

THE TERNARY SYSTEMS

1. MAGNESIUM CHLORIDE - MAGNESIUM SULPHATE - WATER
2. MAGNESIUM SULPHATE - POTASSIUM SULPHATE - WATER

AT THE 100° ISOTHERMAL.

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POTASSIUM SULPHATE - WATER

AT THE 100° ISOTHERMAL.

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who has directed and very kindly  
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### Introduction

When a natural water is concentrated by evaporation it deposits its saline constituents in the reverse order of their solubility, the least soluble first, the most soluble last of all. The process, however, is not so simple as it might appear to be, for the solubility of a salt in pure water is one thing and its solubility in the presence of other compounds is another. Each substance is affected by its associates, and its deposition is partly a matter of concentration and partly a question of temperature. In general, the character of a saline deposit can be predicated from the character of the water which yields it; a chloride water gives chlorides, a sulphate water sulphates, and waters of mixed type furnish mixtures of compounds or even double salts. The more complex the water the greater becomes the range of possibilities.

The behaviour of reciprocal salt pairs is of a special importance in connection with the study of the conditions governing the deposition of oceanic salts, such as takes place at Stassfurt. In sea water there are a number of ions, for example; sodium, potassium, magnesium, calcium, chloride and sulphate ions, which on evaporation of the water can give rise to deposits of single salts or of double salts in large numbers, the nature of the deposit depending on the concentration of the solution and the temperature of evaporation.

Leaving out of consideration the calcium and the sodium salts, we will in this work consider the condition for equilibrium in the systems formed by the reciprocal salt pairs potassium, magnesium, chloride and sulphate.

The Stassfurt deposits have been the subject of elaborate investigation by J. H. Van't Hoff and his school<sup>1</sup>. In 1849 J. Usiglio<sup>2</sup> studied the deposition of salts, when sea water is concentrated by evaporation and examined the residues analytically. He found that calcium carbonate is first eliminated, then calcium sulphate, then sodium chloride and the more soluble salts accumulate in the mother liquor. This method of investigation does not allow sufficient time for the various salts to attain a state of equilibrium and it therefore follows that the natural evaporation of brines probably furnishes somewhat different results. Moreover it is difficult, if not impossible, to identify the several substances, which separate from the mother liquor formed during the later stages of evaporation. Van't Hoff followed the synthetic method in his study of this subject. He started from simple solutions, like those of sodium and potassium chlorides under definite conditions of temperature and gradually added the pertinent constituents, until the subject became so complicated that the crystallization of the constituents from the concentrating sea water was reduced to a special case of a far more comprehensive work.

The work of Van't Hoff shows that the slow evaporation of sea water furnishes salts in the following order (1) a deposit of sodium chloride, (2) sodium chloride, leonite, potassium chloride, (3) sodium chloride, keiserite and carnallite, (4) sodium chloride, keiserite, carnallite and magnesium chloride, (5) the solution dries without further change. Precht and Wittzen<sup>3</sup> have shown that the dehydrating action of magnesium chloride prevented the formation of epsomite, when a mixture of the sulphates and chlorides of magnesium is heated on the

water bath. This dehydrating action of magnesium chloride has made itself evident continually in our work on this subject and its presence in solution will effect considerably the resulting salts.

To obtain an insight into the conditions under which the different salts can be deposited, Van't Hoff and his pupils<sup>4</sup> carried out a large number of solubility determinations and investigated the conditions under which the different salts and mixtures of salts exists in equilibrium with solution. This work was carried on at 25<sup>0</sup> and he found that besides the four single salts, there existed the double salts, carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and schoenite  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  in the before mentioned system  $\text{K}_2\text{SO}_4 \cdot \text{MgCl}_2 - \text{KCl} - \text{MgSO}_4 - \text{H}_2\text{O}$ .

This system was also studied by Janecke,<sup>5</sup> who worked upon the melts of these salts. His results differed from Van't Hoff's 25<sup>0</sup> isothermal in that two new salts formed, namely, langbeinite  $\text{K}_2\text{Mg}(\text{SO}_4)_3$  and a quaternary salt, anhydro kainite  $\text{KMgClSO}_4$  were present besides the anhydrous simple salts themselves and an anhydro carnallite, which occurred at 25<sup>0</sup>. The quaternary is of interest, since it is formed of the four different radicals.

A question may now be raised, where do these salts appear and disappear with respect to the temperature between 25<sup>0</sup> and the temperatures of the melts, which was in the neighborhood of 500<sup>0</sup>? The answer to this question is attempted in this work. The 100<sup>0</sup> isothermal was chosen, since it was midway between the two studies which had already been completed. 100<sup>0</sup> is also the approximate boiling point of water solutions, therefore, our results would give us solubility relations of the salt pairs in boiling solutions or approx-

imately boiling, since the boiling point of the solution will be raised by the dissolved salts.

It was necessary in this work to carry out a complete primary investigation of the salt pairs containing a common radical or metal and then use the data so obtained, to complete the quaternary system containing the two different metal and acid radicals.

Only two of these systems were completed in this work, namely, magnesium sulphate, magnesium chloride and water at 100<sup>0</sup> and magnesium sulphate, potassium sulphate and water at 100<sup>0</sup>. The other two systems, namely, potassium chloride and magnesium chloride and water at 100<sup>0</sup> and potassium chloride, potassium sulphate and water at 100<sup>0</sup> were completed by my co-worker K. Downes<sup>6</sup> and a thorough study of these systems will be found in his work under that title. I have used his results to complete the solubility relations of the quaternary system  $KCl - MgSO_4 - K_2SO_4 - MgCl_2$  at 100<sup>0</sup> along with the results I obtained for the above mentioned two systems that are found in this work.



## The Phase Rule

Gibbs<sup>9</sup> enunciated the general theorem called the phase rule, by which he defined the conditions of equilibrium as a relationship between the number of what are called phases and the components of the system.

**Phases.** When a heterogeneous system is made up of different portions, each in itself homogeneous, but marked off in space and separated from the other portions by bounding surfaces.

These homogeneous, physically distinct and mechanically separable portions are called phases.

**Component.** As the components of a system there are to be chosen the smallest number of the independently variable constituents, by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation; namely three facts: -

(1) The components are to be chosen from among the constituents, which are present when the system is in a state of true equilibrium and which takes part in the equilibrium.

(2) As components are to be chosen the smallest number of such constituents necessary to express the composition of each phase participating in the equilibrium. Zero and negative quantities of the components being permissible.

(3) In any given system the number of components is definite, but may alter with varying conditions of the experiment. A certain freedom of choice however is allowed in the qualitative selection of the components. The choice being influenced by considerations of simplicity, suitability or generality of application.

Degree of freedom. The number of the variable factors, temperature, pressure and concentration of the components, which must be arbitrarily fixed in order that the conditions of the system may be perfectly defined, we may also speak of variability or variance of a system.

The phase rule may be stated as follows: a system consisting of  $n$  components can exist in  $n / 2$  phases only when the temperature, pressure and concentration have fixed and definite values. If there are  $n$  components in  $n / 1$  phases, equilibrium can exist while one of the factors varies and if there are only  $n$  phases, two of the varying factors may be arbitrarily fixed. This rule, the application of which, it is hoped, will become clear in the sequel, may be very concisely and conveniently summarized in the form of the equation

$$F = n - r / 2 \quad \text{or} \quad F = n / 2 - r$$

where  $F$  denotes the variability or degrees of freedom of the system,  $n$  the number of the components, and  $r$  the number of phases. The relation between these is evident from the equation.

Consider first the relation of our investigations to Gibbs' phase rule. According to this there is complete equilibrium, if  $n$  salts occur in  $(n / 1)$  phases. We are dealing with saturated solutions and since two phases are always present, namely salt and solution, the conditions for equilibrium are such that there will be  $(n - 1)$  solid phases.

Consider first a solution saturated with one salt. In this case we will have two components and one solid phase. The two components

being salt and water. Complete equilibrium will be obtained only when three phases are present.

With solutions saturated with two salts of the same base or acid, the number of components will be three existing in three phases.

(a) We deal with solutions of two salts, both of the same acid or base: eg.,  $KCl$ ,  $K_2SO_4$ . In all three components. Therefore the degree of freedom will be zero, when both salts are present as solids.

(b) A special case will occur where a double salt forms to complete equilibrium being possible: eg.,  $KCl - DS$ ,  $K_2SO_4 - DS$ .

(c) A peculiar solution of  $MgSO_4$  as  $7H_2O$  and  $6H_2O$  both forming solid phases. The latter forms from water, magnesium chloride, magnesium sulphate heptahydrate. Magnesium chloride enters solution and withdraws water of crystallization from magnesium sulphate heptahydrate forming  $6aq.$ , until a definite concentration is reached. If more solid magnesium chloride hexahydrate is added, this also dissolves and draws  $1aq.$  from the magnesium sulphate heptahydrate. If sufficient magnesium sulphate heptahydrate is not present, it no longer occurs as a solid phase, but only magnesium sulphate hexahydrate coexists with magnesium chloride hexahydrate in the solid state. Hence two different solutions can be prepared from the salts magnesium sulphate and magnesium chloride, each saturated with respect to the two salts.

