

The System $(\text{NH}_4)_2\text{SO}_4\text{-NH}_4\text{Cl-Ag}_2\text{SO}_4\text{-AgCl-H}_2\text{O}$

A thesis

presented to

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In partial fulfillment

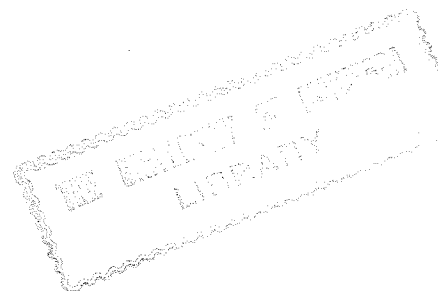
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Master of Science

by

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To DR. A. N. CAMPBELL
who has directed and very kindly
assisted in this work, the thanks
of the writer are most gratefully
offered.

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INTRODUCTION

(1)

Considering a system derived from water and two electrolytes which do not yield a common ion, the equilibrium which must exist between the two electrolytes can be expressed by the equation:



Such equilibria involve a simple interchange between the acidic and basic constituents. Systems of this kind were designated by Meyerhoffer (14) "reciprocal salt pairs", but the term is now generally applied to systems of this kind in which water is present as an additional component. In the presence of water the equilibria are determined almost entirely by the extent to which the four salts are dissociated and by the relative solubilities of these salts and their different hydrates. If the salts are capable of forming double salts or solid solutions the solubility of these are also important factors in the equilibria.

Investigations of such systems are not common in literature but perhaps one of the most interesting is the system $\text{CuSO}_4 - \text{CuCl}_2 - (\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$ studied by Schreinemakers (21) (22). As will be shown in the sequel a case of "reciprocal salt pairs" constitutes a quaternary system; that is, a system of four components and such studies are of interest not only from the point of view of the individual properties of the substances participating but also from the view of the mode of representation. The investigation of Schreinemakers produced several double salts and also introduced a new method of representing quaternary systems.

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Somewhat similar to the work of Schreinemakers, this investigation concerns the system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$. The participating substances are connected by the equation:



A complete study of this equilibrium involves the investigation of the four ternary systems making up the quaternary.

These are as follows:

- (a) $\text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$
- (b) $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O}$
- (c) $\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O}$
- (d) $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$

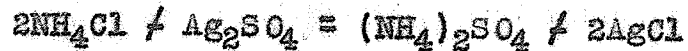
Since Schreinemakers investigated the ternary system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$, his results will be used in this work.

A further point of interest in the investigation involves the formation of double salts. The copper ion and ammonia form a complex in solution and Schreinemakers was able to find double salts of the two salt pairs $\text{CuSO}_4 - (\text{NH}_4)_2\text{SO}_4$ and $\text{CuCl}_2 - \text{NH}_4\text{Cl}$. It is a well known fact that silver chloride because of the complex formed between silver and ammonia will dissolve in dilute ammonia water. It might then be expected that double salts would exist between the pairs $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4$ and $\text{NH}_4\text{Cl} - \text{AgCl}$. Although such double salts were not found at the temperature of the investigation, evidence from increased solubility of the silver salts and constancy obtained in the equilibrium expression indicates their existence.

In industrial analysis valuable silver from silver chloride is recovered by a dangerous process involving

(3)

nitric acid and alcohol. It was thought possible through the existence of the equilibrium



or through formation of double salt, that silver chloride could be reintroduced into solution in some usable form. However, by the ordinary means of analysis no silver ion could be found in solution from the action of a saturated solution of ammonium sulphate on silver chloride, and although the solubility of silver chloride was increased many thousands in ammonium chloride solution, it still was insufficient to warrant use industrially.

THEORETICAL CONSIDERATIONS

The Investigation and Graphical Representation of Two Salts and Water -

As stated previously a complete investigation of the system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$ involves the study of the four ternary systems:

- (a) $\text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$
- (b) $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O}$
- (c) $\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O}$
- (d) $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$

These are special cases of ternary systems since they are all composed of water and two salts with a common ion. The problem of representation of such systems has been solved in many ways (15), (23), (30), (19), (10). The method to be used in this work was first suggested by Gibbs (7) and later independently by Stokes (28). It has since been greatly elaborated by Roozeboom (20). The method of representation consists in employing an equilateral triangle with lines ruled parallel to each side of the triangle, the length of a side is made equal to unity or one hundred; the sum of the fractional or percentage amounts of the three components being represented therefore by a side of the triangle. The composition of a ternary mixture is obtained by determining the distance in a direction parallel to the three sides of the triangle (Figure 1). Conversely, in order to represent a mixture consisting of say a, b, and c parts of the components A, B and C respectively, where $a + b + c = 100$, divide one side, say AB of the triangle into

100 parts. Since apex A represents 100% A we plot from B, the distance Bx representing a parts of A, and since apex B represents 100% B we plot from A the distance Ax' representing b parts of B (Figure 1). Since $AB = 100$ and $a + b + c = 100$ the remainder xx' represents c parts of C. From x and x' lines are drawn parallel to the sides of the triangle and the point of intersection P represents the composition of the ternary mixture of given composition; for as is evident from the figure, the distance of the point P from the three sides of the triangle, when measured in directions parallel to the sides is equal to a, b and c respectively. Since all investigations in this work were carried out at 30° , isothermal diagrams only will be considered here.

We now consider the form that will be taken by the equilibrium diagram of an aqueous solution of two salts when plotted on the equilateral triangle. In the simplest case where no double salts are present a two-branch curve results, represented by acb in Figure 2. In this diagram a represents the solubility of salt A, b represents the solubility of salt B, while the curves ac and bc represent ternary solutions in equilibrium with solid salt A and solid salt B respectively. At c we have an isothermally invariant system in which the solution is in equilibrium with both salts as solid phases.

Where the two components A and B form a compound,

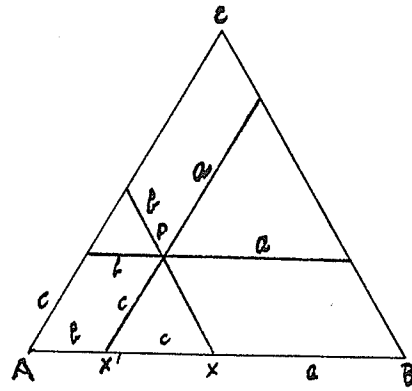


Fig. 1

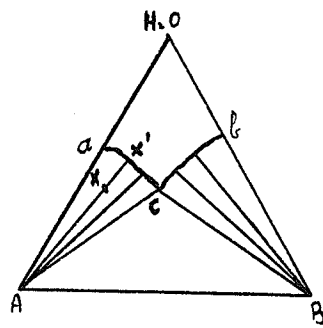


Fig. 2

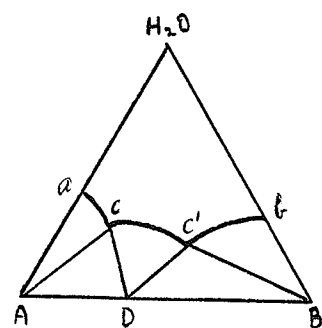


Fig. 3

the isothermal diagram will exhibit three curves such as ac , cc^1 , bc^1 as shown in Figure 3, c and c^1 representing solutions which are in equilibrium with pure A and double salt and pure B and double salt respectively. The composition of the anhydrous double salt is represented by point D on the side of the triangle AB. Should an hydrated double salt be formed intersection of the lines (known as "tie-lines") would take place in the interior of the triangle corresponding to the molecules of water contained in the compound.

A mixture of the three components having a total composition represented by x in the area aAc (Figure 2), will give rise to a heterogeneous system consisting of solid A and a saturated solution represented by the point on the saturation curve ac where the "tie-line" Ax meets ac . Similarly mixtures having a total composition represented by a point in the area bBc will give rise to solid B and a saturated solution represented by a point on the curve bc . From this diagram also the relative amounts of solid phase and saturated solution formed can be obtained. Thus in the case of the mixture x , the amount of saturated solution formed will be represented by the distance Ax , and the amount of solid phase deposited will be represented by the distance of x from curve ac .

There are two methods of determining the composition of the solid phase in contact with the saturated solution, these are due to Bancroft (2) and Schreinemakers (24). The

latter method was used in this investigation. The determination of the solid phase in two salt and water systems is often troublesome owing to the difficulty of separating the solid in equilibrium with the liquid phase from the adhering mother liquor without changing its composition. Schreinemakers' "residue method" consists in making analyses of some of the saturated solution and its corresponding wet solid phase, that is, a mixture of some of this solution and the solid with which it is in equilibrium. The composition of the mixture must correspond to a point on the diagram which is located on the straight line connecting the composition of the solid and the saturated solution. If a line is drawn through the two points representing the two analyses it must pass through the point representing the composition of the solid. If the directions of a number of such lines are ascertained, the point toward which they converge must represent the composition of the pure solid. The determination is more accurate the further the points representing composition of wet solid phase and mother liquor are apart. If the solutions used are not saturated with the same solid or if saturated with more than one solid, these lines will not converge towards a common point.

