

THE SYSTEM: LITHIUM, SODIUM, POTASSIUM,  
SULPHATE, CHLORIDE, WATER AT 25°C.

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by  
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To My Father

## ABSTRACT

The system lithium, potassium, chloride, sulphate, water at 25°C. has been investigated by chemical analysis of the solution and of the wet residues. There are large areas where potassium sulphate and potassium lithium sulphate ( $\text{KLiSO}_4$ ) are, separately, in equilibrium with solutions. Two incongruent invariant points have been found; the solution at the first has a composition of 0.917 mole fractions of chloride, 0.437 mole fractions of lithium, and 19.4 moles of water per total mole of salt, with potassium chloride, potassium sulphate, and the double salt ( $\text{KLiSO}_4$ ) as the solid phases in the wet residues. The second invariant liquid phase has been found to contain 0.967 mole fractions of chloride, 0.870 mole fractions of lithium, and 13.8 moles of water per mole of salt. The solid phases were potassium chloride, double salt, and lithium sulphate monohydrate. At the congruent invariant point the composition of the liquid phase was found to be 1.00 mole fractions of chloride, 0.960 mole fractions of lithium, 9.6 moles of water per mole of salts, and the solid phases; lithium sulphate monohydrate, lithium chloride monohydrate, and potassium chloride.

The system lithium, sodium, chloride, sulphate, water at 25°C. has been investigated by chemical analysis of the

liquid phase and of the wet residues. An incongruent invariant point where sodium chloride, solid solution of sodium and lithium sulphates, and lithium sulphate monohydrate are in equilibrium with solution has been found. The solution composition at this point was 0.873 mole fractions of chloride, 0.668 mole fractions of lithium, and 15.1 moles of water per total mole of salts. The solid phases present at the congruent invariant point are lithium chloride monohydrate, lithium sulphate monohydrate, and sodium chloride. Analysis of the liquid phases showed the solution to consist practically entirely of lithium chloride in water.

The possibility of the existence of an area of the double salt  $\text{NaLiSO}_4$  is discussed, as is the possibility of using X-rays and the petrographic microscope to examine the solid phases.

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## INTRODUCTION

When one pair of salts forms a second pair of salts by double decomposition, then, since one pair is formed from the other, they are known as reciprocal salt pairs.



In studies of reciprocal salt pairs in which the valences of the ions are not all the same it is customary to make all the ions of the same valence by combining enough of the ions of lower valence into radicals so that they have the same valence as that of the ion or radical which, singly, has the highest valence. In the lithium chloride-potassium sulphate reciprocal salt pair, the lithium, potassium, and chloride ions are written as  $\text{Li}_2^{++}$ ,  $\text{K}_2^{++}$ , and  $\text{Cl}_2^-$ . This usage is for stoichiometric reasons, and does not suggest that the ions exist as dimers.

The two reciprocal salt pairs; lithium, sodium, chloride, sulphate, and water, and lithium, potassium, chloride, sulphate, and water, both at  $25^\circ\text{C}$ ., which form the subject of this thesis, are part of the five component system of lithium, potassium, sodium, chlorides, sulphates, and water at  $25^\circ\text{C}$ . which is being studied in this department. The five component system is the analogue of the classical sea salt system, which was first studied by van't Hoff<sup>1</sup>.

In the sea salt system the lithium ion is replaced by magnesium ion.

Phase rule studies, of the type described in this thesis, are of great practical importance, for they can be used to determine the best procedure to be followed in winning salts from solutions, as well as the best procedure for production of one salt pair from the other pair. This is best carried out by a multiple temperature cycling process in which conditions are controlled so that first one of the desired salts is deposited in a pure condition, and then, by altering the conditions, the other is deposited. The process can be made to run indefinitely, by adding the unstable pair at the proper place in the cycle, and removing the salts of the stable pair when they precipitate.

An example of this process is the production of conversion saltpetre. Figure 1 from Findley, Campbell, and Smith<sup>2, 3, 4</sup>, shows the equilibrium diagram of the reciprocal salt pair



in water at 25°C. Each corner of the diagram represents a pure salt; the light lines are the isohydrores, or lines of equal water content. There will be three solid phases in equilibrium with solution at an invariant point. P<sub>1</sub> is the invariant point where potassium nitrate, sodium nitrate, and sodium chloride are in equilibrium with solution, and P<sub>2</sub> is

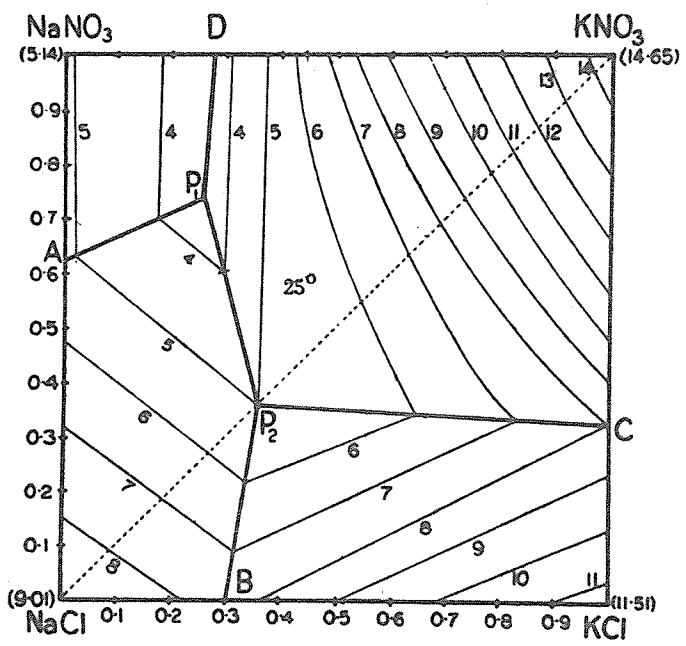


FIGURE 1

CONVERSION SALTPETRE

the invariant point where potassium nitrate, sodium chloride, and potassium chloride are in equilibrium with solution. By consideration of this reciprocal salt pair at 5°C. and 100°C. Reinders<sup>3</sup> has devised a cycling process which gives 100% conversion of potassium chloride into potassium nitrate.

From isothermal studies of reciprocal salt pairs the isothermal crystallization path of any solution can be determined. As an example, take the reciprocal salt pair shown in Figure 2. The point P<sub>1</sub> where B, C, and D are in equilibrium is called a

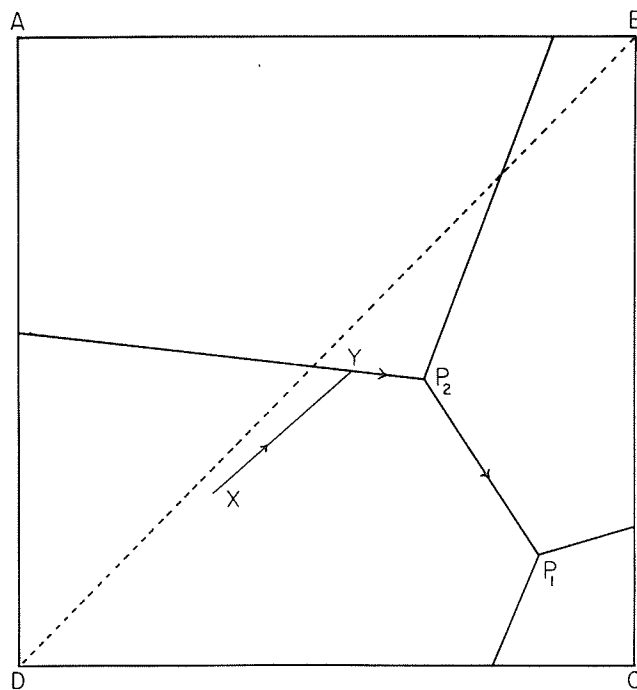


FIGURE 2

## CONGRUENT AND INCONGRUENT INVARIANT POINTS

congruent invariant point, because it lies within the composition triangle BCD and the composition of the liquid phase can be expressed in positive quantities of the solid phases present at  $P_1$ . The point,  $P_2$  where A, B, and D are the solid phases is an incongruent invariant point because it does not lie within the composition triangle BAD, and the composition of the solution at  $P_2$  cannot be expressed in positive quantities of the salts B, A, and D which are present at  $P_2$ .



If a solution of composition X in Figure 2 is subjected to isothermal evaporation the first salt to precipitate will be D, and the composition of the liquid will move directly away from D to point Y where solid A will be thrown down with D. From Y the liquid composition will move to  $P_2$  where B will begin to precipitate, and a reaction between solid A and solution will take place. After all of A has reacted the solid phases will be B and D, and the composition of the solution will move to  $P_1$ , where solid C will be precipitated. The solution will dry up at  $P_1$  because the composition of point X is expressible in positive quantities of the salts present at  $P_1$ , but not in those present at  $P_2$ .

## THEORETICAL CONSIDERATIONS

### 1. THE PHASE RULE

In 1879 J. Willard Gibbs<sup>5</sup> derived the phase rule from thermodynamics, and, sometime later Roozeboom<sup>6</sup> demonstrated its practical importance. The Phase Rule is:

$$F = C - P + 2$$

where F is the variance, C is the number of components, and P is the number of phases present. The phase rule is applicable only when equilibrium amongst all the phases present has been attained.

Since, in graphical representation, every four component system is made up of four three component systems, the method of graphical representation of three and four component systems will be shown.

### 2. THREE COMPONENT SYSTEMS

At constant temperature and pressure ternary systems can be represented on an equilateral triangle by Roozeboom's method. The apices of the triangle represent the pure components, A, B, and C. The length of each side is made equal to one hundred, and the components are plotted in weight percent or mole percent of each component. Thus point D in Figure 3 represents a mixture of a% A, b% B, and c% C.

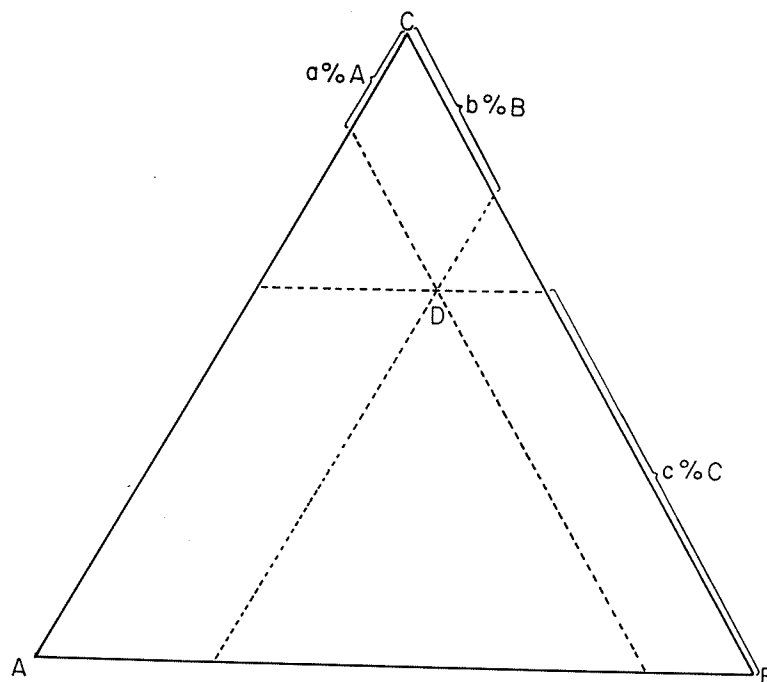


FIGURE 3

## A POINT ON A TRIANGULAR GRAPH

Two salts with a common ion,  $M_1X_1$ ,  $M_2X_1$ , and water constitute a ternary system. In a system of this type there may be hydrate, solid solution, or double salt formation. Figure 4 shows this system as it would appear if  $M_1X_1$  were hydrated, and if a double salt were formed. The double salt is  $M_1M_2(X_1)_2$ , and it is in equilibrium with solutions whose compositions lie along curve BC. At the temperature of this isotherm  $M_1X_1$  exists as the hydrate  $M_1X_1 \cdot nH_2O$ . Point B gives the composition of the solution at the

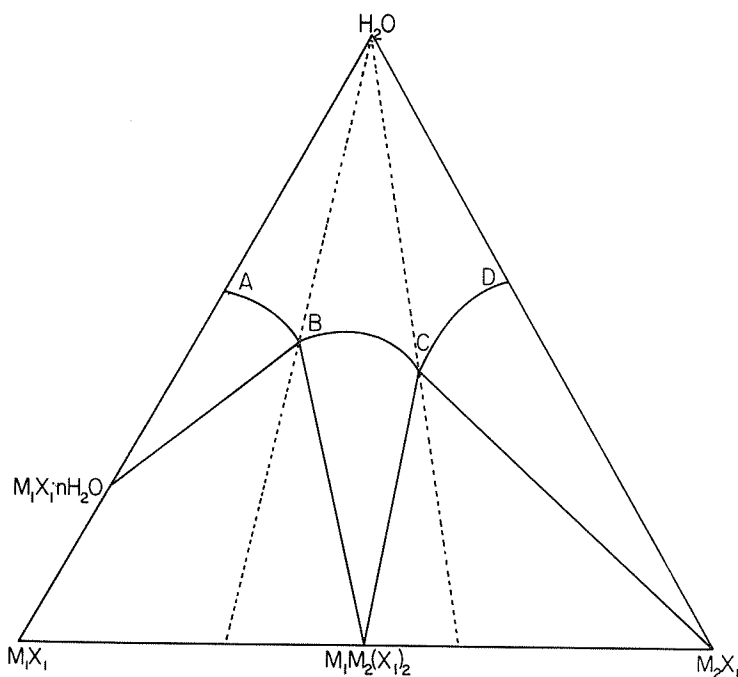


FIGURE 4

TYPICAL THREE COMPONENT SYSTEM SHOWING  
HYDRATE AND COMPOUND

invariant point where  $M_1X_1 \cdot nH_2O$  and  $M_1M_2(X_1)_2$  are the solid phases, and point C gives the solution in equilibrium with  $M_2X_1$  and  $M_1M_2(X_1)_2$ . This diagram is projected onto a line by constructing lines from the water apex, through points B and C, onto the base of the triangle, in order to obtain the ratio of  $M_1X_1$  to  $M_2X_1$  at points B and C. The salts are then represented by the mole fraction of one of the cations in the total cation mixture. If there are  $n_1$  moles

of  $M_1$  and  $n_2$  moles of  $M_2$  at a point, then the mole fraction of  $M_1$  is:

$$\frac{n_1}{n_1 + n_2} = \text{mole fraction of } M_1$$

The water content of points B and C is represented by  $m_B$  and  $m_C$  where  $m$  is the number of moles of water per total mole of salts. Figure 5 shows this system represented on a line.

