

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

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BY

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TO MY PARENTS

## ABSTRACT

The system consisting of the ions  $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ , and water at  $25^\circ\text{C}$ . has been investigated by the chemical analysis of the solutions and of the wet residues. In the solid model eight volumes were found where the following solid phases were in equilibrium with solution:  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ , solid solution of  $\text{Na}_2\text{SO}_4$  and  $\text{Li}_2\text{SO}_4$ ,  $\text{KCl}$ , and  $\text{NaCl}$ . Anhydrous  $\text{Na}_2\text{SO}_4$  was found to exist only as a surface in the solid diagram. Another volume,  $\text{LiCl} \cdot \text{H}_2\text{O}$ , was not obtained experimentally due to its close proximity to the  $\text{LiCl}$  corner of the diagram.

Five invariant points were discovered. For an invariant solution represented by  $\text{Li}_2^{++}$  - 17.0 mole %,  $\text{Na}_2^{++}$  - 13.9 mole %,  $\text{K}_2^{++}$  - 20.7 mole %,  $\text{Cl}_2^-$  - 43.8 mole %,  $\text{SO}_4^-$  - 4.6 mole %, the solid phases present in excess were  $\text{K}_2\text{SO}_4$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{KCl}$ ; for the solution,  $\text{Li}_2^{++}$  - 38.9 mole %,  $\text{Na}_2^{++}$  - 5.8 mole %,  $\text{K}_2^{++}$  - 5.6 mole %,  $\text{Cl}_2^-$  - 48.3 mole %,  $\text{SO}_4^-$  - 1.4 mole %, the solid phases were  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{KLiSO}_4$ ,  $\text{KCl}$ , and  $\text{NaCl}$ ; for the solution  $\text{Li}_2^{++}$  - 28.3 mole %,  $\text{Na}_2^{++}$  - 12.4 mole %,  $\text{K}_2^{++}$  - 8.2 mole %,  $\text{Cl}_2^-$  - 48.7 mole %,  $\text{SO}_4^-$  - 2.4 mole %, the solid phases were  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{KCl}$ , and  $\text{NaCl}$ ; the invariant solution  $\text{Li}_2^{++}$  - 30.2 mole %,  $\text{Na}_2^{++}$  - 14.8 mole %,  $\text{K}_2^{++}$  - 4.8

mole %,  $\text{Cl}_2^-$  - 47.6 mole %,  $\text{SO}_4^-$  - 2.6 mole %, excess solid phases were  $\text{K}_2\text{Na}(\text{SO}_4)_2$ ,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NaCl}$ , and  $\text{KLiSO}_4$ ; finally for the fifth invariant solution,  $\text{Li}_2^{++}$  - 9.8 mole %,  $\text{Na}_2^{++}$  - 34.3 mole %,  $\text{K}_2^{++}$  - 6.2 mole %,  $\text{Cl}_2^-$  - 17.5 mole %,  $\text{SO}_4^-$  - 32.2 mole %, the solid phases were  $\text{K}_2\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

A ternary salt was not found to exist in the interior of the phase model at the temperature of this study,  $25^\circ\text{C}$ .

No lines of equal water content were drawn from the data obtained, due to the complexity of the problem.

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## INTRODUCTION

The completion of this project finishes the comprehensive study of this five component system begun by A.N. Campbell and his associates five years ago. This five component system is itself composed of a number of sub-systems, namely 5 four component systems, and 9 three component systems. Of these various sub-systems all but three of the ternary systems had been reported in the literature with sufficient accuracy. These were:

1. KCl, LiCl, H<sub>2</sub>O at 25°C.
2. Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O at 25°C.
3. K<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O at 25°C.

Only one of the five quaternary systems, (Na<sub>2</sub><sup>++</sup>, K<sub>2</sub><sup>++</sup>), (Cl<sub>2</sub><sup>=</sup>, SO<sub>4</sub><sup>=</sup>), H<sub>2</sub>O at 25°C. had been completed. These ternary and quaternary sub-systems were completed by Campbell and co-workers before work was begun on the quinary system.

The method of graphical representation used was that of Jänecke, the only one possible for a five component system. In this system involving reciprocal salt pairs in solution, to represent the equilibrium at constant temperature and pressure, it was necessary to disregard the water content of the solution and to use a regular triangular prism for the graphical model.

In studies of systems in which the valences of the ions are not all the same, it is customary to make all the ions of the lower valence into radicals so that they have the same value as that of the ion or radical which, singly, has the highest valence. Thus  $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$  are written. This is done for stoichiometric reasons and does not suggest that the ions exist as dimers.

## THEORETICAL CONSIDERATIONS

### 1. THE PHASE RULE

In 1879 J. Willard Gibbs (1) derived the phase rule from thermodynamic principles, and, sometime later Roozeboom (2) demonstrated its practical importance.

The phase rule may be given as:

$$F = C - P + 2$$

where F is the variance, C is the number of components, and P is the number of phases present in the system.

The phase rule is applicable only when equilibrium amongst all the phases present has been attained.

Using constant temperature and pressure conditions, two of the variables have been fixed. Thus, with reservations, a modified phase rule equation may be used. This is:

$$F = C - P$$

It is readily seen that for invariance, where  $F = 0$ , in a ternary system three phases must be present, a solution and two solids. In a quaternary system four phases, solution and three solids yield invariance, while in the five component system five phases, solution in equilibrium with four solid phases, give invariance. Care must be taken in using this modified equation, since it is

possible that at some critical temperature or pressure another phase may appear at the invariant, so that six phases may be in equilibrium.

Jänecke's (3) method of graphical representation has been used in this work. Since every five component system is composed of five quaternary sub-systems, and in turn, every four component system is composed of four ternary sub-systems, the graphical representation of ternary, quaternary, and quinary systems will be shown.

## 2. THREE COMPONENT SYSTEMS

A ternary system consists of water and two salts with one common ion or radical,  $M_1X_1$ ,  $M_2X_1$ ,  $H_2O$ . At

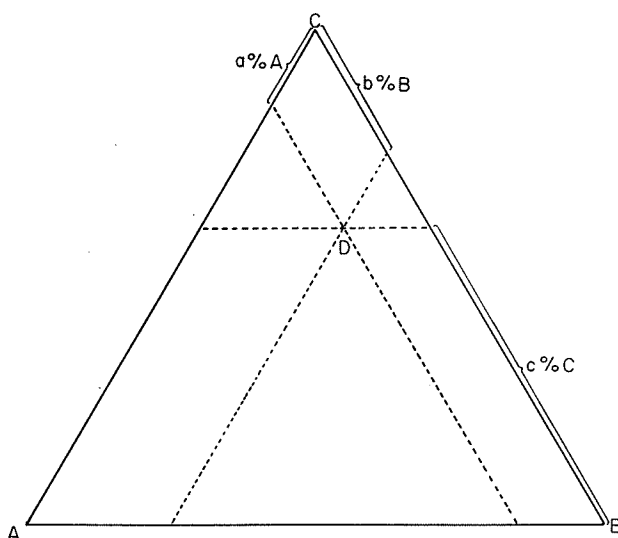


FIGURE 1

A POINT ON A TRIANGULAR GRAPH

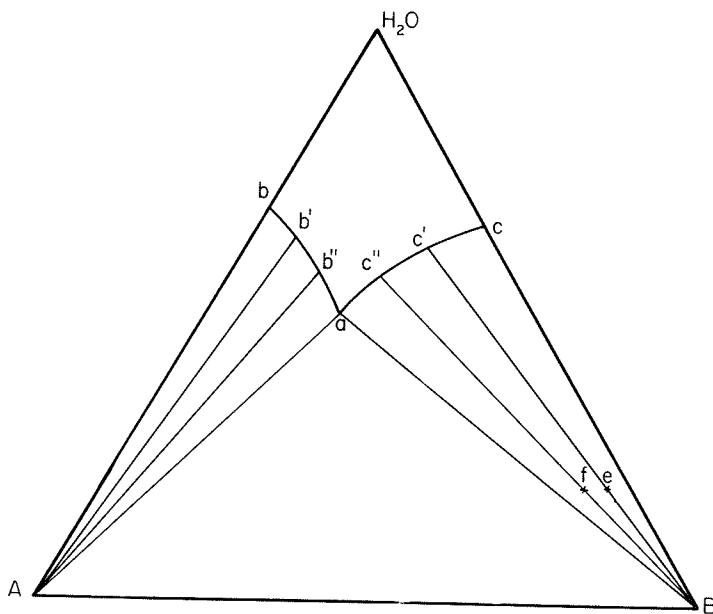


FIGURE 2

## A SIMPLE THREE COMPONENT SYSTEM

constant temperature and pressure a three component system may 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 100, and the components are plotted in weight percent or mole percent of each component. Thus point D in Figure 1 represents a mixture of  $a\%$  A,  $b\%$  B, and  $c\%$  C.

An example of the simplest three component system is shown in Figure 2. The area  $H_2O$ -b-a-c represents unsaturated solution of the salts in water; the line



a-b represents A in equilibrium with saturated solution; a-c gives B in equilibrium with saturated solution; and point a gives both A and B in equilibrium with saturated solution. Point a, where three phases are in equilibrium at a fixed temperature and pressure, is an invariant point, since by the phase rule the variance is zero. The lines  $Ab'$ ,  $Ab''$ ,  $Bc'$ ,  $Bc''$  are called tie lines; they indicate the solid phase in equilibrium with the saturated solutions along the lines ab and ac.

In the analysis of aqueous ternary systems, the method of Schreinemakers (4) is used. For example, a solution is prepared having a composition  $c''$  in equilibrium with an excess of salt B. The greater part of the solution is now separated from the solid phase, and the latter together with the adhering mother liquor is analysed. This composition will be represented by the point e on the line  $Bc'$ , in Figure 2. Another solution, for example  $c''$  in equilibrium with the same salt B, is prepared and analysed, giving a wet residue composition f. Two tie lines  $c'eB$  and  $c''fB$  are drawn and found to intersect at B. For a more complicated system, the method of finding the composition of an unknown double salt consists of obtaining the tie lines, such as  $c'eB$  and  $c''fB$ ; the point of intersection of these lines gives the composition of the double salt, hydrate, or solid solution which is in equilibrium with the solution.

In a system of this type there may be hydrate, solid solution, or double salt formation. Figure 3 shows this system as it would appear if  $M_1X_1$  were hydrated and if a double salt were formed. The double

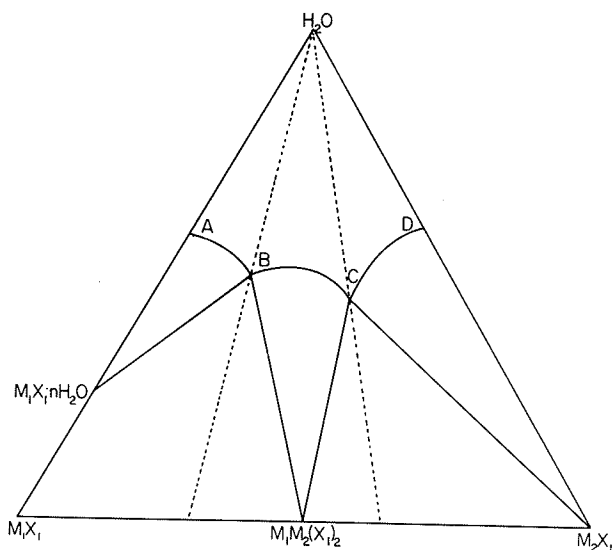


FIGURE 3

TYPICAL THREE COMPONENT SYSTEM SHOWING  
HYDRATE AND COMPOUND

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 invariant point, where  $M_1X_1 \cdot nH_2O$  and  $M_1M_2(X_1)_2$  are the

solid phases; point C gives the solution in equilibrium with  $M_2X_1$  and  $M_1M_2(X_1)_2$ .

If a solid solution is formed with the compound, then the diagram will be as given in Figure 4. B and C are the invariant points, where the solid phases are  $M_1X_1 \cdot nH_2O$  and solid solution at B, and  $M_1X_2$  and solid

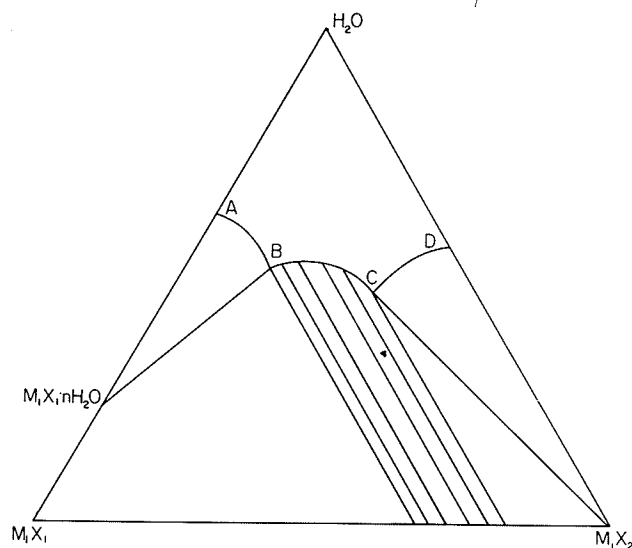


FIGURE 4

TYPICAL THREE COMPONENT SYSTEM SHOWING  
HYDRATE AND SOLID SOLUTION

solution at C. The tie lines obtained from joining the solution composition along BC to that of the wet residues do not meet in a point, indicating solid solution formation rather than the formation of a

compound. If a compound with no solid solution were formed these tie lines would meet at the point representing the composition of the compound; however, solid solution always does occur to some extent, although in many cases it is negligible and it is ignored. Variability in the composition of the solid phase, as in Figure 4, is a criterion of solid solution formation.

In order to represent a quaternary system on a two dimensional graph, it is necessary to represent the ternary systems in one dimension, on a line. The diagram, Figure 3, is projected onto a line by constructing lines from the water apex, through point B and C, onto the base of the triangle. By this method the ratios of  $M_1X_1$  to  $M_2X_1$  at points B and C are maintained.

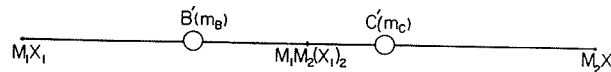


FIGURE 5

FIGURE 3 PROJECTED ON A LINE

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:

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

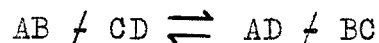
The water contents of points B and C can no longer be represented directly but may be given by  $(m_B)$  and  $(m_C)$ , where  $m$  is the number of moles of water per total mole of salt. Figure 5 shows this system condensed on a line.

### 3. FOUR COMPONENT SYSTEMS

Four component systems of aqueous salts may be divided into two types: reciprocal salt pairs, and three salts with a common ion.