Thus, for example in Figure 2, suppose analysis of saturated solution yields point x' , while analysis of its corresponding wet phase yields point x . The line (that is,

the "tie-line" mentioned above) joining the two points is found to pass through the point representing 100% A. Analysis of another equilibrium mixture in this neighborhood yields another "tie-line" intersecting the first at A, hence both saturated solutions are in equilibrium with solid A. If a double salt is formed then the tie-lines intersect at the composition of the double salt; the point of intersection being on the base line AB if the double salt is anhydrous or up in the body of the triangle if hydrated. The percentage of water in the hydrated salt is given by the percentage of water indicated by this point of intersection of the tie-lines.

This technique was used in the investigation of the four ternary systems and the resulting diagrams will be shown later in this work.

The Investigation and Graphical Representation of
Reciprocal Salt Pairs -

The equation



represents a general case of "reciprocal salt pairs". The liquid phase associated with these systems must contain at least four ions, and although it may contain appreciable concentrations of complex ions and of hydrogen and hydroxyl, the composition of the entire mixture can in general be expressed in terms of the simple ions present. It was first pointed out by Meyerhoffer⁽¹⁶⁾ that the composition of the liquid phase can be expressed in terms of water and any three of the simple ions. This fact is a necessary consequence of the fact that the sum of the number of equivalents of anion must equal the sum of the number of equivalents of the cation, therefore the concentration of the solution with respect to the ion not used as a component can be found by difference. Similarly the composition can also be expressed in terms of any three of the four salts concerned. If, for example, AM, BN and AN are used as components the unused salt, namely BM, can be expressed as $AM \neq BN - AN$, for there is no objection to using negative values in expressing these concentrations⁽⁶⁾. Since these systems can be defined in terms of three, rather than four ions or salts, and water they are four-component systems.

Applying the Phase Rule to "reciprocal salt-pairs", invariance is possible only when six different phases are present. Assuming that the system includes a liquid and a vapour phase, four solids must be present if the values of all variables, namely pressure, temperature and four concentrations are fixed. If it be assumed that the four solids are the four simple salts, the liquid phase must be saturated with the four salts simultaneously, and must have a fixed concentration as to all these salts at the invariant temperature. This is not only required by the Phase Rule but is a consequence of the Mass Law⁽³⁾.

Graphical representation of changes in all six of the variables concerned in these systems is not possible unless certain simplifying assumptions are made. Four such methods are particularly applicable to the case of reciprocal salt pairs. The simplifying assumptions lie in carrying on the investigations at atmospheric pressure (that is, in an open vessel) and at a constant temperature. This study was carried out under these conditions. The first device was suggested by Lowenherz (12) who besides the above assumptions, assumed a constant amount of water present and thus represented the changes in the four remaining variables - the concentration of the substances. He represented the ratios between the number of equivalents of each of the four salts and 1000 moles of water on four axes assumed to intersect in space like the edges of a regular four sided pyramid. Adjacent axes must be used to represent salts which contain a common

ion. If this requirement is not complied with, it is not possible to represent a continuous series of changes in the composition of the system. The resulting diagram would be a number of surfaces intersecting at the points of saturation of the different salts or mixtures of them in the constant amount of water. However, the preparation of such diagrams from numerical data is time-consuming and the resulting figures may fail to indicate clearly the position and extent of the different saturation fields. These difficulties may be eliminated by orthographical projection of the saturation surfaces upon a horizontal plane which then yields a diagram similar to that suggested by Schreinemakers⁽²²⁾.

Schreinemakers' original method involved a square formed by the four substances as corners and the water content represented on a perpendicular axis. As in the method of Lowenherz adjacent axes must be used to represent salts which contain a common ion. The resulting surfaces were then projected on a horizontal plane. A diagram resulting from this method is shown later in Figure 7 where Schreinemakers plots the system $\text{CuSO}_4 - \text{CuCl}_2 - (\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$.

Lodocnikow has devised an entirely different method for the representation of four component systems⁽¹¹⁾. He arrives at the conclusion that for representation of a quaternary system on a plane two points are necessary and

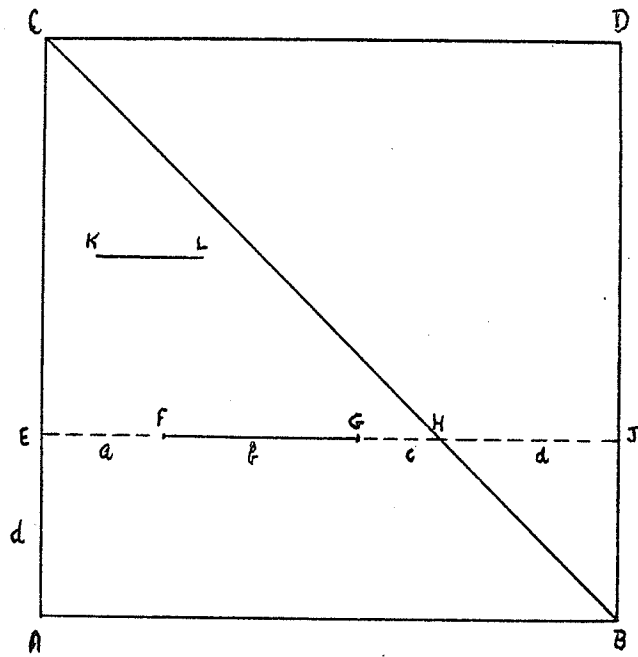


Fig. 4

a vector joining these two points represents that particular equilibrium. A square ABDC as shown in Figure 4 is constructed with the diagonal BC. We assume the quantities a , b , c and d of the participating substances A, B, C and D respectively where $a \neq b \neq c \neq d = \text{constant} = \text{the side of the square}$. To represent a particular equilibrium the outer component d is drawn on the side AC from the point A upwards. Through the obtained point E a straight line is drawn parallel to the side AB. On this straight line we draw in determined sequence $EF = a$ and $FG = b$; then GH indicates the component c since $HJ = JB = EA = d$. The obtained vector $FG = b$ represents the given composition. Inversely from the given vector of formation KL along the straight line which contains it we can read the composition at once in the following manner. From AC out to point K we have the component a , the section KL itself indicates the component b , the section from point L to the diagonal BC indicates the component c and finally the component d is equal to the section from the diagonal to the right hand side BD or, equal to the ordinate of point K (or generally to the ordinate of any point on the straight line).

All components are then situated on a straight line and therefore their quantitative relationships show clearly. The higher the vector lies, the greater is the quantity d and conversely, the further leftwards the left point of the vector lies the smaller is a and so on. Thus all components

have a corresponding geometrical picture on the diagram and hence one can easily recognize the specific compositions which contain less than four components. This method of representation is most useful in cases where a relationship or ratio exists between the solubilities of the components. These special properties are outlined in Lodocnikow's original article. In the particular system under investigation the comparatively small solubility of silver chloride does not lend itself to representation by a vector.

The mode of graphical representation most suited to reciprocal salt pairs and the one used in this work was devised by Janecke⁽¹⁰⁾. By it complete representation of any set of reciprocal salt pairs can be expressed in one diagram. Expressed as a formula the Janecke method is represented by



in which $100m$ is the number of grams or moles of water associated with 100 equivalents of the mixture of salts present; x is the number of equivalents of one of the anions and y is the number of equivalents of one of the cations present in 100 equivalents of that mixture. The relative proportions of the four ions in any mixture are expressed graphically by the position of a point on or within a square, the length of whose sides corresponds to 100 equivalents of salt. The method of locating such points is found in Figure 5. Each of the four corners

of the square corresponds to a pure salt and each of the four edges to mixtures of a pair of salts containing a common ion. The corners which represent the four salts must be so chosen that these relations are complied with. Points in the interior of the square represent mixtures containing four different ions. In order to find the position of a point representing a mixture composed of x equivalents of A anion and y of N cation it is only necessary to measure off x units from the BM - BN line and y units from the AM - BM line which gives the point O.