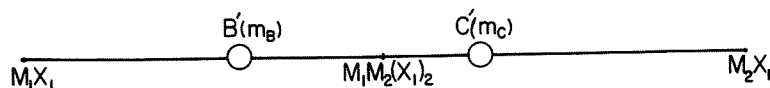


FIGURE 5

FIGURE 4 PROJECTED ONTO A LINE

If a solid solution with the compound is formed, then the diagram will be as given in Figure 6. B and C are the invariant points where the solid phases are  $M_1X_1 \cdot nH_2O$  and solid solution, at B and solid solution and  $M_1X_2$  at C. The "tie lines", obtained from joining the solution composition

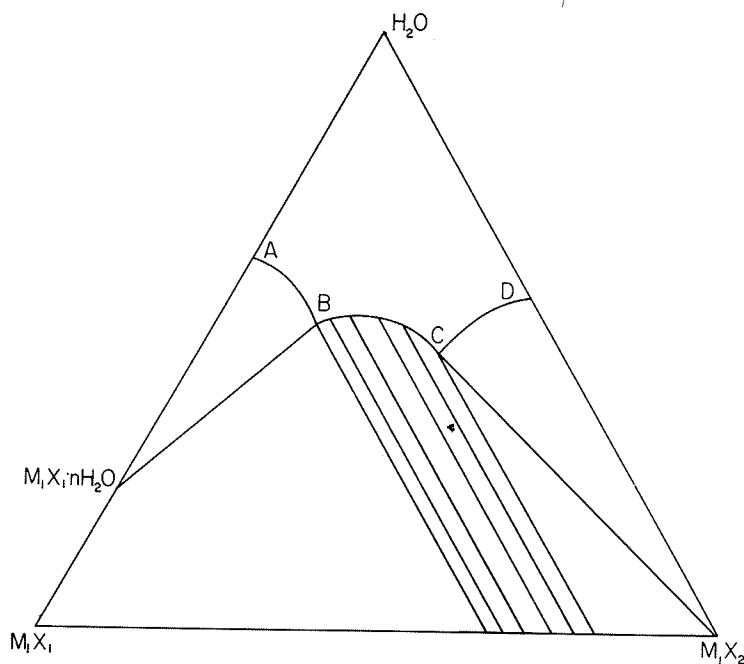


FIGURE 6

TYPICAL THREE COMPONENT SYSTEM SHOWING  
HYDRATE AND SOLID SOLUTION

along BC to that of the wet residues are parallel, indicating the formation of solid solution. If a compound with no solid solution were formed the tie lines would meet at the point representing the composition of the compound, but variability in the composition of the solid phase, in a case like this, is a criterion of solid solution formation.

### 3. RECIPROCAL SALT PAIRS

At constant temperature and pressure reciprocal salt pairs in water are represented on a square by the method of Janecke<sup>7</sup> and Le Chatelier<sup>8</sup>. The pure salts are represented by the corners of the square, and the salts are arranged so that those at adjacent corners have a common ion. The mole fraction of the anions is plotted as the abscissa, and the mole fraction of the cations as the ordinate. A point within the square is plotted by calculating the mole fraction of the

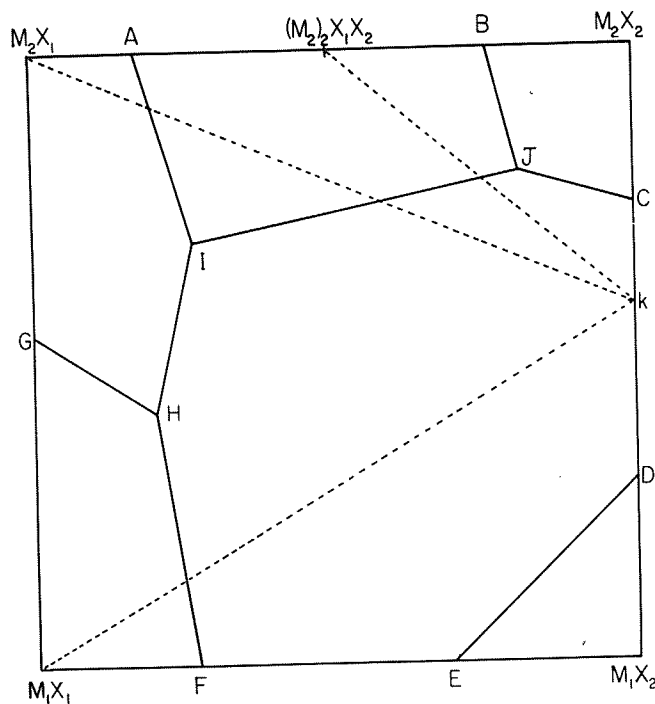
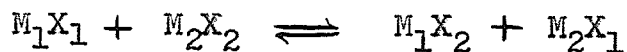


FIGURE 7

RECIPROCAL SALT PAIR EXHIBITING SOLID  
SOLUTION, HYDRATE, AND COMPOUND

anions and of the cations in the salt mixture; the water content is given as  $m$ , the moles of water per total mole of salt.

The reciprocal salt pair



is shown in Figure 7. There is a compound  $((M_2)_2X_1X_2)$ , hydrate  $(M_1X_2 \cdot nH_2O)$ , and solid solution  $(M_2X_2 \text{ in } M_1X_2)$  in this example. The points A, B, C, D, E, F, and G are all points in the four ternary systems that make up the edges of the square in the graphical representation of this reciprocal salt pair. The solid phases present at these points are:

<u>Point</u>	<u>Solid Phases</u>
A	$M_2X_1, (M_2)_2X_1X_2$
B	$M_2X_2, (M_2)_2X_1X_2$
C	$M_2X_2, \text{ solid solution}$
D	$M_1X_2 \cdot nH_2O, \text{ solid solution}$
E	$M_1X_2 \cdot nH_2O, \text{ solid solution}$
F	$M_1X_1, \text{ solid solution}$
G	$M_1X_1, M_2X_1$

The points H, I, and J are invariant points, where there are three solid phases present. These points are invariant points because, from the phase rule, with temperature and pressure fixed, the maximum number of phases possible in a four component system is four, when the variance is zero.



The solid phases present at H, I, and J are:

<u>Point</u>	<u>Solid Phases</u>
H	$M_1X_1, M_2X_1$ , solid solution
I	$M_2X_1, (M_2)_2 X_1X_2$ , solid solution
J	$(M_2)_2 X_1X_2, M_2X_2$ , solid solution

A congruent invariant point is one that lies within the area bounded by the pure salts present at the invariant point. The composition of the solution at a congruent invariant point can be expressed in positive quantities of the solid phases present. If solid solution is present at an invariant point, then the end member of the series of solid solutions is chosen as the composition of the solid phase. This composition is given by point k in Figure 7. Therefore, since point J lies within the triangle k,  $M_2X_2, (M_2)_2 X_1X_2$  it is congruent. Point H is also congruent, whereas point I is not.

#### 4. X-RAY POWDER PHOTOGRAPHS

It is well known that when a beam of monochromatic X-rays is directed at a crystalline substance, a characteristic diffraction pattern is obtained. If a crystalline powder is used, the pattern will appear as a series of arcs on a strip of film mounted coaxially with the specimen. The conditions under which diffraction takes place are defined by the Bragg relation

$$n \lambda = 2 d \sin \theta,$$

where  $n$  = a positive integer denoting the "order" of the reflection

$\lambda$  = the wavelength of the monochromatic radiation  
in Angstrom units

$d$  = the distance between two successive lattice planes,  
also in Angstrom units

$\Theta$  = the angle between the incident beam, and the  
lattice plane (the glancing angle)

Since every crystalline substance has a characteristic pattern, x-ray powder photographs can be used as a means of identifying crystalline substances. In a mixture of two or more crystalline materials, the patterns of each substance will appear superimposed on the strip of film, but the individual patterns can usually be resolved. Thus a mixture of two or three crystalline phases can readily be identified by this means.

## 5. PHASE CHANGES

One of the methods to determine the temperature of a phase change, that is, the transition point where one solid phase undergoes a change to a second solid phase, is by detecting the volume change that usually accompanies such a phase change. This property is utilized to find transition points by enclosing the solid phase in a bulb to which is attached a long capillary tube (a dilatometer). The solid phase in the bulb is covered with an inert liquid. As the bulb is slowly warmed the inert

liquid begins to rise in the capillary, because of normal expansion due to increasing temperature. When a phase change occurs the inert liquid will either rise or fall rapidly in the capillary due to a volume change in the solid phase which has undergone a transition. There is usually a time lag between the transition temperature and the temperature at which the volume change occurs, so that it is necessary to observe the phase change from both sides of the transition point, and to take the mean of the observed temperatures of volume change in order to establish the transition temperature.

#### 6. OPTICAL EXAMINATION OF CRYSTALS

Transparent crystals can frequently be identified from their optical properties; to determine their properties the crystals have to be examined under a petrographic microscope. It is impossible here to describe the detailed features of crystal optics but it can be pointed out that crystals can be divided into three main groups on the basis of their optical properties. The first group consists of those crystals which

are isotropic in all crystallographic directions; all such crystals belong to the cubic system. All non cubic crystals have the ability of breaking a beam of light into two separate rays, except along a special direction in the case of certain crystals, and along two special directions in the case of other crystals. The second optical grouping of crystals consists of those characterized by the one direction along which the crystal is isotropic; these are said to be optically uniaxial and all such crystals belong to either the tetragonal or hexagonal systems. The third optical group is made up of those crystals which have two directions of optical isotropism, and these are said to be optically biaxial. All biaxial crystals belong to the orthorhombic, monoclinic, or triclinic systems. Under the petrographic microscope it is fairly straightforward to determine to which one of these optical groups a given crystal belongs, but to decide whether a uniaxial crystal for example, belongs to the tetragonal or hexagonal system depends upon other optical and physical characteristics of the crystals which may or may not be observable in a given case. It is thus not always possible to determine by optical methods the crystal system to which a given crystal belongs.

Uniaxial and biaxial crystals have refractive indices which are different in different crystal directions, and thus each uniaxial or biaxial crystal is characterized by a range

of refractive indices from a minimum value in one direction, to a maximum value in some other direction. These refractive indices used along with the other optical properties of a crystal can be very useful in the identification of crystals when there is a set of tables<sup>22</sup> giving the optical properties of a large number of crystals.

The refractive index of a crystal is found by comparing it to that of a set of oils of known refractive index, under the petrographic microscope.

## LITERATURE REVIEW

### 1. THE TERNARY SYSTEMS

#### A. The System-Sodium Chloride-Sodium Sulphate-Water

This system was first investigated at 25°C. by Meyerhoffer and Saunders<sup>9</sup> in 1899 as part of the reciprocal salt pair, sodium chloride-potassium sulphate-water. The ternary system was also investigated by Seidell<sup>10</sup>, in 1902, at several temperatures besides 25°C., but his work was not very exact. The composition of the invariant points in the ternary system was reported by Schreinemakers<sup>11</sup> in 1911.

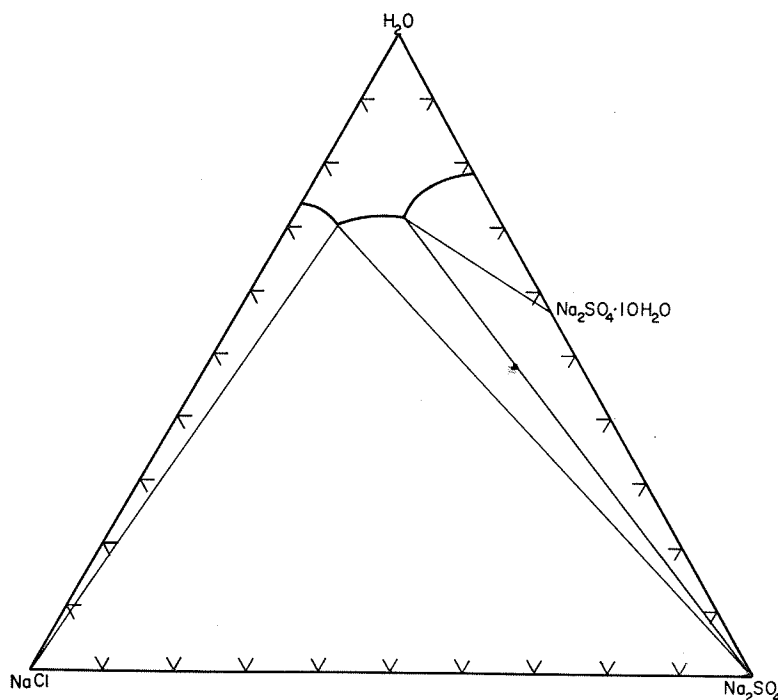


FIGURE 8

THE SYSTEM NaCl - Na<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O at 25°C.

Blasdale<sup>12</sup>, in 1918, and Takegami<sup>13</sup>, in 1921, also investigated this system. Takegami's results differ, but not significantly, from those of Blasdale. Figure 8 shows the equilibrium diagram, drawn from Takegami's data.

B. The System-Sodium Chloride-Lithium Chloride-Water  
at 25°C.

Smits, Elgersma, and Hardenburg<sup>14</sup> investigated this system in 1924. Their work shows the strong "salting out" effect of lithium chloride on sodium chloride. The solution at the only invariant point has very little sodium chloride in it. The equilibrium diagram is shown in Figure 9.