#### A. RECIPROCAL SALT PAIRS

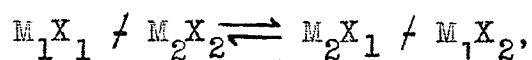
When one pair of salts forms a second pair of salts by double decomposition, then, since one pair is formed from the other, they are known as reciprocal salt pairs.



In this aqueous quaternary system at constant temperature and pressure reciprocal salt pairs are represented on a square by the method of Jänecke (3) and Le Chatelier (5). 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, or vice versa. Water content is given as the number of moles of water per mole of salt at particular points. Isohydres, lines of equal water content, may be constructed.

In a simple reciprocal salt pair the diagram would be represented as in Figure 6. The metathesis is given by:



with  $M_2X_1$  and  $M_1X_2$  being the stable pair. This is evident from diagram, since  $M_1X_1$  and  $M_2X_2$  are unable to

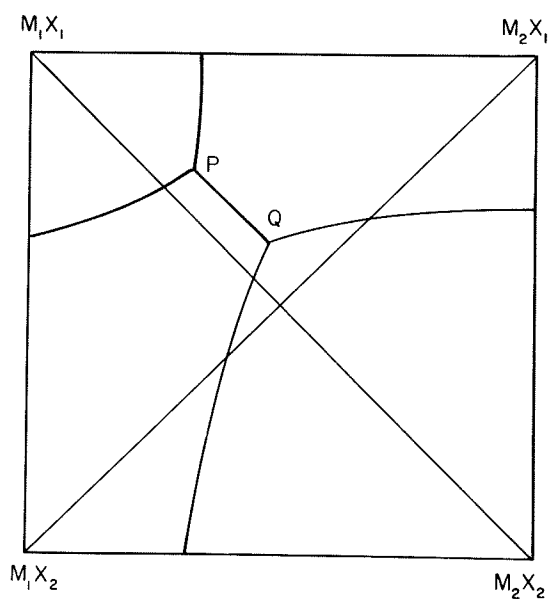


FIGURE 6

A SIMPLE RECIPROCAL SALT PAIR

exist together in contact with their saturated solutions, whereas,  $M_1X_2$  and  $M_2X_1$  are. For invariance in a quaternary system, there must be three salts in equilibrium with solution, at a fixed temperature and pressure. In the system in Figure 6 there are two invariant points P and Q, which may be designated as congruent or incongruent invariants. A congruent invariant point is one which lies within the area bounded by the pure salts present at the invariant point. Thus point P is a congruently saturating solution since it lies within the composition triangle formed by joining  $M_1X_1$ ,  $M_2X_1$ ,

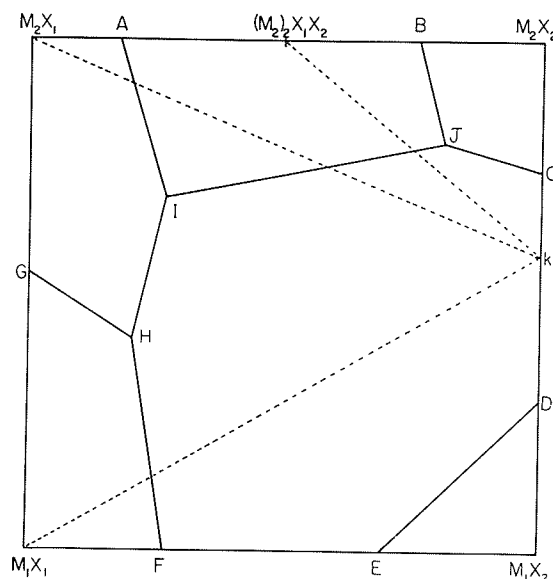
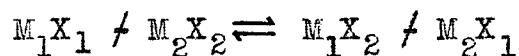


FIGURE 7

RECIPROCAL SALT PAIR EXHIBITING SOLID SOLUTION, HYDRATE, AND COMPOUND

and  $M_1X_2$ , the three solids with which the solution is in equilibrium. Point Q lies outside its composition triangle and is thus incongruent.

Figure 7 illustrates a more complicated reciprocal salt pair exhibiting solid solution, hydrate, and compound formation. This diagram again represents the reciprocal salt pair:



There is a compound  $(M_2)_2X_1X_2$ , hydrate  $M_1X_2 \cdot nH_2O$ , and solid solution  $M_2X_2$  in  $M_1X_2$  in this example. The points A, B, C, D, E, F, and G are all invariant points in the ternary systems that make up the edges of the square.

The solid phases present 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, where there are three solid phases in equilibrium with solution, are invariant points in the quaternary system. 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	$M_2X_1, (M_2)_2X_1X_2$ , solid solution
J	$M_2X_2, (M_2)_2X_1X_2$ , solid solution

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 solid phase. This composition is given by point k in Figure 7. Since point J lies within the triangle k,  $M_2X_2, (M_2)_2X_1X_2$ , it is congruent. Point H is also congruent, whereas point I is not.

#### B. THREE SALTS WITH A COMMON ION

Aqueous quaternary systems consisting of three salts with a common ion are represented on an equilateral triangle. Each apex shows a pure salt, with water content indicated by isohydrates. In plotting a point the common ion is ignored, and the mole fraction of each of the remaining ions is plotted as previously described for a three component system. The existence of compounds, hydrates, and solid solutions, forming congruent and incongruent invariant points is the same as shown for reciprocal salt pairs.

#### 4. FIVE COMPONENT SYSTEMS

Aqueous five component systems may be of at least two kinds: those comprising water and four salts with a common ion, and those involving reciprocal salt pairs. Aqueous quinary salt systems with metathesis, as under study here, may consist of three cations and two anions, or two cations and three anions. Even at constant temperature and pressure, it is necessary that five quantities, water and four salts, must be stated in defining the composition of the solutions. Of necessity the water content must be given as planes of equal water content and only the concentration of the components in the solution may be plotted.

This quinary system at constant temperature and pressure may be represented in space by a regular triangular prism, whose base is an equilateral triangle, and the three sides of which are squares. The salts are arranged so that all the salts on each of the triangular ends have a common ion, and each of the three square faces represents a set of reciprocal salt pairs. In this way each of the nine edges represent two salts with a common ion. Each of the nine edges is a three component system, and each of the five surfaces represents a four component system.

From the invariant points in the quaternary systems on the surfaces of the model, other lines proceed inward and meet at various quinary invariant points. Ordinarily only four such lines meet at an invariant point, since by the phase rule only four salts may be in equilibrium with solution in a five component system at constant temperature and pressure. It is possible, however, that at some critical temperature or pressure five salts could be in equilibrium with solution at an invariant point. The whole model is divided into elements of volume by these intersecting lines, these volumes denoting liquid saturated with one salt. The surfaces separating adjacent volumes indicate two salts in equilibrium with solution; the edges of the volumes, that is the interior lines, denote solution saturated with three salts.

Invariant points may also be designated as congruently saturating or incongruently saturating. A congruent invariant point is one which is enclosed in the volume bounded by the pure salts present at the invariant point.

In plotting points in this five component system the relative mole fractions of dissolved cations and anions must be calculated separately. As indicated in the diagram, Figure 8, the relative mole percent  $A\%$ ,  $A$ ,

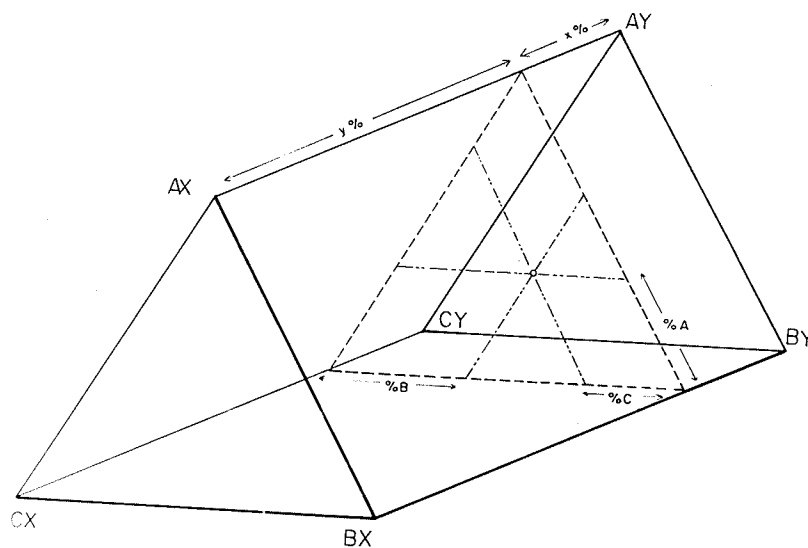


FIGURE 8  
 REPRESENTATION OF A FIVE COMPONENT  
 SYSTEM

$B\%$  B, and  $C\%$  C denotes the points position on an equilateral plane in the prism and the relative mole percent  $X\%$  X and  $Y\%$  Y gives the depth of the plane in the prism.

## LITERATURE REVIEW

### 1. THE TERNARY SYSTEMS

#### A. The System-Sodium Chloride-Sodium Sulphate-Water at 25°C.

This system was first investigated at 25°C. by Meyerhoffer and Saunders (6) in 1899, as part of the reciprocal salt pair, sodium chloride-potassium sulphate-water. This ternary system was also investigated by Seidell (7) in 1902, at several temperatures besides 25°C., but his work was not very exact. The composition of the invariant points were reported by Schreinemakers (8) in 1911. Blasdale (9), in 1918, and Takegami (10),

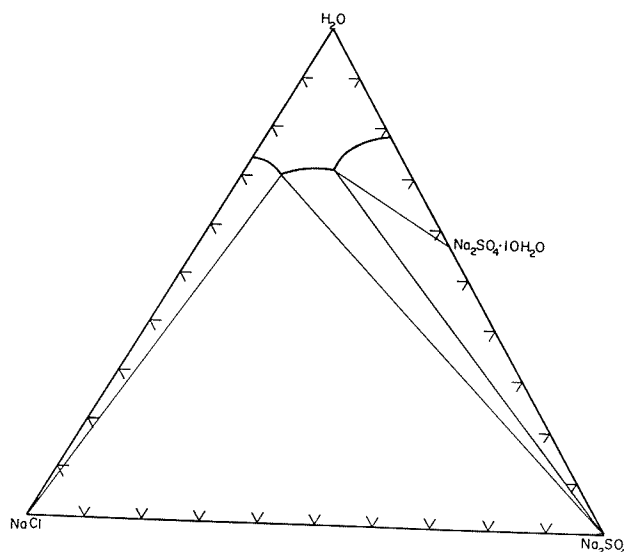


FIGURE 9

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

in 1921, also investigated this system. Takegami's results differ only slightly from the data of Blasdale. Figure 9 shows the equilibrium diagram drawn from Takegami's data.

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

Smits, Elgersma, and Hardenburg's (11) work in 1924 indicated the strong "salting out" effect of LiCl on NaCl. The solution at its invariant point has very little sodium chloride, as the diagram, Figure 10, shows.

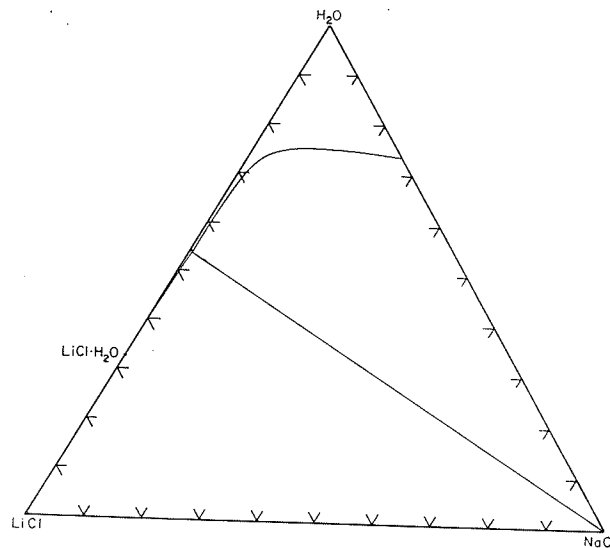


FIGURE 10

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

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

The first study of this system at 25°C. was carried out by Druzhinin and Yanko (12) in 1954, although Schreinemakers and Kayser (13) completed the 30°C. isotherm in 1918. A diagram of the results of Druzhinin and Yanko appears in Figure 11.

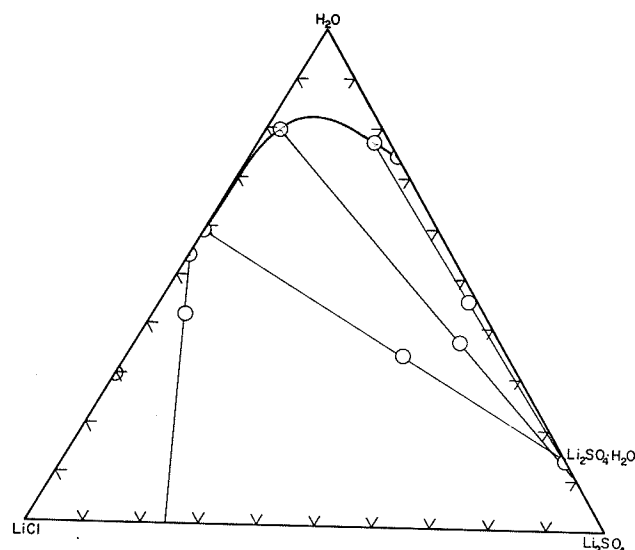


FIGURE 11

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 1952 Cavalca and Nardelli (14) claimed the existence of the double salt  $\text{Na}_2\text{Li}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at 27°C.

This result was contradicted by the later work of Campbell and Kartzmark (15) whose investigation at 25°C. showed extensive solid solution of lithium sulphate in sodium sulphate, rather than compound formation. They have also shown that the double salt does exist at higher temperatures, but that it breaks down to the simple sulphates at 29.5°C. Figure 12 shows the system according to Campbell and Kartzmark.