If the composition is expressed as a mixture of salts rather than of ions the location of the point demands more thought. The two diagonals of the square when considered separately can be thought of as dividing it into four right-angled isosceles triangles. The composition of all points within each of these triangles can be expressed in terms of the three salts at the apices of these triangles. Thus the composition of point O (Figure 5) can be represented by either the set AM - BM - BN or BM - BN - AN but any other set of salts would involve the use of negative quantities. Having located the proper triangle it is only necessary to lay off from the point located at the right angle of this triangle, distances corresponding to salts represented by the points located at the two acute angles of the triangle and get the intersection of lines drawn through these points parallel to the sides of the square. Hence, if the

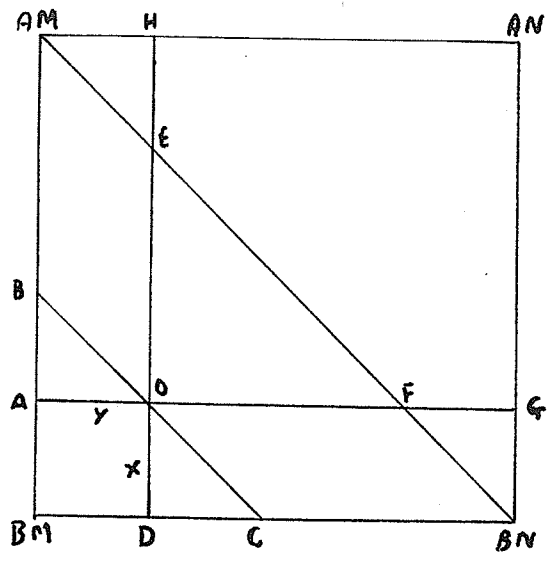


Fig. 5

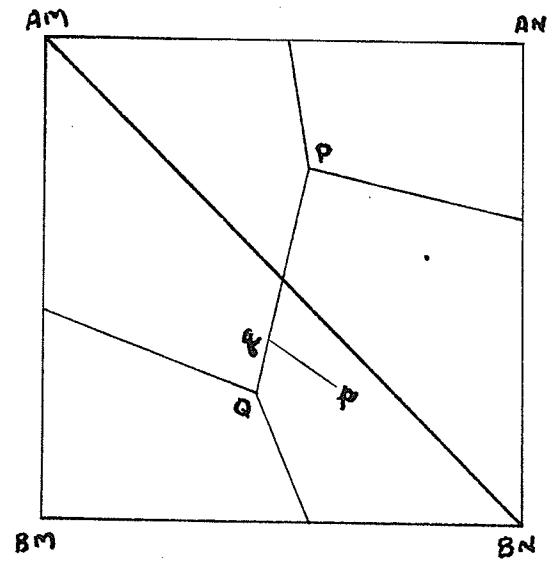


Fig. 6

composition of O is expressed in terms of $AM - BN - BM$ it corresponds to the point found by laying off x equivalents of AM from BM , which gives the point A , and M equivalents of BN which gives the point D , and getting the intersection of the lines AG and DH . It is a simple problem in geometry to see that the percentage of the third salt in the mixture must correspond to the distance of the point found from the longer side of the triangle when measured on a line parallel to the shorter sides, in this case OF or OE .

A representative diagram for a reciprocal salt pair is shown in Figure 6. It assumes that the four component salts are the only solids present and that there are two univariant points each representing systems composed of three solids, a vapour and a liquid. It is obvious that the stable pair of salts is AM and BN . Saturation as to each of the four solids corresponds to points within the four fields and saturation as to two solids to points on the lines separating these fields. Although the diagram does not indicate the proportions of water present, changes in the composition of the dissolved salts which result from evaporation of saturated solutions can be easily followed. If a solution whose composition corresponds to a point in the BN field, such as p , is evaporated that salt must separate and the resulting change in composition must correspond to movement of the point p away from the point BN until q is reached,

at which point AM also begins to separate. Further changes must correspond to movement from q away from the point representing saturation as to both AM and BN which is on the AM - BN diagonal, namely the point R, until saturation as to a third salt is attained at Q. The points, P, Q and R are congruent solutions and P and Q are crystallization end points. A virtue of the Janecke diagram is that changes in the composition of the dissolved salts which result when the liquid phase is evaporated, can be calculated quantitatively.

NATURE OF THE PROBLEM

Investigation of the system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$ involves the study of the solubilities of the different participating substances in water, by themselves and in the presence of some of the other salts and identification of any double salts produced and their corresponding fields of existence. This is accomplished by investigation of the common ion ternary systems and then the quaternary system.

Schreinemakers in his study of the system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{CuSO}_4 - \text{CuCl}_2 - \text{H}_2\text{O}$ found several double salts; the solid substances capable of occurring at 30° in contact with solution were as follows; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$. Since by Schreinemakers' method of representation the quaternary solution saturated with one solid substance is represented by a surface, here must occur six saturation surfaces; their projections are shown in Figure 7.

abmlk	is	the	saturation	area	of	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
iklh	"	"	"	"	"	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
fgope	"	"	"	"	"	NH_4Cl
depe	"	"	"	"	"	$(\text{NH}_4)_2\text{SO}_4$
hlmog	"	"	"	"	"	$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$
bmopc	"	"	"	"	"	$\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

Each saturation surface has been marked with the corresponding solid substance. The curves in which the saturation surfaces meet in twos are the saturation curves; these represent therefore, the solutions saturated

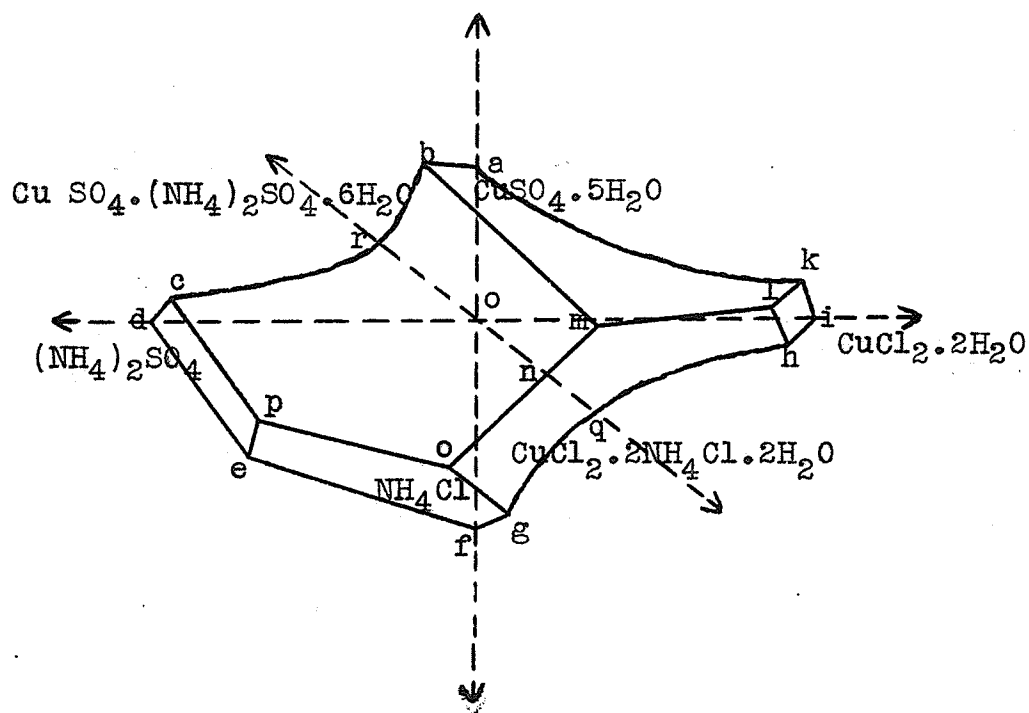


Fig. 7

with two solid materials. In Schreinemakers' projection diagram there are nine such saturation curves.

Figure 8 shows what is obtained when Schreinemakers' results are plotted by Janecke's method of graphical representation. The saturation fields have been represented by the same letters and labels show the substances with which solutions in this area would be saturated. Similar to Schreinemakers' diagram there are nine saturation curves where solutions are saturated with two solid materials. These are as follows:

ep	"	"	"	"	$(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl
op	"	"	"	"	$(\text{NH}_4)_2\text{SO}_4$ and $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
bm	"	"	"	"	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
kl	"	"	"	"	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
hl	"	"	"	"	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$
go	"	"	"	"	NH_4Cl and $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$
po	"	"	"	"	NH_4Cl and $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
om	"	"	"	"	$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
ml	"	"	"	"	$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

The points at which saturation curves meet three at a time are the saturation points, these represent solutions saturated with three solid substances. Four such points occur at l, m, o and p. The substances saturating the solutions at these points depend on which saturation fields meet at the points. Thus at l, the solution is saturated with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$.

