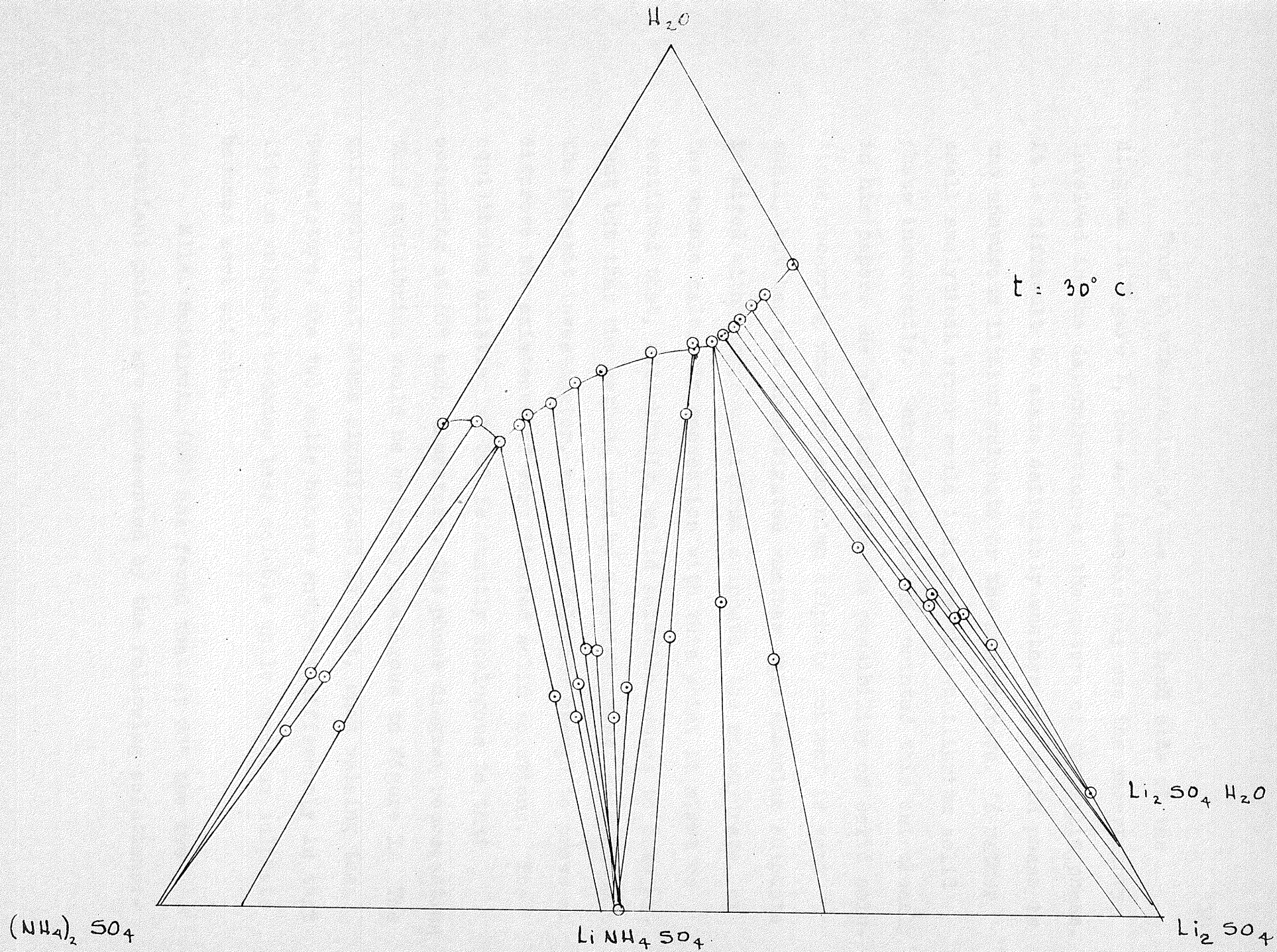


Figure 1. Isotherm for  $30^\circ$

- Point 1. 33 grams  $\text{Li}_2\text{SO}_4$  per 100 grams of solution.  
 14.2 grams  $(\text{NH}_4)_2\text{SO}_4$  per 100 grams of solution.
- Point 2. 11 grams  $\text{Li}_2\text{SO}_4$  per 100 grams of solution.  
 50 grams  $(\text{NH}_4)_2\text{SO}_4$  per 100 grams of solution.

This worker also found that a double salt existed of the form  $\text{Li}_2\text{SO}_4(\text{NH}_4)_2\text{SO}_4$ .

In a later paper Spielrein (29) reported data for three isotherms. The results expressed in Table XI are as they were obtained from the literature.

TABLE XI  
 THE COMPOSITIONS OF THE INVARIANT SOLUTIONS

	t = 20°C		t = 57°C		t = 97°C	
	I	II	I	II	I	II
$\text{Li}_2\text{SO}_4$	38.8	12.6	38.6	18.2	38.0	10.6
$(\text{NH}_4)_2\text{SO}_4$	17.2	72.9	11.3	82.2	19.2	93.1

The solid phases at point I are  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{LiNH}_4\text{SO}_4$  and at point II are  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{LiNH}_4\text{SO}_4$ . It is assumed that the above compositions are in grams of anhydrous salt per 100 grams of water although the point was not established in this paper. These three isotherms were superposed by Spielrein on a horizontal projection, and she subsequently states that their solubility remains sensibly constant with temperature, and therefore, the heat of solution of the double salt is nil at all these temperatures.

The Ternary System, Ammonium Sulphate -

Sodium Sulphate - Water

This system is composed of components rather closely analogous to those under investigation in the present research. One would, therefore, possibly expect to obtain similar behavior in this system to that under investigation. Matignon and Meyer (30) and Dawson (31), working independently, investigated the system ammonium sulphate - sodium sulphate - water. Freeth (32) also investigated the system, but at a somewhat later date.

The components of this system combine to form two compounds namely, Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and the double salt  $\text{Na}_2\text{SO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ . The properties of these two compounds largely determine the characteristic features of this system.

Upon studying the equilibrium relations between  $-20^\circ$  and  $100^\circ$  and illustrating the results on diagrams, these investigators found that the double salt was formed from Glauber's salt and ammonium sulphate at a lower temperature limit of  $-16^\circ$ . This double salt decomposed with the formation of the anhydrous simple salts at  $59.3^\circ\text{C}$ . Between  $-16^\circ$  and  $20^\circ$  the double salt decomposed, upon treatment with water, with the formation of Glauber's salt, while between  $41.5$  and  $59.3^\circ$  it decomposed with the formation of the anhydrous sodium sulphate. The transition temperature for Glauber's salt into anhydrous sodium sulphate was depressed to  $26.5^\circ$  by the addition of ammonium



sulphate. The solid phases in equilibrium with the solution at this temperature were Glauber's salt, anhydrous sodium sulphate, and the double salt.

## EXPERIMENTAL PROCEDURE

### Introduction

The experimental aspect of this work can be classified as follows:

Firstly, the checking of the two binary eutectic temperatures and compositions was carried out by the method of thermal analysis.

Secondly, the checking of Friend's (4) contention that higher hydrates than the monohydrate of lithium sulphate existed at low temperatures was carried out through the use of a dilatometer as well as by a study of the zero degrees isotherm.