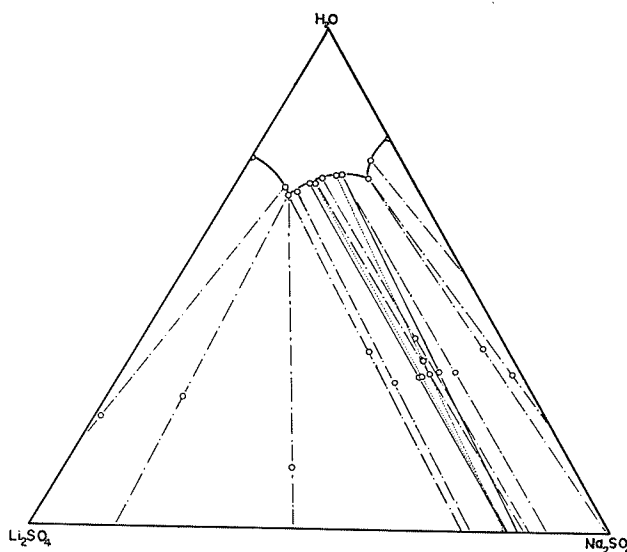


FIGURE 12

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



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

The invariant point of this ternary system was investigated by Meyerhoffer and Saunders (6) and Blasdale (9), as part of the reciprocal salt pair  $(K_2^{++}, Na_2^{++}) (Cl_2^-, SO_4^-)$ , water at 25°C. It has also been investigated by Ya. Anosov and Byzova (16), at a series of temperatures. The equilibrium diagram from Blasdale's data appears as Figure 13.

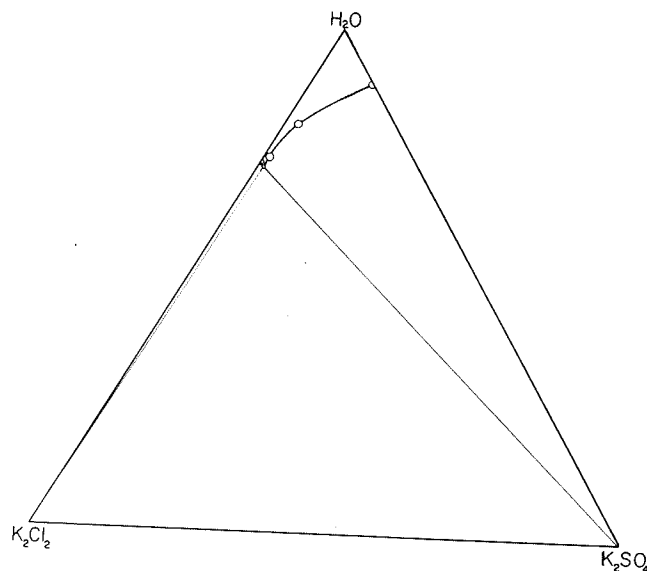


Figure 13

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

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

This system was investigated by Campbell and Kartzmark (17) in 1956. Their diagram, Figure 14, shows the high "salting out" effect of lithium chloride on the potassium salt, in analogy to the LiCl-NaCl-H<sub>2</sub>O system.

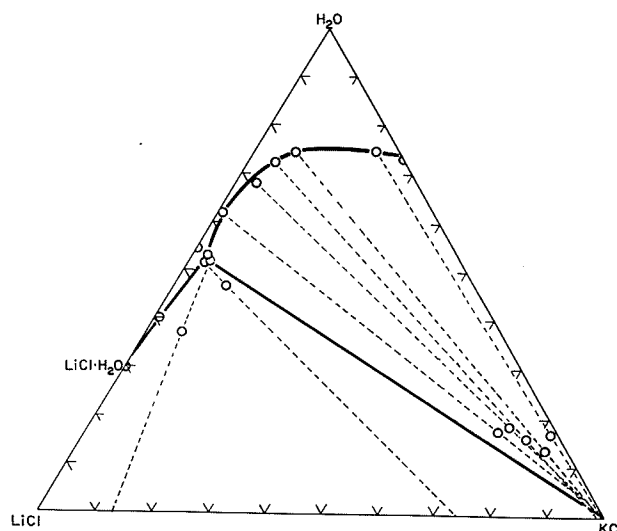


FIGURE 14

THE SYSTEM: LiCl - KCl - 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 Druzhinin and Yanko (18) in 1955. They claimed that LiKSO<sub>4</sub> is formed

only as the limiting case of a series of solid solutions. This system was also studied by Campbell and Kartzmark (15), and their work shows that the double salt exists between  $\text{Li}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  on one side of the diagram, and  $\text{K}_2\text{SO}_4$  on the other. Figure 15 gives the equilibrium diagram as they determined it. In order to compare these results, the data according to Druzhinin and Yanko are given in Figure 16.

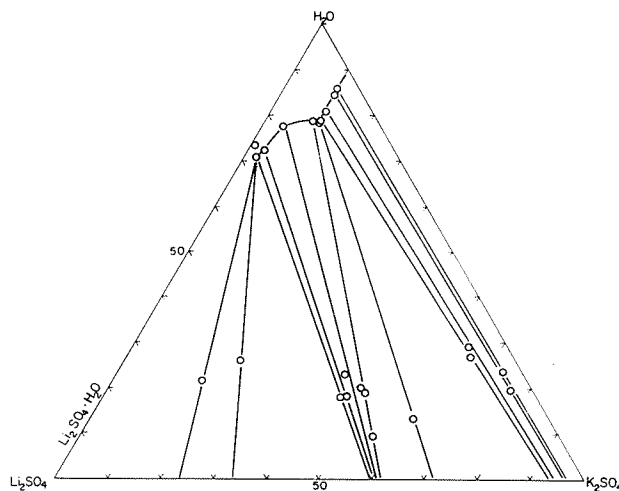


FIGURE 15

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

by Campbell and Kartzmark

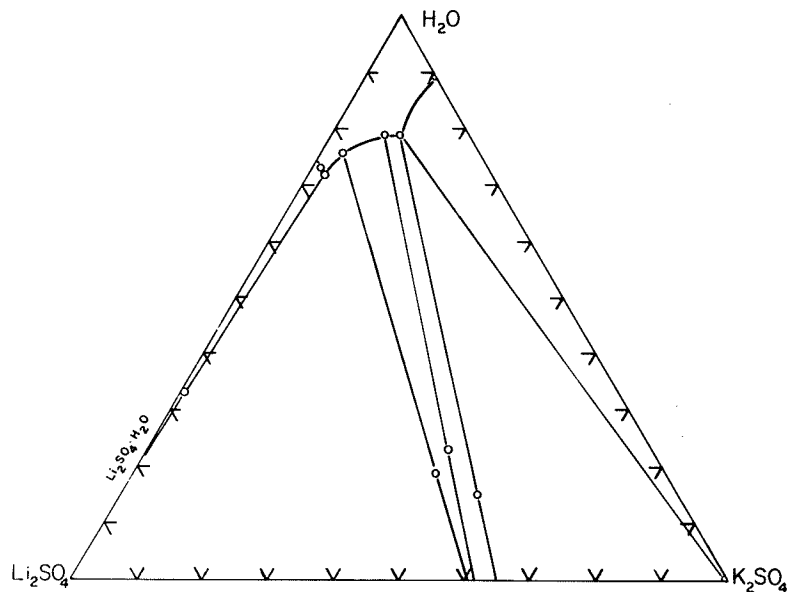


FIGURE 16

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

by Druzhinin and Yanko

H. The System-Sodium Chloride-Potassium Chloride-Water at  $25^\circ\text{C}$

This simple system was completed by Precht and Wittjen (19) in 1891, and repeated by later workers, including Meyerhoffer (6), and Blasdale (9), when investigating ternary and quaternary systems. The equilibrium diagram, Figure 17, was constructed from data taken from Blasdale.

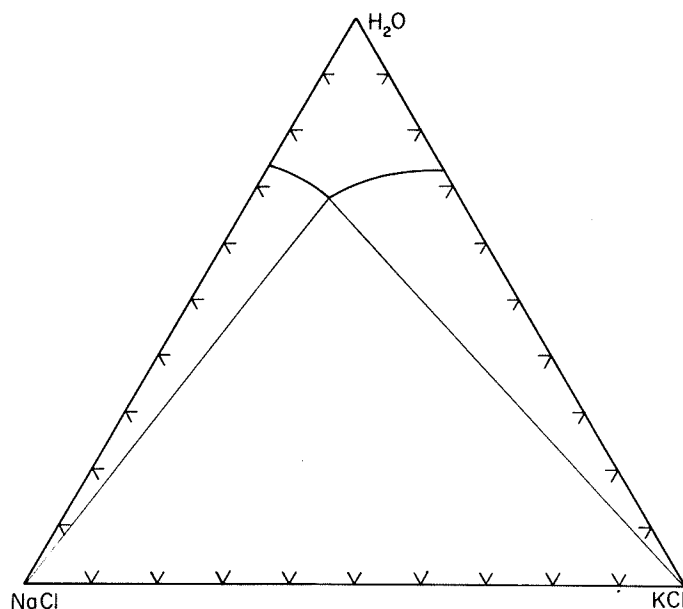


FIGURE 17

THE SYSTEM: NaCl - KCl - H<sub>2</sub>O at 25°C

I. The System-Sodium Sulphate-Potassium Sulphate-Water at 25°C.

This system is complicated by the existence of the double salt glaserite, the correct composition of which was first reported by Penny (20) in 1855. Several others, including Meyerhoffer (6) and Hamid (21) have repeated the work on this system. Hamid's results appear in Figure 18.

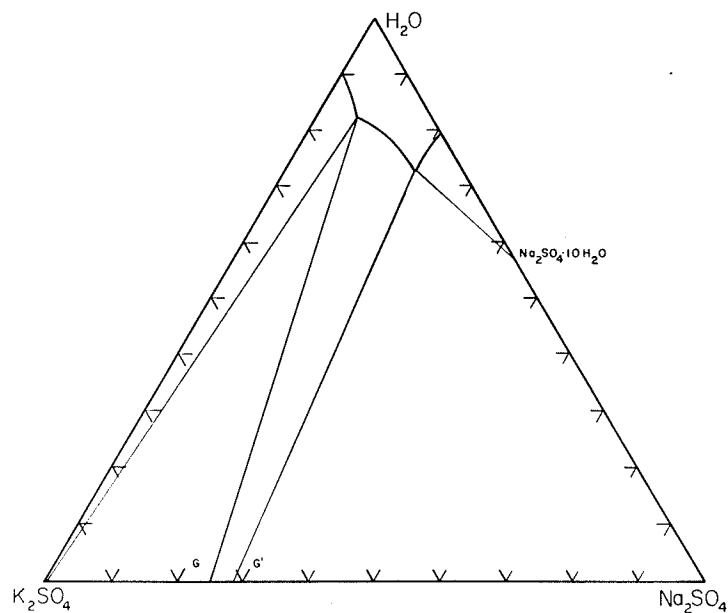


FIGURE 18

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

The point G represents the composition of pure glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ . The point G' represents the maximum amount of sodium sulphate which glaserite can dissolve at  $25^\circ\text{C}$ ., 3.3% according to Hamid (21).

## 2. THE QUATERNARY SYSTEMS

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

This system was completed by Campbell, Kartzmark and Lovering (22), in 1958, the diagram of which is reproduced in Figure 19. The stable pair of solid phases, that is, the pair of salts that can exist in contact with each other and with solution, consists of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KCl}$ . Three invariant points were found. At the invariant point A in Figure 19, the solid phases are

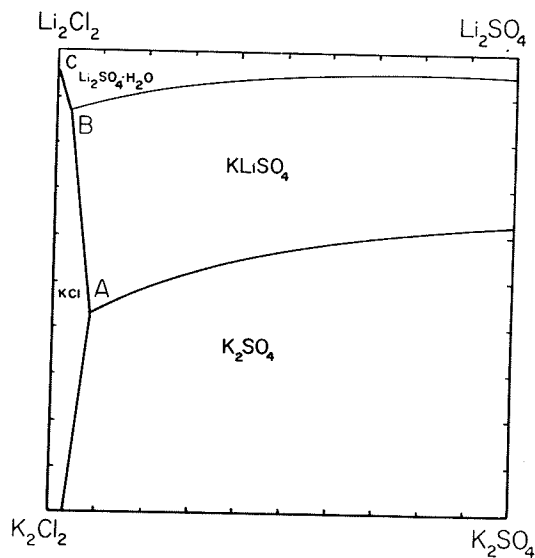


FIGURE 19

THE SYSTEM: Lithium, Potassium, Chloride,  
Sulphate, Water at 25°C.

$K_2SO_4$ ,  $KCl$ , and the double salt  $KLiSO_4$ . Since the invariant point does not fall within the composition triangle whose angular points represent the three solid phases, it is incongruent. The invariant point B, where  $Li_2SO_4 \cdot H_2O$ ,  $KCl$ , and  $KLiSO_4$  are in equilibrium with solution, is also incongruent. Point C, where the solid phases are  $LiCl \cdot H_2O$ ,  $Li_2SO_4 \cdot H_2O$ , and  $KCl$ , is congruent.

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

This quaternary system has just recently been completed by Campbell, Kartzmark and Lovering (22), the diagram of which is given as Figure 20. In this equilibrium diagram the co-existent salts are sodium chloride and lithium sulphate in solution. Since no double salt has been found in this system at 25°C., there are only two invariant points, one congruent, the other incongruent. At the incongruent invariant, point A in Figure 20, the solid phases in equilibrium with solution are  $Li_2SO_4 \cdot H_2O$ ,  $NaCl$ , and a solid solution of lithium sulphate and sodium sulphate. At point B, the congruent invariant point, the solid phases are  $LiCl \cdot H_2O$ ,  $Li_2SO_4 \cdot H_2O$ , and  $NaCl$ ; the solution is very rich in lithium chloride. From the ternary systems involving  $LiCl$ , it is known that the  $LiCl$  field in the quaternary must be extremely narrow; it cannot be investigated experimentally or expressed graphically to scale.



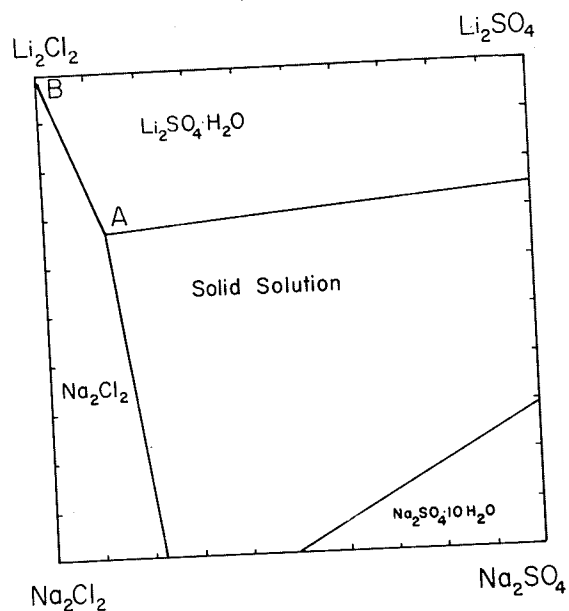


FIGURE 20

THE SYSTEM: Lithium, Sodium, Chloride,  
Sulphate, Water at 25°C.