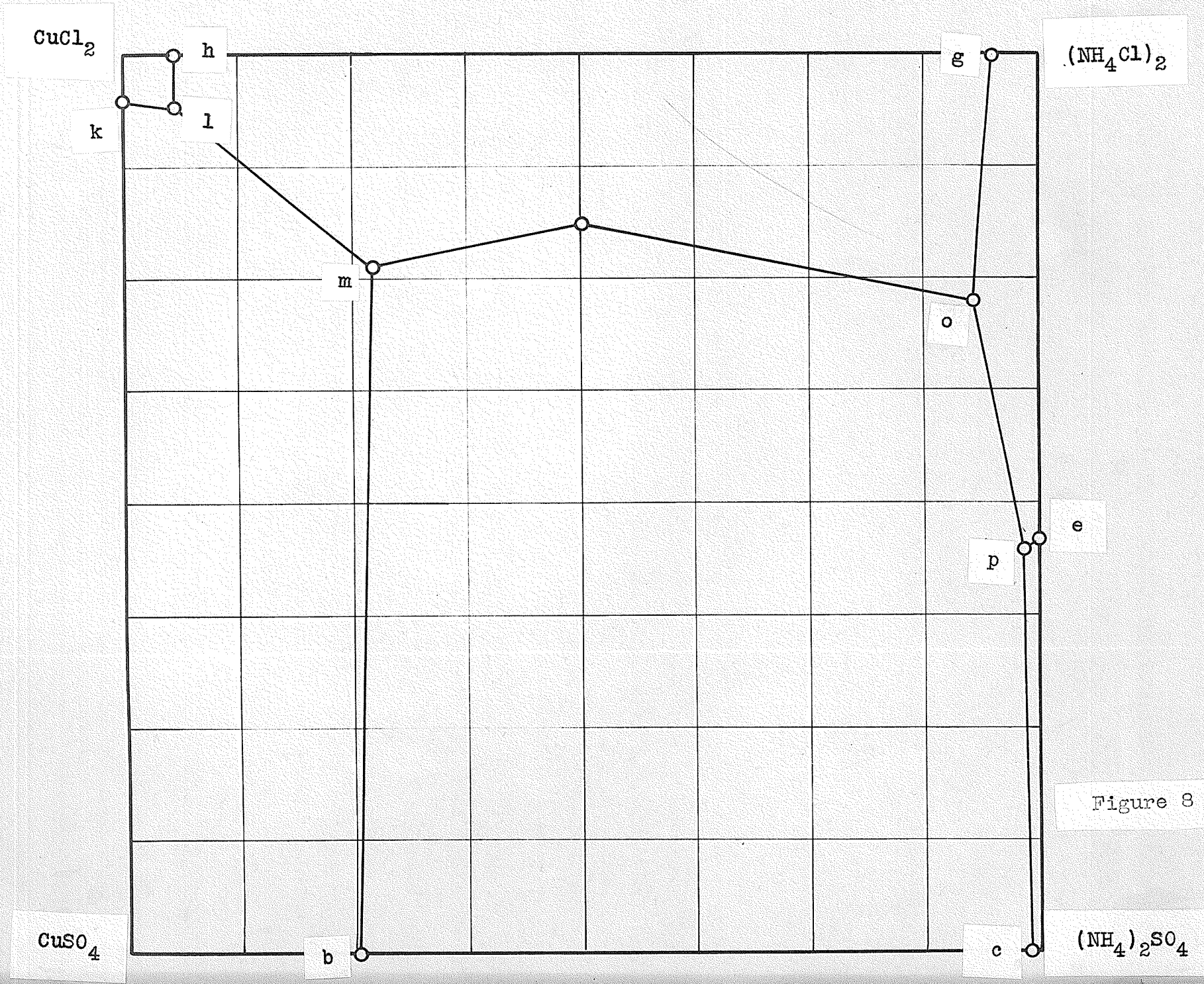


Figure 8

Copper and silver are in the same sub-group of the Periodic Table, hence it was thought similar results would be obtained by substituting silver for copper in the system. With this thought in mind the system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$ was investigated in a manner similar to that used by Schreinemakers. The results though not as interesting as those of Schreinemakers are shown in the sequel.

THE TERNARY SYSTEMS

Materials -

The sulphates used in this investigation were obtained from the British Drug Houses. Merck's U.S.P. Granular ammonium chloride was used of certified molecular weight 53.50. Each was recrystallized and found to be pure within the accuracy of the standard methods of analysis used in the study.

Freshly precipitated silver chloride was employed for each determination. It was prepared ⁽¹³⁾ by adding a solution of silver nitrate to a solution of sodium chloride in the presence of a small amount of nitric acid. The precipitate was well washed with water away from violet light and the final washings tested with silver nitrate solution. The precipitated chloride was then dried and ground ready for use.

Apparatus and Procedure -

All solubilities were determined by stirring a mixture of the components in a closed bottle which was immersed in a constant temperature bath. An ordinary reagent bottle about five inches high was used. Preliminary tests were used in the case of each mixture to determine the time of stirring in order to establish equilibrium. It was found that a period of twenty-four hours was sufficient to ensure equilibrium in each case.

Water was used as the thermostatic fluid - its temperature being controlled by a vacuum-sealed mercury regulator. Checking against a standard thermometer

showed the temperature of the investigation to be 29.91°C with an error of $\pm 0.03^{\circ}$.

Analyses were carried out by sucking off the mother liquor using a simple apparatus shown in Figure 9. A represents a sinter glass filter which is placed in the stirring bottle and is connected by rubber pressure tubing to a weighed testtube represented at B. The testtube B stoppered by a two-hole rubber bung is also connected to a water pump. In order to draw off the mother liquor the weighed testtube is placed in the thermostat and the water pump turned on; since the accuracy of Schreinemakers' "wet residue method" depends on a large difference between the composition of the mother liquor and the wet residue, as much mother liquor as possible is drawn off. The saturated liquor is then weighed, diluted and analyzed in aliquots; a small amount of the corresponding solid residue is taken off, diluted and also analyzed in aliquots. The compositions of the two are then plotted on the equilateral triangle.

Methods of Analysis -

In the ternary system $\text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$, the solid and liquid phases were separated by the suction apparatus. No silver chloride could be detected in solution. The silver sulphate in solution was determined by analyzing for silver by Volhard's method (25). This involves the addition of ferric ammonium sulphate to an aliquot amount of solution acidified with nitric acid

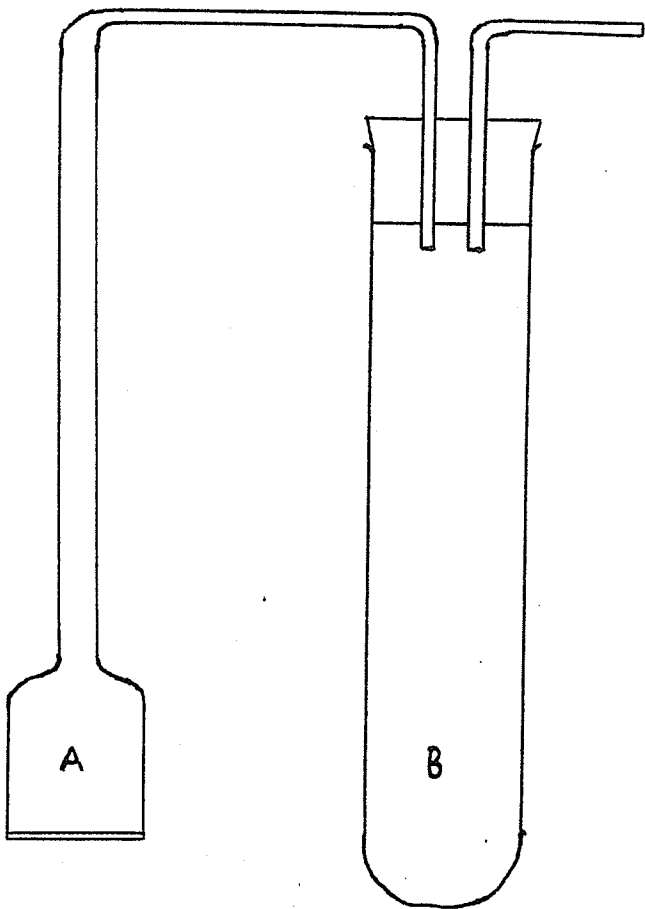


Fig. 9



and titration with potassium thiocyanate. When the precipitation of the white curdy silver thiocyanate is complete, ferric thiocyanate is formed and gives a red colour to the solution.

The wet solid material consisting of silver chloride and silver sulphate was diluted with water. The amount of silver chloride was found by filtering the result through a weighed Gooch crucible, washing with water, then alcohol and drying in an oven at 110°C to constant weight⁽²⁶⁾. The filtrate was then analyzed by the method of Volhard to determine the amount of silver sulphate.

It was thought at first that the analysis of silver in solution in the system $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O}$ would be hampered by the possible formation of double salt. Thus the sample was evaporated to dryness, ammonium sulphate sublimed off and the remaining silver sulphate then dissolved in water and a little nitric acid and titrated as before by Volhard's method. Such a troublesome procedure did not prove satisfactory, difficulty being experienced in introducing the silver back in solution. It was subsequently found that the soluble silver could be determined as described in the previous system in the presence of ammonium sulphate if the sample was first diluted with a large amount of water. This is shown by the following results obtained by making up solutions of ammonium and silver sulphates and analyzing for silver.

<u>Amount of Salts in Solution</u>		<u>Results of Analyses</u>	
<u>(NH₄)₂SO₄</u>	<u>Ag₂SO₄</u>	<u>Sublimation</u>	<u>Dilution</u>
<u>grams</u>	<u>grams</u>	<u>Method</u>	<u>Method</u>
5	1.122	1.120	1.125
10	1.630	1.621	1.630
20	1.641	1.507	1.642
50	2.255	2.005	2.258

Solutions requiring considerable heating to sublime the ammonium sulphate yielded faulty results by this method. The dilution method was used throughout the investigation in analyzing for silver sulphate in the presence of ammonium sulphate.