The third point of interest that was investigated was a determination of the region of stability of the double salt and of the monohydrate of lithium sulphate. This was carried out through the study of the isotherms at 0 and 72 degrees, using the familiar method of "wet residues" as introduced by Schreinemakers.

The determination of the temperature and composition of the two ternary eutectic solutions was the final investigation. This was carried out, once again, by the method of thermal analysis.

Each of these classifications will be dealt with separately in the subsequent discussion.

Preparation and Purification of Starting Materials

All the reagents used were standard reagent grade materials. The lithium sulphate, Analar grade, was a British Drug House product with the following maximum limits of impurities.

Chloride .....	0.002%
Iron .....	0.0005%
Heavy Metals .....	0.001%
Nitrate .....	0.002%

The ammonium sulphate was C.P. Baker's Analyzed, guaranteed to meet A.C.S. standards. It was free of pyridine and assayed 99.1%. Before using it was recrystallized from water and dried.

The double sulphate of lithium and ammonium was prepared by adding these two sulphates, in equi-molecular proportions, to water until the hot solution was just saturated. It was concentrated by evaporation, allowed to cool to room temperature, when the crystals were filtered under suction. The resultant double salt was then recrystallized twice and subsequently dried for some weeks in a sulphuric acid dessicator.

Nichols mercury metal and Analar grade chloroform, which were used in the calibration of the thermocouple, were both redistilled before use. Carbon dioxide, which was used in the solid form for the same purpose, was obtained from a city supply house and was used, for obvious reasons, with no further purification.

### Method of Analysis

A relatively quick and accurate method was desired by which the composition of aqueous solutions of lithium and ammonium sulphate could be determined. It was decided to determine total sulphate content and total ammonia content while the lithium content was determined by difference.

A great deal of research has been carried out concerning the estimation of sulphate. The standard method is, of course, to precipitate the sulphate as barium sulphate. Many investigators, however, stress the inaccuracy inherent in this method due to the great tendency to occlude other ions. E. T. Allen and J. Johnston (33), J. Johnston and L. H. Adams (34) have carried out a number of illuminating investigations upon the phenomena of occlusion in precipitates of barium sulphate. Friend (4) in his determination of the solubility of lithium sulphate, abandons the barium sulphate method completely in favor of slow evaporation of the sample and subsequent volatilization. This method was tested by the present investigator and, while realizing that fundamentally this is a sound method, it was abandoned due to the great susceptibility to splattering with a resulting low estimation of sulphate content. A volumetric method that was formulated by Wiley (35) and that has been used successively by Sanders and Dobbins (36) was investigated, but ammonium acetate, which was formed in the course of the analysis, was found to interfere with the external indicator, and therefore, this method was abandoned.



It was decided to test the method of precipitation as barium sulphate, to measure the actual degree of occlusion with the particular ions under investigation. Using the method as outlined by Kolthoff and Sandell (37), an accuracy of better than 0.5% was consistently obtained. Minimum co-precipitation was ensured by observing the following precautions. The acidified sulphate solution and the barium chloride solution were heated almost to their boiling point before they were rapidly added to each other. Since the non-co-precipitation of cations was desired, the sulphate solution was rapidly added to the chloride solution, and the resultant solution was allowed to stand for a minimum period of twenty four hours before filtration through Whatman's No. 42 filter paper. The first drops of filtrate were tested with silver nitrate solution to ensure complete precipitation of the sulphate ion while avoiding a large excess of barium chloride. The barium sulphate crystals were washed with hot water until the wash water showed a negative chloride ion test. The precipitate was then ignited very slowly in platinum crucibles, care being exercised that the filter paper did not catch fire at any time as this would reduce the barium sulphate. Having observed all these precautions, it was felt that this method of analysis was the most satisfactory for this particular investigation. As previously stated, the maximum error ever obtained on test samples was less than 0.5%, and, in the

majority of cases, the accuracy far exceeded this. These tests were carried out in a manner simulating actual working conditions.

The determination of the ammonia content was carried out by the steam distillation of a basic solution of the sample. The distillate was absorbed in a boric acid solution of approximately 4% strength following the method as outlined in Pierce and Haenisch (38) and originally proposed by Winkler (39). The amount of ammonium borate formed was determined by titration with standard hydrochloric acid, using brom-cresol green as the indicator. The acid was standardized with sodium carbonate (40). A blank was run in both cases. Once again, this method was carefully tested before being adopted, the maximum error obtained being 0.5%.

All glassware used in the analytical work was calibrated before use. Pipets and volumetric flasks, which were used to obtain aliquot portions, were calibrated relative to each other.

#### Calibration of the Thermocouple

To measure differences of temperature, an iron-constantan thermocouple was used in conjunction with a sensitive potentiometer. Through the courtesy of the National Research Council Library, a photostat of the method adopted by Roeser and Dahl (41) for their calibration of an iron-constantan thermocouple was obtained and studied. The method adopted

by the present investigator was essentially that of Roeser and Dahl with the exception that many of the precautions adopted by them were not used. The reasons were two-fold, firstly, an accuracy of  $\pm 1$  degree was all that was desired, and secondly, for the small temperature range over which the present investigation was carried out, the calibration curve was essentially a straight line.

The following fixed temperature points were used to calibrate the thermocouple:

1. the freezing point of mercury.....-38.9 degrees (42)
2. the freezing point of chloroform.....-63.5 degrees (42)
3. the sublimation point of carbon  
dioxide.....-78.5 degrees (42)
4. the melting point of ice..... 0.0 degrees (42)
5. the cold junction used by another  
investigator.....+29.8 degrees (43)

For points 1, 2, and 3, the hot junction was the melting ice, while for point 5 the melting ice served as the cold junction.

The determination of the voltage produced when one junction of the thermocouple was maintained in freezing mercury while the other junction was maintained in melting ice was carried out in the following manner. A beaker containing the liquid mercury was immersed in a large flask. This flask was placed in a large dewar flask, and solid carbon dioxide, which acted as the refrigerant, was placed between the walls

of the dewar and the flask. An insulated top containing two holes was placed over the assemblage, and the thermocouple and motor driven stirrer were inserted into the holes. The hot junction was tested for constancy by continual observation of the readings of a standard thermometer. The difference in temperature between the hot and cold junctions of the thermocouple was recorded by taking two minute readings on the potentiometer until a constant voltage was obtained, indicating that the mercury had reached its freezing point.

A similar procedure was carried out when chloroform replaced the mercury with the exception that the air jacket was omitted. When the solid carbon dioxide was used, the cold junction of the thermocouple was placed directly in the dewar flask containing the carbon dioxide. Point number 5 was obtained by a reversal of the junctions. The hot junction was placed in the water which was maintained at a constant temperature of  $29.8^{\circ}$  (43), while the cold junction was immersed in the melting ice. Finally, the two junctions were placed in the melting ice and the voltage produced was noted. Table XII represents the results that were obtained. The voltages shown are mean values. Figure 2 represents the completed calibration curve. The voltages for the fixed temperature points were checked every six months with no appreciable change being observed.