Saturated solutions of two salts with no common ion will raise the number of components to four. A study of a system of this type at  $100^{\circ}$  isothermal is the aim of this present work. The four salts

are  $\text{MgCl}_2 - \text{K}_2\text{SO}_4 - \text{MgSO}_4 - \text{KCl}$ . They represent three substances, i.e.,  $\text{K}_2\text{SO}_4 = \text{K}_2\text{Cl}_2 / \text{MgSO}_4 / \text{MgCl}_2$ . Since the fourth component is water, the degree of freedom must therefore be zero.

If three salts are present as solids, one having used only two salts, a third will have formed from these two and will appear in the solid phase: eg; excess potassium chloride, magnesium sulphate, water. Magnesium chloride is produced, dissolves and potassium sulphate separates out forming shoenite at  $25^\circ$  with magnesium sulphate. Three solids magnesium sulphate heptahydrate, potassium chloride and shoenite. Conversely if four salts are taken, one will vanish and there will be three remaining as solid phases. The solution being of constant composition.

If in the preparation of these solutions we use potassium chloride and magnesium sulphate, the analysis of the solution will give us the same result as if potassium sulphate and magnesium chloride had been added. As potassium sulphate and magnesium sulphate at  $25^\circ$  unite to form shoenite and magnesium chloride and potassium chloride form carnallite and magnesium sulphate hexahydrate from magnesium sulphate heptahydrate by using the salts potassium chloride, magnesium chloride, potassium sulphate and magnesium sulphate in different proportions, the production of five solutions is possible, in each of which three solid phases are present.

- |              |  |
|--------------|--|
| Solid phases | (1) Shoenite, $\text{K}_2\text{SO}_4$ , $\text{KCl}$   |
|              | (2) " , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , $\text{KCl}$   |
|              | (3) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , $\text{KCl}$ |
|              | (4) $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , $\text{KCl}$ Carnallite                                  |
|              | (5) $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Carnallite   |

In the preparation of these solutions within certain limits, salts may be taken in any quantity, but one must pay particular attention to the quantitative relations in which the salts must be present to form the solid phases. Quantities must be chosen in such a manner, if magnesium sulphate heptahydrate is to be the solid phase, that more potassium sulphate expressed in equivalent quantities is not produced by the double decomposition, than is present as magnesium sulphate heptahydrate. As in this case potassium sulphate and not magnesium sulphate heptahydrate with shoelite will be the solid phase. In our soluble experiments very large quantities of salts were avoided because a paste is obtained and therefore three salts were used whose proportions were calculated approximately from previous experiments with solutions having three salts as solid phases.

### Graphical Representation of Three Component Systems.

If we have three components, five phases are necessary to constitute a nonvariant system, four for a monovariant system and three for a divariant system. Since the number of liquid phases can never exceed the number of the components and since there can be only one vapour phase, it is evident at the quintuple point, as in the case of the other invariant systems, there must always be at least one solid phase present. As the number of phases diminished, the variability of the system may increase from one to four. So that in the last case the condition of the system will not be completely defined, until not only the temperature and the total pressure of the system, but also the concentrations of two of the components have been fixed.

The problem of representation has been solved in several ways. Concentration, temperature diagrams present great difficulties when the number of components equals three. Schreinemakers<sup>10</sup> uses the  $x$  and  $y$  axes to represent the amounts of the components in a constant quantity of the third. Here we find ourselves unable to express the anhydrous double salt or solutions containing very little of the third component. Meyerhoffer<sup>11</sup> uses a diagram in which the temperature is one of the coordinates. In a system of two salts and water he measures the ratio of one salt to the other along one axis and the temperature along the other. This method neglects the relative quantities of both salts in respect to the third component.

Van Rijn van Alkermade's<sup>12</sup> method has no advantage over the method of Schreinemakers. In the method proposed by Gibbs<sup>13</sup> an equilateral triangle was used. The sum of the components was kept constant, the triangle being of unit height. The corners of the triangle will represent some definite mixtures of the three substances. This was used by Thurston<sup>14</sup> in some work on alloys and also suggested by Stokes<sup>15</sup>.

Roozeboom<sup>16</sup> suggested first an isosceles right angle triangle, the equal sides being of unit length. This distorted the three sides or hypotenuse so that one of the components seems to occupy an exceptional position and is found impossible, when the system of three components is considered, as a subdivision of one containing four. This he modified to an equilateral triangle, which is distinctly superior to any others considered before. It consists in employing the equilateral triangle, the length of whose side is made equal to unity or one hundred. The sum of the fractional or percentage amounts of the three components being represented by the sides of the triangle. In employing the triangular diagram it will be of use to note a property of the equilateral triangle. A line drawn from one corner of the triangle to the opposite side represents the composition of all mixtures, in which the relative amounts of the two components remain unchanged. Thus, in figure 1 we see that if the component C is added to a mixture x, in which A and B are present in the proportions of a:b, a mixture x', which is thereby obtained, also contains A and B in the ratio a:b. For the two triangles ACx and BCx are similar to

the two triangles  $HCx'$  and  $KCx'$ ; and, therefore,  $AX; Bx = Hx' ; Kx'$ . But  $Ax = Dx$  and  $Bx = Ex$ ; further,  $Hx' = Fx'$  and  $Kx' = Gx'$ . Therefore,  $Dx: Ex = Fx' : Gx' = b;a$ . At all points on the line  $Cx$ , therefore, the ratio of A to B is the same.

If it is desired to represent at the same time the change of another independent variable, e. g. temperature, this can be done by measuring the latter along axes drawn perpendicular to the corners of the triangle. In this way a right prism is obtained, and each section of this cut parallel to the base represents therefore an isothermal surface.

Systems of two salts and water. In studying these systems, one restriction must be made, namely; that the single salts are salts either of the same base or of the same acid or in other words capable of yielding a common ion in solution; otherwise the system would be one of four components.

If to a pure solution of A a small quantity of B is added, the solubility of A will in general be altered. Fig. (2). The curve AC represents the varying composition of the solution in equilibrium with the solid component A. Similarly the curve BC represents the composition of the solutions in contact with pure B as solid phase. At the point C, where these two intersect, there are two solid phases, namely; pure A and pure B in equilibrium with the solution and the system becomes invariant. At this point the solution is saturated with respect to both A and B and at a given temperature must have a perfectly definite composition. The curve ACB is the boundary curve for saturated



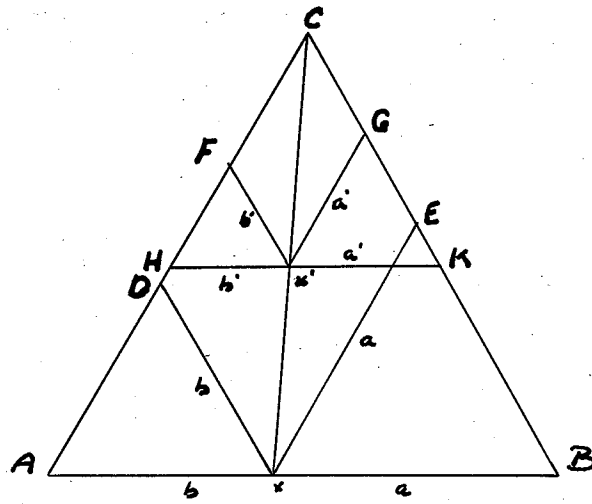


Fig. 1

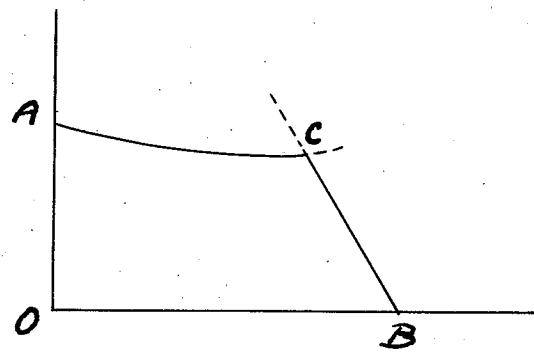
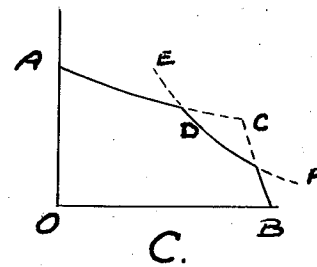
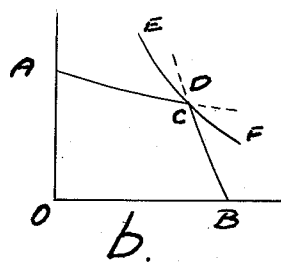
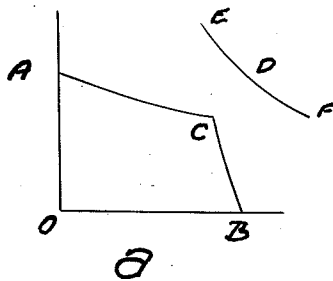


Fig. 2



solutions. While solutions represented by a point lying within the area ACBO are unsaturated, the points outside the area are supersaturated or mixtures of solid phases and saturated solution. Since we are dealing with a three component system, one solid phase in contact with solution will constitute a bivariant system, at any given temperature. Therefore the concentration of the solution in equilibrium with the solid can undergo change.

Consider now the formation of a double salt. This will give us the solubility curve for the double salt and those for the two constituent salts. We shall suppose that the double salt is formed from the single salts, when the temperature is raised above a certain point. We can therefore have three cases:

(a) At a temperature below the transition temperature, the solubility of a double salt is greater than that of a mixture of the single salts. Therefore the curve EFD lies above the point C. This would be metastable and decomposed when brought in contact with the simple salts.