During the experimental work on this system the possibility arose that an area of the double salt  $\text{NaLiSO}_4$  could exist within the body of the diagram, as a result of the transition point of 29.6°C. being lowered by the presence of chloride ions. Attempts to find it, however, were fruitless.

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

This quaternary system was first studied by Meyerhoffer and Saunders (6) at a series of temperatures, which included the isotherm at 25°C. This work was repeated by D'Ans (23), in 1915, and Blasdale (9), in 1918. Blasdale's results, almost identical to those of Meyerhoffer, are reproduced in Figure 21.

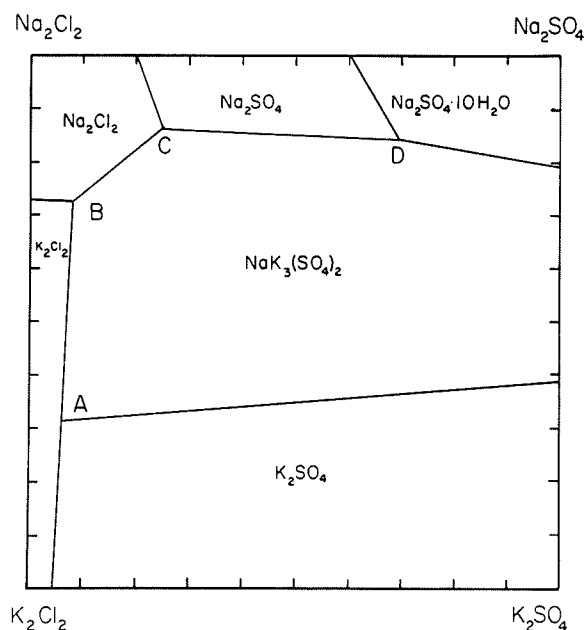


FIGURE 21

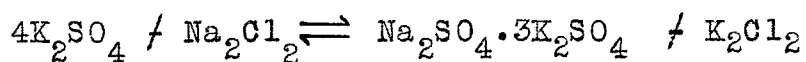
THE SYSTEM: Sodium, Potassium, Chloride  
Sulphate, Water at 25°C.

In this system there are four invariant points, the salts in equilibrium with solution being:

<u>Point</u>	<u>Solid Phases</u>
A	KCl, $K_2SO_4$ , $K_3Na(SO_4)_2$
B	KCl, NaCl, $K_3Na(SO_4)_2$
C	NaCl, $Na_2SO_4$ , $K_3Na(SO_4)_2$
D	$Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$ , $K_3Na(SO_4)_2$

The invariant point B and C are congruently saturating, while point A and D are incongruently saturating.

Salts which do not occupy adjacent areas on the diagram cannot exist in equilibrium with themselves and their saturated solutions. Thus, if saturated solutions of potassium sulphate and sodium chloride are brought together, the following reaction, or a similar one depending on the relative amounts of each salt present, will occur;



Likewise neither  $Na_2SO_4$  and KCl, nor  $K_2SO_4$  and  $Na_2SO_4$  will exist in equilibrium with their saturated solutions.

D. The System-Lithium, Sodium, Potassium, Chloride, Water at 25°C.

This quaternary system, as completed by Campbell and Kartzmark (24), is represented in the diagram, Figure 22. The system is of the simple type with only

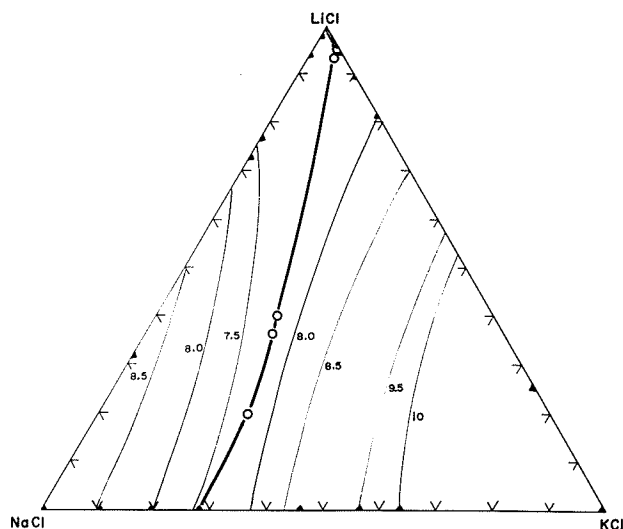


FIGURE 22  
 THE SYSTEM: Lithium, Sodium, Potassium,  
 Chloride, Water at 25°C.

one invariant point,  $\text{LiCl} \cdot \text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{NaCl}$  in equilibrium with solution. The highly hydrated lithium ion acts very powerfully in displacing other salts from solution, so that the invariant contains very little salt other than lithium chloride. Thus this invariant point is near the  $\text{LiCl}$  corner and can only be represented on an enlarged scale, as shown in Figure 23.

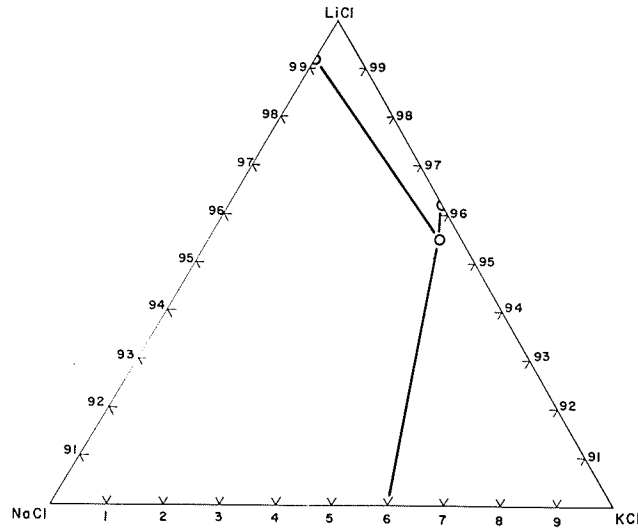


FIGURE 23

## ENLARGEMENT OF THE QUATERNARY AREA

E. The System-Lithium, Sodium, Potassium, Sulphate, Water at 25<sup>o</sup>C.

The equilibrium diagram of Campbell and Kartzmark (25), who completed the 25<sup>o</sup>C. isotherm in 1959, appears as Figure 24. The double salts which were found to occur are  $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$  and  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ; solid solution of lithium and sodium sulphates was also found. The possibility exists that a ternary salt containing all three metallic ions could be present, but was not found to exist at 25<sup>o</sup>C.

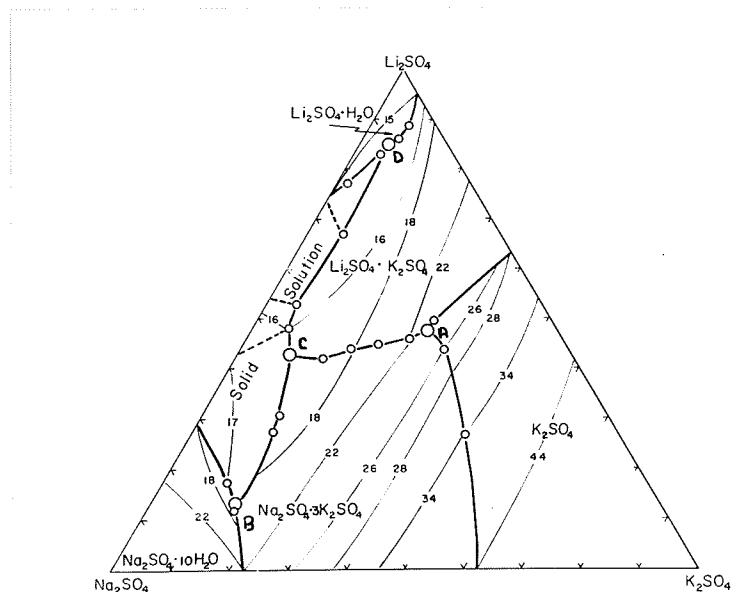


FIGURE 24

THE SYSTEM: Lithium, Sodium, Potassium,  
Sulphate, Water at 25°C.

There are four invariant points, where the salts  
in equilibrium with solution are:

<u>Point</u>	<u>Solid Phase</u>
A	$K_2SO_4$ , $KLiSO_4$ , $K_3Na(SO_4)_2$
B	$Na_2SO_4 \cdot 10H_2O$ , $K_3Na(SO_4)_2$ , $Na_2SO_4$
C	$KLiSO_4$ , $K_3Na(SO_4)_2$ , $Na_2SO_4$
D	$Li_2SO_4 \cdot H_2O$ , $KLiSO_4$ , solid solution

Invariants A and C are incongruent, and B and D are  
congruent points.

### 3. THE QUINARY SYSTEM

No mention of the aqueous five component system:  
 $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . can be  
found in the literature.

## EXPERIMENTAL METHOD

### 1. PURITY OF MATERIALS

All the chemicals were used as supplied by the manufacturer without further purification, since very slight traces of impurity are without effect on studies of this kind. With only one exception, analysed materials were used, as listed in Table I.

TABLE I  
THE REAGENTS

Salt	Supplier	Grade
LiCl	Fisher Scientific Co.	Certified Reagent
Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	Fisher Scientific Co.	Certified Reagent
NaCl	Fisher Scientific Co.	Certified Reagent
Na <sub>2</sub> SO <sub>4</sub>	Fisher Scientific Co.	Certified Reagent
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	British Drug Houses Ltd.	Analar
KCl	Mallinckrodt Chemical Works	Analytical Reagent
K <sub>2</sub> SO <sub>4</sub>	Mallinckrodt Chemical Works	Low Nitrogen

The silver nitrate used in the gravimetric determination of chloride was the analysed material as supplied by Mallinckrodt Chemical Works.



## 2. GENERAL METHOD

After the five quaternary sub-systems had been completed and represented as the surfaces of the equilateral prism, the procedure to investigate the quinary system was to trace the univariant lines from the quaternary invariant points to invariant points in the five component system. This is accomplished by the addition of ions not participating in the quinary equilibrium, to bring it into the body of the prism. As an example, consider the system as given in Figure 25,

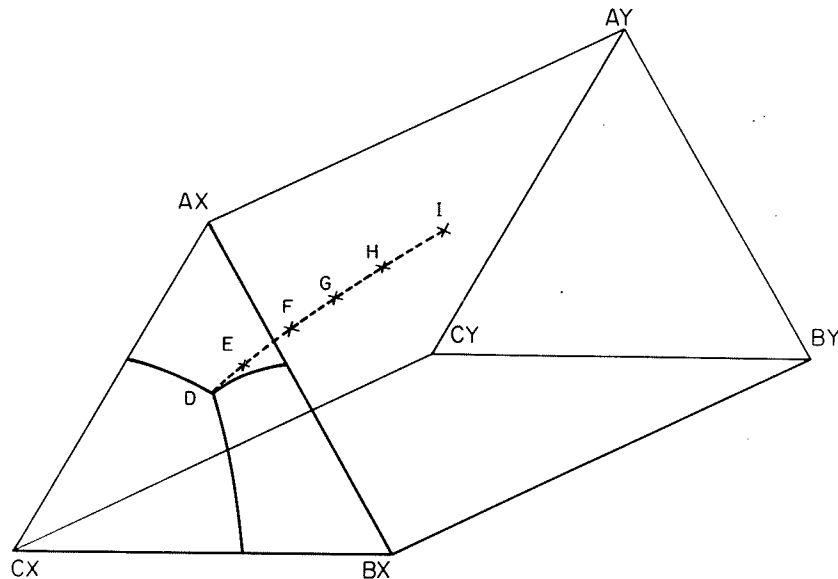


FIGURE 25

OBTAINING AN INVARIANT POINT IN A QUINARY SYSTEM

where quaternary invariant point D consists of AX, BX, and CX in equilibrium with solution. An equilibrium solution with the solid phases present at D is prepared, and a small amount of AY, BY, and CY is added. Analysis of the liquid phase indicated the point E, while analysis of the solid phase showed that only AX, BX, CX are the solids present; no AY, BY, or CY remained in the solid phase. In a second attempt, larger amounts of AY, BY, and CY are added, resulting in point F by analysis; this process is continued along to G, H, and finally to I, the quinary invariant point. Here, for invariance in a five component system, another phase must be present, as indicated by the appearance of one of AY, BY, or CY in the analysis of the solid phase.

In a similar manner all the quaternary invariant points are traced to a quinary invariant. Here, it should be remembered, for invariance there would be four salts in equilibrium with solution, so generally quinary invariant points must be the intersection of four lines. Approaching an invariant point from more than one direction gave excellent confirmation of the position of the invariant point.

In order to trace a line to its invariant point,

it was found convenient to suspend a series of the determined points, plotted on their individual planes, in the body of the diagram at their respective distances from the ends of the prism. By this procedure the direction of the line in space could be visualized. A line parallel or nearly parallel to the anion bases would naturally require only one plane.

### 3. APPARATUS

In order to attain equilibrium, the salts and water were placed in a solubility cell and stirred for twenty-four hours in a constant temperature bath regulated at  $25.00^{\circ}\pm .05^{\circ}\text{C}$ . Using the first type of cell, the liquid phase was removed by suction through a sintered glass disk built into the bottom of the cell, as shown in Figure 26 a. 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 this plug. This method of separating the phases was not entirely satisfactory, since it frequently left the solid phase very wet. To correct this a second type of cell without the sintered disk was made, as illustrated in Figure 26 b. The salts and solution were simply emptied quickly into a large sintered glass funnel to separate solid and liquid phases by suction.

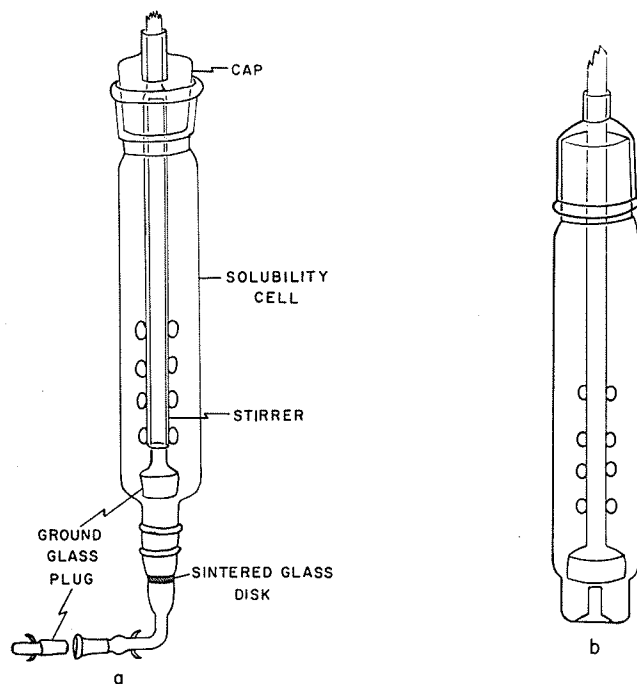


FIGURE 26

## SOLUBILITY CELLS

- a) WITH SINTERED GLASS DISK  
 b) WITHOUT SINTERED GLASS DISK

The flame photometer used was of a standard type, Perkin-Elmer, model 146.