CALIBRATION CURVE - IRON-CONSTANTAN THERMOCOUPLE

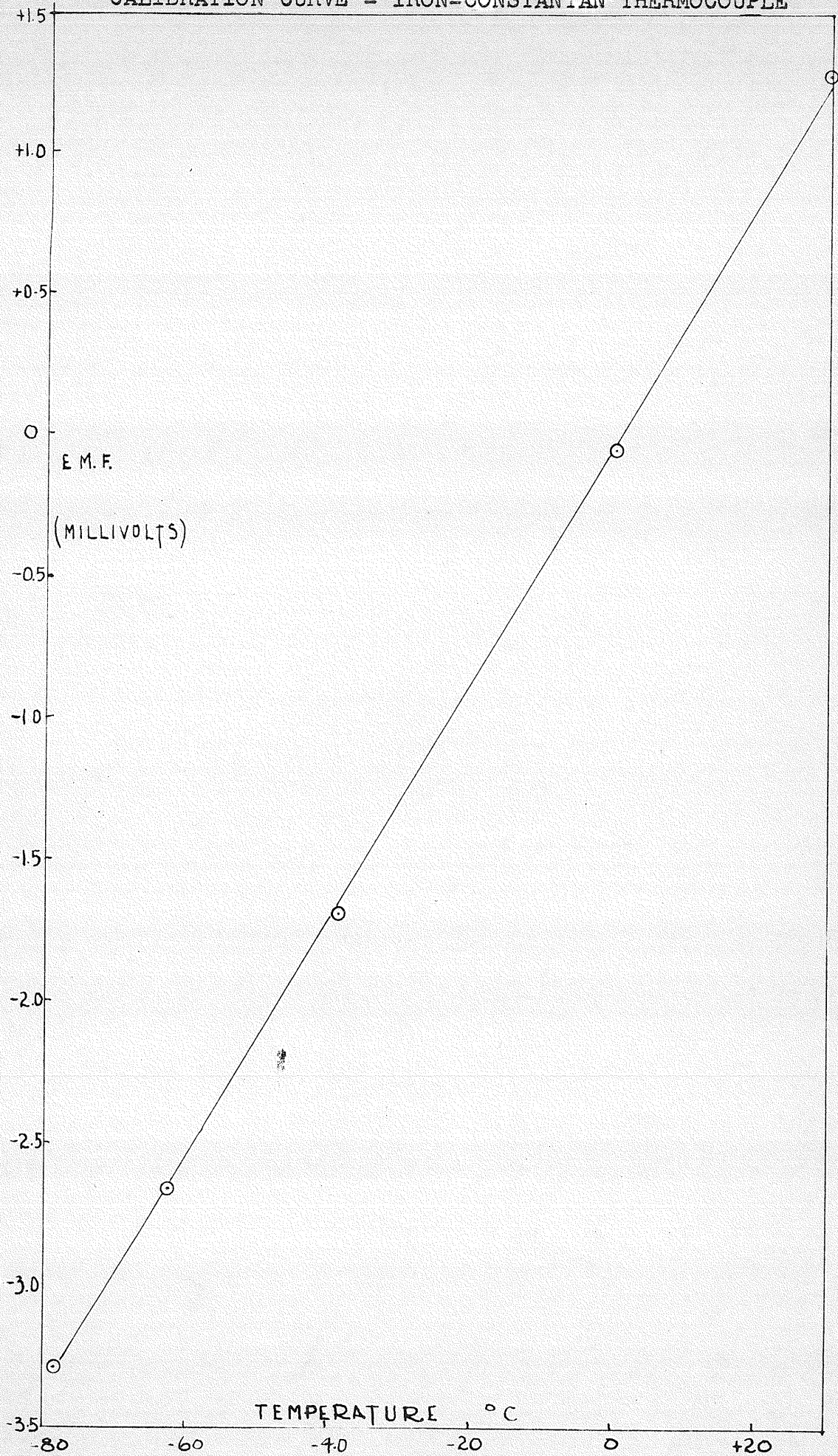


Figure 2.

TABLE XII  
IRON-CONSTANTAN THERMOCOUPLE CALIBRATION CURVE RESULTS

Hot Junction Temperature °C	Cold Junction Temperature °C	E.M.F. millivolts
29.8	0.0	1.27
0.0	0.0	-0.05
0.0	-38.9	-1.69
0.0	-63.5	-2.66
0.0	-78.5	-3.29

The Binary Eutectic: Ammonium Sulphate - Ice

Table VII gives a compilation of various experimental determinations of the eutectic temperature and composition for ammonium sulphate and ice. These determinations were checked in the present investigation. The apparatus used was identical with that used in the calibration of the thermocouple with the exception that two air jackets were used to lessen the rate of cooling. Differences of temperature between the solution of ammonium sulphate and the melting ice were measured by the calibrated thermocouple. The ammonium sulphate solution was agitated at all times by a motor driven stirrer to maintain equilibrium. When the observed voltage attained a constant value, a sample of the equilibrium solution was removed by means of a fritted glass filter stick of fine porosity. The

filter stick had been carefully dried and chilled before inserting it into the eutectic mixture. Gentle suction was applied to the filter stick by means of a water suction pump. The withdrawn sample was quickly transferred to a weighed container and the weight of the sample was ascertained. It was transferred to a 250 millilitre volumetric flask and distilled water was added to bring the solution up to the mark. A 50 millilitre pipet, which had been calibrated relative to the flask, was used to obtain an aliquot portion. The percentage ammonium sulphate content was determined by analyzing for ammonia content, and this value was checked by analyzing for total sulphate. These analyses were carried out in the manner indicated in "Methods of Analysis". The following results were obtained from two different samples.

TABLE XIII  
EUTECTIC TEMPERATURE AND COMPOSITION,  
AMMONIUM SULPHATE - WATER

Constant E.M.F. Reading mvs.	Eutectic Temp. °C	$\%(\text{NH}_4)_2\text{SO}_4$ via ammonia anal.	$\%(\text{NH}_4)_2\text{SO}_4$ via sulphate anal.
1. -0.79	-19.0	38.9	39.5
2. -0.83	-19.9	39.1	39.4

The mean of these results, yields a eutectic temperature of  $-19.5^\circ\text{C}$  and a eutectic composition of 39.2% ammonium sulphate.



The Binary Eutectic, Lithium Sulphate - Water

According to Campbell (1), the eutectic temperature for this system was  $-23.0$  degrees while the eutectic composition was 27.9% anhydrous lithium sulphate. The eutectic composition was obtained through the extrapolation of Friend's (4) solubility curve and Campbell's ice line. The present investigator attempted to check this temperature and composition in a manner analogous to that used in checking the eutectic temperature and composition for the ammonium sulphate - water system. 27.9 grams of anhydrous lithium sulphate and 72.1 grams of distilled water were thoroughly mixed. A similar procedure was carried out with this solution as with the ammonium sulphate solution. A constant E.M.F. value, however, was never obtained. It was thought that possibly the rate of cooling was too rapid and masked the break in the cooling curve. The rate of cooling was accordingly lessened, but once again no definite E.M.F. value, corresponding to the value at the eutectic temperature, was attained. Excess of lithium sulphate was added to the initial solution and a better system of stirring was devised, but no value was obtained which could be interpreted as being the eutectic temperature. Samples were withdrawn at a temperature of  $-23.0$  degrees which were found, upon analysis, to contain 26.1% lithium sulphate. This indicates rough agreement with Campbell's results. The present investigator is unable to



state why a check of the eutectic temperature and composition was impossible. The above rough agreement and a later result, however, are a strong indication that Campbell's are correct.