(b) At the temperature of the transition temperature the double salt can exist together with the single salts in contact with the solution. The solubility curve of the double salt must therefore pass through C.

(c) With a still greater alteration of the temperature in the same direction as before, the relative shifting of the double salt curves becomes more marked. In this case the double salt now lies in a region of distinct unsaturation with respect to the double salts and can exist as solid phase in contact with the solution

of relatively more of B than is contained in a double salt itself.

The method of determining the composition of the solid phase in contact with the saturated solution is due to Schreinemaker.<sup>17</sup>

He showed that by analysing the solution and its corresponding wet solid phase and plotting the two points, thus obtained, on the triangular diagram, that the line joining these two points (called tie line) would intersect the side of the triangle at the composition of the solid phase.

## Graphical Representation of Four Component Systems.

For the graphical representation of the isothermal equilibria in systems formed by two reciprocal salt-pairs and water, two methods are employed, one due to Lowenherz<sup>18</sup> the other due to Janecke<sup>19</sup>. Let us deal first with the system of Lowenherz where he considers the simple case  $\text{KNO}_3 - \text{NaNO}_3 - \text{KCl} - \text{NaCl}$ . As the relation  $\text{KCl} / \text{NaNO}_3 = \text{KNO}_3 / \text{NaCl}$  exists, we can express the composition of all solutions in terms of three salts. The graphical representation of any given concentration can be done on a system of four axes, drawn like the edges of a regular octohedron OA, OB, OC, OD meeting at O; that is two neighboring axes form an angle of  $60^\circ$ , while opposite axes (OA and OC) form an angle of  $90^\circ$ . If we express along OA the content of KCl, NaCl on OB,  $\text{NaNO}_3$  on OC,  $\text{KNO}_3$  on OD, any given point P expresses the content by drawing from P a parallel to DO which cuts the plane OCB in a and ac parallel to CO, ab parallel to BO. Then aP expresses the quantity of  $\text{KNO}_3$ , ac of  $\text{NaNO}_3$ , ab of NaCl. The same concentration can be expressed as the sum of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , KCl, or of  $\text{NaNO}_3$ , NaCl and KCl or of  $\text{KNO}_3$ , NaCl, KCl. But if an octohedron is chosen these values are identical, because  $\text{KNO}_3$  and NaCl is graphically identical with KCl and  $\text{NaNO}_3$ . In the four possible methods of expressing, there may also occur one having, for example, negative KCl and this of course limits the choice. As the four salts can only coexist at the transition temperature, we have for any other temperature

the following cases of saturated solution.

Solutions saturated with 1. one 2. two 3. three salts.

Case 1. Where  $KCl$  and  $NaNO_3$ , but not  $NaCl$  and  $KNO_3$  can coexist.

We then have to express the above three kinds of solutions by lines and surfaces. Solutions saturated with one salt are immediately expressible by plotting the solubilities of  $KCl$ ,  $NaCl$ ,  $NaNO_3$  and  $KNO_3$  as  $Oa$ ,  $Ob$ ,  $Oc$ ,  $Od$  respectively. Further there then exists in the plane between  $Oa$ ,  $Ob$  a line, consisting of two parts, of which  $aP$  expresses the solubility of  $KCl$  in the presence of increasing quantities of  $NaCl$ ,  $bP$  the solution of  $NaCl$  in the presence of increasing quantities of  $KCl$ , and  $P$  the solution saturated with  $KCl$ ,  $NaCl$ . Similarly for  $bQc$ ,  $cRd$ ,  $dSa$ . There is thus a closed curve  $aPbQcRdSa$ , which expresses solutions saturated with one salt and at the points  $PQRS$ , solutions saturated with two salts are as follows:

$P - KCl - NaCl$ ,  $Q - NaCl - NaNO_3$ ,  $R - NaNO_3 - KNO_3$

$S - KNO_3 - KCl$ .

For saturated solutions with three salts, as  $NaCl - KNO_3$  cannot coexist, only two cases are possible, the former  $KCl - NaNO_3 - NaCl$  at  $P_1$ , and  $KCl - NaNO_3 - KNO_3$  at the point  $P_2$ . Both will correspond to a different concentration, which is given by the points  $P_1$  and  $P_2$  lying within the octohedron. We now join  $P_1p$  by the curve of the solution saturated with  $NaCl$  and  $KCl$ , by  $P_1$  with  $q$  for the solutions saturated with  $NaNO_3$  and  $NaCl$ ;  $P_2$  with  $R$  for solutions saturated with  $NaNO_3$  and  $KNO_3$ ;  $P_2$  with  $S$  for  $KNO_3$  and  $KCl$  and  $P_1$  and  $P_2$  for  $KCl$  and  $NaNO_3$ . We then have four surfaces:

$P_1P_2S$  a p expresses solution with  $KCl$

$P_1P_2RcQ$  " " "  $NaNO_3$

$P_1pbQ$  " " "  $NaCl$

$P_2RdS$  " " "  $KNO_3$

1. Unsaturated solutions below  $aPbQcRdSaP_1P_2$ .
2. Supersaturated solutions above " " .
3. Solutions with one solid phase, the four surfaces just mentioned.
4. Solutions saturated and with two solid phases, the five lines of contact of these four surfaces.
5. Solutions saturated and with three solid phases, the two points  $P_1P_2$  or the intersection of three lines.

At the transition temperature  $P_1$  and  $P_2$  will coincide in  $P$ , where  $NaCl - NaNO_3 - KNO_3 - KCl$  are in contact. Hence these can exist at one temperature with a saturated solution of each.

Above the transition temperature  $P_1$  and  $P_2$  will vanish as  $KCl$  and  $NaNO_3$  can no longer coexist.  $P_3$  and  $P_4$  now occur corresponding to solutions at  $P_4$  of three salts  $NaCl$ ,  $KNO_3$  and  $KCl$  or at the point  $P_3$  with  $NaCl$ ,  $NaNO_3$ , and  $KNO_3$  and therefore the projection lines received another interpretation.

Let us deal now with a special case of the four salts  $MgCl_2$   $KCl - K_2SO_4 - MgSO_4 \cdot 7H_2O$ , but these form double salts shoenite, carnallite and magnesium sulphate hexahydrate. Hence in the interior we have not two but five points where the three fields meet.

We proceed as above, with four axes inclined to one another and plot the solubilities of the four salts taking  $KCl$  as twice its molecular weight or  $K_2Cl_2$ . The necessity for doing this results

from the following considerations. If OA, OB, OC, OD are the axes on which  $MgSO_4 - K_2SO_4 - K_2Cl_2 - Mg_2Cl_2$  are plotted and let P be a point lying on one hand in the plane through OA and CO and on the other hand in the plane through BO and DO. The position of the point must then be determined whether the abscissae OA' and OC' or the abscissae OB' and OD'. Hence it is indifferent which of the two pairs of abscissae are given, but they must correspond and this is only the case if OA' and OC' equal OB' and OD' that is if OC' equals  $K_2Cl_2$  and not KCl.

The sides of the fig. 5 express the horizontal projection corresponding to the projection of fig. 4 discussed in connection with the assumed simple case. The values for the present case are those taken from the literature. Consider first figure 5. We have four lines cutting the whole figure and meeting at right angles. These represent the solubilities of the simple salts, the salts in question being indicated on the graph. The Roman figures correspond with solution experiments; the Arabic figures with crystallization experiments. We must imagine the four axes arranged as the edges of a regular octohedron. The ends of the axes are joined by dotted lines. These lines are really curves. Line I, II passing downwards from KCl. I expresses the solubility of KCl with increasing content of  $K_2SO_4$ , and the line III, II going to the right from  $K_2SO_4$ . III gives the solubility of  $K_2SO_4$  with increasing content of KCl. The intersection point II represents a solution in equilibrium with KCl and  $K_2SO_4$ . Line III lies between  $K_2SO_4$  and  $MgSO_4$ . VI

means to the left of III a solution of  $K_2SO_4$  in the presence of shoenite and at the point IV a solution saturated with  $K_2SO_4$  and shoenite. V a solution saturated with shoenite and  $MgSO_4 \cdot 7H_2O$ ; and from V to VI a solution of  $MgSO_4 \cdot 7H_2O$  calculated free from water of crystallization, with decreasing content of shoenite. The line going upwards from  $MgSO_4 \cdot 7H_2O$  (VI) gives the solubility of this with increasing  $MgCl_2$ , which at the same time has a dehydrating action, so that one can look upon the solution as containing  $MgSO_4 \cdot 6H_2O$  in increasing quantities until VII is reached, where  $MgSO_4 \cdot 7H_2O$ ,  $MgSO_4 \cdot 6H_2O$  is the solid phase. So that solutions containing  $MgCl_2$  are saturated with these two compounds. The line continues above VII expressing solutions saturated with  $MgSO_4 \cdot 6H_2O$  and containing increasing quantities of  $MgCl_2$  at VIII.  $MgCl_2 \cdot 6H_2O$  can be the solid phase, that is, solution is saturated with  $MgCl_2$  and  $MgSO_4 \cdot 6H_2O$ .