Ammonium sulphate was determined by analyzing for ammonia by the standard method⁽²⁹⁾. The sample was heated with an excess of strong sodium hydroxide solution, the vapours passing through a condenser into an Erlenmeyer flask containing a known quantity of standard acid and equipped with a drying tube containing glass beads to ensure no loss of ammonia. The standard acid was then titrated with standard sodium carbonate solution using methyl orange as an indicator and the ammonia content determined. As a check a sample was also analyzed for sulphate gravimetrically. The solid residue was diluted with water and analyzed similarly.

Volhard's process failed to show any silver in solution in the system NH₄Cl - AgCl - H₂O even though it was known that increasing amounts of silver chloride were entering solution. The silver chloride content was found by boiling the solution with a large excess of water whereby

the silver salt was precipitated. Complete precipitation of the silver chloride dissolved by 100 millilitres of a saturated solution of ammonium chloride required dilution to two litres. The weight of the precipitated silver chloride was then found by filtering through a Gooch crucible as discussed above. Ammonium chloride content was determined by the aforementioned ammonia analysis. The solid residue was washed with a considerable quantity of water and analyzed by the same method.

The fourth ternary system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$ was investigated by Schreinemakers⁽²²⁾. His results will be used in this work.

SOLUBILITY DATA AND DIAGRAMS

System $\text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O} -$

Analyses of phases obtained from stirring different proportions of silver sulphate and silver chloride in water at 30°C are shown below; the compositions are expressed in weight percent.

Table 1.

<u>Liquid</u>		<u>Residue</u>		<u>Nature of Solid Material</u>
<u>% Ag_2SO_4</u>	<u>% AgCl</u>	<u>% Ag_2SO_4</u>	<u>% AgCl</u>	
0.875	-	-	-	Ag_2SO_4
0.875	-	23.65	25.80	$\text{Ag}_2\text{SO}_4 / \text{AgCl}$

Results show that there was no change in the solubility of silver sulphate in the presence of silver chloride and no silver chloride was detected in solution. Since silver sulphate possesses a low solubility in water and is unaffected by the presence of silver chloride, these data are a sufficient investigation of this system. Should a double salt be formed some silver chloride would have to be brought into solution but results show this is not the case.

System $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{H}_2\text{O} -$

In this system which has been studied previously, no double salts are formed, that is, only ammonium sulphate and ammonium chloride occur as solid materials in contact with solution. The isothermally invariant solution was found to contain 17.93% NH_4Cl and 25.81% $(\text{NH}_4)_2\text{SO}_4$. This point is plotted on the quaternary diagram later in this paper (Fig.12).

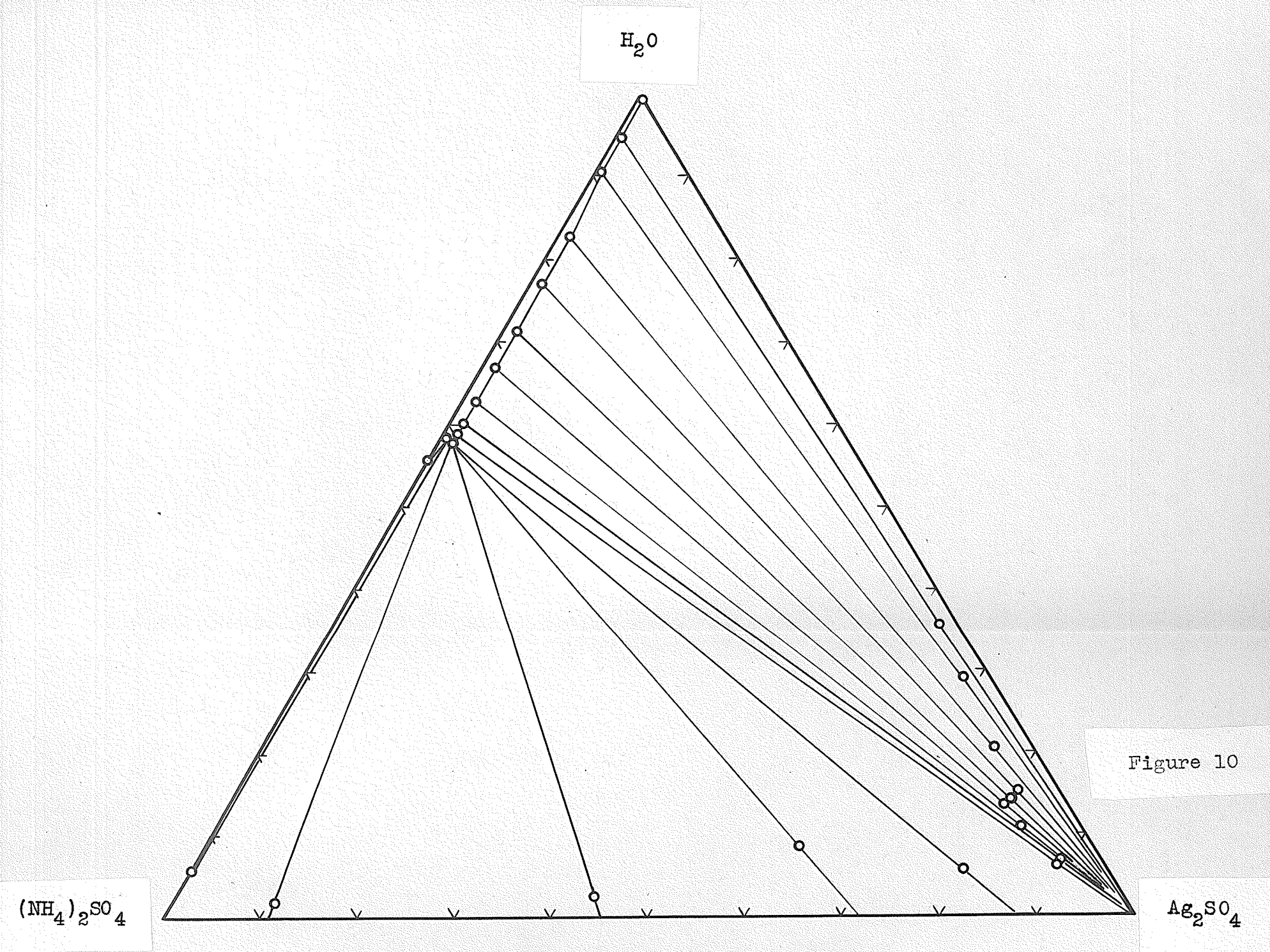
System $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O} -$

Analyses of phases obtained from stirring different proportions of ammonium sulphate and silver sulphate in water at 30° are shown below; the compositions are expressed in weight percent.

Table 2.

	<u>Liquid</u>		<u>Residue</u>		<u>Nature of Solid Material</u>
	<u>$\%(\text{NH}_4)_2\text{SO}_4$</u>	<u>$\%\text{Ag}_2\text{SO}_4$</u>	<u>$\%(\text{NH}_4)_2\text{SO}_4$</u>	<u>$\%\text{Ag}_2\text{SO}_4$</u>	
0		0.875	-	-	Ag_2SO_4
4.83		0.83	1.78	62.64	Ag_2SO_4
8.835		0.80	2.69	68.38	Ag_2SO_4
16.005		1.22	3.88	75.82	Ag_2SO_4
21.76		1.35	4.19	80.77	Ag_2SO_4
27.11		1.42	5.46	80.13	Ag_2SO_4
31.75		1.55	6.46	79.98	Ag_2SO_4
35.445		1.56	6.08	83.00	Ag_2SO_4
38.10		1.52	4.15	88.96	Ag_2SO_4
39.73		1.51	4.35	89.09	Ag_2SO_4
40.26		1.49	14.68	79.63	$\text{Ag}_2\text{SO}_4 \neq (\text{NH}_4)_2\text{SO}_4$
40.35		1.50	29.99	61.23	$\text{Ag}_2\text{SO}_4 \neq (\text{NH}_4)_2\text{SO}_4$
40.20		1.495	53.98	43.37	$\text{Ag}_2\text{SO}_4 \neq (\text{NH}_4)_2\text{SO}_4$
40.32		1.53	87.45	10.49	$\text{Ag}_2\text{SO}_4 \neq (\text{NH}_4)_2\text{SO}_4$
40.85		.95	94.10	.75	$(\text{NH}_4)_2\text{SO}_4$
43.88		0	-	-	$(\text{NH}_4)_2\text{SO}_4$

These results are plotted in Figure 10.



System $\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O} -$

Analyses of phases obtained from stirring different proportions of ammonium chloride and silver chloride in water at 30° are shown below; the compositions are expressed in weight percent.

Table 3.