#### Lithium Sulphate

In an attempt to prove or disprove Friend's (4) contention that higher hydrates than the monohydrate of lithium sulphate existed at low temperatures, and to corroborate Campbell's (1) research concerning this controversial point, use was made of the fact that, if such a transition did occur, it would undoubtedly be accompanied by a change in volume. A dilatometer was constructed to measure this volumetric change. This dilatometer was constructed in the usual manner, a long capillary tube being attached to a bulb containing the lithium sulphate monohydrate in contact with a small amount of distilled water. Toluene served as the indicator fluid. The height of this indicator fluid was measured with a cathetometer.

The bulb of the dilatometer, containing the moistened lithium sulphate monohydrate, was immersed in an ice-sodium chloride eutectic mixture and the lithium sulphate was cooled slowly. Temperature was recorded with a calibrated toluene thermometer. Table XIV is a compilation of the temperatures of the moistened salt and corresponding heights of the indicator fluid.

TABLE XIV

DILATOMETER READINGS FOR  $\text{Li}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ 

Height of Capillary centimetres	Temperature °C
61.73	- 0.5
57.93	- 1.7
54.57	- 2.6
52.93	- 3.0
49.23	- 4.0
45.38	- 5.0
42.30	- 6.0
38.53	- 7.0
34.81	- 8.0
31.44	- 9.0
28.28	-10.0
24.92	-11.0
21.30	-12.0
18.16	-13.0
14.09	-14.1
9.40	-15.1
5.55	-16.3
3.23	-17.0
1.19	-17.6
0.28	-17.9

Figure 3 represents the plot of these results. The straight line indicates that a transition from the monohydrate to a higher hydrate does not occur.

It was thought that the transition might take place if more time was allowed for it to occur. Accordingly the bulb of the dilatometer was immersed in a large mixture of ice and sodium chloride, and the containing dewar flask was very well insulated. Cathetometer readings were noted until a constant reading was obtained. This reading was, of course, the volume of the moistened lithium sulphate at the eutectic temperature of ice and sodium chloride. The temperature was noted. The entire assemblage was then allowed to stand for twenty four hours, at which time, the temperature and height of the indicator fluid were again recorded. Table XV gives the values that were obtained.

TABLE XV  
DILATOMETER READINGS FOR  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

	Height of Capillary centimetres	Temperature °C
July 3	43.11	-21.0
July 4	44.00	-20.0

Once again, the evidence points to the non-occurrence of a transition.

VOLUMETRIC CHANGE OF  $\text{Li}_2\text{SO}_4$

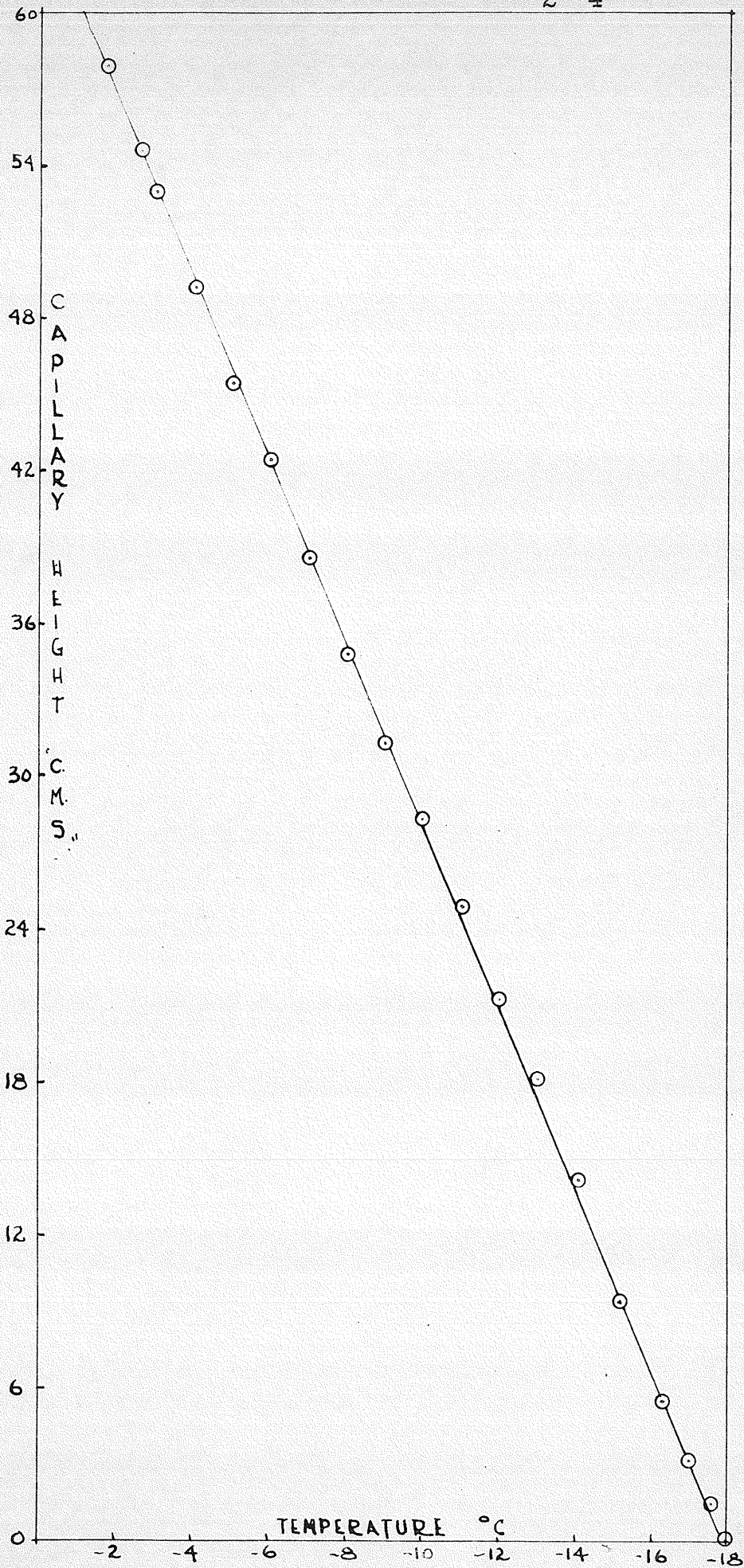


Figure 3.



An attempt was made to see if one could detect, upon cooling, any visible change in the crystal structure and water content of a moistened sample of lithium sulphate monohydrate. Accordingly, samples were sealed in glass containers and cooled in ice - sodium chloride mixtures. These samples were examined after periods of immersion ranging from twenty four to seventy two hours. No visible change in either the crystal structure or the water content could be detected.

The Zero Degree Isotherm,  $\text{Li}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$

The isothermal solubility curve of the sulphates of lithium and ammonia in water was determined by saturating the solutions by stirring in contact with solid phase in tubes suspended in a kerosene thermostat. The stirring time was never less than twenty four hours. The composition of the equilibrium solid phase was determined through the employment of Schreinemaker's method of 'wet residues'.