From VIII to IX the line represents the solution at  $MgCl_2$  with decreasing content of  $MgSO_4 \cdot 6H_2O$  and at the point IX the solubility of  $MgCl_2$  alone. The line going down from IX to I represents solutions containing  $MgCl_2$  and  $K_2Cl_2$ . This is so great at X, that the  $KCl$  can exist as solid phase as carnallite. Finally at XI a point representing the solution saturated with carnallite and  $KCl$ , the  $MgCl_2$  is only present in solution and its content decreases to zero at I. The five points in the interior namely XII, XIII, XIV, XV, XVI which are constructed from the solubility determinations represent solutions saturated with respect to three salts. The solid phases at the following points are XII carnallite,  $MgSO_4 \cdot 6H_2O$ ,  $MgCl_2 \cdot 6H_2O$ ; XIII carnallite,  $MgSO_4 \cdot 6H_2O$ ,  $KCl$ ; XIV  $MgSO_4 \cdot 6H_2O$



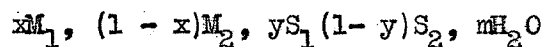
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{KCl}$ ; XV  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  shoenite,  $\text{KCl}$  XVI  $\text{K}_2\text{SO}_4$ , shoenite  $\text{KCl}$ .

As from can be seen directly from figure 5, the horizontal projection contains the seven fields of the seven salts.

Construction of a point representing a saturated solution may be performed by taking for example a solution saturated with shoenite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{K}_2\text{Cl}_2$ . The results will be as follows: 64 mols  $\text{Cl}_2$ , 16 mols  $\text{SO}_4$ , 9 mols  $\text{K}_2$ , 71 mols  $\text{Mg}$  per 1000 mols of water. Expressing as molecules of the three salts  $\text{KCl}$ ,  $\text{MgCl}_2$  and  $\text{MgSO}_4$ , we get the solution of XV to contain per 1000 mols of water, 9 mols of  $\text{K}_2\text{Cl}_2$ , 16 mols of  $\text{MgSO}_4$ , 55 mols of  $\text{MgCl}_2$ . In figure 5 the unit is 1 mol equals 1 mm. To plot this point we must take the point c on the vertical line of figure 5 corresponding to the  $\text{MgSO}_4$  axis, which is as far removed from the point of intersection of the 4 axes as the point c is in the vertical projection from the  $\text{MgCl}_2$  axis. Through c in the horizontal projection, a parallel is drawn to the  $\text{MgCl}_2$  axis, a line 55 units long, its upper end representing the desired point on the horizontal projection. The point c is obtained by taking first a point A on the  $\text{MgSO}_4$  axis, which is 16 units removed from the mean vertical axis cutting the figure, which expresses the  $\text{MgSO}_4$  axis and point B on the  $\text{KCl}$  axis, 19 units distant from the same vertical line. Through A we draw a parallel to the  $\text{K}_2\text{Cl}_2$  axis and through B a parallel to the  $\text{MgSO}_4$  axis. The parallel must meet in the point C. From the point C, as was before stated, a line parallel to  $\text{MgCl}_2$ , 55 units long. Its upper end point gives us the point we desire.

A second method was put forth later by Janecke<sup>19</sup> and Le Chatelier<sup>20</sup> possesses the advantage over the method employed by Lowenherz, that the composition of the solution is expressed not in terms of salts,

but in terms of ions, or of solid and basic radicals. Thus the composition of aqueous solutions formed from the salt-pair  $M_1S_1 / M_2S_2$  and its reciprocal pair,  $M_1S_2 / M_2S_1$ , can be represented in accordance with the scheme.



where  $x$ ,  $(1-x)$ ,  $y$ ,  $(1-y)$  are the number of gram-molecules of the ions dissolved in  $m$  gram-molecules of water. For the complete representation of the isothermal equilibria a three-dimensional model is required, and as such Janecka selects a rectangular column on a square base. The four corners of the base represent the pure salts, salts with a common ion being placed at adjacent corners of the square (Fig. 6). The sides AB and CD of the square will represent solutions containing different proportions of  $M_1$  and  $M_2$ , and by dividing these sides in the ratio of  $x$  to  $(1-x)$ , and joining the points  $a$  and  $b$  so obtained, the line  $ab$  will represent quaternary solutions in all of which the ratio of  $M_1$  to  $M_2$  is as  $x$  to  $(1-x)$ .

Similarly, the line  $cd$  represents the composition of solutions in which the radicals  $S_1$  and  $S_2$  are present in the ratio  $y$  to  $(1-y)$ . The point of intersection  $O$  will then, obviously, represent the solution having the composition  $xM_1, (1-x)M_2, yS_1, (1-y)S_2$  dissolved in a given amount of water. To represent the amount of water, a perpendicular is erected at  $O$ , and a length corresponding with  $m$  gram-molecules is measured off; or better, a length  $N = \frac{100m}{100 - m}$ . The point in space so obtained represents the solution of the composition  $xM_1 / (1-x)M_2 / yS_1 / (1-y)S_2 / mH_2O$ . Generally, however, only the plane quadrangular diagram is employed,

the relative proportions of the salts only being represented graphically, the amounts of water being indicated, when desired, by numerals.

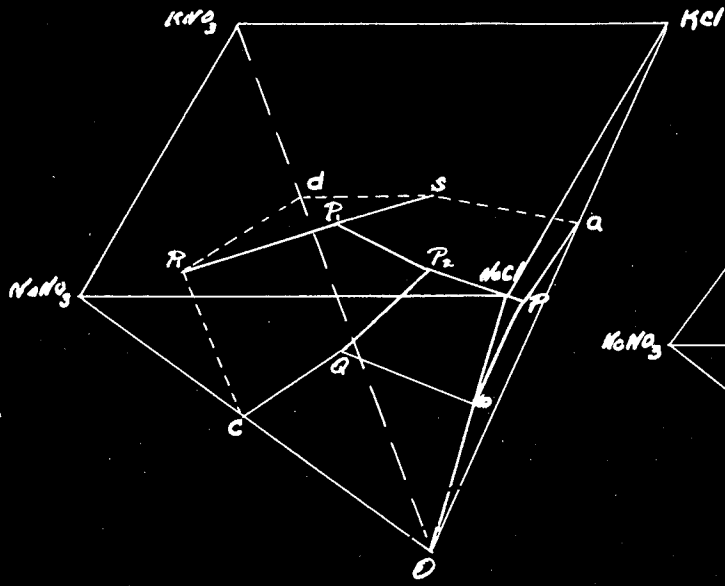


Fig. 3

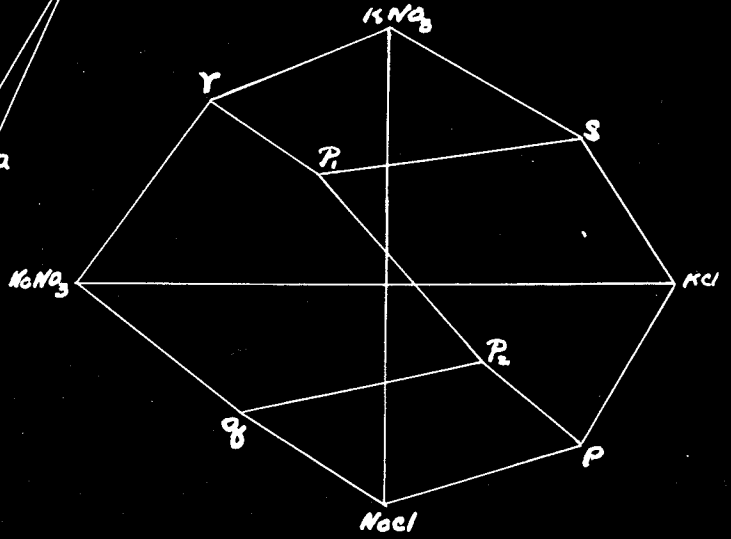


Fig. 4

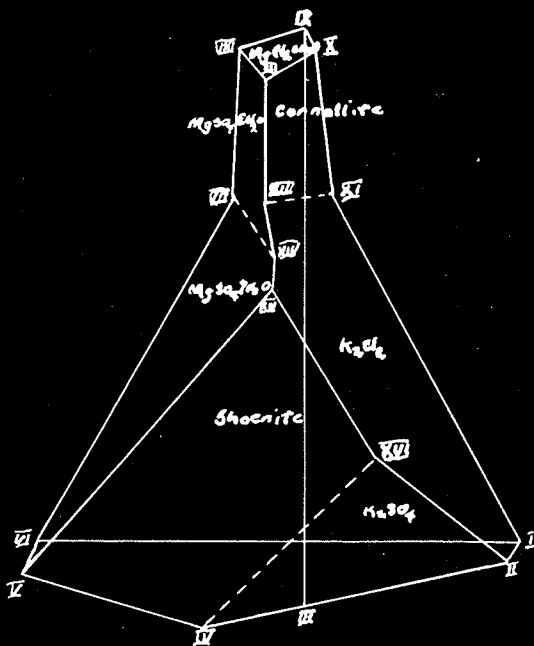


Fig. 5.