<u>Liquid</u>		<u>Residue</u>		<u>Nature of Solid Material</u>
<u>% NH_4Cl</u>	<u>% AgCl</u>	<u>% NH_4Cl</u>	<u>% AgCl</u>	
5.62	0	1.12	80.64	AgCl
10.225	.01	2.31	77.99	AgCl
14.58	.02	2.69	81.37	AgCl
18.49	.07	2.92	82.29	AgCl
22.43	.14	4.38	80.02	AgCl
25.29	.24	4.12	81.41	AgCl
27.26	.365	3.81	85.97	AgCl
28.47	.45	9.64	79.23	AgCl / NH_4Cl
28.41	.46	27.08	61.82	AgCl / NH_4Cl
29.43	0	-	-	NH_4Cl

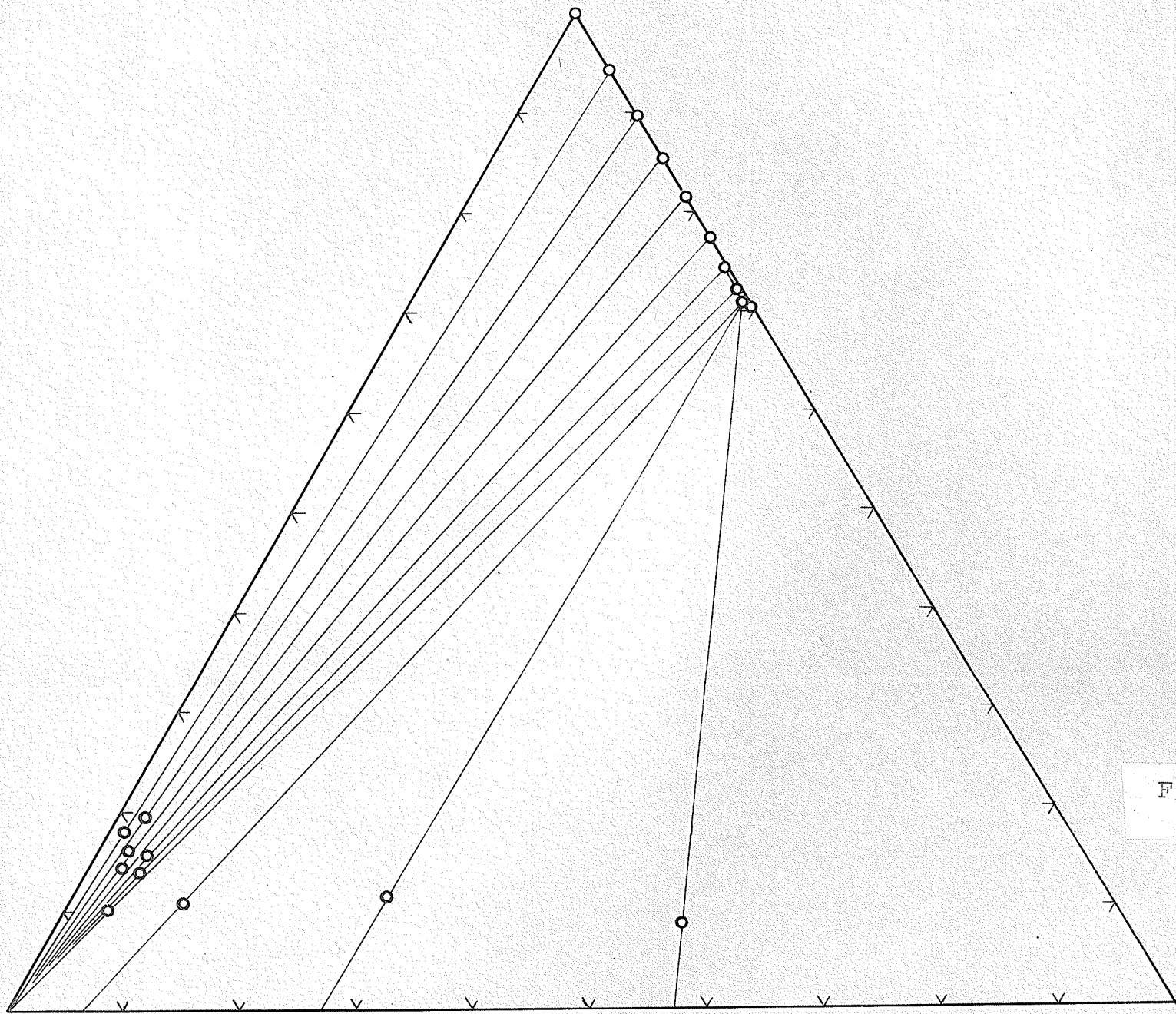
These results are plotted in Figure 11.

H₂O

AgCl

NH₄Cl

Figure 11



Discussion of Results -

As a result of the investigation of the ternary systems, calculations were made of the solubility of each salt in 100 grams of water at 30°. The values obtained were as follows: 0.8824 grams Ag_2SO_4 , 78.20 grams $(\text{NH}_4)_2\text{SO}_4$ and 41.71 grams NH_4Cl . These solubilities result from an average of values obtained by approaching saturation from both under and over saturation. The table below compares the solubilities with some previous results.

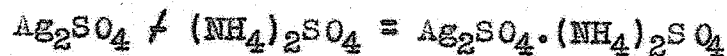
Solubility in grams per 100 grams of H_2O

<u>Salt</u>	<u>Calculated Value</u>	<u>Previous Values</u>
Ag_2SO_4	0.8824	0.8866 ⁽⁸⁾ , 0.8887 ⁽⁴⁾ .
$(\text{NH}_4)_2\text{SO}_4$	78.20	78.95 ⁽²⁷⁾ , 78.16 ⁽¹⁸⁾ , 77.31 ⁽³¹⁾ , 78.57 ⁽²²⁾ ,
NH_4Cl	41.71	41.64 ⁽⁵⁾ , 41.84 ⁽²²⁾ , 41.76 ⁽¹⁷⁾ , 41.36 ⁽¹⁸⁾ , 41.72 ⁽¹⁾ .

No double salts were found in any of the four systems, that is, no double salt was capable of existing as a solid phase in equilibrium with solution. However, evidence from the increased solubility of the silver salts in the systems $(\text{NH}_4)_2\text{SO}_4 - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O}$ and $\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O}$ might point to the existence of double salts in these systems. The solubility of a difficultly soluble salt is always increased initially, by the addition of another salt with no common ion. This change is generally the consequence of metathesis⁽⁸⁾. Also, an increase in solubility is sometimes exhibited when a salt with a common ion is introduced into the solution⁽⁹⁾. However, the comparatively large increase in the solubility of the silver salts would seem

to indicate changes greater than those caused by these effects. With this thought in mind different equilibrium expressions were tried with the object of determining quantitatively the probable double salt formed.

If there exists in solution a complex salt of the formula $Ag_2SO_4 \cdot (NH_4)_2SO_4$ it would be formed by the following reaction



This equation yields an equilibrium constant represented by

$$K = \frac{(Ag_2SO_4 \cdot (NH_4)_2SO_4)}{(Ag_2SO_4) \times ((NH_4)_2SO_4)}$$

where brackets indicate concentrations in moles per litre. It was found in this study that in the presence of increasing amounts of ammonium sulphate, the solubility of silver sulphate increased from 0.8824 grams per 100 grams of water to 2.576 grams per 100 grams of water. The additional silver sulphate entering solution is suspected to go into a complex, the difference between the moles of silver sulphate in solution and the moles of silver sulphate in a solution containing only water gives the number of moles of complex formed. Table 4 shows the moles of ammonium sulphate in solution and the total moles of silver sulphate in solution (subtracting solubility of silver sulphate in moles yields moles of complex formed) per 100 grams of water. It also shows the different equilibrium expressions attempted in order to obtain constancy where

$$K_1 = \frac{(Ag_2SO_4 \cdot (NH_4)_2SO_4)}{(Ag_2SO_4) \times ((NH_4)_2SO_4)}$$

$$K_2 = \frac{(Ag_2SO_4 \cdot 2(NH_4)_2SO_4)}{(Ag_2SO_4) \times ((NH_4)_2SO_4)^2}$$

$$K_3 = \frac{(Ag_2SO_4 \cdot 4(NH_4)_2SO_4)}{(Ag_2SO_4) \times ((NH_4)_2SO_4)^4}$$

Table 4.

<u>Solubilities</u>		<u>Equilibrium Constants</u>		
<u>$(NH_4)_2SO_4$</u>	<u>Ag_2SO_4</u>	<u>K_1</u>	<u>K_2</u>	<u>K_3</u>
.074	.00283	-	-	-
.146	.00471	4.60	32.8	1807.
.214	.00564	4.75	22.7	584.
.287	.00638	4.42	15.9	228.
.360	.00744	4.57	13.2	119.
.426	.00795	4.30	10.8	66.9
.477	.00804	3.89	8.4	55.5
.512	.00823	3.77	7.60	33.0
.530	.00826	3.66	7.11	28.6

Values of K indicate an equilibrium established of the form



The falling off of the value of the equilibrium constant at very high concentrations of ammonium sulphate shows that the solubility of silver sulphate is increasing through some other agency besides the suspected complex formed. Schreinemakers in the investigation

of his system found the analogous double salt $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Thus constancy in K might be overthrown by the fact that $\text{Ag}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ takes on some water of hydration or by the formation of an entirely new complex at high concentrations of ammonium sulphate.