The thermostat was regulated by means of a mercury thermo-regulator with a precision of  $\pm .05$  degrees. A Beckmann thermometer, which had been previously set in melting ice, was used to indicate any possible temperature variation. The kerosene thermostat consisted of a large glass cylinder filled with kerosene. This cylinder was placed in an outer tank which was also filled with kerosene. Cooling was supplied by a cooling coil placed in the outer bath. This cooling coil was attached to a refrigerating unit, the refrigerant being

methyl chloride. Heating was supplied by a 30 watt light bulb which was partially immersed in the inner bath. The bulb, the thermo-regulator, and the refrigerator, were controlled through use of a standard American Instrument Company double tube, double throw, eight point control. This control utilized super sensitive mercury relays.

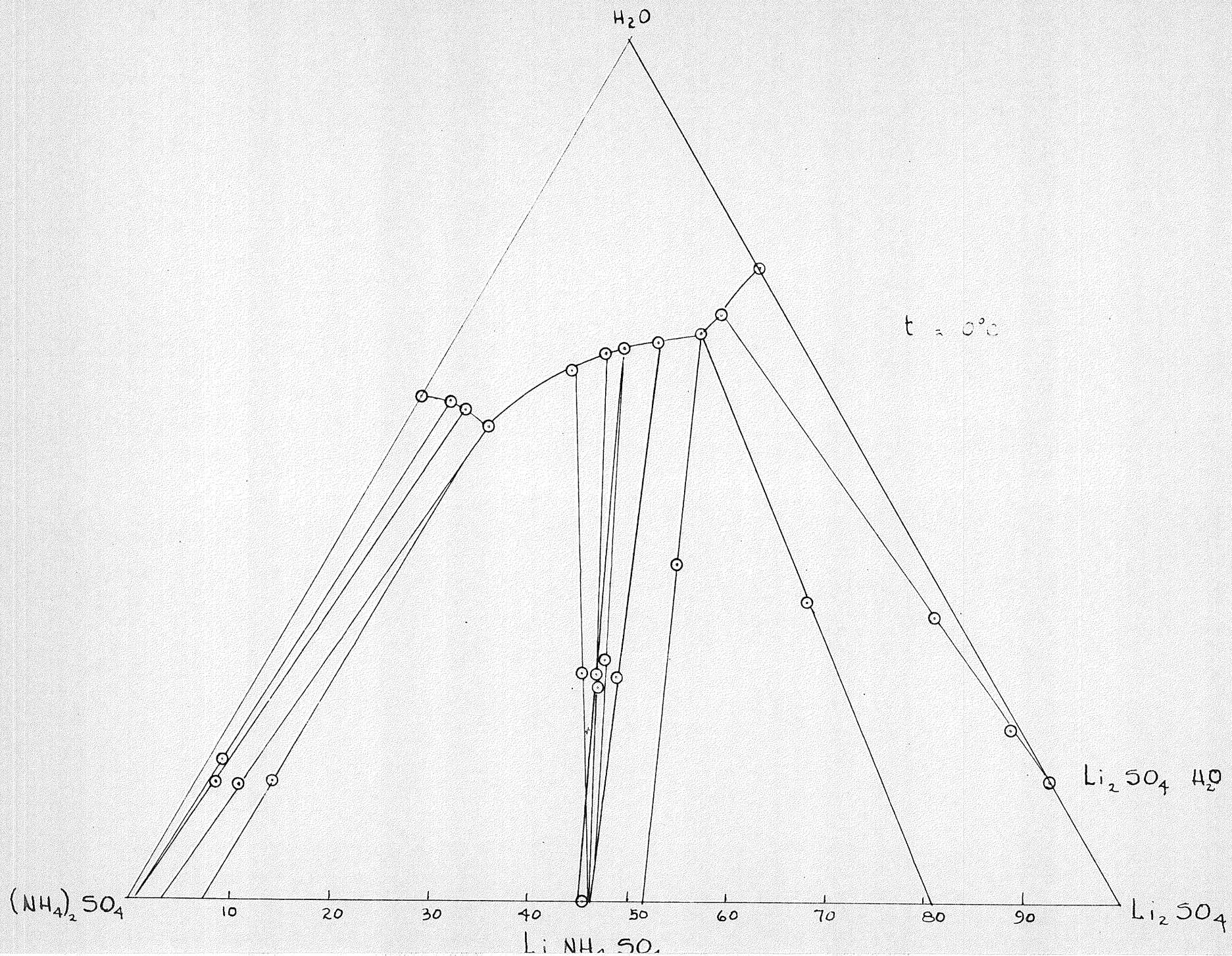
Samples of the solutions, after sufficient stirring in contact with the solid phase to ensure that equilibrium had been established, were drawn off by suction into a weighed receiver. For this purpose, fine fritted-glass filter sticks were used. This equilibrium liquid phase was drawn away from the solid as completely as possible without the risk of appreciable dehydration due to the passage of air through the solid mass. A sample of the moist residue was removed and weighed in a glass stoppered bottle. Approximately two gram samples of both liquid and solid phases were taken. Both the liquid and moist solid samples were dissolved in water to yield 250 millilitres of solution. Separate aliquot portions of these solutions were analyzed for total sulphate content and ammonia content in the manner previously discussed. From the weight of barium sulphate obtained and the number of millilitres of standard acid required to titrate the ammonium borate, the lithium sulphate and ammonium sulphate content were calculated. The results expressed in terms of weight percent are represented in Table XVI. The corresponding isothermal phase diagram is



given in Figure 4, the end of each tie line in each case indicating the composition of the pure equilibrium solid phase.

TABLE XVI  
ISOTHERM FOR 0.10° ( $\pm 0.05^\circ$ )

	Solution		Wet Residue		Nature of the Solid Phase
	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	
1.	0.0	26.5	-	-	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
2.	6.4	25.4	2.3	64.4	"
3.	6.2	25.2	1.0	78.8	"
4.	9.7	24.4	14.1	51.0	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{LiNH}_4\text{SO}_4$
5.	9.8	24.3	25.3	35.7	"
6.	14.1	20.9	38.0	36.1	$\text{LiNH}_4\text{SO}_4$
7.	18.4	17.4	38.1	33.9	"
8.	18.5	17.3	40.0	34.0	"
9.	20.5	16.0	40.6	34.4	"
10.	24.8	13.8	41.6	32.2	"
11.	36.1	8.4	78.6	7.6	$\text{LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$
12.	36.2	8.1	82.1	4.1	"
13.	37.7	5.3	84.5	2.1	$(\text{NH}_4)_2\text{SO}_4$
14.	38.7	3.5	82.4	1.4	"
15.	41.8	0.0	-	-	"



### The 71.8 Degree Isotherm

The isothermal solubility curve was determined by saturating the solutions by stirring in contact with solid phase in tubes suspended in an aqueous bath. The procedure followed, was similar to that adopted in the investigation of the zero degree isotherm with two minor changes. The outer bath and the cooling coil were removed while a heating coil was substituted for the light bulb. The thermostat was heavily insulated and a coating of oil was placed upon the aqueous layer to minimize evaporation.

The mercury thermo-regulator was again employed to regulate the thermostat, but the precision that could be attained in this case, when checked with a Beckmann thermometer, was not better than  $\pm 0.1$  degrees. The solutions in the suspended tubes were agitated, in contact with the respective solid phases, for a minimum period of twelve hours before samples were withdrawn, under suction, by means of the fritted glass filter sticks. The procedure followed from this point on was exactly similar to that employed in the determination of the zero degree isotherm. The results, expressed in weight percent, are compiled in Table XVII, while the corresponding phase diagram is given in Figure 5.