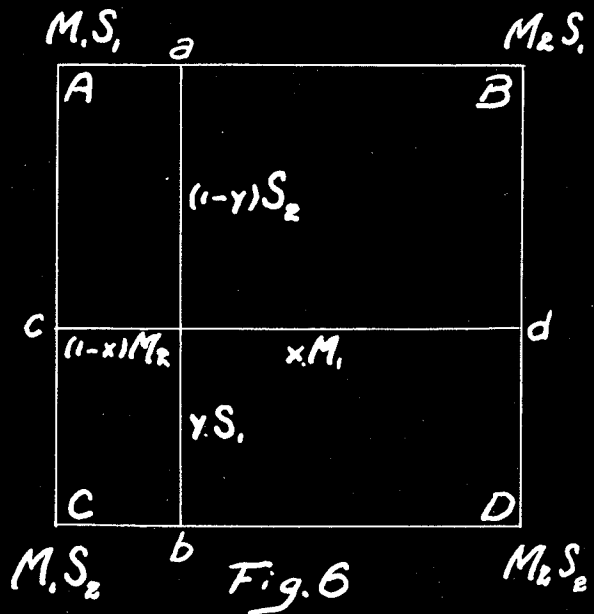


Fig. 6

### Apparatus

All of the solubilities were carried out at 100° and determined by analysing the solutions which were constantly stirred for fifteen hours in a bottle of the type shown in fig. 7. A mercury seal was used to prevent the escape of the vapour phase. These were placed in an electrically heated oil bath, in which a high grade oil was used, since a poor grade was found to decompose after several days, it was necessary to find an oil that could be maintained at this temperature without decomposing. Quaker State electric bath oil was found to be the most satisfactory.

A small heater was placed in the bottom of a thermally insulated tin tank and constantly heated by the AC mains. A rheostat was placed in the circuit to roughly control the temperature. The fine heat change was supplied by means of an electric light bulb, controlled by relay which itself was operated by a regulator of the mercury, xylene B.P. (136°) type. The variation was found to be within .1 of a degree. The oil was found to slowly carbonize, due to its contact with the hot element. The latter was kept at a temperature which maintained the bath almost at 100° and the bulb regulated it. A standard thermometer was used to adjust it.

Special stands were used to hold the solubility bottles fig. 8 which were clamped in these. The two bolts were supplied with wing nuts to hold the top in place.

### Filtration Apparatus.

Since the solubilities of the salts at  $100^{\circ}$  were extremely high and hydration occurred on cooling magnesium sulphate and magnesium chloride hexahydrate being hydrated, removal by a pipette was impossible, because of the solutions solidifying in the cold pipette. A filtration device was used similar to the type devised by Campbell<sup>21</sup> and worked very satisfactorily, giving a well filtered solid phase and ease in removing the filtrate. The apparatus consists, as shown in fig. 7, of a large rubber stopper which fits into the top of the solubility bottle C. The small tube D passes into the bottle C just to the bottom of the rubber stopper. A sintered glass filter M was placed through the other hole going to the bottom of the vessel. A sintered glass filter of about  $\frac{1}{4}$ " in diameter and of a very fine mesh was made by filling a nickel mould, the size and thickness of a penny, with powdered glass. The mould was then placed in a furnace at  $900^{\circ}$  for one minute, this was sufficient time to cause the glass to sinter together to form a porous plate. The plate was removed from the mould and fused into a funnel shaped tube and the end ground flat. To this filter through the cork was connected a U tube which passes into the vessel O containing a side arm tube, which was drawn to a fine point at N to allow the air to escape and also to condense any vapour on the side of the cold glass.

The apparatus both cleaned and dried was placed together as shown and when the solution was ready to be filtered the stirrer was removed as quickly as possible and the stopper placed in the top of the vessel with the filter and the solid phase at the bottom of

the vessel. The metal top was placed in position and screwed by means of two thumb screws thus holding the cork tightly in place. The whole apparatus was then immersed in the oil bath allowing the tube T and D to protrude from the oil. To D was attached the hose from the air line. It was found that suction could not be used with such a concentrated solution at 100° since it would completely dry the liquid and solid phase at once. Therefore, it was necessary to use air pressure, which, when applied, forced the saturated solution through the filter and over the tube and into the vessel O and any steam passing over condensed on the tube T. The apparatus was allowed to stand until it had reached 100° before it was filtered. When the filtration was complete, the apparatus was removed from the bath. The vessel O removed, stopped and weighed. The cork was then removed from the vessel C and the solid phase removed and weighed in a weighing bottle. This method of separating liquid and solid phase was both rapid and accurate.

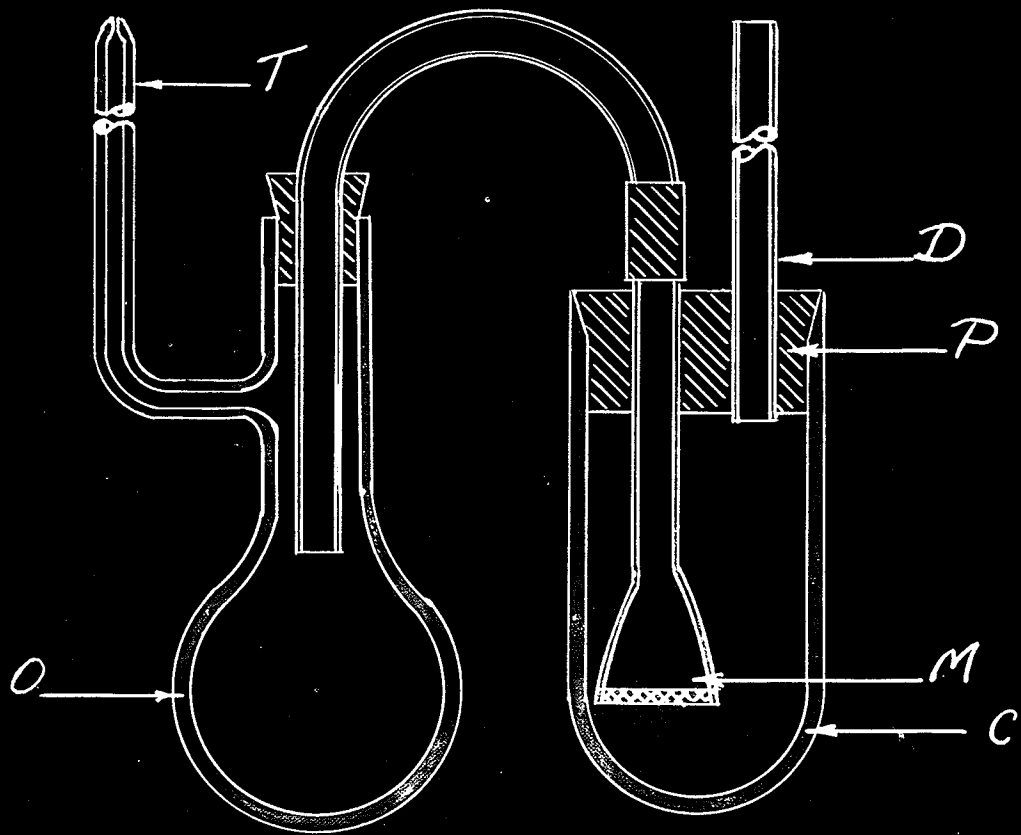


Fig. 7

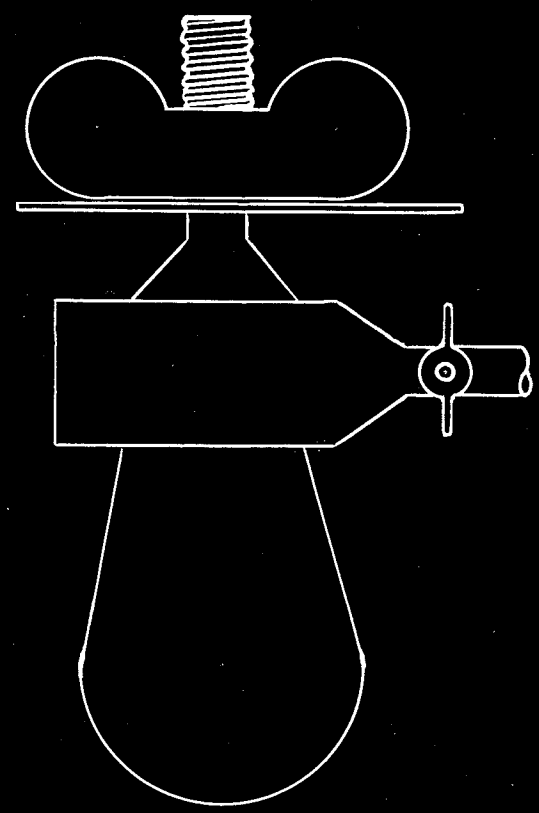


Fig 8

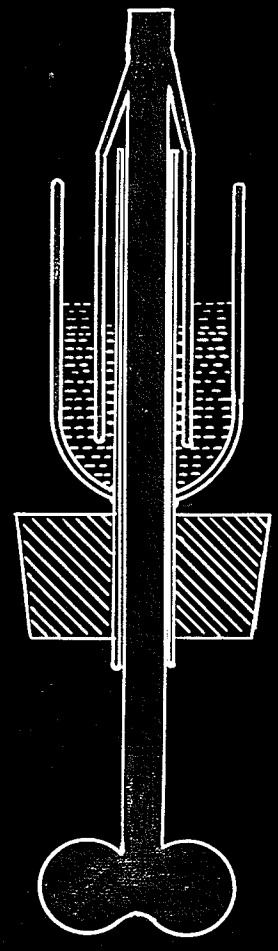


Fig. 9



## Methods of Analysis.

The following volumetric methods of analysis were secured from Sutton's Volumetric Analysis and were tried and found satisfactory both with respect to accuracy and speed of manipulation before use in this work. The chloride was determined by the method devised by Volhard<sup>21</sup>. The method is as follows: the solution to be titrated is treated with nitric acid and a known volume of N/10 silver nitrate in excess is added, the mixture is well shaken and the supernatant liquid is filtered off through a small filter, the chloride well washed, and to the filtrate and washing 5 cc's of ferric indicator is added. The flask is then brought under the thiocyanate burette and titrated till a permanent bright brown color appears.