The 25°C. thermostat was a conventional water bath regulated by a thyatron tube relay circuit. The temperature of the bath was set, and checked periodically,



by a platinum resistance thermometer. Temperature control was better than  $\pm 0.05^{\circ}\text{C}$ .

#### 4. CHEMICAL ANALYSIS

After the separation of the equilibrium mixture, both the solid phase and the liquid phase were dried in platinum crucibles over night; to ensure the complete evaporation of water, the liquid phase was fused. Both weighed salts were dissolved in solutions of known weight, and stored in polyethylene bottles until analysed.

The percentage of chloride was determined gravimetrically as  $\text{AgCl}$  according to the procedure given by Kolthoff and Sandell (26). Since the estimation of sulphate as barium sulphate has been shown to be unreliable in the presence of alkali metal ions (cf Reference 15), it was determined by differences for the purpose of calculation. The use of spectrophotometry methods for sulphate, (27,28) using barium chloroanilate, was contemplated for solutions of low concentration sulphate; it was found to be adequate but unnecessary in the experiments.

Analysis of the phases for cations was made by use of the flame photometer. The flame photometer is an instrument designed for the rapid determination of the alkali and alkaline earth metals in solution. It measures quantitatively the light emitted by the various

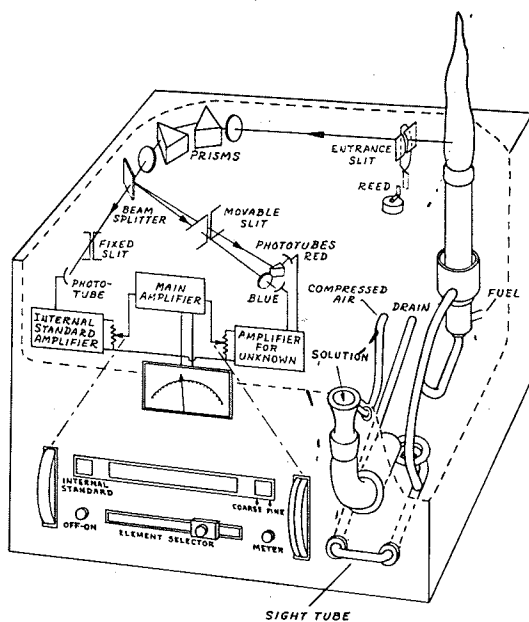


FIGURE 27

## PERKIN-ELMER FLAME PHOTOMETER

metals when atomized from solution, fed to a propane burner, and excited to spectral emission in a flame. Because the intensity of light emitted by each element depends upon the concentration of atoms of the element in the flame at a given instant, a measure of the light intensity produced makes possible the quantitative determination of that element.

In Figure 27, a diagram of the Perkin-Elmer model 146 flame photometer, the liquid samples are introduced into the atomizer where they are blown into the atomizer chamber by a stream of compressed air, and thence into the base of the meker type burner. The atomizer is designed to retain the large liquid particles and to pass the fine liquid mist to the burner, causing spectral emission by the following rapid steps:

1. The water evaporates, leaving minute particles of salt.
2. At the elevated temperature of the flame, decomposition or chemical reaction may take place.
3. The salts or their decomposition products vaporize, and may also dissociate into constituent atoms or radicals.
4. The vapours of the metal atoms are then excited by the thermal energy of the flame.

The process of excitation results in the raising of an electron to a higher energy level followed by the loss of a discrete amount of energy in the form of radiation energy, as the excited electron returns to a lower state.

The entrance slit allows a beam of light from the flame to fall upon a monochromator, where it is dispersed

into a spectrum by a prism. Another slit is used to limit the bandwidth of radiation passed on to the phototube detectors. The phototube converts the selected wavelength to an electric current, which is amplified and indicated on the meter.

Standard solutions for lithium, sodium, and potassium were made from fused salts of these metals in concentrations of 10, 20, 40, 60, 80, and 100 parts per million of the alkali metal. These were used to draw a calibration curve from which the experimental solutions, diluted to the proper range, could be found graphically. The direct intensity method was used; this assumed that the atomizer delivery was constant, the portion of the sample nebulized remained the same, and the flame characteristics did not vary for both the standard and experimental solutions. Since these assumptions are not strictly valid, accuracy of only two percent can be obtained. Relative interferences among the three alkali metals, as well as the interferences due to chloride and sulphate in the solution are negligible.

##### 5. IDENTIFICATION OF THE SOLID PHASES

Ideally one should have an unequivocal means of identifying each solid phase, but the usual methods of X-ray powder photographs, or measurement of the optical



properties of the crystals cannot be applied here because of the necessity of keeping the solid phases wet with mother liquor at all times. It is by no means unlikely that a phase change could occur upon drying the solid phases, even at room temperature. Furthermore, by coincidence, the strong X-ray reflections of NaCl and  $\text{Na}_2\text{SO}_4$  are very close together, making this method less sensitive than usual.

As a result, determination of the solid phases rested only on the identification of the new phase which appeared at each invariant point. When a new ion suddenly appeared in the solid phase, there was usually no question as to the nature of the new phase. Also, the intersection of two solubility lines left little doubt as to the nature of the four phases present at the invariant point.

#### 6. EXAMPLE OF A CALCULATION

In a typical experiment, after separating the solid and liquid phases and evaporating both to dryness, it was found that 9.2029 gms. of salt were associated with 21.105 gms. of water from the liquid phase; the adhering mother liquor on the solid phase was composed of 19.0% liquid.

A. The Solid Phase

By analysis of the dried solid phase, the following data were found experimentally:

<u>Ion</u>	<u>Weight Percentages</u>
$\text{Li}_2^{++}$	3.51%
$\text{Na}_2^{++}$	15.34%
$\text{K}_2^{++}$	11.79%
$\text{Cl}_2^-$	3.23%

The sulphate calculated by difference was found to be 66.13%.

These are converted to the number of moles by the division of the weight percentage by the formula weight of the ion.

$$\begin{aligned}
 \text{Moles of } \text{Li}_2^{++} &= \frac{\text{Wt. \% Li}_2^{++}}{\text{Mol Wt. Li}_2^{++}} = \frac{3.51}{13.88} = 0.2529 \\
 \text{Moles of } \text{Na}_2^{++} &= \frac{\text{Wt. \% Na}_2^{++}}{\text{Mol Wt. Na}_2^{++}} = \frac{15.34}{45.994} = 0.3335 \\
 \text{Moles of } \text{K}_2^{++} &= \frac{\text{Wt. \% K}_2^{++}}{\text{Mol Wt. K}_2^{++}} = \frac{11.79}{78.20} = 0.1508 \\
 \text{Moles of } \text{Cl}_2^- &= \frac{\text{Wt. \% Cl}_2^-}{\text{Mol Wt. Cl}_2^-} = \frac{3.23}{70.91} = 0.0456 \\
 \text{Moles of } \text{SO}_4^- &= \frac{\text{Wt. \% SO}_4^-}{\text{Mol Wt. SO}_4^-} = \frac{66.13}{96.06} = 0.6884 \\
 & \hspace{15em} \text{Total Moles} \hspace{10em} \underline{\hspace{2em}} \hspace{2em} 1.4712
 \end{aligned}$$

These moles of the constituents are converted to mole percentages:

$$\begin{aligned} \text{Mole \% Li}_2^{++} &= \frac{\text{moles}}{\text{total no. moles}} \times 100 = \frac{.2529}{1.4712} \times 100 = 17.2 \% \\ \text{Mole \% Na}_2^{++} &= \frac{.3335 \times 100}{1.4712} = 22.7\% \\ \text{Mole \% K}_2^{++} &= \frac{.1508 \times 100}{1.4712} = 10.2\% \\ \text{Mole \% Cl}_2^{-} &= \frac{.0456 \times 100}{1.4712} = 3.1\% \\ \text{Mole \% SO}_4^{-} &= \frac{.6884 \times 100}{1.4712} = 46.8\% \end{aligned}$$

Total mole percent cations 50.1%, anions 49.9%. Since the mole percent cation/ anion should be 50/50, this ratio as found experimentally was an indication of the accuracy of the determination.

This solid phase was composed of the sulphates of lithium, sodium, and potassium. The 3.10 mole percent chloride was not a constituent of the solid phase, but was due to the 19% adhering mother liquor.

#### B. Liquid Phase

In a similar manner the liquid phase was determined and calculated:

<u>Ion</u>	<u>Weight %</u>	<u>No. Moles</u>	<u>Mole %</u>
$\text{Li}_2^{++}$	2.28%	0.1643	10.2%
$\text{Na}_2^{++}$	24.60%	0.5349	33.4%
$\text{K}_2^{++}$	8.67%	0.1109	6.9%
$\text{Cl}_2^-$	33.09%	0.4666	29.1%
$\text{SO}_4^-$	<u>31.36%</u>	<u>0.3265</u>	<u>20.4%</u>
	100.00%	1.6032	100.0%

Mole percent cations 50.5%, anions 49.5%

In order to plot the position of the liquid phase in the three dimensional diagram, these mole percentages were converted to relative mole percent cations and relative mole percent anions.

<u>Ion</u>	<u>No. of Moles</u>	<u>Relative Mole Percent</u>
$\text{Li}_2^{++}$	0.1643	$\frac{\text{No. moles Li}_2^{++} \times 100}{\text{total moles cations}}$ $= \frac{.1643 \times 100}{.8101} = 20.3\%$
$\text{Na}_2^{++}$	0.5349	$\frac{.5349 \times 100}{.8101} = 66.0\%$
$\text{K}_2^{++}$	<u>0.1109</u>	$\frac{.1109 \times 100}{.8101} = 13.7\%$
	0.8101	100.0%
<u>Ion</u>	<u>No. of Moles</u>	<u>Relative Mole Percent</u>
$\text{Cl}_2^-$	0.4666	$\frac{\text{No. Moles Cl}_2^- \times 100}{\text{total moles anions}}$ $= \frac{.4666 \times 100}{.7931} = 58.8\%$
$\text{SO}_4^-$	<u>0.3265</u>	$\frac{.3265 \times 100}{.7931} = 41.2\%$
	0.7931	100.0%

The relative mole percentages of the cations indicated the position on an equilateral triangle in the prism, the relative mole percentages of the anions gave the depth of the plane in the prism. (cf Figure 8)

To find  $m$ , the number of moles of water per total "mole" of salt, it was necessary to know the amount of salt associated with a certain weight of water. In the example which was under consideration, it was stated that, for the liquid phase, 9.2029 gms. of salt were dissolved in 21.105 gms. of water.

$$\text{No. of Moles of Water} = \frac{21.105}{18.016} = 1.172$$

Since 100 weight percent was converted to 1.6032 moles, 100 gms. of salt must represent 1.6032/2 "moles of salt". Therefore, the number of moles of salt in 9.2029 gms.:

$$\frac{9.2029 \times 1.6032}{100 \times 2} = 0.07377$$

Therefore the number of moles of water per "mole" of salt is:

$$m = \frac{\text{no. moles water}}{\text{no. moles salt}} = \frac{1.172}{0.07377} = 15.9$$

## EXPERIMENTAL RESULTS

The experimental results are collected in Tables II, III, and IV, pages 52 to 57, which list the compositions of the liquid phases and wet residues of the salt system under study. Table IV gives the mole percent of each of  $\text{Li}_2^{++}$ ,  $\text{Na}_2^{++}$ ,  $\text{K}_2^{++}$ ,  $\text{Cl}_2^-$ , and  $\text{SO}_4^-$  in both the solid phase and the liquid phase, as well as  $m$ , the number of moles of water per "mole" of salt, and the nature of the solid phase.

Photographs of the solid model appear in Figure 28, and a series of cross sections at constant anion composition are shown in Figure 30 - 33.

TABLE II

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

Point No.	Wt. % $\text{Li}_2^{++}$	Wt. % $\text{Na}_2^{++}$	Wt. % $\text{K}_2^{++}$	Wt. % $\text{Cl}_2^-$	Wt. % $\text{SO}_4^-$
1	0.86	6.09	32.77	0.61	59.67
2	4.96	4.70	20.28	11.42	58.34
3	3.06	3.06	29.13	4.42	60.33
4	2.81	0.14	38.61	22.09	36.35
5	3.67	2.34	28.93	3.34	62.72
6	6.52	8.46	14.02	15.85	55.15
7	0.21	6.03	39.12	10.98	43.56
8	0.18	4.61	43.85	21.20	30.16
9	0.17	6.80	40.11	12.92	40.00
10	1.17	1.16	46.64	35.71	14.32
11	.09	25.53	17.99	43.62	12.77
12	2.11	23.39	12.05	37.79	24.66
13	2.51	21.51	11.48	38.66	25.84
14	4.49	7.05	23.45	29.65	35.36
15	2.40	22.88	12.53	37.53	24.66
16	2.15	23.04	11.45	41.59	21.77
17	5.98	8.47	13.79	28.48	43.43
18	1.55	25.42	11.47	44.36	17.20
19	2.14	25.83	10.93	37.48	23.62
20	2.08	0.58	39.58	26.09	31.67
21	4.94	0.59	27.63	3.36	63.48
22	3.93	5.30	24.14	33.99	33.64
23	6.39	0.14	26.57	27.14	39.76
24	5.61	5.41	22.00	31.46	35.52
25	4.66	14.47	12.42	38.66	29.79
26	5.01	7.37	21.71	33.35	32.56
27	4.75	14.75	13.20	32.75	34.55
28	8.93	4.92	7.21	3.05	75.89
29	7.41	6.67	10.45	7.25	68.22
30	7.22	7.88	11.46	13.95	59.49
31	7.64	7.82	10.58	20.57	53.39
32	6.27	9.92	15.07	13.85	54.89
33	3.06	21.59	10.93	45.97	18.45
34	3.97	20.02	10.52	44.18	21.31
35	3.66	18.40	11.39	47.19	19.36
36	0.30	22.56	15.51	27.53	34.10
37	3.01	20.92	9.69	26.94	39.44
38	2.99	21.59	7.47	31.06	36.89
39	3.68	20.63	7.54	35.34	32.81
40	5.72	19.27	2.65	31.45	40.88

TABLE II (Continued)

Point No.	Wt.% Li <sup>++</sup> <sub>2</sub>	Wt.% Na <sup>++</sup> <sub>2</sub>	Wt.% K <sup>++</sup> <sub>2</sub>	Wt.% Cl <sub>2</sub> <sup>=</sup>	Wt. % SO <sub>4</sub> <sup>=</sup>
41	6.08	16.20	6.39	29.15	42.18
42	6.42	11.02	12.37	17.14	53.05
43	4.89	10.03	12.57	16.09	56.42
44	5.76	9.02	13.11	11.84	60.36
45	5.39	9.87	12.84	13.08	58.82
46	5.64	9.27	13.28	7.05	64.76
47	5.49	10.93	12.90	5.10	65.58
48	3.51	15.34	11.79	3.23	66.13
49	1.18	28.05	2.41	1.11	67.25
50	1.14	21.44	9.65	1.68	66.09
51	2.59	26.77	1.87	0.91	67.86
52	1.92	21.67	9.71	1.75	64.95
53	0.15	26.14	9.50	0.39	63.82
54	0.24	12.36	29.00	0.52	57.88
55	1.50	19.87	11.39	0.63	66.61
56	1.71	22.78	7.25	1.47	66.79
57	4.70	10.20	14.11	0.66	70.33
58	5.17	11.20	12.45	2.11	69.07
59	3.86	10.27	16.68	1.86	67.33



TABLE III

COMPOSITION DATA OF THE LIQUID PHASE OF THE SYSTEM:

 $\text{Li}_2^{++}$  ,  $\text{Na}_2^{++}$  ,  $\text{K}_2^{++}$  ,  $\text{Cl}_2^-$  ,  $\text{SO}_4^-$  ,  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ .

Point No.	Wt.% $\text{Li}_2^{++}$	Wt.% $\text{Na}_2^{++}$	Wt.% $\text{K}_2^{++}$	Wt.% $\text{Cl}_2^-$	Wt.% $\text{SO}_4^-$
1	4.84	5.98	20.17	10.32	58.69
2	4.75	6.29	24.02	23.88	41.06
3	3.61	9.96	25.58	52.97	7.88
4	4.99	3.26	31.47	53.71	6.57
5	4.19	11.22	28.00	49.86	6.73
6	1.69	10.24	35.69	49.59	2.84
7	1.58	9.98	35.51	49.56	3.37
8	2.60	7.89	33.21	50.42	5.88
9	3.19	9.22	30.10	51.46	6.03
10	3.73	9.89	28.00	52.49	5.89
11	1.31	23.13	18.28	52.79	4.49
12	4.44	17.47	16.44	58.23	3.42
13	6.02	13.79	14.39	62.01	3.79
14	6.71	12.80	14.83	62.77	2.89
15	10.73	6.48	9.95	70.15	2.69
16	10.16	6.77	10.99	69.69	2.39
17	9.18	9.02	9.66	66.14	6.00
18	8.28	10.30	11.36	65.55	4.51
19	7.45	10.73	11.84	65.69	4.29
20	5.02	9.93	22.14	56.37	6.54
21	6.41	10.78	17.85	60.05	4.91
22	7.41	10.90	12.38	65.04	4.27
23	11.92	2.89	10.00	72.17	3.02
24	11.44	4.11	8.32	73.73	2.40
25	11.00	4.90	8.98	71.79	3.33
26	11.10	5.32	9.56	71.55	2.48
27	11.23	6.49	8.76	70.71	2.81
28	11.22	5.40	1.55	16.90	64.93
29	11.27	6.68	1.95	42.24	37.86
30	11.68	6.53	2.79	53.85	25.15
31	11.36	7.39	3.93	63.58	13.74
32	11.64	4.63	8.65	70.03	4.85
33	11.40	4.90	8.91	71.91	2.88
34	12.60	2.72	6.63	76.35	1.70
35	14.35	0.91	4.32	79.61	0.81
36	1.47	26.98	7.24	43.20	21.11
37	3.13	23.91	9.35	53.09	10.52
38	5.51	19.83	7.34	60.33	6.99
39	8.33	12.95	7.98	66.24	4.50
40	9.76	14.19	1.55	64.91	9.59

TABLE III (Continued)

Point No.	Wt.% $\text{Li}_2^{++}$	Wt.% $\text{Na}_2^{++}$	Wt.% $\text{K}_2^{++}$	Wt.% $\text{Cl}_2^{\bar{}}$	Wt.% $\text{SO}_4^{\bar{}}$
41	10.09	14.81	1.57	65.32	8.04
42	8.68	14.57	5.33	64.15	7.11
43	8.05	13.77	6.51	66.07	5.60
44	7.94	11.56	9.25	62.53	8.62
45	8.05	14.90	6.04	60.76	10.25
46	7.71	12.60	9.45	50.40	19.84
47	5.41	18.95	4.81	32.13	38.70
48	2.28	24.60	8.67	33.09	31.36
49	0.89	28.86	5.99	18.97	45.29
50	0.88	27.68	5.94	19.67	45.83
51	1.72	24.39	7.47	18.78	47.64
52	2.02	24.19	7.72	18.32	47.75
53	1.58	23.16	7.17	4.71	63.38
54	1.64	25.04	6.42	6.89	60.01
55	1.64	24.07	7.00	9.71	57.58
56	2.04	23.89	7.65	19.68	46.74
57	4.40	17.40	5.51	5.34	67.35
58	4.27	19.82	4.35	10.51	61.05
59	2.31	24.42	7.03	18.83	47.41

No.	Mole Percent Solid Phase			Cl <sub>2</sub>	SO <sub>4</sub>	Mole Percent Liquid Phase			Cl <sub>2</sub>	SO <sub>4</sub>	Water Content *	Nature of Solid Phase	
	Li <sub>2</sub> <sup>++</sup>	Na <sub>2</sub> <sup>++</sup>	K <sub>2</sub> <sup>++</sup>			Li <sub>2</sub> <sup>++</sup>	Na <sub>2</sub> <sup>++</sup>	K <sub>2</sub> <sup>++</sup>					
1	5.0	10.6	33.7	0.7	50.0	23.3	8.7	17.3	9.8	40.9	24.2	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub>	
2	24.1	6.9	17.4	10.8	40.8	22.1	8.8	19.8	21.7	27.6	20.0	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub>	
3	16.4	4.9	27.6	4.6	46.5	16.0	13.3	20.0	45.7	5.0	17.3	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , KCl	
4	14.5	0.2	35.6	22.6	27.1	21.6	4.3	24.3	45.7	4.1	18.4	K <sub>2</sub> SO <sub>4</sub> , KLiSO <sub>4</sub> , KCl	
5	19.1	3.7	26.7	3.4	47.1	18.0	14.6	21.4	41.9	4.2	18.2	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , KCl	
6	28.8	11.3	11.0	13.7	35.2	3.2	15.3	31.4	48.1	2.0		K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
7	1.2	10.5	39.9	12.3	36.1	7.5	14.2	29.7	45.7	2.9	18.5	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
8	1.0	7.8	43.6	23.2	24.4	12.0	11.0	27.3	45.7	4.0	18.4	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
9	1.0	11.6	40.3	14.3	32.8	14.3	12.5	24.0	45.3	3.9	17.7	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
10	6.2	1.9	43.9	37.1	11.0	16.3	13.1	21.8	45.1	3.7	17.0	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
	Average Invariant Point # 1						17.0	13.9	20.7	43.8	4.6	17.3	K <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , KCl
11	0.4	36.1	14.9	40.0	8.6	5.8	31.0	14.4	45.9	2.9	14.4	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
12	9.5	31.7	9.6	33.2	16.0	18.1	21.5	11.9	46.5	2.0	14.4	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
13	11.2	29.1	9.1	33.9	16.7	23.7	16.4	10.1	47.7	2.2	14.3	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
14	20.7	9.8	19.2	26.7	23.6	25.9	14.9	10.2	47.4	1.6	14.3	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
15	10.7	30.8	9.9	32.7	15.9	37.5	6.8	6.2	48.1	1.4	13.0	KLiSO <sub>4</sub> , NaCl, KCl	
16	9.6	31.0	9.1	36.3	14.0	36.1	7.3	6.9	48.5	1.2	13.4	KLiSO <sub>4</sub> , NaCl, KCl	
17	26.2	11.2	10.7	24.4	27.5	33.5	9.9	6.2	47.2	3.2	15.6	KLiSO <sub>4</sub> , NaCl, KCl	
18	6.9	34.2	9.1	38.7	11.1	30.8	11.6	7.5	47.7	2.4	22.5	KLiSO <sub>4</sub> , NaCl, KCl	
19	9.5	34.4	8.6	32.4	15.1	28.4	12.3	8.0	48.9	2.4	14.1	KLiSO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
20	11.0	0.9	37.1	26.9	24.1	21.0	12.5	16.4	46.1	4.0	16.5	KLiSO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
21	24.9	0.9	24.7	3.3	6.2	25.3	12.9	12.5	46.5	2.8	16.1	KLiSO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl	
22	18.4	7.5	20.1	31.2	22.8	28.2	12.5	8.4	48.5	2.4	14.0	KLiSO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl	
	Average Invariant Point # 2						28.3	12.4	8.2	48.7	2.4	14.1	KLiSO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KCl, NaCl
23	28.8	0.2	21.2	23.9	25.9	40.9	3.0	6.1	48.5	1.5	25.6	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O, KCl	
24	25.0	7.3	17.4	27.4	22.9	39.5	4.3	5.1	49.9	1.2	12.5	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O, KCl	

\* Moles of water per mole of salt

25	20.2	18.9	9.5	32.8	18.6	38.4	5.2	5.6	49.1	1.7	12.9	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, KCl	
26	22.5	10.0	17.3	21.6	28.6	38.6	5.6	5.9	48.7	1.2	12.8	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, KCl, NaCl	
27	20.7	19.4	10.2	27.9	21.8	38.7	6.8	5.4	47.7	1.4	12.8	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, KCl, NaCl	
28	38.4	6.4	5.5	2.6	47.1	43.5	6.3	1.1	12.8	36.3	16.9	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, solid solution	
29	32.9	8.9	8.2	6.3	43.7	41.2	7.3	1.3	30.2	20.0	18.0	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, solid solution	
30	31.4	10.4	8.9	11.9	37.4	41.2	7.0	1.8	37.2	12.8	17.8	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, solid solution	
31	32.3	10.0	8.0	17.0	32.7	39.6	7.8	2.4	43.3	6.9	16.8	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, solid solution	
32	27.8	13.3	11.8	12.0	35.1	40.2	4.8	5.3	47.3	2.4	14.6	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, solid solution	
33	13.2	28.1	8.4	38.8	11.5	39.4	5.1	5.5	48.6	1.4	12.7	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, KCl	
	Average Invariant Point # 3						38.9	5.8	5.6	48.3	1.4	12.8	KLiSO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, KCl
34	16.8	25.6	7.9	36.6	13.1	42.3	2.8	3.9	50.2	0.8	11.9	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, KCl	
35	15.7	23.9	8.7	39.7	12.0	46.1	0.9	2.5	50.1	0.4	10.0	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, KCl	
36	1.5	33.7	13.7	26.7	24.4	6.5	36.4	5.7	37.8	13.6	14.3	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , NaCl, solid solution	
37	13.7	28.7	7.8	23.9	25.9	13.1	30.2	6.9	43.4	6.4	15.3	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , NaCl, solid solution	
38	14.0	30.4	6.2	28.4	21.0	21.5	23.4	5.1	46.1	3.9	15.4	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , NaCl, solid solution	
39	16.0	27.2	5.9	30.2	20.7	30.6	14.3	5.2	47.5	2.4	14.8	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, KLiSO <sub>4</sub> , NaCl	
40	23.9	24.1	2.0	25.5	24.5	34.4	15.1	1.0	44.7	4.9	15.0	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, solid solution	
41	25.4	20.5	4.7	23.9	25.5	35.1	15.5	1.0	44.4	4.0	14.9	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, solid solution	
42	27.9	14.5	9.6	14.6	33.4	31.5	15.9	3.4	45.5	3.7	15.8	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, NaCl, solid solution	
43	22.8	14.1	10.4	14.7	38.0	29.8	15.3	4.3	47.7	2.9	15.2	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , NaCl	
	Average Invariant Point # 4						30.2	14.8	4.8	47.6	2.6	15.0	Li <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O, K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , NaCl
44	26.1	12.5	10.7	10.6	40.1	29.9	13.1	6.2	46.1	4.7	16.4	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , solid solution	
45	24.8	13.7	10.5	11.8	39.2	29.8	16.6	4.0	44.1	5.5	17.0	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , solid solution	
46	26.2	13.0	10.9	6.4	43.5	29.7	14.7	6.5	38.0	11.1	19.1	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , solid solution	
47	25.5	15.3	10.6	4.6	44.0	22.7	24.0	3.6	26.3	23.4	18.4	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , solid solution	
48	17.2	22.7	10.2	3.1	46.8	10.2	33.4	6.9	29.1	20.4	15.9	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , KLiSO <sub>4</sub> , solid solution	
49	5.9	42.3	2.1	1.1	48.6	4.3	41.6	5.1	17.7	31.3	15.1	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	
50	5.9	33.7	8.9	1.7	49.8	4.2	40.3	5.1	18.5	31.9	15.3	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	
51	12.3	38.5	1.6	0.9	46.7	8.2	35.1	6.3	17.5	32.9	16.1	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	

## 57-A

52	9.6	32.6	8.6	1.7	47.5	9.5	34.5	6.5	16.9	32.6	16.6	$K_3Na(SO_4)_2$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$ , $KLiSO_4$	
53	0.8	41.5	8.8	0.4	48.5	7.9	35.1	6.4	4.6	46.0	15.8	$K_3Na(SO_4)_2$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$	
54	1.4	21.2	29.3	0.6	47.5	8.1	37.1	5.6	6.6	42.6	15.1	$K_3Na(SO_4)_2$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$	
55	7.8	31.1	10.5	0.6	50.0	8.1	35.7	6.1	9.3	40.8	15.6	$K_3Na(SO_4)_2$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$	
56	8.6	34.7	6.5	1.5	48.7	9.6	34.0	6.4	18.2	31.8	16.3	$K_3Na(SO_4)_2$ , $KLiSO_4$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$	
57	22.8	15.0	12.2	0.6	49.4	20.5	24.5	4.6	4.9	45.5	16.5	$K_3Na(SO_4)_2$ , $KLiSO_4$ , $Na_2SO_4$	
58	24.4	16.0	10.4	2.0	47.2	19.5	27.3	3.5	9.4	40.3	17.2	$K_3Na(SO_4)_2$ , $KLiSO_4$ , $Na_2SO_4$	
59	19.3	15.5	14.8	1.8	48.6	10.3	34.5	5.8	17.3	32.1	16.2	$K_3Na(SO_4)_2$ , $KLiSO_4$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$	
	Average Invariant Point # 5						9.8	34.3	6.2	17.5	32.2	16.4	$K_3Na(SO_4)_2$ , $KLiSO_4$ , $Na_2SO_4$ , $Na_2SO_4 \cdot 10H_2O$