In the ternary system $\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O}$ the solubility of silver chloride due to the presence of ammonium chloride rises from 17.44×10^{-7} moles to $4462. \times 10^{-6}$ moles per 100 grams of water, an increase in solubility of about 2560 times. Table 5 shows the moles of ammonium chloride and total moles of silver chloride in solution per 100 grams of water. If the solubility in moles, of silver chloride in water is subtracted from the total moles of silver chloride in solution, the result is the number of moles of complex formed. The equilibrium constants tried are as follows:

$$K_1 = \frac{(\text{AgCl} \cdot 2\text{NH}_4\text{Cl})}{(\text{AgCl}) \times (\text{NH}_4\text{Cl})^2}$$

$$K_2 = \frac{(2\text{AgCl} \cdot 3\text{NH}_4\text{Cl})}{(\text{AgCl})^2 \times (\text{NH}_4\text{Cl})^3}$$

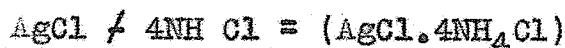
$$K_3 = \frac{(\text{AgCl} \cdot 3\text{NH}_4\text{Cl})}{(\text{AgCl}) \times (\text{NH}_4\text{Cl})^3}$$

$$K_4 = \frac{(\text{AgCl} \cdot 4\text{NH}_4\text{Cl})}{(\text{AgCl}) \times (\text{NH}_4\text{Cl})^4}$$

Table 5.

<u>Solubilities</u>			<u>Equilibrium Constants</u>		
<u>NH₄Cl</u>	<u>AgCl</u>	<u>K₁</u>	<u>K₂</u>	<u>K₃</u>	<u>K₄</u>
.319	15.38x10 ⁻⁵	.874x10 ³	1.53x10 ⁹	2.69x10 ³	8.46x10 ³
.424	57.37x10 ⁻⁵	1.83x10 ³	2.48x10 ⁹	4.34x10 ³	10.3 x10 ³
.541	126.2 x10 ⁻⁵	2.49x10 ³	2.64x10 ⁹	4.65x10 ³	8.73x10 ³
.635	228.3 x10 ⁻⁵	3.29x10 ³	3.03x10 ⁹	5.28x10 ³	8.54x10 ³
.704	352.2x 10 ⁻⁵	4.14x10 ³	3.47x10 ⁹	6.05x10 ³	8.90x10 ³

Calculations of K show the probable existence of the equilibrium



to explain the increased amount of silver chloride entering solution. The double salt corresponding to this combination in Schreinemakers' study was $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$.

It is quite understandable that the double salts found by Schreinemakers and those calculated from this work should not correspond. Schreinemakers showed the existence of the salts $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$. In general, ammonium salts are anhydrous while on the other hand copper salts, especially the sulphate and chloride, are hydrated; thus the water of hydration in these salts is due to the presence of the copper salt rather than the ammonium. Such is not the case however on replacing copper by silver, silver salts (even though copper and silver are in the same sub-group of the Periodic Table) are not prone to taking on water of hydration. Thus a double salt formed from a silver and an ammonium salts would in all probability be anhydrous.

The solubility diagrams show that the double salts $\text{Ag}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and $\text{AgCl} \cdot 4\text{NH}_4\text{Cl}$ are not capable of existing as solid materials in equilibrium with solution at 30° . However, it is possible that they possess a stable existence at some other temperature.

Conclusions -

The solubility relations in the ternary systems Ag_2SO_4 - AgCl - H_2O , $(\text{NH}_4)_2\text{SO}_4$ - Ag_2SO_4 - H_2O and NH_4Cl - AgCl - H_2O at 30°C have been determined.

No double salts were found in any of these systems at this temperature. However, evidence has been given to point to the existence of the salts $\text{Ag}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and $\text{AgCl} \cdot 4\text{NH}_4\text{Cl}$ at some other isotherm.

THE QUATERNARY SYSTEM

Procedure -

Four isothermally invariant compositions were realizable in the four ternary systems. They in the quaternary diagram will be represented by points on the edges of the Janecke square. An investigation of the quaternary system is accomplished by adding a third salt to each ternary system. Analyses of the resulting solutions would yield curves starting at the isothermally invariant point of the corresponding ternary system and moving out into the body of the diagram. Four such curves are expected representing the following sets of salts in solution:

- (a) $\text{AgCl} - \text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$
- (b) $\text{Ag}_2\text{SO}_4 - \text{NH}_4\text{Cl} - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$
- (c) $(\text{NH}_4)_2\text{SO}_4 - \text{AgCl} - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$
- (d) $\text{NH}_4\text{Cl} - \text{AgCl} - \text{Ag}_2\text{SO}_4 - \text{H}_2\text{O}$

The first named salt in each set is added to the ternary system represented by the last three compounds in each set. Thus in (a) varying amounts of silver chloride are added to the ternary system $\text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$.

The curves, starting at the isothermally invariant point of the ternary system would run out to an isothermally invariant point of the quaternary system. In general if no ternary or quaternary solids are formed, two isothermally invariant points in the quaternary system are expected and these would be joined by a curve representing equilibrium between two substances without a common ion. With this thought in mind mixtures of ammonium sulphate, silver chloride and water were prepared and analyzed.

Thus the Janecke square would be divided into four areas in each of which, one of the four salts is in equilibrium with solutions. If any ternary or quaternary solids are formed they also would have areas representing the compositions of solutions with which they were in equilibrium, although the fact that no double salts were found at this temperature in the ternary systems makes the existence of ternary or quaternary solids unlikely.

The study of the mixtures was carried out by the same method used in the ternary system. The different sets of salts were stirred in the reagent bottle immersed in the thermostat. Preliminary tests showed that a minimum of forty-eight hours of stirring was necessary to ensure the establishment of equilibrium of the reaction mixtures. The same solubility apparatus (Figure 9) was employed.

In the analysis of each set of salts the liquid phase was drawn off, diluted with a large quantity of water and filtered through a Gooch crucible to determine the silver chloride content. The filtrate was analyzed in aliquots by Volhard's method for silver in solution and by back titration with standard sodium carbonate solution for ammonium in solution. Since in sets (b) and (c) both ammonium chloride and ammonium sulphate exist in the liquid phase, sulphate analyses were also necessary to determine the composition. The solid residue was diluted with a large quantity of water,

filtered through a Gooch crucible for determination of silver chloride and the filtrate analyzed in a way similar to the liquid phase above.

Results and Diagram -

Investigation of set (a) yielded no curve on the Janecke diagram (Figure 12). Adding silver chloride to the ternary system $\text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ caused no change in the composition of the isothermally invariant point of the ternary system.

Investigation of set (b) yielded curve op. This is a very short curve since the only silver that can exist in solution with the chloride ion is that held in one of the suspected double salts.

Investigation of set (c) yielded curve qp. Table 6 shows the results of analyses in equivalents of each ion considering 100 equivalents of each of the cation and anion present.

Table 6.

<u>Ag</u>	<u>NH₄</u>	<u>Cl</u>	<u>SO₄</u>	<u>Point</u>
3.41	96.59	100	-	q
2.53	97.47	74.55	25.45	
1.90	98.10	54.69	45.31	
1.20	98.80	38.91	61.09	
1.26	98.74	37.71	62.29	p
-	100	38.61	61.39	o

Investigation of set (d) yielded curve lm. Since no chloride enters solution and there is only an increase

in the ammonium radical, no results will be given.

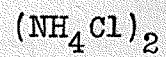
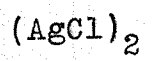
Investigation of the system $(\text{NH}_4)_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$ showed no silver chloride in solution using the described methods of analysis.

The Janecke diagram is completed by a curve joining mp. The line represents the addition of ammonium chloride to the system $\text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$.

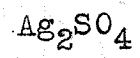
Table 7 shows the solid phases in equilibrium with the liquid phase at the different points on the quaternary diagram.

Table 7.