The sulphate method of Wildenstein<sup>22</sup> was applied to determine the sulphate content of the samples. The solution containing sulphate is precipitated in a test tube with a slight excess of standard barium chloride delivered from a burette. As the precipitate rapidly settles from a boiling solution, it is easy to avoid any great excess of barium, which prevents the liquid from clearing rapidly. The solution is then heated to boiling and a chromate solution added, until the liquid is of a light yellow color, each time removing the test tube and allowing the precipitate to settle. The quantity of chromate is then deducted from the barium solution and the remainder calculated as sulphate.

Meade's<sup>23</sup> method for the determination of magnesium from Sutton's volumetric analysis was used as follows: the magnesia solution formed by adding ammonium chloride to the solution to be determined was placed in a conical flask. One third of its volume of strong ammonia was added and

50 cc's. of sodium arsenate was run in. This was stirred vigorously for ten minutes. The precipitate was allowed to settle somewhat and then filtered and washed with strong ammonia, till the washings ceased to react for arsenic. The precipitate was dissolved in dilute HCl allowing the acid solution to run into a flask containing a solution of potassium iodide. The solution was allowed to stand for several minutes and then titrated with standard thiosulphate. No indicator being used, the iodine giving a one drop end point.

## Chemicals

## Preparation and purity of materials.

Throughout this work Mallinckrodt's U.S.P. magnesium sulphate was used. The magnesium chloride was B.P.H. certified chemicals and J. T. Baker chemicals N.F.V. crystal purified. The potassium sulphate was Mallinckrodt's N.F. powdered  $K_2SO_4$ , which was recrystallized to remove all impurities. Mallinckrodt's potassium chloride was used throughout this work. One recrystallization of the salt was sufficient purity for our requirements.

THE TERNARY SYSTEM

1. MAGNESIUM CHLORIDE - MAGNESIUM SULPHATE - WATER

AT THE 100° ISOTHERMAL.

## Historical

In the case of the system  $\text{MgCl}_2 - \text{H}_2\text{O}$  the solubility relations are as follows<sup>37</sup>: with ice as the solid phase, the solubility falls from 11.1 per cent at  $-10^\circ$  to the eutectic with the solubility of 20.6 per cent at  $-33.6^\circ$ . When the solid phase is a mixture of ice and  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , the solubility with  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$  then rises to 31.6 per cent at  $-16.8^\circ$ , where the solid phase is a mixture of  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$  and alpha  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ , at  $-17.4^\circ$  the solubility is 23.3 per cent the solid phases being  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$  and beta  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ . At  $-19.4^\circ$  the solubility of 33.3 per cent has the solid phases  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . At  $-3.4^\circ$  with solubility of 34.4 per cent the solid phases are alpha  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and the last named salt is a solid phase from  $-3.4^\circ$  to  $116.7^\circ$  where the solubility is 46.2 per cent and the solid phases are  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . At  $152.6^\circ$  the solubility is 49.1 per cent and the solid phase is  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . At  $181.5^\circ$  the solubility is 55.8 per cent,  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  being the solid phases. At  $186^\circ$  the solubility is 56.1 the solid phase being  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ .

The critical tables give the solubility of  $\text{MgCl}_2$  at  $100^\circ$  at 7.59 mols of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  per 1000 grams of  $\text{H}_2\text{O}$ , while Mellor<sup>38</sup> gives the solubility of  $\text{MgCl}_2$  in grams per 100 grams of solution from  $0^\circ$  to  $100^\circ$ , where the solid phase is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , as  $0^\circ - 34.9$ ,  $10^\circ - 34.9$ ,  $20^\circ - 35.5$ ,  $40^\circ - 36.5$ ,  $60^\circ - 37.9$ ,  $80^\circ - 39.8$  and  $100^\circ - 42.2$ . He states that  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is the solid phase from  $-3.4^\circ$  to  $116.7^\circ$ , the best representative values of the solubility of  $\text{MgSO}_4$  were compiled by R. Kremann<sup>39</sup> for the stable binary system  $\text{MgSO}_4 - \text{H}_2\text{O}$ . The ice line by F. Rudorff and L.C. de Coppet corresponds with the percentage solubility of 13.9 per cent magnesium sulphate at  $-29^\circ$  and according to Van't Hoff

and Meyerhoffer with a eutectic at  $-3.9^{\circ}$  and 19 per cent  $\text{MgSO}_4$ .

The next solubility curve refers to the system with the dedecahydrate  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$  at  $1.8^{\circ}$  and 21.1 per cent of magnesium sulphate. At the transition temperature of  $1.8^{\circ}$  both the dodeca and the rhombic hepta hydrates are in equilibrium as solid phases. Van der Heide gave  $48.5^{\circ}$  for the transition temperature of the hepta to the hexa hydrate and C.P. Carpenter gave  $48.4^{\circ}$ . This curve represents the solubility of the hexahydrated magnesium sulphate, where according to Van't Hoff the transition temperature between the hexa and the monohydrate occurs at  $68^{\circ}$  and 37 per cent of  $\text{MgSO}_4$ . Lowel represents the solubility of the hexagonal heptahydrate with the solubilities at  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$  or 25.8 per cent, 27.9 per cent and 30 per cent  $\text{MgSO}_4$ . While Mulder represents the percentage solubility of the hexahydrate as

$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$30^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$	$100^{\circ}$
	29	29.7	30.8	31.2	37.3	39.1	40.8	42.5

Robson<sup>40</sup> investigated the system  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  from  $68^{\circ}$  to  $240^{\circ}$  and he found that the solutions came to equilibrium with the hexahydrate in a few minutes and with the penta and tetra hydrates fairly rapidly. Three to seven days were required for solutions to come to equilibrium with kieserite under  $100^{\circ}$  unless an abundance of the solid phase was present. Equilibrium was not obtained in less than twenty four hours stirring under  $160^{\circ}$ , nor with less than 40 hours stirring under  $90^{\circ}$ , but was obtained after stirring for half an hour at  $238^{\circ}$ . Many trials, that were well inoculated, which were stirred for shorter periods gave a high result. He states that kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  is poorly crystallized under  $200^{\circ}$  and comes to equilibrium slowly. His

results for 100° are as follows:

Temperature.	Liquid phase . gr. MgSO <sub>4</sub> per 100 grams of water.	Solid phases.
95°	51.6	Kieserite
99.4°	68.5	by Meyerhoffer
100°	74.6	2 min. after concen- tration by boiling
100°	68.1	penta and tetra hydrates
100°	67.7	penta and tetra hydrates
100°	50.4	Kieserite

Van't Hoff obtained the following results for the system at 25°: he found two invariant points, the systems solid phases occur in and the solubility relations as shown in the following table:

25° isothermal System	Solid phases	1000 mols water dissolves
MgSO <sub>4</sub> , MgCl <sub>2</sub> , H <sub>2</sub> O	MgSO <sub>4</sub> , MgCl <sub>2</sub> .	58 mols MgSO <sub>4</sub> , 108 mols MgCl <sub>2</sub>
" " "	MgSO <sub>4</sub> ·6H <sub>2</sub> O MgCl <sub>2</sub> ·6H <sub>2</sub> O	104 mols MgCl <sub>2</sub> , 14 mols of MgSO <sub>4</sub> .
" " "	MgSO <sub>4</sub> ·6H <sub>2</sub> O MgSO <sub>4</sub> ·7H <sub>2</sub> O	15 mols MgSO <sub>4</sub> , 73 mols of MgCl <sub>2</sub> .

Tyrahon<sup>41</sup> showed that the odd molecule of water was not expelled from the monohydrate at 210° and 238°, and applied the term the water of constitution or halyhydration. The critical tables give the solubility of magnesium sulphate at 100° as 5.9 mols of magnesium sulphate monohydrate per 1000 grams of water.

Janecke in his study of the theoretical behaviour of the melting of the salt pairs in particular cases, in considering the system MgCl<sub>2</sub>, MgSO<sub>4</sub>, found it to have only one eutectic, besides the melting

point of  $1185^{\circ}$ , others were found due to the decomposition of the salts. No compound was formed and the eutectic was found to occur at  $K_2SO_4$  20 mol per cent and  $MgSO_4$  at 60 mol per cent.