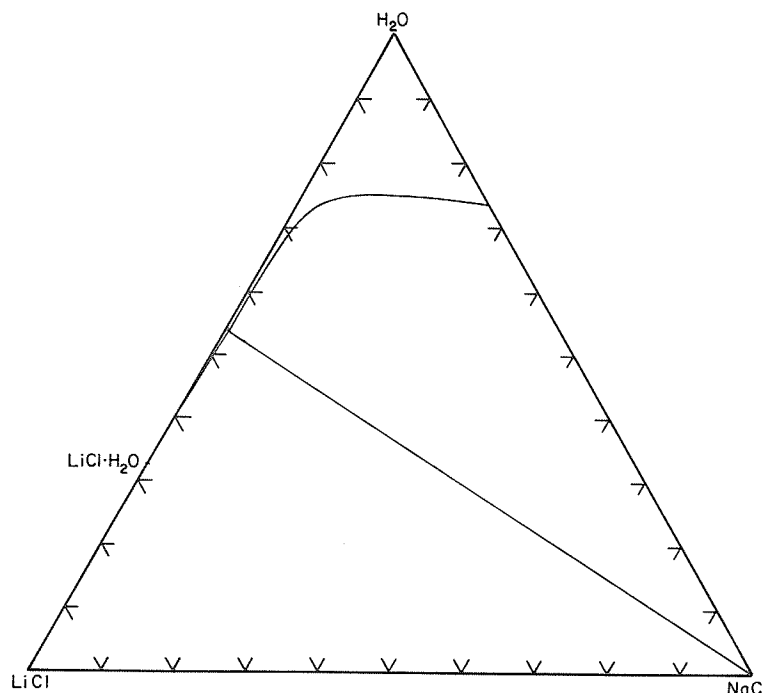


FIGURE 9

THE SYSTEM LiCl - NaCl-H<sub>2</sub>O at 25°C.

C. The System - Lithium Chloride-Lithium Sulphate-Water  
at 25°C.

Apart from the work carried out by Schreinemakers and Kayser<sup>15</sup> at 30°C., the first study of this system at 25°C. was made by Druzhinin and Yanko<sup>16</sup>. Their equilibrium diagram is reproduced in Figure 10.

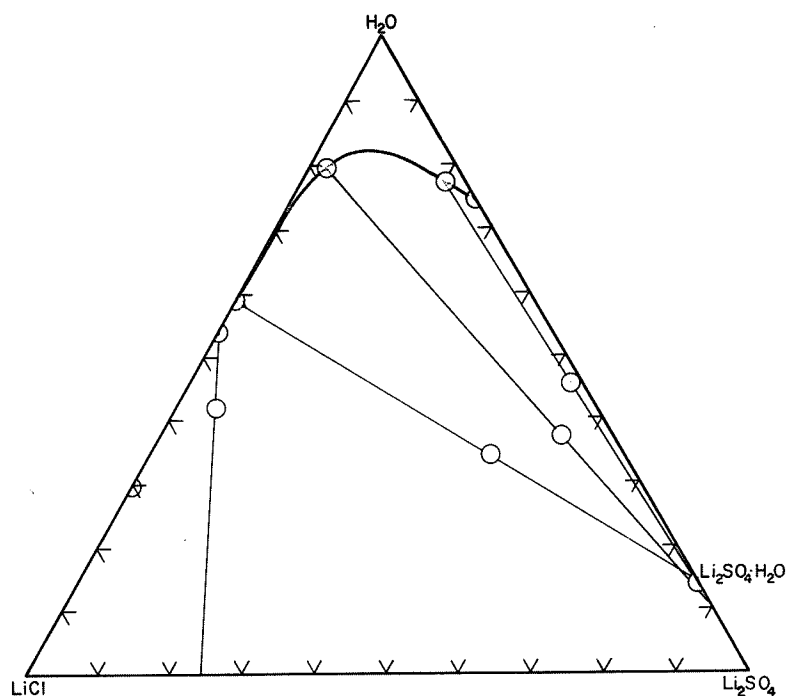


FIGURE 10

THE SYSTEM  $\text{LiCl} - \text{Li}_2\text{SO}_4 - \text{H}_2\text{O}$  AT 25°C.

D. The System-Lithium Sulphate-Sodium Sulphate-Water  
at 25°C.

In the past there has been a good deal of controversy (see the addendum) as to whether there is a solid solution of



the sulphates in this system, or whether double salts are formed. Cavalca and Nardelli<sup>17</sup> claim that the double salt  $\text{Na}_3\text{Li}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  exists at  $27^\circ\text{C}$ . However, the work of Campbell and Kartzmark<sup>18</sup> shows that there is no such salt at  $25^\circ\text{C}$ . They have also shown that the double salt  $\text{LiNaSO}_4$  does exist at higher temperatures, but that it breaks down to the simple sulphates at  $29.3^\circ\text{C}$ . Figure 11 shows the system according to Campbell and Kartzmark.<sup>18</sup>

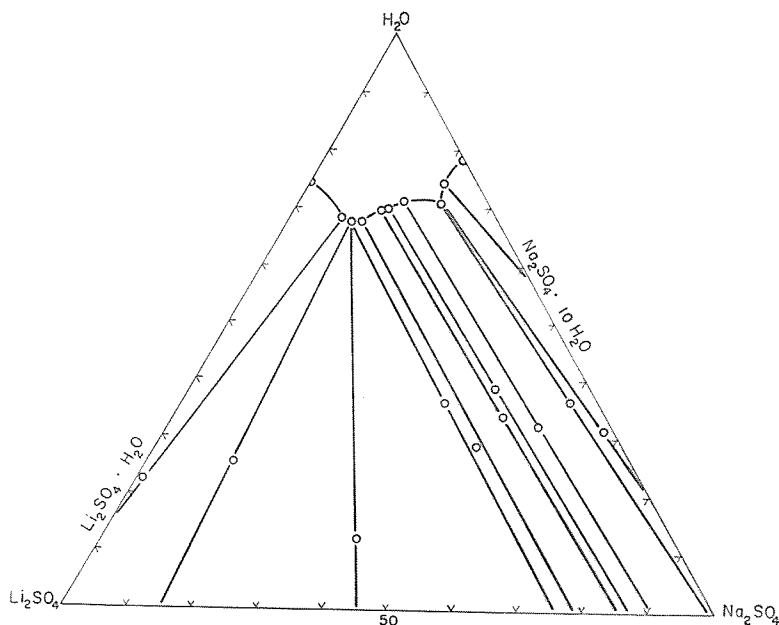


FIGURE 11

THE SYSTEM  $\text{Li}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  AT  $25^\circ\text{C}$ .

E. The System-Potassium Sulphate-Potassium Chloride-  
Water at 25°C.

The invariant point of this ternary system appears in the reciprocal salt pair  $(K_2^{++}, Na_2^{++})(Cl_2^-, SO_4^-)$  water at 25°C., which has been investigated by Meyerhoffer and Saunders<sup>9</sup> and Blasdale<sup>12</sup>. It has also been investigated by Ya. Anosov and Byzova<sup>19</sup>, at a series of temperatures.

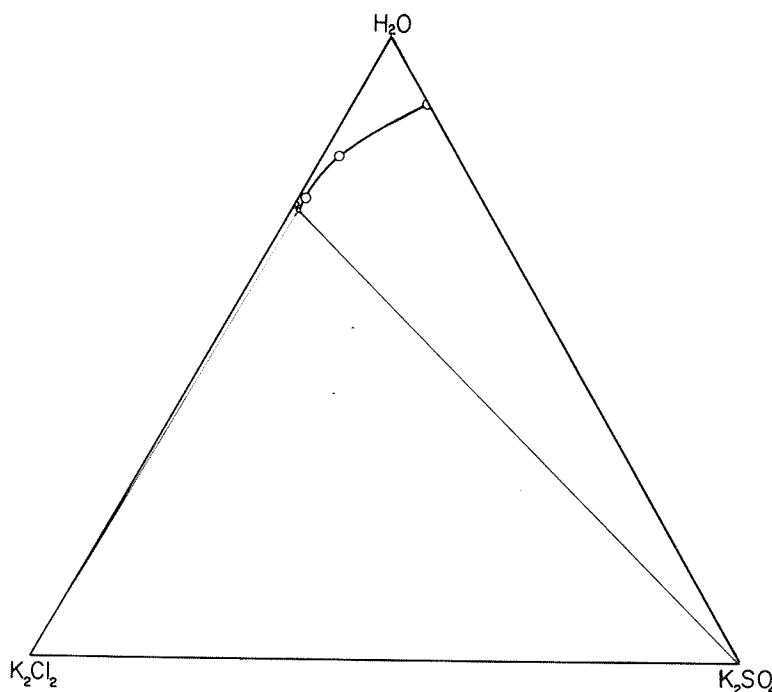


FIGURE 12

THE SYSTEM  $K_2SO_4 - KCl - H_2O$  at 25°C.

F. The System- Potassium Chloride-Lithium Chloride-  
Water at 25°C.

This system was investigated by Campbell and Kartzmark<sup>20</sup> in 1956. Their equilibrium diagram appears in Figure 13.

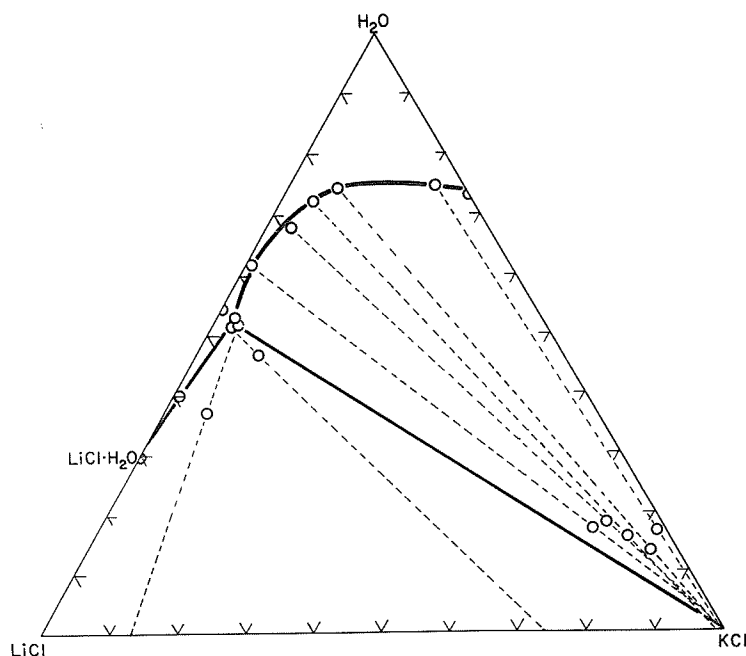


FIGURE 13

THE SYSTEM KCl - LiCl - H<sub>2</sub>O at 25°C.

G. The System-Lithium Sulphate-Potassium Sulphate-Water  
at 25°C.

This system was first investigated by Yanko and Druzhinin<sup>21</sup> in 1955. They claim that lithium potassium sulphate (LiKSO<sub>4</sub>) is formed only in the limiting case of a

series of solid solutions. The system has also been made a subject of study by Campbell and Kartzmark<sup>18</sup>, and their work shows that double salt exists between  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  on one side of the diagram, and  $\text{K}_2\text{SO}_4$  on the other. Figure 14 gives the equilibrium diagram, as they determined it.

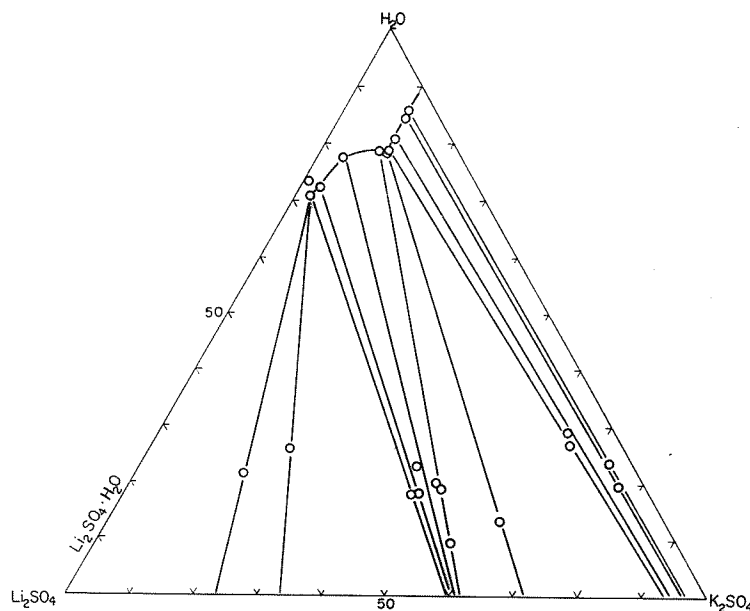


FIGURE 14

THE SYSTEM  $\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$  at  $25^\circ\text{C}$ .

2. THE QUATERNARY SYSTEMSA. The Reciprocal Salt Pair Lithium, Sodium, Chloride, Sulphate, Water at 25°C.

No mention of the reciprocal salt pair  $(\text{Na}_2^{++}, \text{Li}_2^{++})(\text{Cl}_2^-, \text{SO}_4^-)$  water at 25°C. can be found in the literature.

B. The Reciprocal Salt Pair Lithium, Potassium, Chloride, Sulphate, Water at 25°C.

Reference to the reciprocal salt pair  $(\text{K}_2^{++}, \text{Li}_2^{++})(\text{Cl}_2^-, \text{SO}_4^-)$  water at 25°C. could not be found in the literature.

## PURITY OF MATERIALS

All the chemicals were used as supplied by the manufacturer without further purification. In every case, except one, analysed materials were used. The grade and manufacturer of the salts employed are given in Table I.