<u>Point</u>	<u>Solid Phases</u>
l	$\text{AgCl}, \text{Ag}_2\text{SO}_4$
m	$\text{AgCl}, \text{Ag}_2\text{SO}_4, (\text{NH}_4)_2\text{SO}_4$
o	$\text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4$
q	$\text{AgCl}, \text{NH}_4\text{Cl}$
p	$\text{AgCl}, \text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4$

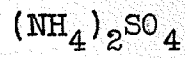


q



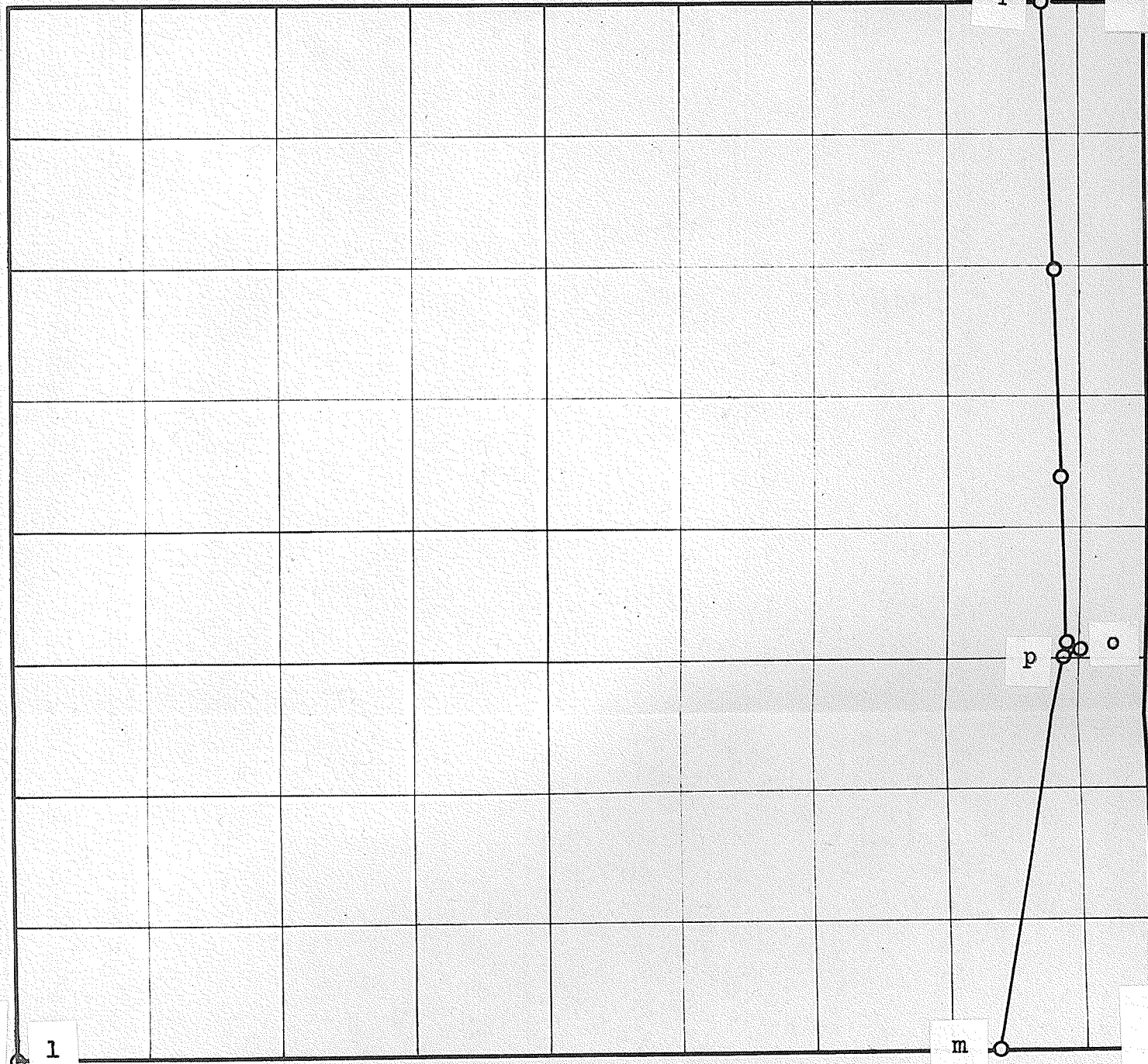
l

m



p

Figure 12



Discussion of Results -

Participants in the quaternary system are connected by the equation



Since silver chloride is only sparingly soluble the reaction produces the right-hand components almost completely.

The only cases where the silver ion and chloride ion could exist simultaneously in solution were in the addition of ammonium sulphate to $\text{AgCl} - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$, the addition of silver chloride to $\text{NH}_4\text{Cl} - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ and the addition of ammonium chloride to $\text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$. Thus these cases represented by *ap*, *op* and *mp* are the only curves which move out into the body of Jancke's square. This also provides more evidence for the formation of double salts. Although silver chloride was in solution it was not free to react with the ammonium sulphate but rather was held in solution by combination with the ammonium chloride. Similarly silver sulphate was in solution but would not all react with ammonium chloride.

The isothermally invariant points of the four ternary systems are represented (Figure 12) as follows:

<u>System</u>	<u>Point</u>
$\text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$	l
$\text{Ag}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$	m
$\text{NH}_4\text{Cl} - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$	o
$\text{NH}_4\text{Cl} - \text{AgCl} - \text{H}_2\text{O}$	q

Although these no longer represent isothermal invariance all curves in the quaternary system have their beginnings at these points. Only one isothermally invariant point

could be experimentally realized from the quaternary investigation, that being point p.

The curve qp represents solutions in equilibrium with solids ammonium chloride and silver chloride, curve mp represents solutions in equilibrium with solids ammonium sulphate and silver chloride and curve op represents solutions in equilibrium with solids ammonium sulphate and ammonium chloride. The point p represents a solution in equilibrium with solid ammonium sulphate, ammonium chloride and silver chloride.

A solution represented by a point in the area bounded by qpo will be in equilibrium with solid ammonium chloride and a solution represented by a point in the area bounded by mpo will be in equilibrium with solid ammonium sulphate. The remainder of the diagram represents the compositions of solutions in equilibrium with solid silver chloride. Under no conditions can a solution exist in equilibrium with silver sulphate since any excess silver sulphate over and above that entering the complex will react with the chloride ion yielding silver chloride.

Conclusions -

The quaternary system $(\text{NH}_4)_2\text{SO}_4 - \text{NH}_4\text{Cl} - \text{Ag}_2\text{SO}_4 - \text{AgCl} - \text{H}_2\text{O}$ has been investigated at 30°C and the results plotted by the method of Jänecke.

Bibliography -

1. Alluard, M.: Compt. rend. 59, 500-504 (1864).
2. Bancroft, W.: J. Phys.Chem. 6, 178-185 (1902).
3. Blasdale, W.C.: "Equilibria in Saturated Salt Solutions"
(Chemical Catalog Co., 1927) p.137.
4. Caven, R.M., and Mitchell, T.C.: J.Chem.Soc. 127, 2550-2551
(1925).
5. Fedotieff, P.P.: Z. physik.Chem. 49, 162-188 (1904).
6. Findlay, A.: "The Phase Rule"
(Dover Publications Inc., 1945) p.9.
7. Gibbs, W.H.: Trans.Conn.Acad. 3, 174 (1891).
8. Harkins, W.D.: J.Am.Chem.Soc. 33, 1807-1827 (1911).
9. Harkins, W.D.: J.Am.Chem.Soc. 33, 1836-1873 (1911).
10. Janecke, E.: Z.anorg. Chem. 51, 132-157 (1906).
11. Lodocnikow, W.H.: Z.enorg. Chem. 151, 185-213 (1926).
12. Lowenherz, R.: Z.physik. Chem. 13, 459-491 (1894).
13. Mellor, J.W.: "Inorganic and Theoretical Chemistry"
Vol.3, (Longmans, 1923) p.392.
14. Meyerhoffer, W.: Sitzungsber.Wien.Akad. 104, IIb, 840
(1895).
15. Meyerhoffer, W.: Z. physik. Chem. 5, 97 (1890).
16. Meyerhoffer, W.: "Phasenregel", (Leipzig, 1892) p.60.
17. Mohr, E.C.J.: Z.physik. Chem. 27, 193-221 (1898).
18. Rivett, A.C.D.: J.Chem.Soc. 121, 379-393 (1922).
19. Roozeboom, H.W.B.: Z.physik.Chem. 12, 357-389 (1893).
20. Roozeboom, H.W.B.: Z.physik.Chem. 15, 145-158 (1894).
21. Schreinemakers, F.A.H.: Proc.K.Akad. Wetensch.Amsterdam,
11, 615-620 (1908-9).
22. Schreinemakers, F.A.H.: Z.physik.Chem. 69, 557-568 (1909).
23. Schreinemakers, F.A.H.: Z.physik.Chem. 9, 57-77 (1892).
24. Schreinemakers, F.A.H.: Z.physik.Chem. 11, 75-109 (1893).

25. Scott, W.W.: "Standard Methods of Chemical Analysis"
(Van Nostrand Co., 1927) p.456.
26. Scott, W.W.: "Standard Methods of Chemical Analysis"
(Van Nostrand Co., 1927) p.454.
27. Sommer, F., and Weise, K.: Z.anorg.Chem. 94, 51-91 (1916).
28. Stokes, G.: Proc.Roy.Soc. 49, 174-188 (1891).
29. Sutton, F.: "Volumetric Analysis"
(J. and A. Churchill, 1924) p.75.
30. Van Rijn van Alkemade, A.C.:
Z. physik. Chem. 11, 289-309 (1893).
31. Weston, A.: J. Chem. Soc. 121, 1223-1237(1922).

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