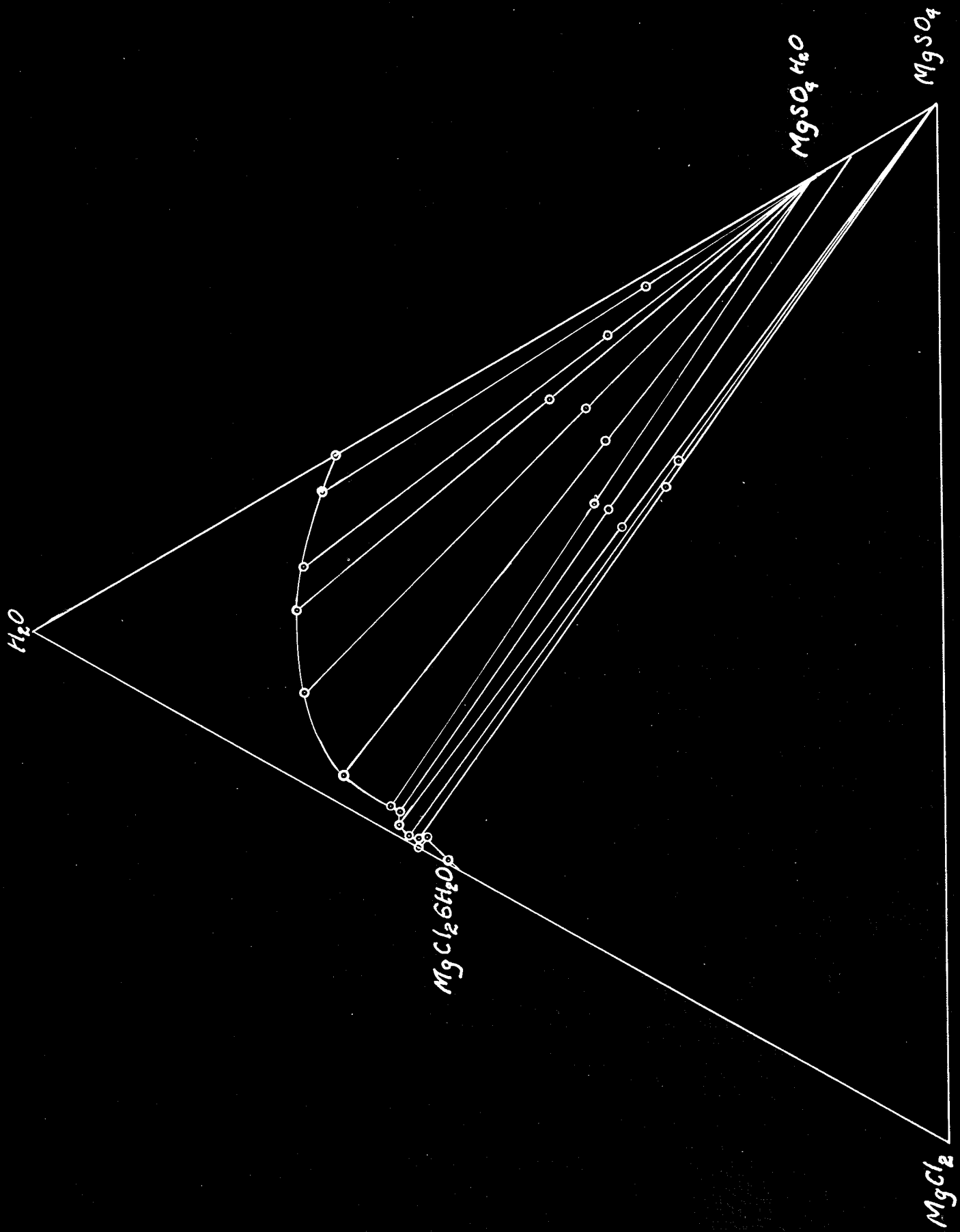
Lowel, Basch and Mulder give the following table as the stable hydrates of magnesium sulphate and their transition temperatures, with the solubility per 100 grams of the solution. The solid phase in each case being given:

$10^{\circ}$	$20^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$	$60^{\circ}$	$80^{\circ}$	$99.4^{\circ}$	$164^{\circ}$	$188^{\circ}$
23.6	26.2	29	31.3	33.5	35.5	38.6	40.6	29.3	20.3
$MgSO_4 \cdot 7H_2O$				$MgSO_4 \cdot 6H_2O$		$MgSO_4 \cdot H_2O$			



## Solubility Data.

Solubility per 100 grams of water.		Percentage solubility.		Percentage solid phase analysis.	
Grams MgCl <sub>2</sub>	Grams MgSO <sub>4</sub>	%MgCl <sub>2</sub>	%MgSO <sub>4</sub>	%MgSO <sub>4</sub>	%MgCl <sub>2</sub>
71.25	1.87	41.2	1.085	47.03	21.05
72.4	2.11	41.5	1.23	.565	45.00
70.5	1.535	40.25	.876	42.5	23.00
69.4	1.025	40.6	.6	51.25	19.3
64.7	1.652	29.00	.990	43.00	22.5
62.3	3.52	37.6	2.12	30.3	27.05
61.3	4.7	37.00	2.832	42.8	19.02
61.00	4.67	36.8	2.81	43.00	20.85
60.8	4.67	37.35	2.82	42.65	20.88
47.25	5.02	31.00	3.3	49.05	14.00
29.76	12.91	20.85	9.05	51.4	9.35
27.9	12.14	19.85	8.65	51.5	9.98
17.65	22.8	12.5	16.3	50.6	6.52
12.1	31.65	8.42	21.2	60.00	3.5
4.26	43.6	2.88	29.5	67.00	1.01
.559	49.75	33.1	.372	45.00	.176



### Conclusions.

The isothermal at  $100^{\circ}$  for the system  $\text{MgCl}_2 - \text{MgSO}_4 - \text{H}_2\text{O}$  has been completed at this temperature. No double salt formation takes place, but the solubility isothermal at this temperature consists of three intersecting curves, representing isothermally univariant equilibrium between the solutions and one solid phase, and two isothermally invariant points, where two solid phases are in equilibrium with the solution.

The left hand of the isothermal solubility curve on the percentage diagram represents the equilibrium between the saturated solution and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  as solid phase. This curve starts at the solubility of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and on addition of  $\text{MgSO}_4$ , the solubility increases and the curve runs down to the first invariant point at  $\text{MgCl}_2$  41.5% and  $\text{MgSO}_4$  .565%. The tie lines on this solubility curve cut the sides of the graph at  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , showing that  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is a solid phase in contact with the solution up to the invariant point. The right hand of the isothermal solubility curve represents the equilibrium between the saturated solution and  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  as solid phase. This curve starts at the solubility of pure  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  and on the addition of  $\text{MgCl}_2$ , the solubility increases and the curve continues down to the second invariant point at  $\text{MgCl}_2$  37.5% and  $\text{MgSO}_4$  2.6%, where there are two solid phases present and therefore invariant.

It may be observed in this work that numerous references have been made to the dehydrating action of  $\text{MgCl}_2$ . It was found to be very marked on this isothermal, resulting in the dehydrating of the keiserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  and producing a new phase  $\text{MgSO}_4$ . This accounts for the two

invariant points occurring, even though a double salt was not formed. The solubility curve, between the two before mentioned points, represents the solubility curve in equilibrium with  $\text{MgSO}_4$  as solid phase which will be obvious, if we examine the isothermal diagram. The solid phase analyses tie into  $\text{MgSO}_4$  on this curve, while on the solubility curve to the right of the second invariant point, the solid phase analyses tie into the monohydrate or  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . At the two invariant points we have solutions of their percentage composition in equilibrium with (1)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSO}_4$  as solid phases and (2)  $\text{MgSO}_4$  and  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  as solid phases. These results are similar to Lowenherz, who found  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  to occur with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  at the  $25^\circ$  isothermal of this system.

It may be pointed out, that it is extremely difficult to obtain a wandering tie line from the first invariant point  $\text{MgSO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  on this isothermal diagram, since the solid phase of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and the invariant point and  $\text{MgSO}_4$  are almost in a straight line and the solid phase will therefore travel up the  $\text{MgSO}_4$  tie line and the distance from this tie line to the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solid phase is so small, that it was found very difficult to obtain a wandering tie line from this invariant point,

Another interesting fact may be pointed out here. In the before mentioned work of Robson and others, the solubility of  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  was determined and they found their varying results to be due to penta and tetra hydrates in the metastable condition. and conditions of equilibrium to be difficult to establish. The writer also found this difficulty in obtaining the solubility of  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , but on addition

of the smallest quantity of  $MgCl_2$ , the dehydrating effect at once becomes apparent and we have equilibrium with the monohydrate established at once. This dehydrating action increases, as the  $MgCl_2$  content increases, and finally results in dehydrating the monohydrate of  $MgSO_4$ . The solubility of  $MgSO_4 \cdot H_2O$  was found to agree with Robson's value of 50.5 grams per 100 grams of water or 33.5%.

If we examine the rectangular graphs, representing the relative quantities of  $MgSO_4$  and  $MgCl_2$  per 100 grams of water, we find again the three curves. The  $MgSO_4 \cdot H_2O$  curve runs from 50.5 grams of  $MgSO_4$  per 100 grams of water down to the invariant point at 4.67 grams of  $MgSO_4$  and 61 grams of  $MgCl_2$  per 100 grams of  $H_2O$ . The  $MgSO_4$  curve then runs to the invariant point with  $MgSO_4$  and  $MgCl_2 \cdot 6H_2O$  as solid phase, at 72.4 grams of  $MgCl_2$  and 2.11 grams of  $MgSO_4$  per 100 grams of water. The  $MgCl_2$  curve joins this point to the solubility of  $MgCl_2$  72.1 grams per 100 grams of water.

THE TERNARY SYSTEM

2. MAGNESIUM SULPHATE - POTASSIUM SULPHATE - WATER

AT THE 100° ISOTHERMAL.