TABLE I  
THE REAGENTS

Salt	Supplier	Grade
$\text{LiCl} \cdot \text{H}_2\text{O}$	Fisher Scientific Co.	Certified Reagent
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	British Drug Houses Ltd.	Analar
$\text{NaCl}$	Fisher Scientific Co.	Certified Reagent
$\text{Na}_2\text{SO}_4$	Fisher Scientific Co.	Certified Reagent
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	British Drug Houses Ltd.	Analar
$\text{KCl}$	Mallinckrodt Chemical Works	Analytical Reagent
$\text{K}_2\text{SO}_4$	Mallinckrodt Chemical Works	Low Nitrogen

The sulphates used to determine the viscosity curves, which formed a part of the analysis scheme, were not further purified, but they were dried by fusion in a platinum dish. After fusion they were ground in a mortar, and stored in a desiccator over Drierite. It was found that exposure to the

atmosphere for short periods of time did not lead to any appreciable increase in the weight of either lithium sulphate or sodium sulphate.

The silver nitrate used in the gravimetric determination of chloride was the analysed material supplied by the Merck Company, in both the "Reagent" and "Chemically Pure" grades.

The sulphuric and nitric acids used were the "Chemically Pure" analysed materials manufactured by Canadian Industries Limited.

## METHOD OF ANALYSIS

The analytical scheme makes use of a physical property of sulphate solutions to determine the amounts of lithium and potassium or sodium present in the liquid and solid phases. Solutions of lithium sulphate in water, and of sodium sulphate in water, prepared by dissolving the same weight of each salt in water, and made up to the same volume, exhibit a considerable difference in viscosity. The viscosities of the solutions of the two sulphates lie between the viscosities of solutions of the pure sulphates. By preparing a series of solutions of mixed sulphates, and determining their viscosities, a curve of viscosity versus the amount of one of the sulphates in the sulphate mixture can be drawn. Therefore, the amount of each sulphate in an unknown mixture of the two sulphates can be found by preparing the specified solution, and finding the viscosity of this solution.

After a gravimetric determination of chloride, enough information about a mixture of the four ions  $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$  or  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$  and  $\text{SO}_4^-$  is known so the percentage of each can be calculated, determining sulphate by difference.



1. Liquid Phase of the Potassium, Lithium, Chloride, Sulphate, Water System

The water in the liquid phase of this system was determined by weighing the solution in a platinum dish, and then evaporating it overnight in an oven at  $140^{\circ}\text{C}$ . The last traces of water were removed by fusion of the remaining salts, and the total water content was found by weighing the dried salts, in the weighed platinum dish.

The dried salts were coarsely ground in a mortar and well mixed; a small portion was dried at  $140^{\circ}\text{C}$ . for an hour, to be used for the gravimetric analysis of chloride. To the remainder of the salts an excess of 1:1 sulphuric acid was added to convert the chlorides to sulphates. The water and excess acid were removed by heating; first gently with a Bunsen burner under a sand bath, and then more strongly with a Meker burner applied directly to the platinum dish, until sulphur trioxide fumes were no longer visible. Finally, the dish and its contents were heated in a furnace at  $600^{\circ}\text{C}$ ., for a period of not less than six hours, to drive off the last traces of sulphuric acid. The sulphated salts were finely ground and tested for the presence of chloride ion and sulphuric acid, with silver nitrate solution and litmus paper respectively. The weight of potassium sulphate in ten grams of the sulphated salts was found by dissolving ten grams of the salts in water, making the volume up to one hundred



FIGURE 15

## MODIFIED OSTWALD VISCOMETER

millilitres at  $25^{\circ}\text{C}$ ., and determining the viscosity of the resulting solution in a modified Ostwald viscometer at  $25^{\circ}\text{C}$ .

To prepare the standard viscosity curve a series of solutions, ranging from pure potassium sulphate to pure lithium sulphate was prepared. Each solution contained a total weight of ten grams of sulphates, and was made up to a volume of one hundred millilitres at  $25^{\circ}\text{C}$ . The solutions were filtered rapidly through sintered glass to remove any

insoluble material, and then the viscosities at 25°C. were found by using a modified Ostwald viscometer. The density of each solution at 25°C. was found by using a modified Ostwald pyknometer. The viscosities of the salt solutions were compared to the arbitrarily chosen standard of  $\eta_{\text{H}_2\text{O}} = 1.0000$  at 25°C., where  $\eta_{\text{H}_2\text{O}}$  is the viscosity of water.

TABLE II

VISCOSITIES AND DENSITIES OF LITHIUM SULPHATE-POTASSIUM  
SULPHATE-WATER SOLUTIONS AT 25°C.

Wt. $K_2SO_4$ (gms)	Wt. $Li_2SO_4$ (gms)	Density (gms/ml)	Viscosity ( $\eta_{H_2O} = 1.0000$ )
10	0	1.0738	1.1342
9	1	1.0741	1.1751
8	2	1.0748	1.2174
7	3	1.0752	1.2594
6	4	1.0758	1.3048
5	5	1.0757	1.3460
3	7	1.0770	1.4482
2	8	1.0776	1.4999
1	9	1.0780	1.5559
0	10	1.0780	1.6141

The percentage of chloride was determined gravimetrically according to the procedure given by Kolthoff and Sandell<sup>23</sup>. Each analysis was carried out in quadruplicate, and the mean of the four values for chloride was taken as the percentage of chloride.

The sulphate radical was determined by difference.

## 2. Liquid Phase of the Sodium Lithium Chloride Sulphate Water System

The analysis of this liquid phase was carried out in exactly the same manner as that of the previous liquid phase, except that twenty grams of the sulphated salts were made up to a volume of one hundred milliliters at 25°C. for the determination of the viscosity. The standard viscosity curve was determined by preparing a series of solutions, in which a total of twenty grams of sulphates was made up to a volume of one hundred milliliters at 25°C., and the viscosities determined. Once again the viscosities of the salt solutions are given (see Table III) in comparison to the arbitrarily chosen standard of water having a viscosity of 1.0000 at 25°C. The curve is given in Figure 16.

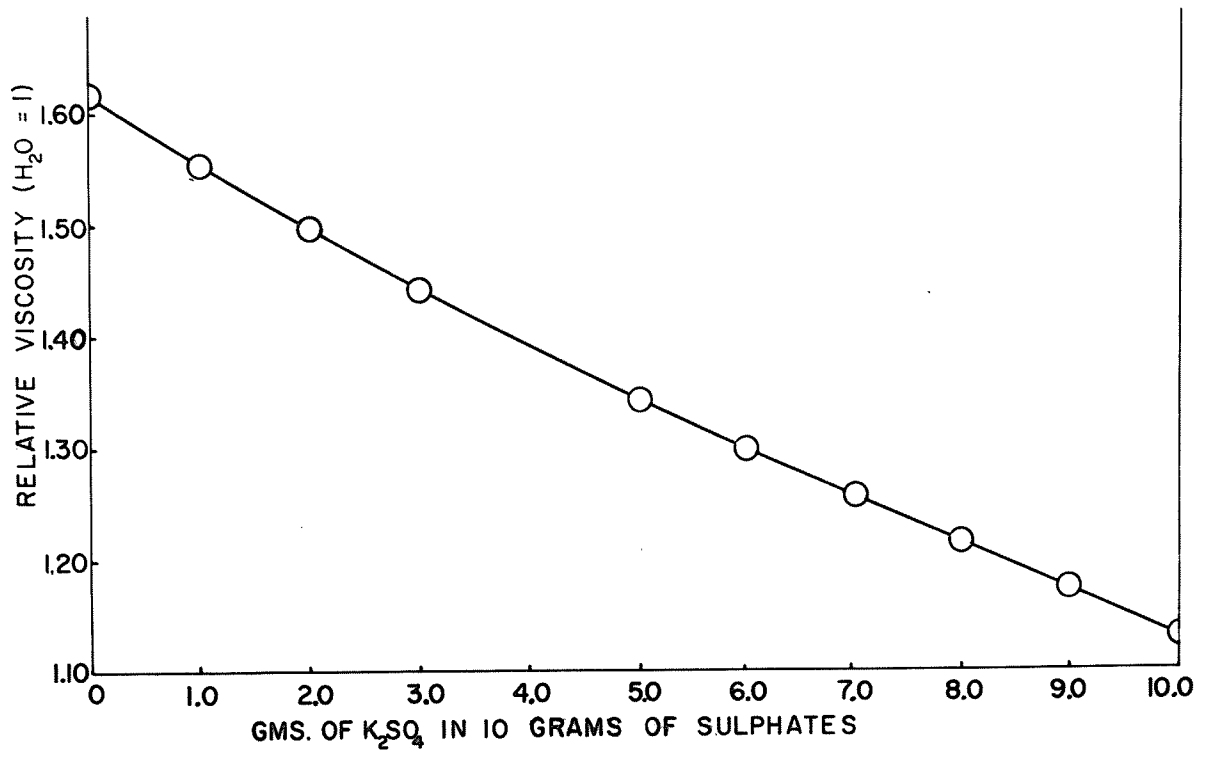


FIGURE 16

VISCOSITIES OF SOLUTIONS CONTAINING POTASSIUM  
SULPHATE AND LITHIUM SULPHATE

TABLE III

VISCOSITIES AND DENSITIES OF SODIUM SULPHATE-LITHIUM  
SULPHATE-WATER SOLUTIONS AT 25°C.

Wt. $\text{Na}_2\text{SO}_4$ (gms)	Wt. $\text{Li}_2\text{SO}_4$ (gms)	Density (gms/ml)	Viscosity ( $\eta_{\text{H}_2\text{O}} =$ 1.0000)
20	0	1.1606	1.9057
18	2	1.1604	1.9699
16	4	1.1591	2.0369
14	6	1.1583	2.1071
12	8	1.1573	2.1817
10	10	1.1565	2.2552
8	12	1.1554	2.3356
6	14	1.1551	2.4231
4	16	1.1545	2.5163
2	18	1.1532	2.6125
0	20	1.1524	2.7016

The curve showing the viscosity plotted against the weight of sodium sulphate is given in Figure 17.

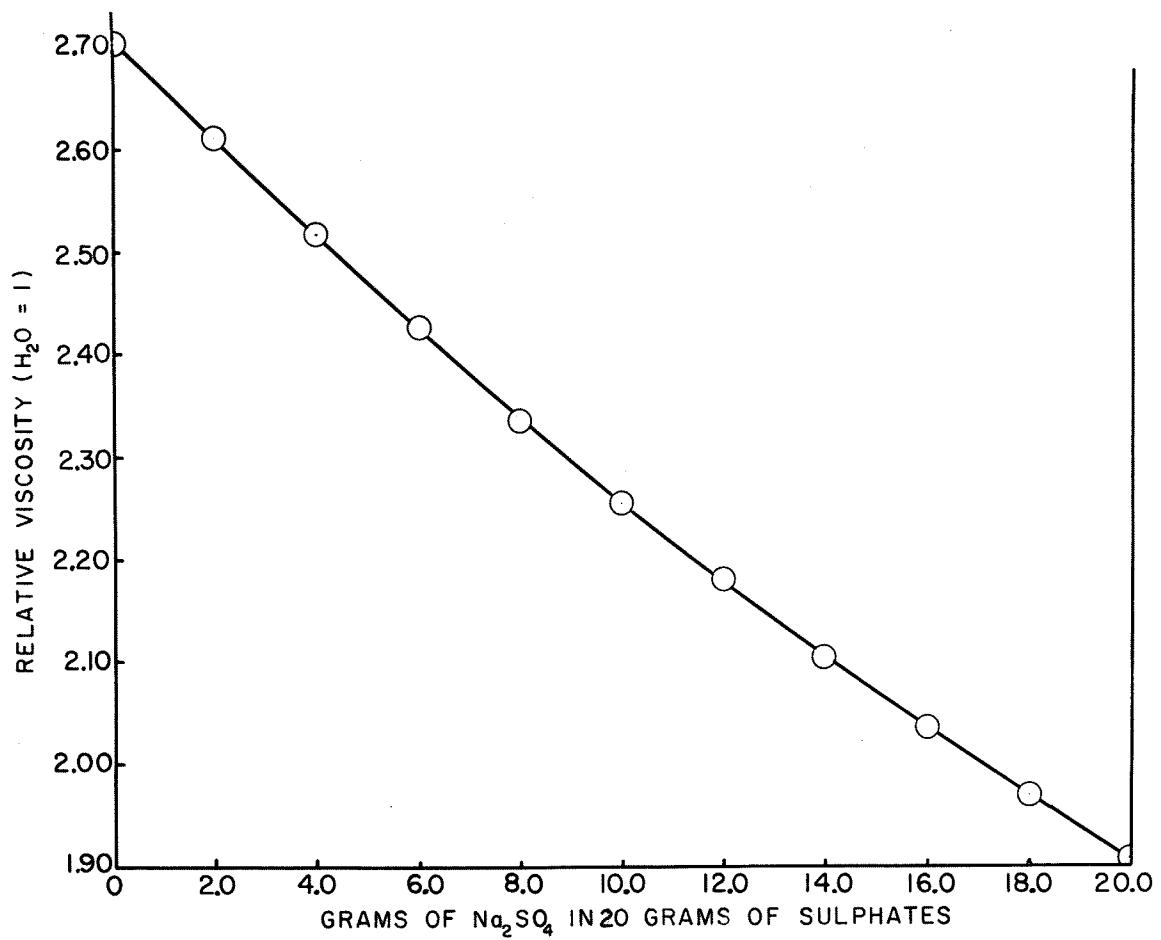


FIGURE 17

VISCOSITIES OF SOLUTIONS CONTAINING SODIUM  
SULPHATE AND LITHIUM SULPHATE



3. Solid Phase of the Potassium, Lithium, Chloride, Sulphate, Water System at 25°C.

The solid phases of this system were identified by chemical analysis, using the same method that was employed to analyse the liquid phase of this system. At all points where one, two, or three solid phases were believed to be in equilibrium with solution it was possible to ascertain that such was actually the case from the amount of each ion present in the solid phase, and from the knowledge that lithium chloride would be present as a solid phase only when the amount of lithium chloride in the liquid phase was exceedingly high.