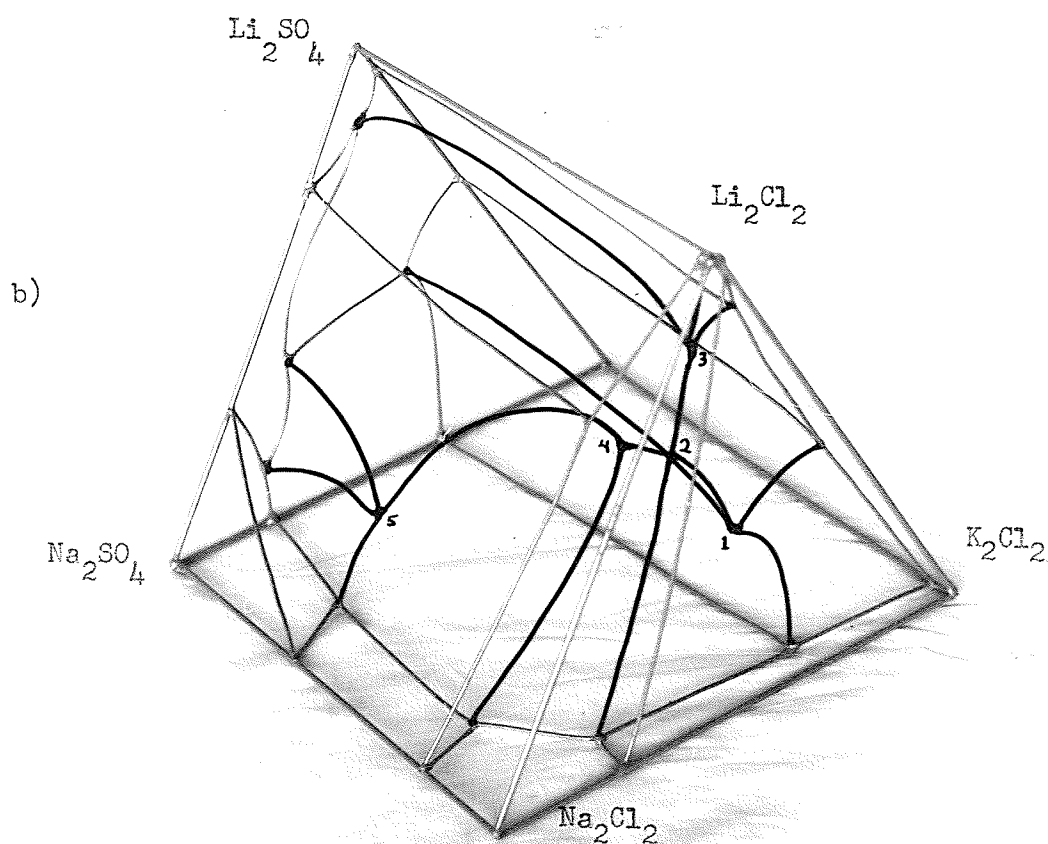
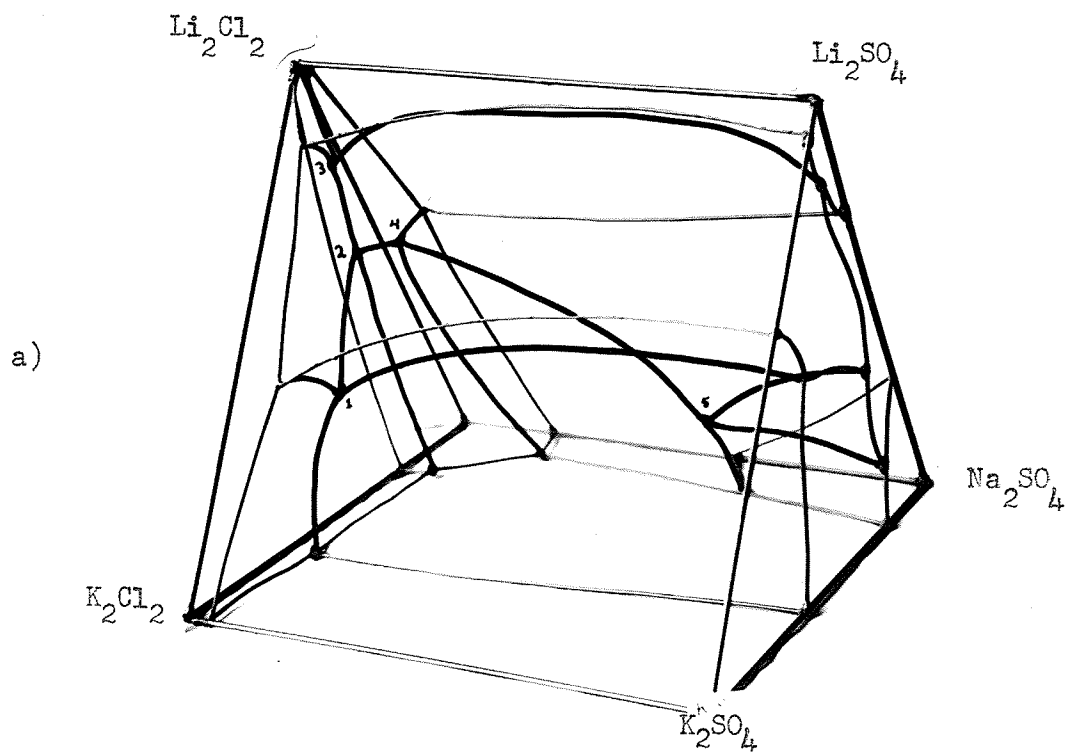


FIGURE 28

PHOTOGRAPHS OF THE EQUILIBRIUM DIAGRAM

## DISCUSSION OF RESULTS AND CONCLUSIONS

The results of the chemical analysis of the liquid phases and of the wet residues are given in Tables II to IV, pages 52 to 57. Pictures of the equilibrium diagram are shown in Figure 28, with the invariant points marked as outlined below. With the exception of the univariant lines with  $\text{LiCl}\cdot\text{H}_2\text{O}$  as one of the equilibrium solids, evidence given in Table IV was obtained for the univariant lines indicating the equilibrium of three solids and solution. One was completed by extrapolation, the  $\text{KLiSO}_4$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{NaCl}$  line, due to the proximity of the two invariant points it joins.

Five invariant points were found in this system:

1.  $\text{K}_2\text{SO}_4$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{KCl}$
2.  $\text{KLiSO}_4$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KCl}$ ,  $\text{NaCl}$
3.  $\text{KLiSO}_4$ ,  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ ,  $\text{NaCl}$ ,  $\text{KCl}$
4.  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ ,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{NaCl}$
5.  $\text{K}_3\text{Na}(\text{SO}_4)_2$ ,  $\text{KLiSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$

These are the solids in equilibrium with solution at  $25^\circ\text{C}$ . The photographs in Figure 28 show the approximate positions of the quinary invariant points. To help differentiate the various lines in the prism, the quaternary lines on the surface are grey, while the quinary lines inside the prism are black. Picture a) is shown with the  $\text{K}_2\text{SO}_4$

corner nearest the right front; in picture b) the NaCl corner is forward, presenting a view diagonally opposite to the first picture. Due to the difficulties in assembling this solder and wire diagram, the lines and invariant points are positioned only approximately. With the experimental data obtained, the invariants marked 2 and 4 in the photographs, Figure 28, should be closer than indicated, actually almost touching.

One other invariant point,  $\text{LiCl}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , NaCl, KCl, in equilibrium with solution, exists in this system, but could not be obtained experimentally or even represented on this diagram. It is situated in the LiCl corner of the prism and theoretically is represented by the expanded diagram, Figure 29.

The small volume which the lithium chloride salt occupies is the result of the powerful action of this chloride in displacing other salts from solution. This was expected from the data of the quaternary systems.

To illustrate the existence of the volumes indicating solution saturated with one salt, approximate cross sections at constant anion composition were drawn, using the three dimensional wire model as



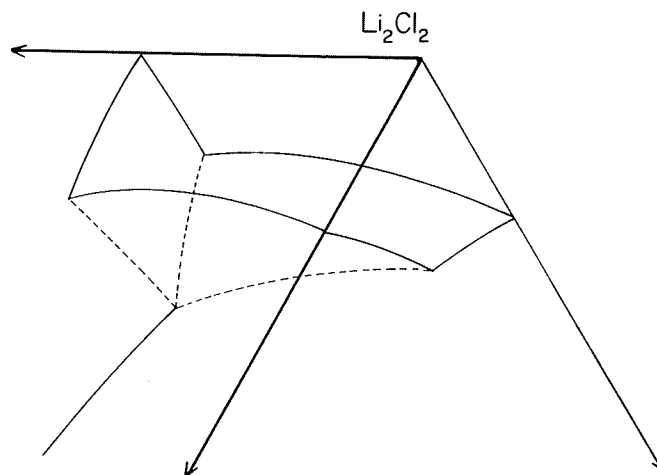


FIGURE 29

ENLARGEMENT OF THE  $\text{LiCl} - \text{NaCl} - \text{KCl} - \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$   
INVARIANT POINT

a guide. The sixteen diagrams are represented in Figures 30 - 33.

Diagram 1 is the sulphate end of the prism. In this system all the sulphates -  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  are present, with  $\text{Na}_2\text{SO}_4$  anhydrous

represented by the line  $ab$ , and  $ab'$ . Only two addition compounds,  $KLiSO_4$  and  $K_3Na(SO_4)_2$ , exist; at this temperature solid solution occurs between the lithium and sodium sulphates. Diagrams 2 and 3 show the change of the  $Li_2SO_4 \cdot H_2O$ , solid solution, and  $Na_2SO_4 \cdot 10H_2O$  areas. In Diagram 4, at the quinary invariant point (#5) where  $K_3Na(SO_4)_2$ ,  $KLiSO_4$ ,  $Na_2SO_4$ ,  $Na_2SO_4 \cdot 10H_2O$  are the solids in excess in solution, another small wedge of solid solution appears;  $Na_2SO_4$  anhydrous is still represented on the surface of the solid solution, that is  $ab$ ,  $ab'$ , and  $ab''$ . Past this quinary invariant, in Diagram 5,  $Na_2SO_4 \cdot 10H_2O$  is still evident, with the anhydrous form existing on the base below the solid solution. Finally in Diagram 6 the decahydrate volume has vanished. In this interval the  $KLiSO_4 - K_3Na(SO_4)_2$  surface has been tilted upward at the  $KLiSO_4$ ,  $K_3Na(SO_4)_2$ , solid solution line, as evident in Diagram 7. The first appearance of a chloride,  $NaCl$ , is observed in Diagram 8, its area increasing in Diagrams 9 and 10, at the expense of the solid solution region. Diagram 11 is drawn through the quaternary invariant point  $Li_2SO_4 \cdot H_2O$ , solid solution,  $NaCl$  in the Lithium, Sodium, Chloride, Sulphate, Water System. Solid solution here is completely in the body of the diagram and in

Diagram 12 it is quickly disappearing as another quinary invariant is approached. Number 12 also represents the quinary invariant <sup>(\*)</sup> $\text{KLiSO}_4, \text{K}_3\text{Na}(\text{SO}_4)_2, \text{K}_2\text{SO}_4, \text{KCl}$ ;  $\text{KCl}$  appears for the first time, but cannot be represented since it is on the plane immediately behind Diagram 12. In Diagram 13, the <sup>(\*\*)</sup> invariant  $\text{K}_3\text{Na}(\text{SO}_4)_2, \text{KLiSO}_4, \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{NaCl}$  has been reached, with this being one extremity of solid solution, that is lithium sulphate; as well  $\text{K}_2\text{SO}_4$  has all but disappeared. This surface represents the last plane of existence of the double salts  $\text{KLiSO}_4$  and  $\text{Na}_3\text{K}(\text{SO}_4)_2$ . Between Diagrams 13 and 14, the  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} - \text{NaCl}$  line has moved rapidly upward. Two quinary invariants are evident in Diagram 14, the  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{KLiSO}_4, \text{NaCl}, \text{KCl}$  and <sup>(\*\*\*)</sup> $\text{Na}_3\text{K}(\text{SO}_4)_2, \text{KLiSO}_4, \text{NaCl}, \text{KCl}$  <sup>(\*\*\*)</sup> invariants, although not all the salts can be represented. Diagram 15 shows the existence of the chlorides of sodium and potassium but the sulphate of lithium. The last Diagram, where only the chlorides are present, represents only the sodium and potassium chlorides. Lithium chloride so strongly displaces other salts from solution that its area of existence cannot be indicated on the diagram with the scale used. The other quinary invariant point  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}, \text{LiCl} \cdot \text{H}_2\text{O}, \text{NaCl}, \text{KCl}$  was not represented due to its position extremely close to the  $\text{LiCl}$  corner of the prism.