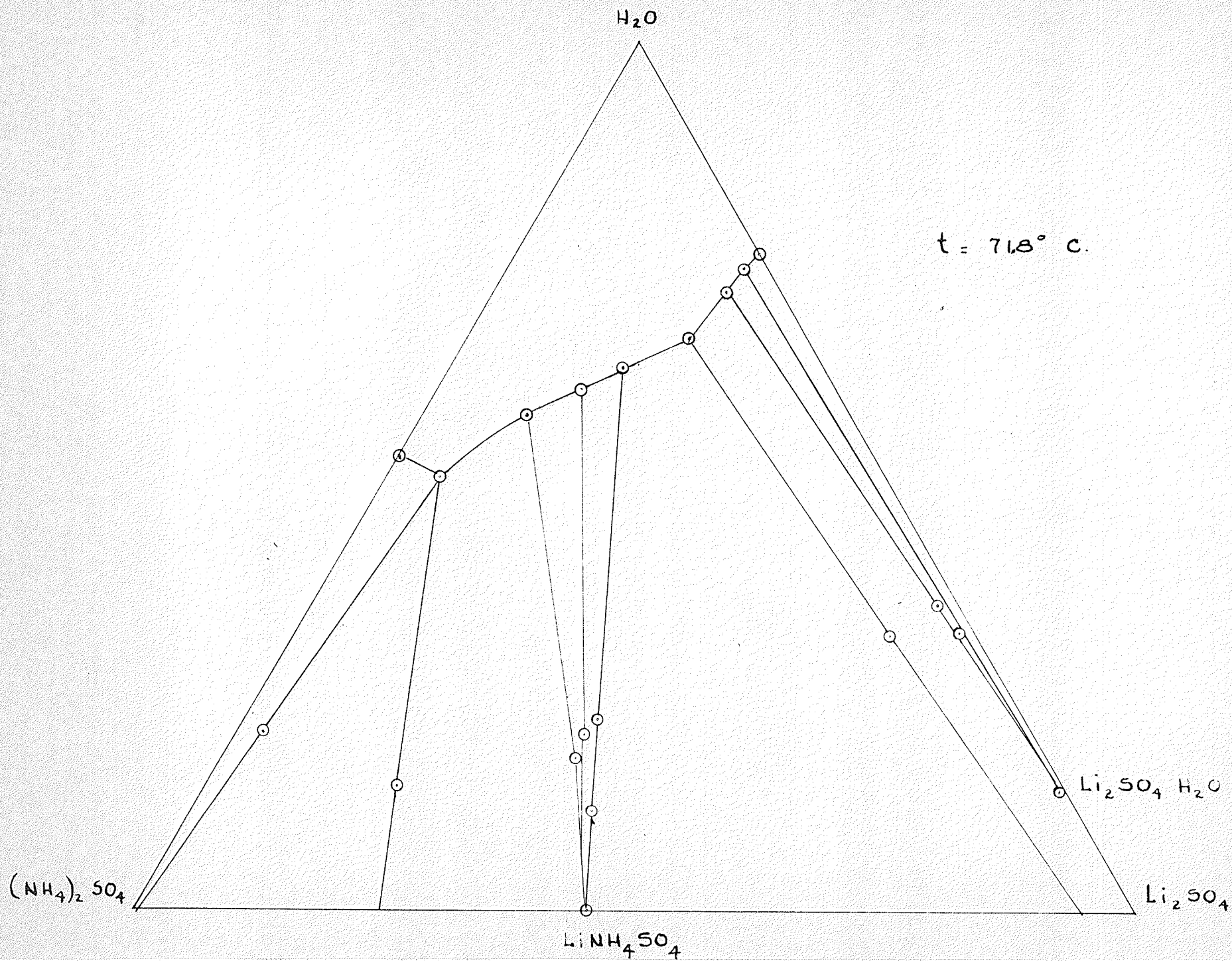
TABLE XVII  
ISOTHERM FOR 71.8° ( $\pm 0.10^\circ$ )

	Solution		Wet Residue		Nature of the Solid Phase
	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$	
1.	0.0	24.2	-	-	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
2.	2.4	23.5	1.2	66.3	"
3.	5.6	23.1	2.1	62.5	"
4.	12.1	21.8	8.5	59.6	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{LiNH}_4\text{SO}_4$
5.	20.1	17.1	48.2	40.0	$\text{LiNH}_4\text{SO}_4$
6.	20.4	17.2	42.4	35.2	"
7.	25.6	14.2	44.9	35.0	"
8.	32.1	10.5	46.8	35.4	"
9.	44.9	5.2	66.2	19.3	$\text{LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$
10.	45.1	5.5	76.8	2.7	$(\text{NH}_4)_2\text{SO}_4$
11.	47.9	0.0	-	-	"

### The Ternary Eutectics

It is well known, that in a ternary system consisting of two salts and an aqueous liquid phase, there will be two ternary eutectic points when the two salts combine to form a compound (44). These ternary eutectic points represent an invariant system: three solid phases can exist in equilibrium with a ternary solution, only when the latter has one fixed composition and when the temperature has a definite value. The three solid phases in equilibrium with the ternary solution in the system under examination were  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{LiNH}_4\text{SO}_4$ , ice, and for the other eutectic point  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{LiNH}_4\text{SO}_4$ , ice. The determination of these two eutectic temperatures, the lowest temperatures attainable with the particular three solid phases, was desired. The two eutectic compositions were also to be determined, as well as an outline of the shape of the three eutectic curves.

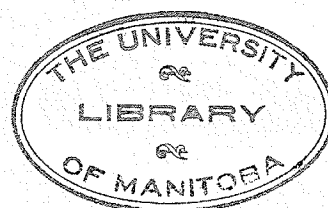
Thermal analysis was employed to supply this information. The procedure followed was similar to that employed in the determination of the temperatures and compositions of the two binary eutectic points. Two air jackets were used in all cases to lessen the rate of cooling. Differences of temperature were again recorded through the use of the calibrated iron-constantan thermocouple, melting ice serving as the hot junction. The salt mixture was agitated at all times by a motor driven stirrer.





The initial composition of the solution was determined by weighing each salt and the amount of water necessary to dissolve this salt mixture. Knowing the initial composition, one was able to determine the shape of the eutectic curves. The composition of the final equilibrium solution was determined by withdrawing, with gentle suction, samples of this solution and analyzing as before. The fritted glass filter sticks were used for this purpose. Theoretically, if one commenced with any initial solution containing the three components one should, by continued cooling, obtain a final solution corresponding to one or other of the eutectic compositions. It was found, in actual practice, that one had to have initial solutions having a composition rather close to the ternary eutectic solution composition to obtain a final solution corresponding to the eutectic composition. This point is, of course, readily understandable. The three intermediate points were obtained by cooling an aqueous solution of the previously prepared double salt. Table XVIII compiles the values obtained, while Figure 6 indicates the general shape of the three eutectic curves. These curves represent univariant systems; at a given temperature two solid phases can exist in equilibrium with a ternary solution, only when the latter has a definite composition.

From an examination of the table and the accompanying



figure, one notes the following eutectic temperatures and compositions.