4. Solid Phase of the Sodium, Lithium, Chloride, Sulphate, Water System at 25°C.

Along the curve which shows sodium sulphate decahydrate and solid solution of lithium and sodium sulphate in equilibrium with solution, in this system, chemical analysis, carried out as in the liquid phase, shows that the number of equivalents of sodium considerably exceeded the equivalents of lithium indicating decahydrate in the solid phase. Sodium sulphate decahydrate was identified by picking out a few crystals, and warming them slightly. These crystals dehydrate immediately because of the transition from the decahydrate to anhydrous sodium sulphate and water, which takes place at approximately 32.5°C. It was not possible to identify the

solid solution in such a direct manner, but its presence was shown by the appearance of lithium in the solid phase.

At points where one of the solid phases was lithium sulphate monohydrate it was identified by the prismatic habit of the crystals, and by the fact that it would not dehydrate on a steam bath. This salt loses its water of hydration at  $128^{\circ}\text{C}$ .

At the sodium chloride, lithium sulphate monohydrate, solid solution invariant point the only salt that could be identified unequivocally was lithium sulphate monohydrate and this by the method just given. At this invariant point all of the solid phases including lithium sulphate monohydrate were investigated by using a plane polarizing microscope, but in order to be able to use this it was necessary to dry the solid phases. It was quite possible that one or more of the solid phases which were stable in the presence of solution, would be unstable in its absence, and hence would undergo a phase change on drying. This limitation makes results obtained from investigating the dried salts of questionable value.

A dilatometer was used to determine the behavior of the transition point of the double salt\* in the presence of chloride ions. In order to master the technique an equimolar mixture of the sulphates of lithium and sodium was put into the dilatometer, and the transition point of the double salt was found to lie at  $29.9^{\circ}\text{C}$ .; within  $0.6^{\circ}\text{C}$ . of the value of  $29.3^{\circ}\text{C}$ . found by

\*  $\text{NaLiSO}_4$

Campbell and Kartzmark<sup>18</sup>. The experiment was repeated using an equimolar mixture of lithium sulphate monohydrate, and sodium chloride, but the only transition point found in this mixture was at approximately  $12^{\circ}\text{C}$ . An equimolar mixture of the sulphates does not exhibit a transition point at this temperature, so the transition point found was not likely to be of sodium sulphate decahydrate undergoing dehydration in the presence of chloride ions. The transition point found at  $12^{\circ}\text{C}$ . could have been caused by the breaking down of sodium lithium sulphate but, it could also have been caused by some other phase change. If the transition point found at  $12^{\circ}\text{C}$ . was, in fact, due to the  $\text{NaLiSO}_4$  double salt breaking down to solid solution, then, there would be an area within the  $25^{\circ}\text{C}$ . isotherm of this reciprocal salt pair, in which the double salt would be in equilibrium with solution. No such area was found.

It was originally hoped that the solid phases could be identified by means of X-ray powder photographs. Attempts to do this were made by enclosing the wet solid phases in glass capillaries, but, pictures taken in this way gave only a darkened film with one or two strong lines. Wrapping the wet solid phase in an envelope of collodian gave the same results. The poor photographs in both cases apparently resulted from excessive X-ray scattering by the glass or collodian, and from water in the sample.

In order to determine the practicability of the method for the salts concerned, two mixtures of dry, reagent grade salts were prepared and photographed. The first mixture consisted of 75 weight percent sodium sulphate and 25 weight percent lithium sulphate monohydrate Figure 18 (Film 1), and the second of 25 weight percent sodium sulphate, and 75 weight percent sodium chloride Figure 18 (Film 2). Film 1 shows only very weak lines due to lithium sulphate. By comparison, the sodium sulphate lines on Film 2 are stronger, but the strongest lines on the sodium chloride and sodium sulphate powder photographs coincide, making this method less sensitive than usual. The sodium sulphate lines are weak, but distinguishable. In the practical case of wet solid phases in glass the lines would all be much weaker, and the background would be much darker, the net effect of which would be to obscure most of the weak lines. Photographs of pure sodium chloride, sodium sulphate, and lithium sulphate monohydrate are shown in Figure 18 (Films 3, 4, and 5). For the reasons given above, no further attempt was made to utilize this method as a means of analyzing the solid phases.

##### 5. Example of the Calculations

Consider the lithium potassium sulphate ( $\text{LiKSO}_4$ ), potassium chloride, potassium sulphate invariant point in the  $(\text{K}_2^{++}, \text{Li}_2^{++})(\text{Cl}_2^{\ominus}, \text{SO}_4^{\ominus})$  system, and the analysis of the liquid and

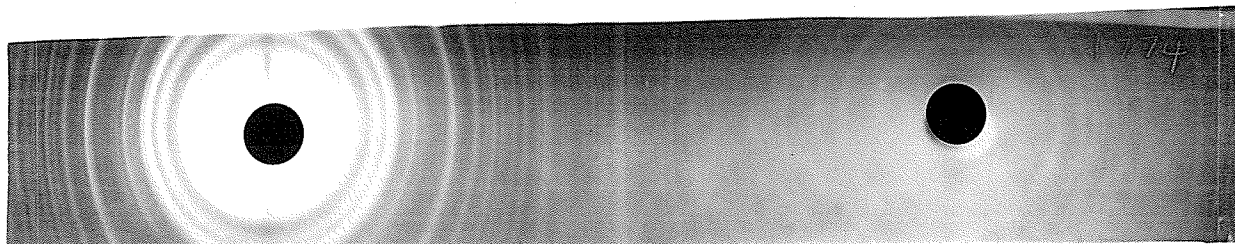
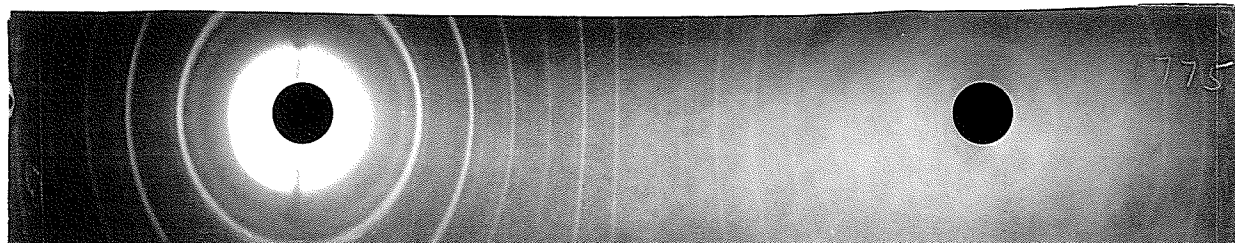
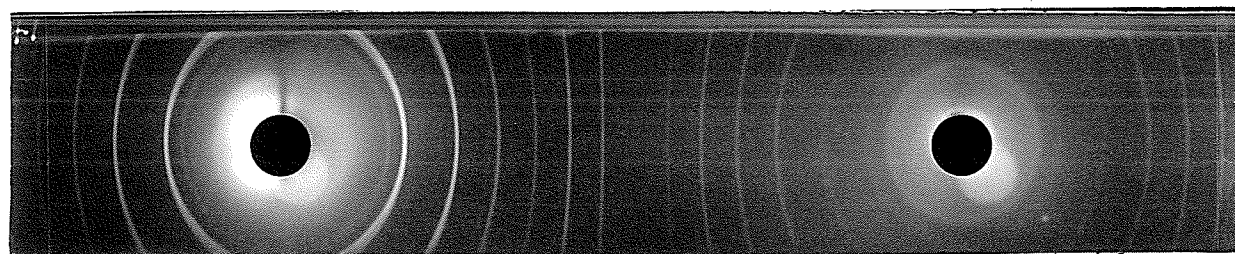
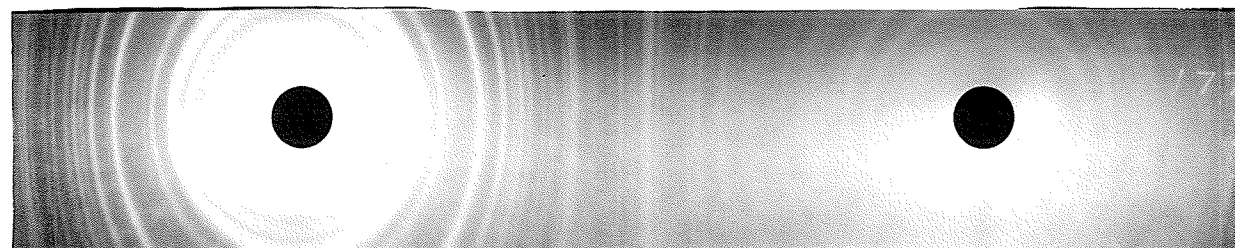
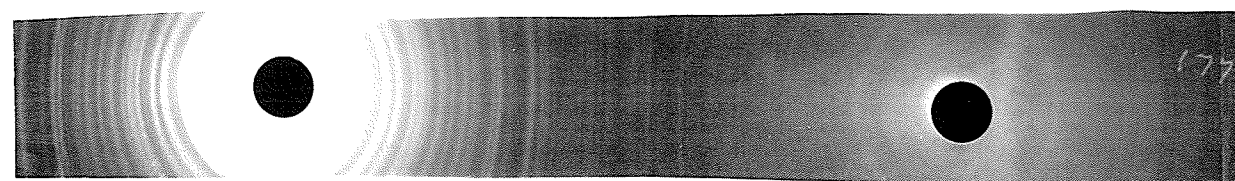
Film 1 (75%  $\text{Na}_2\text{SO}_4$  - 25%  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ )Film 2 (25%  $\text{Na}_2\text{SO}_4$  - 75%  $\text{NaCl}$ )Film 3 ( $\text{NaCl}$ )Film 4 ( $\text{Na}_2\text{SO}_4$ )Film 5 ( $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ )

FIGURE 18

X-RAY POWDER PHOTOGRAPHS

the solid phases at this point (point #10 , Fig. 21, Table IV).

A. Liquid Phase. The following data were determined experimentally: 44.9311 grams of water were associated with 15.8422 grams of salts. The salts were 52.96% chloride, and 10 grams of sulphated salts contained 6.70 grams of potassium sulphate, and 3.30 grams of lithium sulphate.

If 100 grams of the original salt mixture were considered, then 52.96% of this mixture was chloride. Treatment with sulphuric acid will replace the chloride with sulphates, resulting in a weight increase of the original 100 grams. The weight of the sulphated salts can be found by multiplying the weight of chloride by the ratio of sulphate to chloride, subtracting the weight of chloride, and adding the difference to one hundred

$$\left( \frac{96.06}{70.92} \times 52.96 \right) - 52.96 + 100 = 117.77 \text{ grams of sulphated salts.}$$

In 10 grams of mixed sulphates there were 6.70 grams of potassium sulphate, and therefore, in 117.77 grams of mixed sulphates there were

$$117.77 \times \frac{6.70}{10} = 78.91 \text{ grams of potassium sulphate}$$

$$\text{of which there were } 78.91 \times \frac{K_2}{K_2SO_4} = 78.91 \times 0.4488 = 35.72$$

grams  $K_2$  in the original 100 grams of salts, or 35.72%  $K_2$  in the original 100 grams.

$$\text{There were } 117.77 - 78.91 = 38.86 \text{ grams of lithium}$$

sulphate in the sulphated salts, of which

$38.86 \times \frac{\text{Li}_2}{\text{Li}_2\text{SO}_4} = 38.86 \times 0.1262 = 4.95$  grams was  $\text{Li}_2^{++}$  or  
the original salts contained 4.95%  $\text{Li}_2^{++}$

The sulphate was found by difference:

$$100 - 4.95 - 35.72 - 52.96 = 6.37\% \text{ sulphate.}$$

In order to be able to plot this point on the diagram,  
the percentages must be converted to the mole fraction of  
 $\text{Li}_2$  in the cations and the mole fraction of  $\text{Cl}_2$  in the anions.  
In 100 grams of the salts the number of moles of each ion was

$$\frac{\text{weight Cl}_2}{\text{molecular weight Cl}_2} = \frac{52.96}{70.92} = 0.747 \text{ moles Cl}_2$$

$$\frac{\text{Wt. K}_2}{\text{Mol. Wt. K}_2} = \frac{35.72}{78.20} = 0.457 \text{ moles K}_2$$

$$\frac{\text{Wt. Li}_2}{\text{Mol. Wt. Li}_2} = \frac{4.95}{13.88} = 0.356 \text{ moles Li}_2$$

$$\frac{\text{Wt. SO}_4}{\text{Mol. Wt. SO}_4} = \frac{6.37}{96.06} = 0.066 \text{ moles SO}_4$$

$$\text{moles of anions} = 0.813$$

$$\text{moles of cations} = 0.813$$

$$\text{mole fraction Cl}_2 = \frac{0.747}{0.813} = 0.918$$

$$\text{mole fraction Li}_2 = \frac{0.356}{0.813} = 0.439$$

To find  $m$ , the number of moles of water per total mole

of salts, it was necessary to find how many grams of salts there were per total mole.

$$\frac{100 \times 1}{0.813} = 123.00 \text{ grams of salts per mole.}$$

There were  $\frac{44.93}{18.01} = 2.50$  moles of water associated with 15.84 grams of salts. Therefore,

$$m = \frac{2.50 \times 123.00}{15.84} = 19.4 \text{ moles of water}$$

B. Solid Phase. The solid phase was analysed by the same procedure except that  $m$  was not determined. The percentage, and the number of moles per 100 grams in the solid phases, of each ion is given below.

	<u>Weight %</u>	<u>Moles per 100 grams</u>
$\text{Cl}_2^-$	13.24	0.187
$\text{K}_2^{++}$	40.74	0.521
$\text{Li}_2^{++}$	1.76	0.127
$\text{SO}_4^-$	44.26	0.461

All the chloride at this point where potassium chloride, potassium sulphate, and  $\text{KLiSO}_4$  are in equilibrium with solution, must be present as potassium chloride, which means that there were 0.187 moles of  $\text{K}_2\text{Cl}_2$  in 100 grams of the solid phase. Since all the lithium existed as  $\text{KLiSO}_4$ , then there were 0.254 moles of double salt present, leaving 0.204 moles of potassium sulphate in 100 grams of the solid phase.