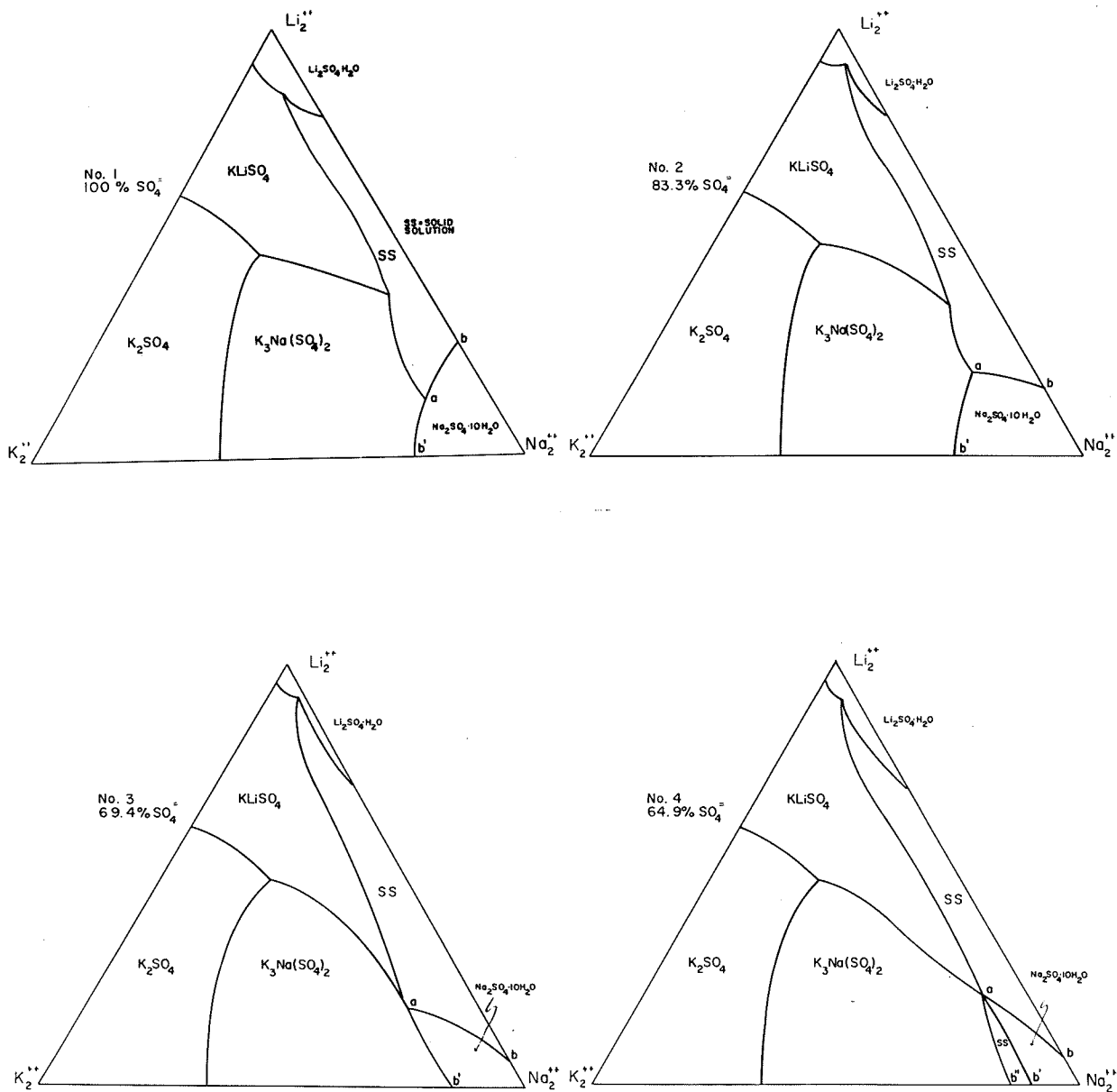


FIGURE 30

CROSS SECTIONS OF EQUAL ANION CONTENT

DIAGRAMS 1 - 4

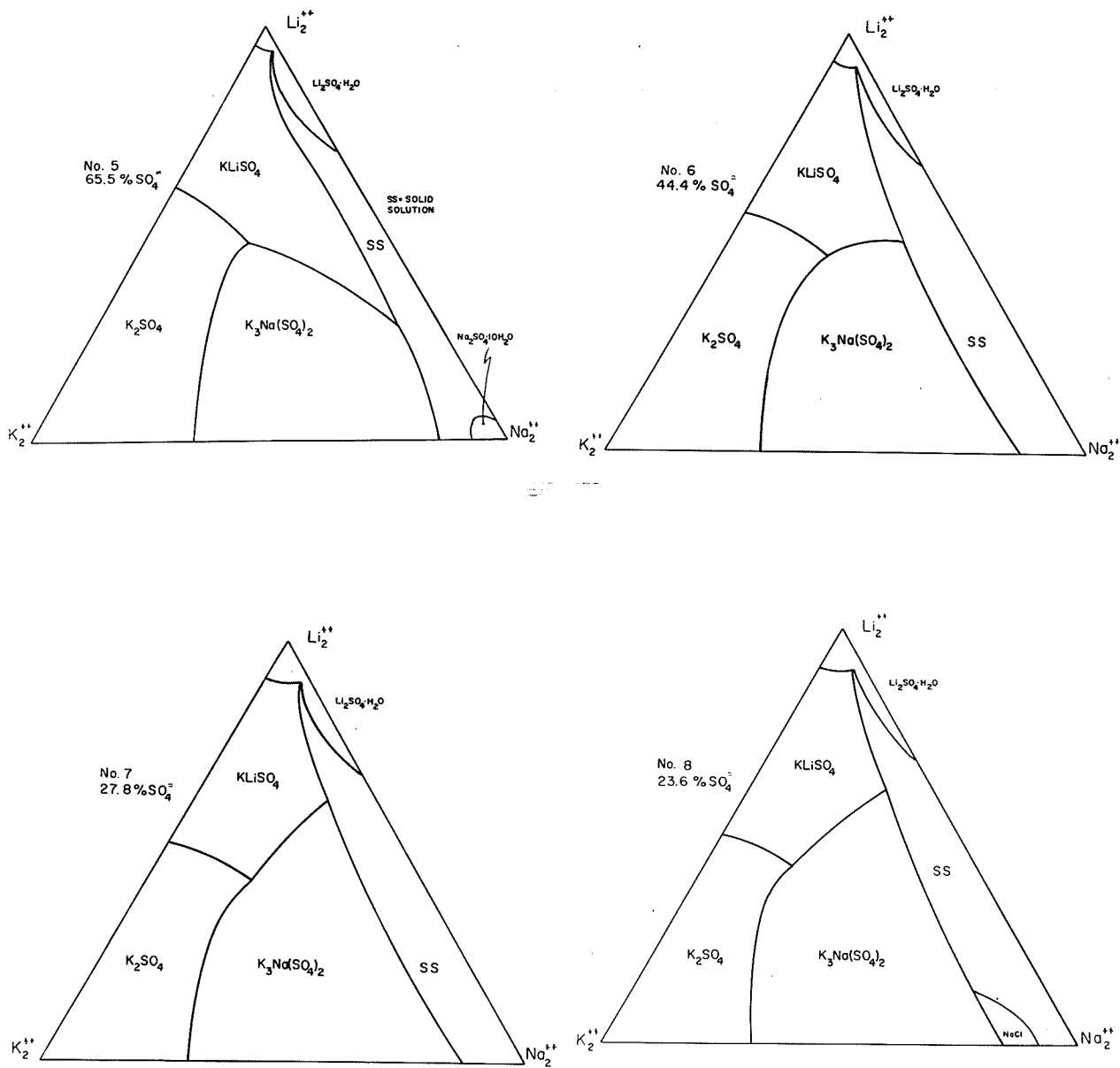


FIGURE 31

CROSS SECTIONS OF EQUAL ANION CONTENT

DIAGRAMS 5 - 8

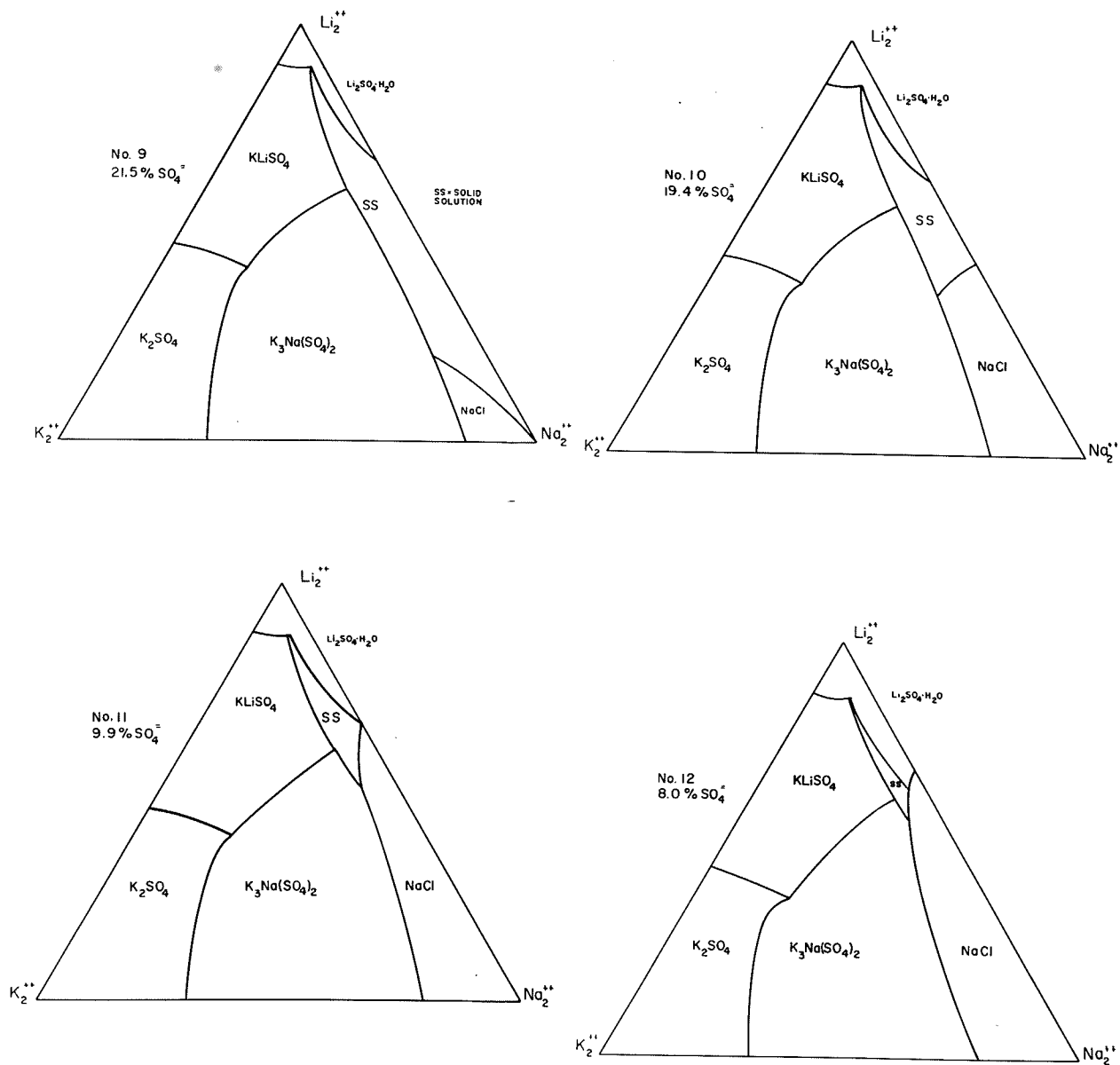


FIGURE 32

CROSS SECTIONS OF EQUAL ANION CONTENT

DIAGRAMS 9 - 12

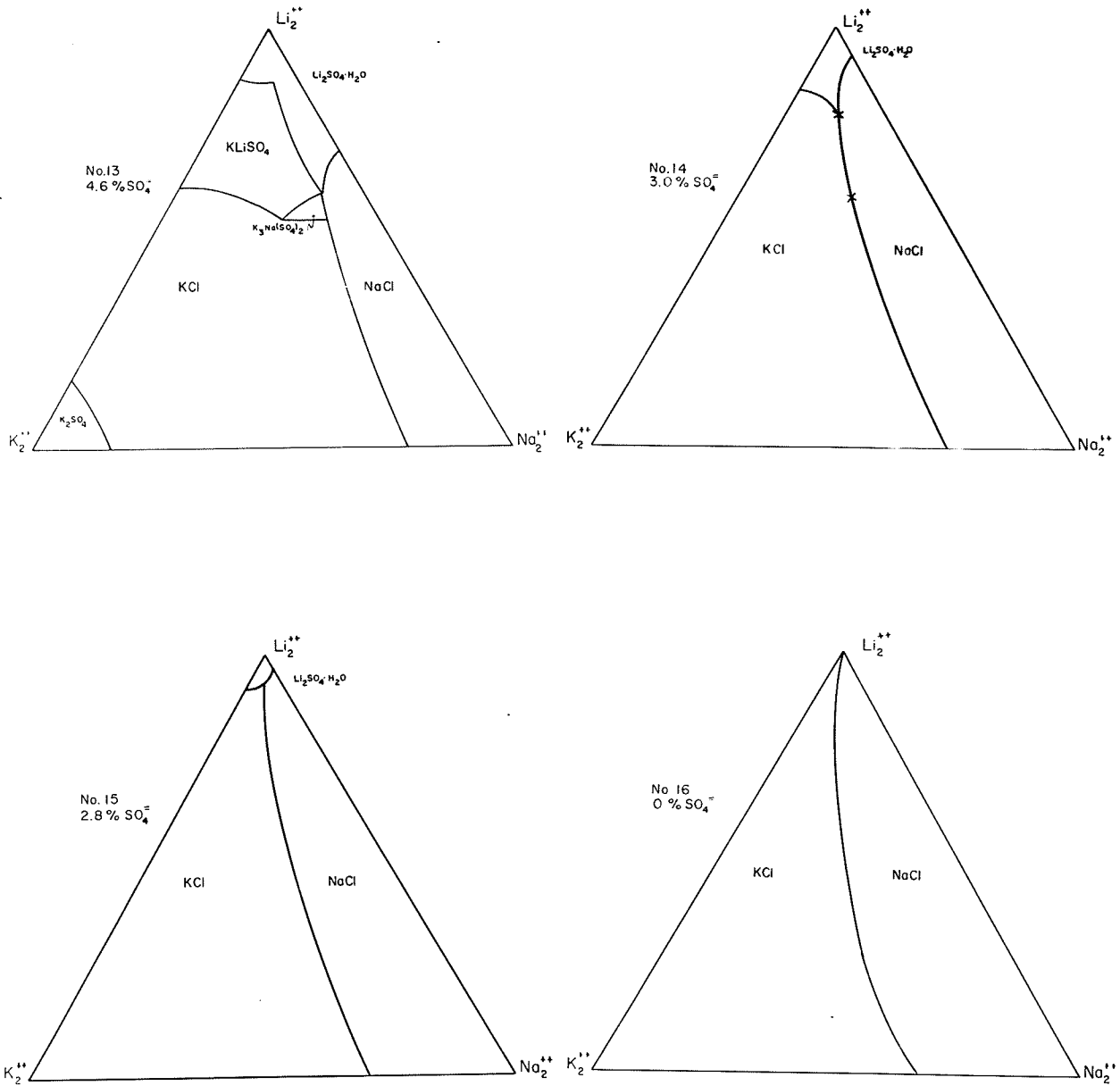


FIGURE 33  
 CROSS SECTIONS OF EQUAL ANION CONTENT  
 DIAGRAMS 13 - 16

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