-27°C with 33%  $(\text{NH}_4)_2\text{SO}_4$  and 10%  $\text{Li}_2\text{SO}_4$

-30°C with 10%  $(\text{NH}_4)_2\text{SO}_4$  and 27%  $\text{Li}_2\text{SO}_4$

The solid phases that separated out at -27°C are ammonium sulphate, double salt, ice while at -30° they are the monohydrate of lithium sulphate, double salt and ice.

TABLE XVIII  
THE TERNARY EUTECTIC CURVES

Temperature	% $(\text{NH}_4)_2\text{SO}_4$	% $\text{Li}_2\text{SO}_4$
-19.5	39.2	0.0
-22.5	37.0	5.1
-27.0	33.2	10.5*
-26.0	23.3	16.2
-26.0	20.4	18.8
-23.0	18.3	20.8
-30.0	10.6	27.4*
-24.0	6.0	26.8
-23.0	0.0	27.9

\*These determinations represent the two eutectic temperatures and compositions. They are mean values.

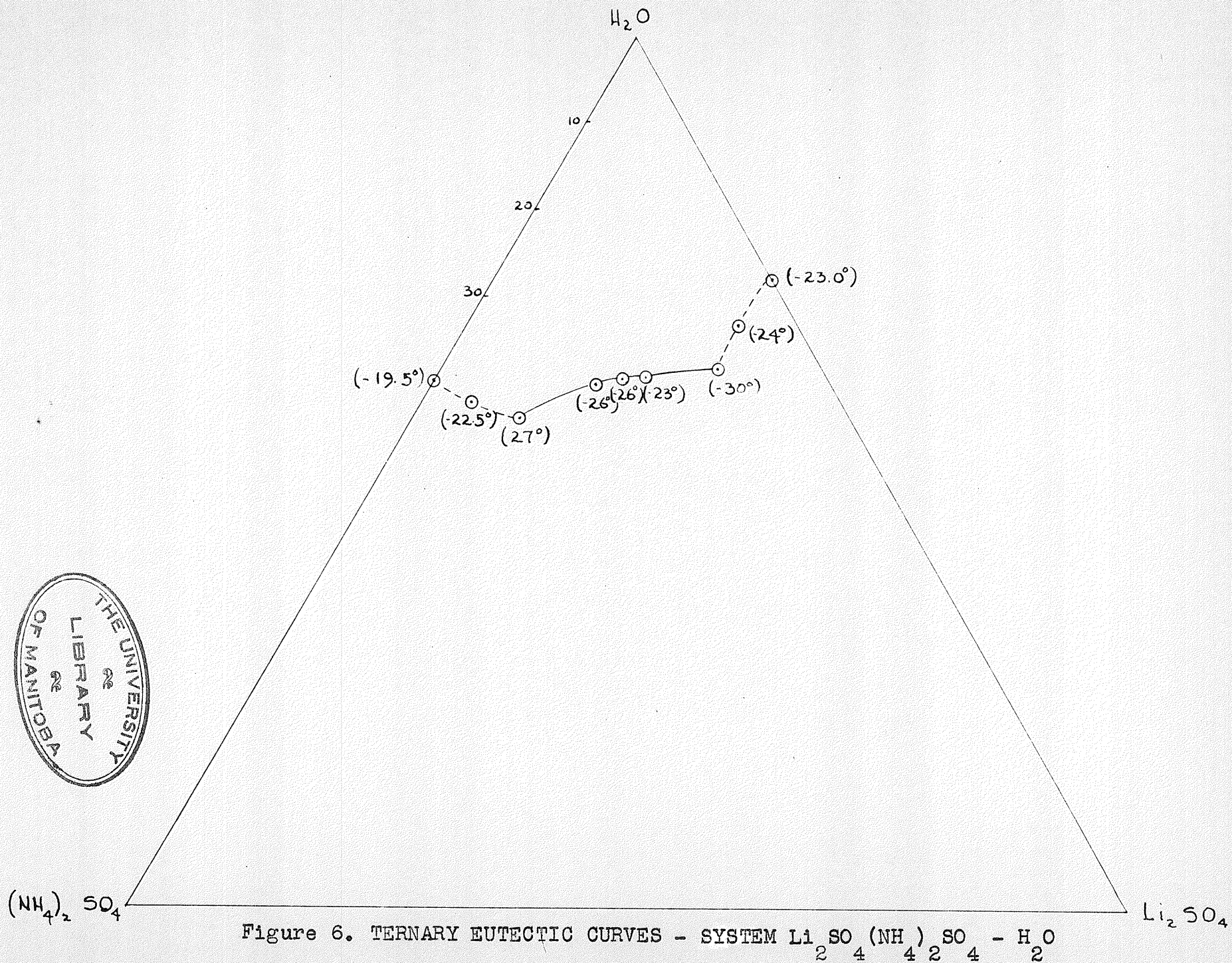


Figure 6. TERNARY EUTECTIC CURVES - SYSTEM  $\text{Li}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$

## DISCUSSION OF RESULTS

### The Binary Eutectic, Ammonium Sulphate - Water

The value for the eutectic temperature and the eutectic composition obtained by the present investigator, agrees well, within the limits of experimental error, with those listed in the literature as indicated in Table VII. The eutectic temperature obtained was  $-19.5^{\circ}\text{C}$ , while the eutectic composition was 39.2% ammonium sulphate.

### The Binary Eutectic, Lithium Sulphate - Water

A definite check for the eutectic temperature and composition for this system as listed by Campbell (1) was not obtained. One of the cooling curves exhibited a change in slope at a temperature of  $-23^{\circ}$ . A sample withdrawn at this temperature analyzed 26.1% lithium sulphate. This value is in rough agreement with Campbell's value of 27.9%. The above cooling curve did not, however, exhibit a definite halt and thus this figure is, at the best, uncertain. Later evidence, as depicted in Table XVIII and Figure 6, tends to substantiate Campbell's results. Upon examination of the right hand eutectic curve in Figure 6, one notes the smooth curve obtained when Campbell's values are included. The depression of  $1^{\circ}$  of the binary eutectic temperature upon the addition of 6% ammonium sulphate seems feasible. In the light of these two pieces of evidence, the present investigator concurs with Campbell's values of  $-23.0^{\circ}$  for the eutectic temperature and 27.9% anhydrous



lithium sulphate for the eutectic composition.

### Lithium Sulphate

The dilatometric experiments carried out in the present research, all indicate that the highest hydrate of lithium sulphate that exists at low temperatures is the monohydrate. This is in disagreement with Friend's (4) contention and substantiates Campbell's (1) research. Visible evidence also indicated the non-existence of a transition from the mono to a higher hydrate. More evidence in support of the view that a transition does not occur, was obtained from the zero and higher degree isotherms. The equilibrium solid phase was at all times the monohydrate. This last piece of evidence, of course, has merely disproved the possibility of a transition occurring at temperatures above zero degrees, but when one includes all the evidence obtained in the present investigation together with Campbell's (1) results, the possibility of a transition to a higher hydrate is virtually excluded.

The Zero Degree Isotherm,  $\text{Li}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$

The results obtained for this isotherm indicate very good agreement with Schreinemakers' results for the 30° isotherm and with Spielrein's limited results for the 20° isotherm. The double salt is still quite stable with no indication of a downwards transition. All attempts to establish the existence of other unknown double salts by varying the initial amounts



of the simple salts used for the equilibrium measurements, failed. An examination of the equilibrium solid phases shows no evidence of any higher hydrate of lithium sulphate than the monohydrate. The phase diagram, in addition, indicates that the equilibrium solid phase is the lithium sulphate monohydrate rather than the anhydrous salt. As previously pointed out, however, a very small analytical error could conceivably result in an incorrect interpretation of the equilibrium solid phase. If solid solution does occur, the present research proves that the extent to which it occurs is very limited.