## APPARATUS

In order to attain equilibrium, the salts and water were placed in the solubility cell, and stirred for twenty-four hours at 25°C. In the original solubility cell, the liquid phase was removed by suction through a sintered glass filter stick that replaced the stirrer. The liquid phase was collected in a receiver attached by a ground glass joint, as shown in Figure 19. This method of separating the phases was not satisfactory because it frequently left the solid phases very wet. To correct this disadvantage a second type of cell, which had a sintered glass disk built into its bottom, was used. During the long period of stirring the sintered glass disk was covered by a long handled glass plug. The stirrer was designed to fit over the long handle of the plug. Figure 20a shows the cell set up for stirring, and 20b shows the method of separating the liquid from the solid phases.

Densities were determined in a modified Ostwald pycnometer, and viscosities were found by means of modified Ostwald viscometer; both were calibrated in the usual way. The 25°C. thermostat was of the conventional type, and controlled the temperature to  $\pm 0.05^\circ\text{C}$ .

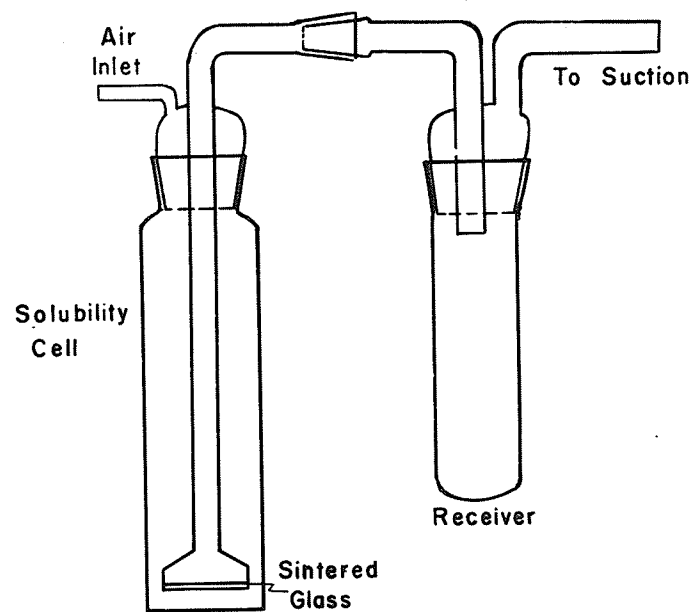
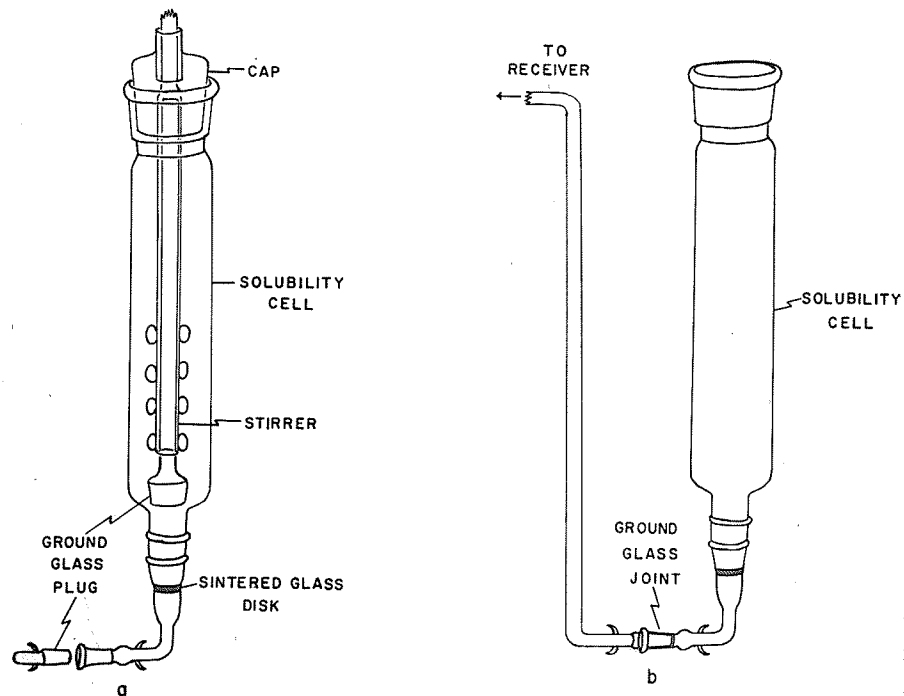


FIGURE 19

THE SOLUBILITY CELL, SHOWING THE TECHNIQUE OF  
SEPARATING SOLUTION FROM THE WET RESIDUES

**FIGURE 20****THE IMPROVED SOLUBILITY CELL**

- a) SHOWS THE CELL ASSEMBLED FOR STIRRING  
b) SHOWS THE TECHNIQUE USED TO SEPARATE  
THE LIQUID FROM THE WET RESIDUES

## EXPERIMENTAL PROCEDURE

### 1. GENERAL METHOD

The general method of attack consisted of first plotting the invariant points of the four ternary systems, comprising the particular reciprocal salt pair, on the edges of the square upon which the experimental data were to be plotted. At any one of these ternary invariant points there would be three of the four possible ions present in the liquid phase. Points within the square were found experimentally by adding the fourth ion, and moving into the square from the invariant points in the ternary systems. This was accomplished by making up solutions which were very near to being saturated, and which contained a small amount of the fourth ion that was being added to the three ions of the ternary system; large amounts of the two solid phases that were in equilibrium with solution in the ternary system were also present. The solution and the solid phases were stirred for at least twenty- four hours in the solubility cell; the solid and liquid phases were separated, and then both phases were analysed. After analysis, the point was plotted on the square, and the next point was made up to fall further into the square by adding more of the fourth ion.

In a three component system the method of analysing

solid phases, wet with mother liquor, is Schreinemakers' wet residue method for determining the nature of the solid phase, but in this problem, only points where two or three solid phases were in equilibrium with solution were investigated. If one phase points had been investigated, and the water content plotted in the third dimension, then the lines joining the composition of the liquid phase to that of the wet residue would have met at a point, giving the composition of the solid phase present. When two or more phases are present, the lines joining the composition of the liquid phase to that of the wet residue are scattered.

Invariant points revealed themselves in two ways. The first was by the sudden appearance of a new ion in the wet residue, on what had been a curve of two phases in equilibrium with solution, thus indicating the presence of a third solid phase. Secondly, at an invariant point various ratios of salts can be stirred to equilibrium to give solutions identical in composition.

It was found that solutions containing a large amount of lithium chloride exhibited a much stronger tendency to adhere to the residue than solutions low in lithium chloride content. In order to get a more accurate estimation of the composition of the solid phases at points of this nature, it was necessary to determine the water content of the wet residue, and then to subtract the ions that would be dissolved

in this water, from the composition of the solid phases.

2. THE SYSTEM LITHIUM, POTASSIUM, CHLORIDE, SULPHATE, WATER  
AT 25°C.

The general method of determining the equilibrium curves and points in this system, as given above, was followed. The invariant points were determined by both criteria of invariance.

3. THE SYSTEM LITHIUM, SODIUM, CHLORIDE, SULPHATE, WATER AT  
25°C.

It was possible to identify the sodium chloride, lithium sulphate monohydrate, solid solution invariant point when approaching it from along the curve upon which solid solution and lithium sulphate monohydrate were in equilibrium, by the sudden appearance of chloride. The invariance of this point was also shown by various ratios of salts giving solutions of the invariant composition.

## EXPERIMENTAL RESULTS

The experimental results are collected in Tables IV to VII, pages 53 to 56, which list the compositions of the liquid phases and wet residues of the reciprocal salt pairs investigated. Tables VIII and IX, pages 57 and 58, give the mole fractions of the ions, the moles of water per mole of salt, and the solid phases present at each point for each salt pair.

TABLE IV

COMPOSITION DATA OF THE LIQUID PHASE OF THE SYSTEM  
 $K_2^{++}$ ,  $Li_2^{++}$ ,  $Cl_2^-$ ,  $SO_4^-$ ,  $H_2O$  AT  $25^\circ C$ .

Point No.	Wt. % $Cl_2^-$	Wt. % $K_2^{++}$	Wt. % $Li_2^{++}$	Wt. % $SO_4^-$
1	48.16	47.65	1.37	2.82
2	52.73	37.08	4.55	5.64
3	9.04	24.13	6.24	60.59
4	33.32	28.00	6.24	32.44
5	40.73	29.43	6.17	23.67
6	47.66	32.79	5.53	14.02
7	51.18	34.14	5.31	9.37
8	52.77	35.75	4.93	6.55
9	53.99	34.32	5.38	6.31
10	52.96	35.72	4.95	6.37
11	57.73	29.89	6.80	5.58
12	64.31	22.43	9.19	4.17
13	10.18	3.39	12.12	74.31
14	33.58	4.17	12.95	49.30
15	54.87	5.41	13.55	26.17
16	68.85	7.26	13.66	10.23
17	72.28	10.52	12.95	3.25
18	73.25	11.87	12.56	2.32
19	72.82	10.78	12.84	3.56
20	77.01	7.48	13.96	1.55
21	81.11	3.64	15.22	0.03



TABLE V

COMPOSITION DATA OF THE WET RESIDUES OF THE SYSTEM  
 $K_2^{++}$ ,  $Li_2^{++}$ ,  $Cl_2^-$ ,  $SO_4^-$ ,  $H_2O$  AT  $25^\circ C$ .

Point No.	Wt. % $Cl_2^-$	Wt. % $K_2^{++}$	Wt. % $Li_2^{++}$	Wt. % $SO_4^-$
1	25.58	48.46	0.14	25.82
2	29.28	46.57	0.84	62.73
3	trace	34.29	2.98	23.31
4	2.82	30.37	4.21	62.60
5	trace	31.73	3.70	64.57
6	3.50	38.39	1.98	56.13
7	1.65	37.51	2.15	58.69
8	18.78	38.74	2.57	39.91
9	18.55	36.40	3.21	41.84
10	13.24	40.74	1.76	44.26
11	23.30	37.53	3.06	37.11
12	27.87	38.81	2.95	30.37
13	trace	13.64	8.78	77.58
14	trace	11.35	9.43	79.22
15	5.83	10.21	10.01	73.95
16	trace	9.71	11.35	79.88
17	18.79	26.99	5.88	48.35
18	14.37	23.63	6.62	55.39
19	5.48	11.08	8.95	74.49
20	20.03	23.61	6.88	49.48
21	33.09	23.12	7.60	36.19

TABLE VI

THE COMPOSITION OF THE SOLUTIONS, AND THE  
NATURE OF THE SOLID PHASES IN THE SYSTEM  
 $\text{Li}_2^{++}$ ,  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}$  AT  $25^\circ\text{C}$ .

Point No.	Composition of the Liquid Phase		Moles of $\text{H}_2\text{O}$ per Mole of Salt	Nature of the Solid Phases
	Mole Fraction $\text{Cl}_2^-$	Mole Fraction $\text{Li}_2^{++}$		
1	0.959	0.140	21.9	$\text{K}_2\text{Cl}_2 + \text{K}_2\text{SO}_4$
2	0.927	0.408	19.6	" "
3	0.167	0.594	29.2	$\text{K}_2\text{SO}_4 + \text{LiKSO}_4$
4	0.582	0.557	27.5	$\text{K}_2\text{SO}_4 + \text{LiKSO}_4$
5	0.700	0.543	26.3	" "
6	0.822	0.487	23.6	" "
7	0.467	0.880	21.0	" "
8	0.916	0.437	19.4	$\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{K}_2\text{SO}_4$
9	0.917	0.435	19.4	" " "
10	0.918	0.439	19.4	" " "
11	0.933	0.562	18.5	$\text{LiKSO}_4 + \text{K}_2\text{Cl}_2$
12	0.956	0.698	17.1	" "
13	0.157	0.952	17.7	$\text{LiKSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
14	0.480	0.946	19.2	" " "
15	0.740	0.933	19.0	" " "
16	0.902	0.914	17.2	" " "
17	0.967	0.874	13.8	$\text{K}_2\text{Cl}_2 + \text{KLiSO}_4 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
18	0.967	0.870	13.8	" " "
19	0.966	0.870	13.8	" " "
20	0.985	0.913	12.3	$\text{K}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
21	1.000	0.960	9.6	$\text{Li}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O} + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{K}_2\text{Cl}_2$

TABLE VII

COMPOSITION DATA OF THE LIQUID PHASE OF THE SYSTEM  
 $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}$  AT  $25^\circ\text{C}$ .

Point No.	Wt. % $\text{Cl}_2^-$	Wt. % $\text{Na}_2^{++}$	Wt. % $\text{Li}_2^{++}$	Wt. % $\text{SO}_4^-$
1	4.00	25.73	2.77	67.50
2	8.04	27.56	2.24	62.16
3	16.01	31.25	1.16	51.58
4	46.33	34.36	1.30	18.01
5	54.56	23.63	5.86	15.95
6	59.02	18.40	8.08	14.50
7	62.55	15.43	9.40	12.62
8	62.84	15.00	9.58	12.58
9	62.43	15.76	9.26	12.55
10	64.83	14.40	9.91	10.86
11	68.18	12.88	10.65	8.29
12	53.14	14.53	9.34	22.99
13	48.53	14.19	9.26	28.02
14	32.23	13.17	8.93	45.67
15	14.93	12.09	8.57	64.41

TABLE VIII

COMPOSITION DATA OF THE WET RESIDUES OF THE SYSTEM  
 $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}$  AT  $25^\circ\text{C}$ .

Point No.	Wt. % $\text{Cl}_2^-$	Wt. % $\text{Na}_2^{++}$	Wt. % $\text{Li}_2^{++}$	Wt. % $\text{SO}_4^-$
1	trace	29.82	1.11	69.07
2	trace	29.07	1.28	69.65
3	trace	27.85	1.77	70.38
4	14.76	31.27	1.09	52.87
5	44.83	34.24	1.30	19.62
6	24.75	26.31	3.27	45.66
7	42.62	33.71	1.38	22.22
8	43.83	16.41	8.17	31.58
9	33.35	23.43	4.98	38.24
10	34.47	19.97	6.38	39.18
11	38.58	23.11	5.34	32.97
12	1.25	15.17	6.23	77.35
13	4.42	15.33	6.85	73.40
14	-	-	-	-
15	trace	20.55	4.62	74.83

TABLE IX

THE COMPOSITION OF THE SOLUTIONS, AND THE  
NATURE OF THE SOLID PHASES IN THE SYSTEM  
 $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}$  AT  $25^\circ\text{C}$ .

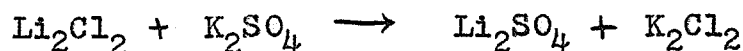
Point No.	Composition of the Liquid Phase		Moles of $\text{H}_2\text{O}$ per Mole of Salt	Nature of the Solid Phase
	Mole Fraction $\text{Cl}_2^-$	Mole Fraction $\text{Li}_2^{++}$		
1	0.074	0.263	18.1	$\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
2	0.149	0.212	18.0	" " "
3	0.296	0.110	17.9	" " "
4	0.777	0.112	15.7	$\text{Na}_2\text{Cl}_2 + \text{Solid Solution}$
5	0.822	0.451	15.6	" " "
6	0.846	0.592	15.4	" " "
7	0.872	0.669	15.1	$\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{Solid Solution}$
8	0.871	0.679	15.1	" " "
9	0.880	0.660	15.2	" " "
10	0.918	0.733	15.3	$\text{Na}_2\text{Cl}_2 + \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
11	0.890	0.695	-	" " "
12	0.758	0.681	16.2	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{Solid Solution}$
13	0.701	0.683	16.4	" " "
14	0.489	0.692	16.2	" " "
15	0.240	0.700	13.5	" " "

## DISCUSSION OF RESULTS

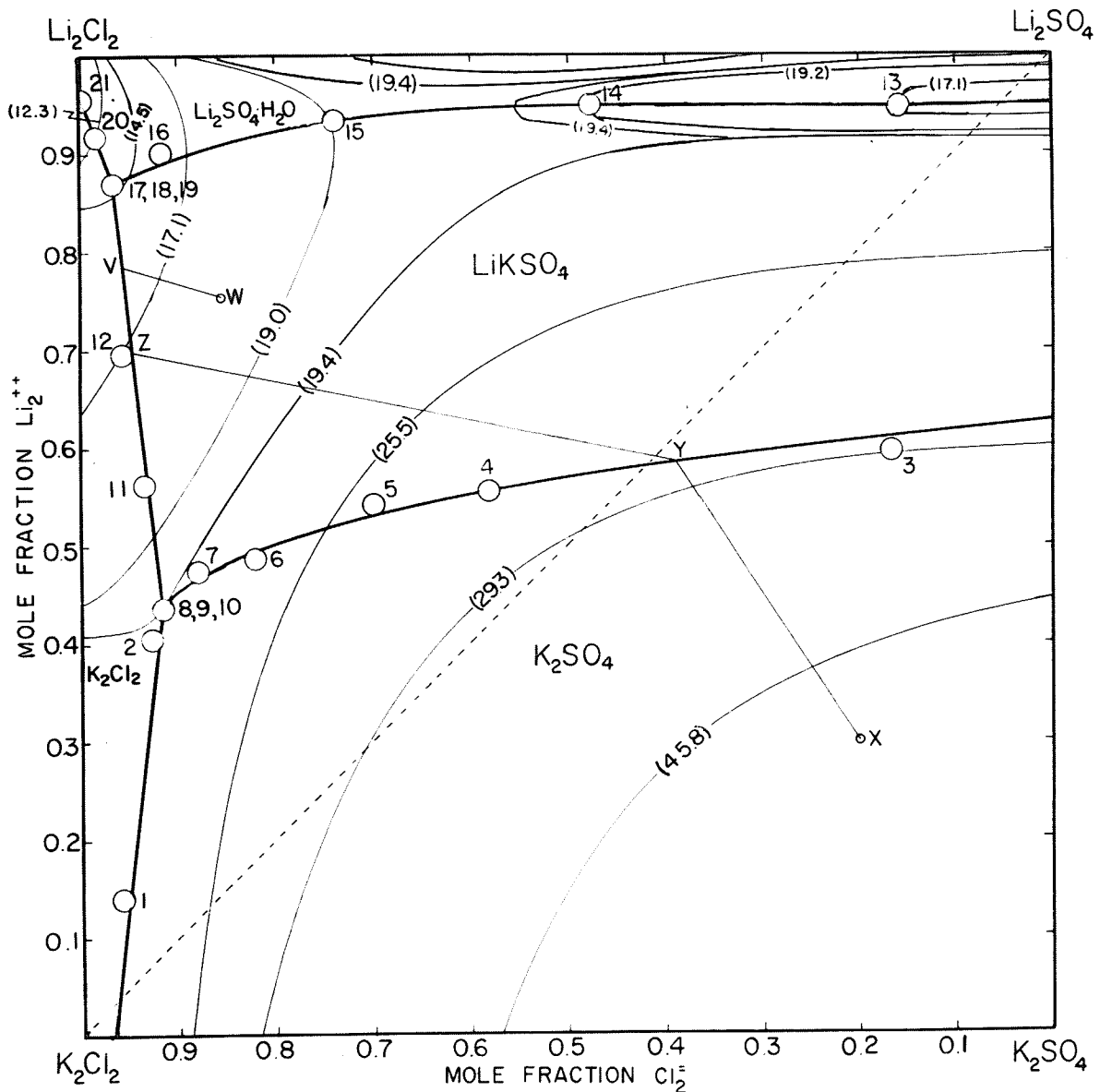
### 1. THE SYSTEM, POTASSIUM, LITHIUM, CHLORIDE, SULPHATE, WATER AT 25°C.

The results of the chemical analyses of the liquid phase, and the wet residues of this system are listed in Tables IV, V and VI, pages 53 to 55; the equilibrium diagram is shown in Figure 21. The curves which represent two solid phases in equilibrium with solution are shown as the heavy lines, and the lighter lines are the isohydrates.

In the reciprocal salt pair,



the stable pair, that is the pair of salts that can exist in contact with each other and with solution, is lithium sulphate monohydrate, and potassium chloride. There are three invariant points in this system. At the invariant point 8, 9, 10 in Figure 21 the solid phases are potassium sulphate, potassium chloride, and the double salt ( $\text{KLiSO}_4$ ). Since the invariant point does not fall within the area bounded by the pure phases present at the invariant point, it is incongruent. The invariant point, 17, 18, 19 where lithium sulphate monohydrate, potassium chloride, and double salt are in equilibrium is also incongruent. The only congruent invariant point in this system at 25°C. is point 21 where lithium chloride monohydrate,



THE SYSTEM: LITHIUM, POTASSIUM, CHLORIDE,  
SULPHATE, WATER AT 25° C.

FIGURE 21

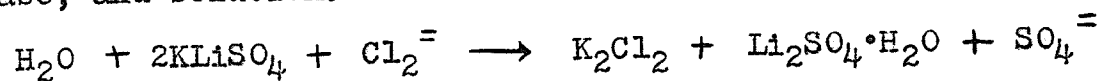
lithium sulphate monohydrate, and potassium chloride are in equilibrium with solution.

#### A. Isothermal Evaporation

Isothermal evaporation is of considerable practical importance because it can often show how pure salts may be obtained from salt mixtures in solution. A qualitative illustration of isothermal evaporation where the solid phases are not removed as they precipitate, and a quantitative case when they are removed as they form is given.

##### 1. Qualitative Example of Isothermal Evaporation

If a solution whose composition is given by point W (Figure 21) is allowed to evaporate at 25°C., the first salt to come out of solution will be the double salt (KLiSO<sub>4</sub>). As double salt precipitates the composition of the solution will move directly away from that of the double salt, until point V is reached, and potassium chloride begins to precipitate along with the double salt. From V the composition of the solution moves towards the invariant point 17, throwing down double salt and potassium chloride as it proceeds. When this point is reached the monohydrate of lithium sulphate begins to precipitate. At this point (an incongruent invariant point) there will be a reaction between the double salt in the solid phase, and solution.





This reaction will continue until the double salt in the solid phase is exhausted, and then the composition of the liquid will move away from 17 towards 21 where it will finally dry up.

## 2. Quantitative Example of Isothermal Evaporation

Point X, in Figure 21, represents a solution containing one total mole of salts, in the proportions of 0.30 mole fractions of  $\text{Li}_2^{++}$  and 0.20 mole fractions of chloride  $\text{Cl}_2^-$  in 53 moles of water. The weight of each ion in this solution is shown below.

	$\text{Cl}_2^-$	$\text{K}_2^{++}$	$\text{Li}_2^{++}$	$\text{SO}_4^-$
mole fraction	.20	.70	.30	.80
weight in grams	14.2	54.7	4.2	76.8
moles	.20	.70	.30	.80

As evaporation takes place potassium sulphate will precipitate, and the composition of the solution will move directly away from that of pure potassium sulphate, until point Y is reached. At Y all the precipitated potassium sulphate is removed. The composition of the solution, in mole fractions, is read from the equilibrium diagram (Figure 21), and since no chloride or lithium has precipitated the amount of these ions, in moles, is the same as it was in the original solution. The composition of point Y in mole fractions and in grams is:

	$\text{Cl}_2^-$	$\text{K}_2^{++}$	$\text{Li}_2^{++}$	$\text{SO}_4^-$
mole fractions	.39	.42	.58	.61
weight in grams	14.2	16.4	4.2	29.8
moles	.20	.21	.30	.31

Thus, in going from point X to point Y, 47 grams of sulphate and 38.3 grams of potassium were precipitated, as 85.3 grams of potassium sulphate, and 38.2 moles of water evaporated.

At point Y, as evaporation continues, the double salt,  $\text{KLiSO}_4$ , will begin to precipitate, and since the potassium sulphate has been removed, the composition of the solution will move directly away from that of double salt, to point Z. At Z the solution composition is:

	$\text{Cl}_2^-$	$\text{K}_2^{++}$	$\text{Li}_2^{++}$	$\text{SO}_4^-$
mole fractions	0.94	0.30	0.70	0.06
weight in grams	14.2	4.9	2.1	1.1
moles	0.20	0.064	0.15	0.013

In going from Y to Z by isothermal evaporation 42.5 grams of double salt were deposited, and 11.2 moles of water were evaporated.

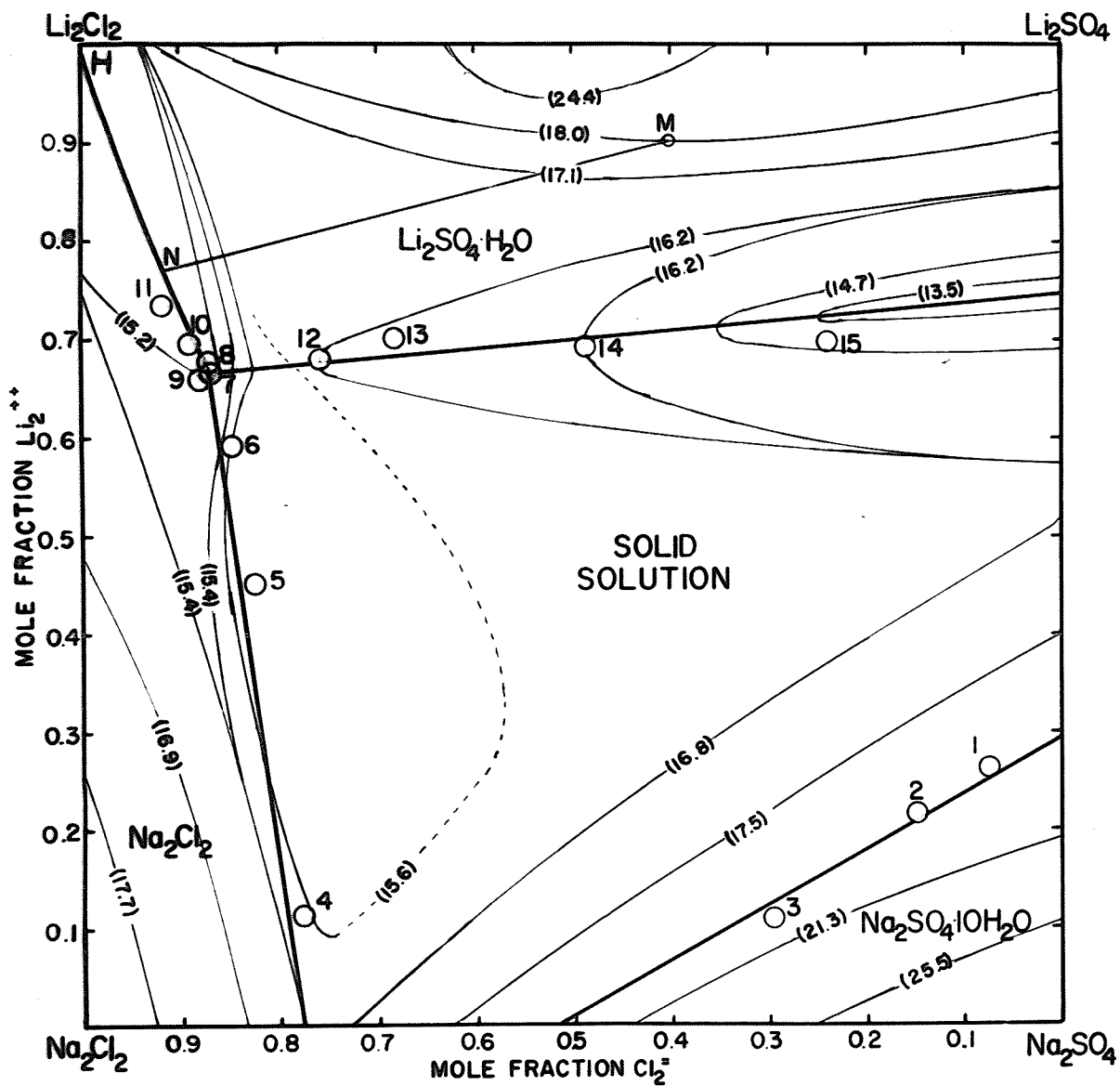
At point Z potassium chloride will begin to precipitate, along with double salt, so that further evaporation will yield mixed solid phases, which are of little interest from the point of view of preparing pure salts.