#### The 71.8 Degree Isotherm

The results for this isotherm again correspond closely to those for the 50° isotherm of Schreinemakers. The agreement is not so close with Mlle. Spielrein's results for the 57 and 97 degree isotherms, but, as previously mentioned, the accuracy of this investigator's results is somewhat doubtful. An examination of Figure 5 points to the stability of the double salt at this temperature and the non existence of an upper transition. Once again the existence of other unknown double salts is excluded. It would also indicate, as in the zero degree isotherm, that if solid solution does occur, the extent of this solid solution is very limited.

#### The Ternary Eutectics

The two eutectic temperatures and compositions have

been determined from thermal phenomena obtained from the system of two phases when a third phase appears. The values as listed in Table XVIII are mean values.

The three eutectic curves were obtained through the use of cooling curve measurements. Two of the curves are dotted because difficulty was encountered in analyzing the cooling curves.

#### Further Discussion

Figure 7 represents a composite diagram that includes the coordinates of all the isotherms studied for the system lithium sulphate - ammonium sulphate - water. When this diagram is contrasted with the similar diagram for the system sodium sulphate - ammonium sulphate - water, as shown by Dawson (31), one notes the sharp contrast in the limits of stability of the respective double salts. The double salt  $\text{LiNH}_4\text{SO}_4$  is stable over the entire temperature range studied. From the examination of Figure 6, it is extremely difficult to state whether a downward or upward transition is favored. The double salt  $\text{Na}_2\text{SO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  however, is formed from Glauber's salt and ammonium sulphate at  $-16^\circ$  and decomposes with the formation of the anhydrous simple salts at  $59.3^\circ$ .

The lithium sulphate - ammonium sulphate - water system differs from the sodium sulphate - ammonium sulphate - water system in that the components of this latter system combine to form two compounds, namely Glauber's salt  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and the double salt  $\text{Na}_2\text{SO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ .

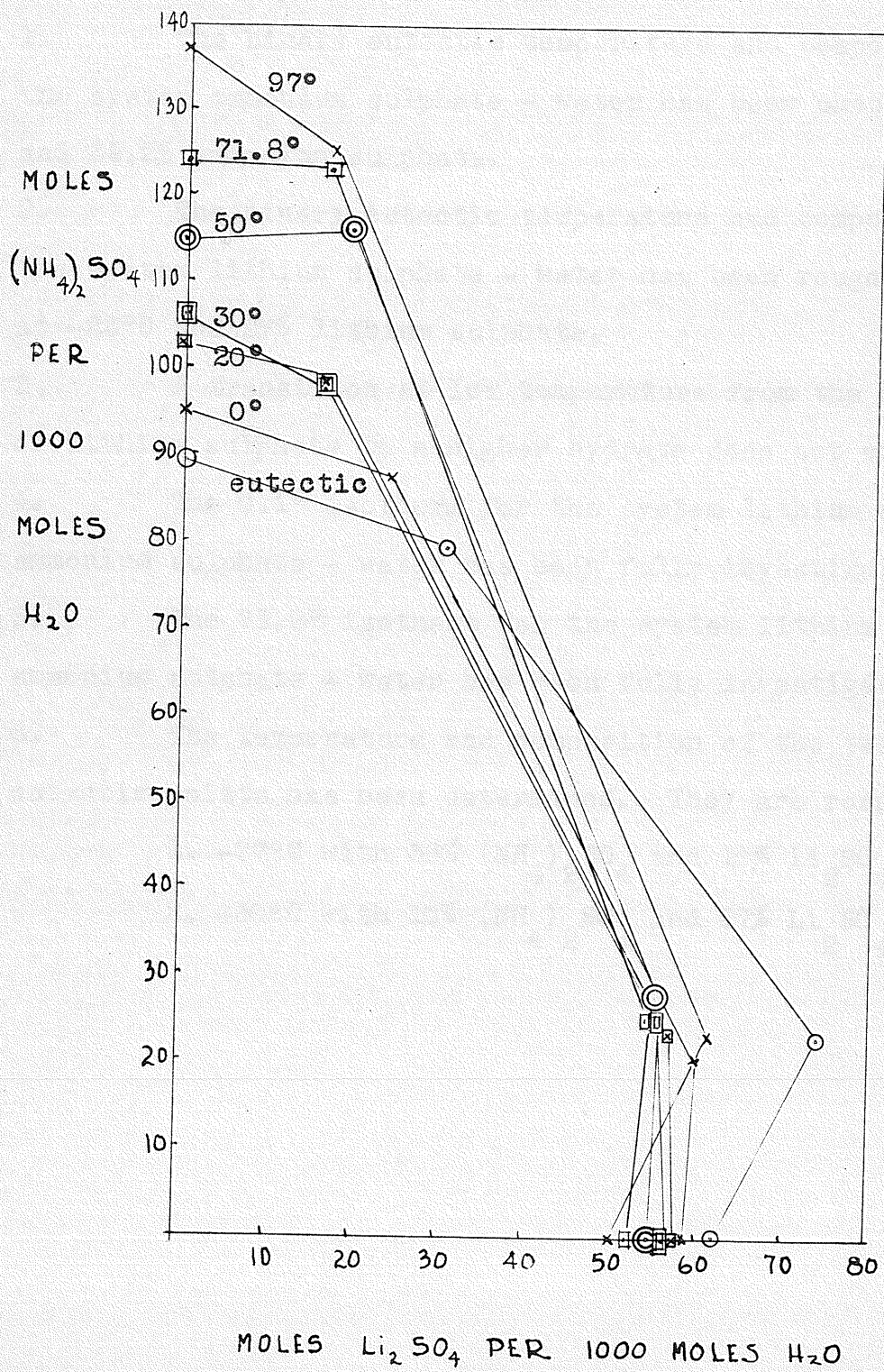


Figure 7.

SUMMARY

1. The binary eutectic temperature and composition for the system ammonium sulphate - water has been checked at  $-19.5^{\circ}\text{C}$  and 39.2% ammonium sulphate.
2. The binary eutectic temperature and composition for the system lithium sulphate - water has been roughly checked at  $-23^{\circ}\text{C}$  and 27% lithium sulphate.
3. A transition at low temperature from the monohydrate of lithium sulphate to a higher hydrate does not exist.
4. The  $0.1^{\circ}$  isotherm for the system lithium sulphate - ammonium sulphate - water has been fully investigated.
5. The  $71.8^{\circ}$  isotherm for the system lithium sulphate - ammonium sulphate - water has been fully investigated.
6. The temperature and composition of the two ternary eutectic points has been determined. They are respectively:
  1.  $-27^{\circ}\text{C}$  with 33%  $(\text{NH}_4)_2\text{SO}_4$  and 10%  $\text{Li}_2\text{SO}_4$
  2.  $-30^{\circ}\text{C}$  with 10%  $(\text{NH}_4)_2\text{SO}_4$  and 27%  $\text{Li}_2\text{SO}_4$



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