2. THE SYSTEM, SODIUM, LITHIUM, CHLORIDE, SULPHATE, WATER  
AT 25°C.

The results of the chemical analyses of the liquid phase, and of the wet residues, are given in Tables VII, VIII, and IX, pages 56 to 58; the equilibrium diagram is shown in Figure 22. Analogously to the previous reciprocal salt pair, the stable salt pair of this system is sodium chloride and lithium sulphate monohydrate.

Two invariant points were found in this system, one of which is incongruent. At the incongruent invariant point (point 7) the solid phases in equilibrium with solution are lithium sulphate monohydrate, sodium chloride, and a solid solution of sodium and lithium sulphates. The amount of lithium in the solid solution increases as the concentration of lithium in the liquid phase increases. The solution at H, the congruent invariant point where lithium chloride monohydrate, lithium sulphate monohydrate, and sodium chloride are the solid phases, is very rich in lithium chloride.

As was mentioned in the section dealing with the analysis of the solid phases of this system, there is a possibility that an area of the double salt,  $\text{NaLiSO}_4$ , exists within the body of the diagram, as a result of its transition temperature being lowered by the presence of chloride ions.



THE SYSTEM: LITHIUM, SODIUM, CHLORIDE,  
SULPHATE, WATER AT 25° C.

FIGURE 22

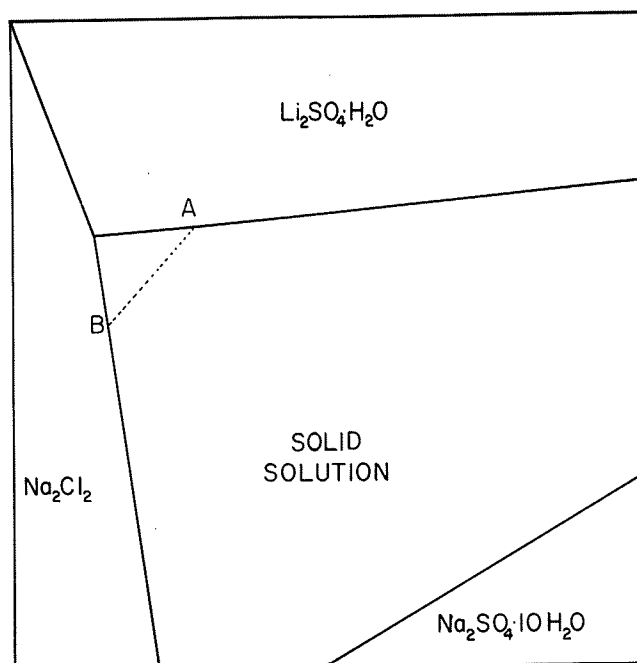


FIGURE 23

## POSSIBLE AREA OF DOUBLE SALT

If the double salt does exist, then there will be a curve (A B) where double salt and solid solution are in equilibrium. The approximate location of this curve is shown by the dotted line A B in Figure 23. If curve A B exists there will be invariant points at A and B. Attempts to find one of these, or a point on curve A B were fruitless. There is, however, a possibility that such an area does exist.

### A. Isothermal Evaporation

At point M, one mole of salts are dissolved in 18 moles of water. The composition of this solution is:

	$\text{Cl}_2^-$	$\text{Na}_2^{++}$	$\text{Li}_2^{++}$	$\text{SO}_4^-$
mole fractions	0.40	0.10	0.90	0.60
weight in grams	28.4	4.6	12.5	57.6
moles	0.40	0.10	0.90	0.60

As evaporation takes place the composition of the liquid phase moves directly away from that of lithium sulphate, as lithium sulphate precipitates. In going from M to N the solution composition changes to:

	$\text{Cl}_2^-$	$\text{Na}_2^{++}$	$\text{Li}_2^{++}$	$\text{SO}_4^-$
mole fractions	0.91	0.23	0.77	0.09
weight in grams	28.4	4.6	4.7	3.8
moles	0.40	0.10	0.34	0.04

showing that 7.8 grams of lithium and 53.8 grams of sulphate precipitated as 71.7 grams of lithium sulphate monohydrate.

At point N sodium chloride begins to contaminate the precipitate and there is no further interest in isothermal evaporation to prepare pure salts.

## SUMMARY AND CONCLUSIONS

The reciprocal salt pair lithium, potassium, chloride, sulphate, water at 25°C. was investigated by chemical analysis of the liquid phase and of the wet residues. Two incongruent invariant points were found, the first having the composition of 0.917 mole fractions of chloride, 0.437 mole fractions of lithium, and 19.4 moles of water per total mole of salts. At the second invariant point the composition was found to be 0.967 mole fractions of chloride, 0.870 mole fractions of lithium, and 13.8 moles of water per total mole of salts. At the congruent invariant point there were 9.6 moles of water per total mole of salts, whose composition was 1.000 mole fractions of chloride and 0.960 mole fractions of lithium. The stable salt pair of this reciprocal salt pair was found to be lithium sulphate monohydrate and potassium chloride. Qualitative and quantitative crystallization paths have been discussed.

The system, sodium, lithium, chloride, sulphate, water was investigated at 25°C. Of the two invariant points found, one was incongruent, and its composition was found to be 0.873 mole fractions of chloride, and 0.668 mole fractions of lithium, with 15.1 moles of water per total mole of salts. At the congruent invariant point chemical analysis showed the

liquid phase to consist almost entirely of lithium chloride. The stable salt pair was found to be sodium chloride and lithium sulphate monohydrate. An example of a crystallization path has been shown.

There is a possibility that an area, in which the double salt  $\text{NaLiSO}_4$  is in equilibrium with solution, exists in this isotherm. However, only weak, inconclusive, and ambiguous evidence for this was found, in the form of an unexplained transition point at  $12^\circ\text{C}$ . Attempts to find a third and fourth invariant point were fruitless. If such an area does exist it would probably be quite small.



APPENDIX

## APPENDIX I

### THE X-RAY POWDER DATA OF LITHIUM SULPHATE MONOHYDRATE

While attempting to make use of X-ray powder diffraction photographs to identify the crystalline phases in equilibrium with solutions of the sodium, lithium, chloride, sulphate and water reciprocal salt pair, the author found that the X-ray powder diffraction data for lithium sulphate monohydrate given in the X-ray powder data file of the American Society for Testing Materials were not particularly complete. Therefore two X-ray powder photographs, one on a camera 57.3 mm. in diameter and the other on a camera 114.6 mm. in diameter, were taken of Mallenckrodts' Analytical Reagent lithium sulphate monohydrate. Two photographs were taken because the large camera gave better resolution, which facilitated reading the positions of the X-ray powder lines in the front reflection region. The photograph on the small camera gave a better picture on the whole, although the front reflection region was darkened, and the resolution was poor. Both pictures were taken with iron K radiation which has a wavelength of 1.9360 Angstrom units. The diameters of the rings on the films were read as carefully as possible, and the relative intensities of the rings were estimated visually. The relative intensities

$I_{\text{obs}}$  and the lattice spacings  $d_{\text{obs}}$ , in Angstrom units, are given below. The values in parentheses for  $I_{\text{obs}}$  and for  $d_{\text{obs}}$  have been taken from the X-Ray Powder Data File (A. S. T. M.) for lithium sulphate monohydrate.

TABLE X

X-RAY POWDER DATA FOR  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$   
 USING  $\text{FeK}\alpha$  RADIATION

$I_{\text{obs}}$	$d_{\text{obs}, \text{\AA}}$	$I_{\text{obs}}$	$d_{\text{obs}, \text{\AA}}$
15 (7)	7.84 (7.8)	40 (7)	1.558 (1.55)
100 (67)	5.12 (5.1)	3	1.504
90 (100)	4.17 (4.12)	5 (7)	1.492 (1.49)
10	3.95	3	1.478
80 (58)	3.88 (3.84)	3	1.456
30 (7)	3.71 (3.68)	5	1.442
80 (67)	3.59 (3.54)	3	1.420
60 (50)	3.08 (3.02)	10	1.402
60 (33)	2.97 (2.93)	50 (7)	1.382 (1.38)
60 (33)	2.75 (2.72)	5	1.365
15 (3)	2.68 (2.65)	40	1.339
3	2.62	bd 10	1.314
5	2.55	bd 10	1.286
50 (3)	2.45 (2.48)	5	1.260
3 (27)	2.42 (2.41)	5	1.250
5 (3)	2.36 (2.33)	10	1.233
20 (3)	2.30 (2.28)	10	1.223
20 (7)	2.21 (2.18)	10	1.214
30 (7)	2.06 (2.04)	5	1.202
3	2.04	bd 10	1.188
10	2.01	10	1.176
30	1.930	5	1.166
3 (7)	1.898 (1.91)	bd 10	1.155
10 (7)	1.813 (1.81)	3	1.141
20 (7)	1.741 (1.72)	20	1.135
20 (7)	1.703 (1.70)	3	1.119
3	1.668	20	1.114
5 (3)	1.640 (1.63)	bd 10	1.104
30 (7)	1.597 (1.59)		

## APPENDIX II

THE SYSTEM: SODIUM SULPHATE, LITHIUM SULPHATE,  
WATER AT 25°C.

In their paper of 1952 L. Cavalca and M. Nardelli<sup>17</sup> claim that the double salt  $\text{Na}_3\text{Li}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  exists in the system  $\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{H}_2\text{O}$  at 27°C. The results of their work are contradicted by the more recent study of Campbell and Kartzmark<sup>18</sup> whose investigation does not show the presence of double salt, but rather extensive solid solution of lithium sulphate in sodium sulphate. As an independent check on the work of these authors two points in this ternary system were investigated.

Each solution was stirred for a period of one week in the presence of the solid phase. The solutions and wet residues were analysed, both by determination of the sulphate radical with barium, and by the viscosity of solutions of 20 grams of the anhydrous sulphates made up to a volume of 100 mls. at 25°C. The results of these analyses for the two points are given in Tables XI and XII.

TABLE XI  
SULPHATE ANALYSIS

Liquid Phase		Wet Residues		Solid Phase
Na <sub>2</sub> SO <sub>4</sub> Wt.%	Li <sub>2</sub> SO <sub>4</sub> Wt.%	Na <sub>2</sub> SO <sub>4</sub> Wt.%	Li <sub>2</sub> SO <sub>4</sub> Wt.%	
12.9	17.9	51.9	17.2	Solid Solution
16.3	12.7	52.1	16.1	Solid Solution

TABLE XII  
VISCOSITY ANALYSIS

Liquid Phase		Wet Residues		Solid Phase
Na <sub>2</sub> SO <sub>4</sub> Wt.%	Li <sub>2</sub> SO <sub>4</sub> Wt.%	Na <sub>2</sub> SO <sub>4</sub> Wt.%	Li <sub>2</sub> SO <sub>4</sub> Wt.%	
13.6	17.2	51.5	17.6	Solid Solution
17.3	11.7	54.1	14.1	Solid Solution

These points are shown below. The tie lines between the solutions and wet residues, as determined by the sulphate method, are shown in dotted lines, and those determined by physical means are shown in solid lines. It is interesting to note that the tie lines found by the erratic barium sulphate precipitation cross, but that those found by the viscosity method do not. The complete solubility curve in Figure 24 is from the paper by

Campbell and Kartzmark, with their tie lines shown in alternating dots and dashes. In no case do the tie lines cross to indicate the compound claimed by Cavalca and Nardelli at 27°C.

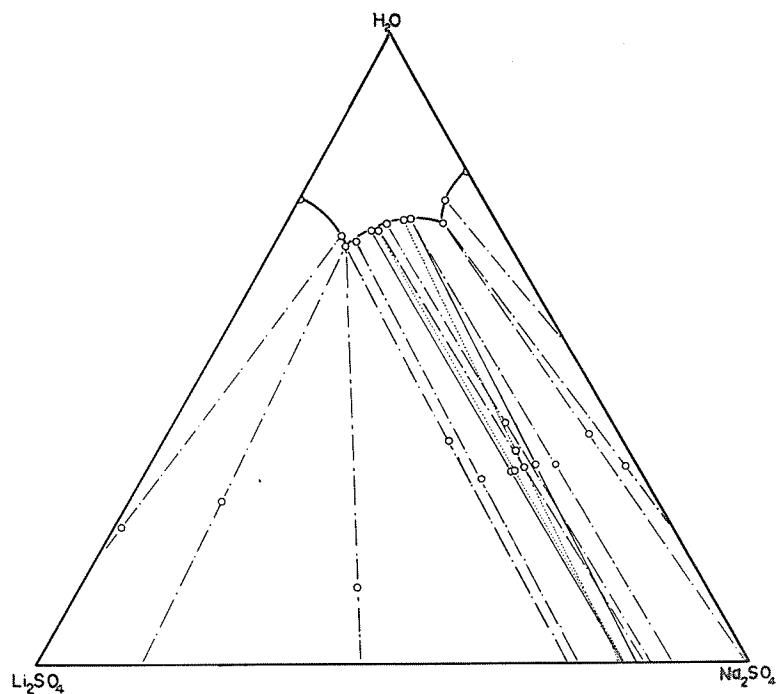


FIGURE 24

THE SYSTEM  $\text{Na}_2\text{SO}_4$ - $\text{Li}_2\text{SO}_4$ - $\text{H}_2\text{O}$  AT 25°C.

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