## Historical.

Many investigators have studied this system and in general have limited themselves to a determination of the isothermal invariant points. Precht and Wittgen<sup>24</sup> investigated the decomposition of shoenite by water from 10<sup>0</sup> to 90<sup>0</sup>C. inclusive. Van der Heide<sup>25</sup> made the first detailed study of the system and also found the double salt leonite. Van't Hoff and his co-workers determined many transition temperatures, as well as a number of univariant points and their work showed that Van der Heider's results did not represent equilibrium conditions. D'Ans<sup>26</sup> later determined several more invariant points. Van Klooster<sup>27</sup> determined the complete 25<sup>0</sup> isothermal and Weston<sup>28</sup> that at 30<sup>0</sup>. Starrs and Clark redetermined the 30<sup>0</sup> data. Levi<sup>29</sup> secured data for univariant points at temperatures of zero, 19.8, 20.4, 26.1, 34.4, 37.8, 44.7, 49.6, 55.2 and 63.4 degrees.

The data listed above in the case that the stable solid phases in this system are potassium sulphate, shoenite, leonite, langbeinite and hydrates of magnesium sulphates 12Aq., 7Aq., 6Aq., 1Aq. This accumulated data fixes rather definitely the nature of the system below 50<sup>0</sup>, but above this temperature the data is insufficient. Selected values may be found in the international critical tables.<sup>30</sup> When their data are examined, it is found that the points are in poor agreement. Mainly those of Precht, Wittgen, Van der Heide, Geiger and Levi. The results of Precht and Wittgen are at best only approximations of the values of the invariant points potassium sulphate and double salt. It is not to be supposed that the

magnesium sulphate concentrations would be more in error than the potassium sulphate concentrations. Van der Heide was working with solutions not in equilibrium with the stable solid phase, as has been established by Van't Hoff. Greiger's determination of the solubility of keiserite of 67.29 grams of  $\text{MgSO}_4$  per 100 grams of water shows definitely that the solid phase was not  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . It is very likely that this invariant point for langbeinite, keiserite is an error for the same reason. His invariant point langbeinite, leonite shows a greater magnesium sulphate and a smaller potassium sulphate concentration than would be expected. His invariant point potassium sulphate, leonite is in fair agreement with the other data. Levi agitated his mixtures for only four hours and the comparison with the results of D'Ans shows he did not have equilibrium conditions above  $40^\circ$ .

Starrs and Storch<sup>31</sup> did the ternary system potassium sulphate, magnesium sulphate at  $85^\circ$  and  $100^\circ$ . They used pure chemicals in pyrex tubes, stirring for 20 and 658 hours. They filtered these solutions by means of warm pipettes placed in the solutions and filtered through a glass wool filter. Solid phases were obtained by filtering the solutions through heated gooch crucibles. The solid phases were examined chemically and with a petrographic microscope. No analytical figures were given or triangular diagrams determined. They point out, that the values obtained for the solubility of magnesium sulphate are much lower than those usually given in the literature, and are slightly lower than those obtained by Robson<sup>32</sup>. They suggested their values for  $100^\circ$  closely approx-



imates the true value, while the values for  $85^{\circ}$  may be too low. They point out that it was found repeatedly that the composition of the saturated solution did not fall on the equilibrium curve, in some cases even after a month of agitation, while often the stable solid phases would not be present. If the stable phases were present, the solution was supersaturated in respect to the apparent saturation curve. In this sense, these factors have caused the largest errors in the determinations. There was no absolute certainty that equilibrium was reached except in the middle of the langbeinite curve of the  $100^{\circ}$  isothermal. In this case the curve was approached from two directions. He points out that many points that were found were not included in the data, since it was thought that they were not in equilibrium. Several of these points fall on a well defined langbeinite curve at  $85^{\circ}$ , which passed through the invariant at one end and was about 1.3 grams of magnesium sulphate to the right of the leonite, langbeinite invariant on the  $85^{\circ}$  isothermal. This may be due to the existence of an unknown unstable solid phase, whose crystallization path must approximate that of langbeinite. An unstable solid phase  $K_2SO_4 \cdot 4MgSO_4 \cdot 5H_2O$  was found by Kassatkin<sup>33</sup>, to occur at  $72.5^{\circ}C$ . and it was found that this unstable phase was very slow in changing to the stable langbeinite. But the unstable substance could not have given the above higher solubility curve from that of langbeinite. The value for the invariant point was somewhat doubtful, especially the langbeinite, leonite point, which was not located experimentally, but by the intersection of the leonite and langbeinite curves. The langbeinite and magnesium

sulphate invariant is doubtful, since its value is fixed by only one determination. However he states that it seems very likely that these points are situated very near their correct position. It may be noted there is a metastable extension of the leonite curve into the langbeinite field. This is confirmed by Van der Heide's work, in which he failed to find langbeinite, although he was in the langbeinite field. If the initial concentration were taken far out in the langbeinite field, langbeinite rapidly formed although it is not known whether or not the leonite formation proceeds it.

Langbeinite was named by S. Zuckochvert from specimens which he found near Holberstradt. It occurs as a polyhalite in the regions of Wilhelmshall and accompanies the sylvite of Wisteregeln. Analysis agree with  $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ . G. Mulcher<sup>34</sup> made this compound in 1864 and Mullet obtained by fusing together at a dull red heat molecular proportions of the two components. The best crystals were obtained by pouring the fused salt into a hot nickel crucible and allowing the mass to cool. According to Van't Hoff, W. Meyerhoffer and Coterel, the salt crystallizes from a solution of its component salts at  $85^\circ$  and at a lower temperature in the presence of dehydrating salts like  $\text{MgCl}_2$ . They recommended evaporating a boiling solution of 17 grams of potassium sulphate, 49 grams heptahydrated magnesium sulphate and 75 grams of hexahydrated magnesium chloride, until the langbeinite, which is formed, no longer dissolves and then further evaporating on the water bath till  $\text{MgCl}_2$  begins to separate. Although the transition temperature of leonite to langbeinite is  $89^\circ$ , the transformation is extremely slow at  $100^\circ$  and requires a temperature of  $120^\circ$ . The tem-

perature of formation of langbeinite from a mixture of leonite and hexahydrated  $\text{MgCl}_2$  is  $61^\circ$ . The presence of hexahydrated magnesium sulphate depresses the temperature of formation of langbeinite from leonite down to  $61^\circ$ , but this temperature may be easily passed without the change taking place and at  $72^\circ$  the unstable  $\text{K}_2\text{Mg}_4(\text{SO}_4)_5 \cdot 5\text{H}_2\text{O}$  is formed and readily passes into langbeinite when a little of the latter is added. The presence of  $\text{NaCl}$  lowers the temperature still further. Van der Heide showed that shoenite decomposes into its components below  $-3^\circ$  and above  $72^\circ$  in the presence of magnesium sulphate hexahydrate passes into leonite while in the presence of potassium sulphate the transition temperature is  $92^\circ$ , Van't Hoff and Williams found that shoenite passes into leonite at  $47.5^\circ$  provided an excess of  $\text{K}_2\text{SO}_4$  is present at  $41^\circ$ , if magnesium sulphate is present at  $20^\circ$ , if the latter salt and also  $\text{KCl}$  is present.

Melts of the binary system  $\text{K}_2\text{SO}_4 - \text{MgSO}_4$  were investigated by Nachan and A. S. Ginsberg<sup>35</sup>. The former found the compound langbeinite to occur, forming two eutectics with  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$ . Above  $595^\circ$  the more stable salt is alpha  $\text{K}_2\text{SO}_4$ , which forms mixed crystals with  $\text{MgSO}_4$  to a limited extent. Beta  $\text{K}_2\text{SO}_4$  does not. Levi<sup>36</sup> studied saturated solutions of  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$ . The solubility of shoenite was investigated up to its transition point to leonite and it was found that at  $37.8^\circ$ , 100 grams of water contained 44.71 grams of  $\text{MgSO}_4$  and 6.63 grams of  $\text{K}_2\text{SO}_4$  the solid phases in equilibrium being  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and shoenite. At  $63.4$  degrees 100 grams of water contains 25.28 grams of  $\text{MgSO}_4$  and 20.65 grams of  $\text{K}_2\text{SO}_4$ , solid phases being  $\text{K}_2\text{SO}_4$  and leonite. At  $88.5$  degrees 1000 mols of water contain 41 mols of

MgSO<sub>4</sub> and 27 mols of K<sub>2</sub>SO<sub>4</sub>, solid phases being K<sub>2</sub>SO<sub>4</sub> and leonite. At 98<sup>0</sup>, 1000 mols of water contains 43.6 mols of MgSO<sub>4</sub> and 29.3 mols of K<sub>2</sub>SO<sub>4</sub>. The solid phases being MgSO<sub>4</sub>·7H<sub>2</sub>O and shoenite, below 45<sup>0</sup> it changes to MgSO<sub>4</sub>·6H<sub>2</sub>O and shoenite and about 70<sup>0</sup> to MgSO<sub>4</sub>·5H<sub>2</sub>O and shoenite. Where solid phase is K<sub>2</sub>SO<sub>4</sub> and shoenite, it changes about 50<sup>0</sup> to K<sub>2</sub>SO<sub>4</sub> and leonite. When the solid phase is MgSO<sub>4</sub>·7H<sub>2</sub>O and shoenite there is no change. He also suggests that at 95<sup>0</sup> Mg<sub>4</sub>K<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·5H<sub>2</sub>O exists.

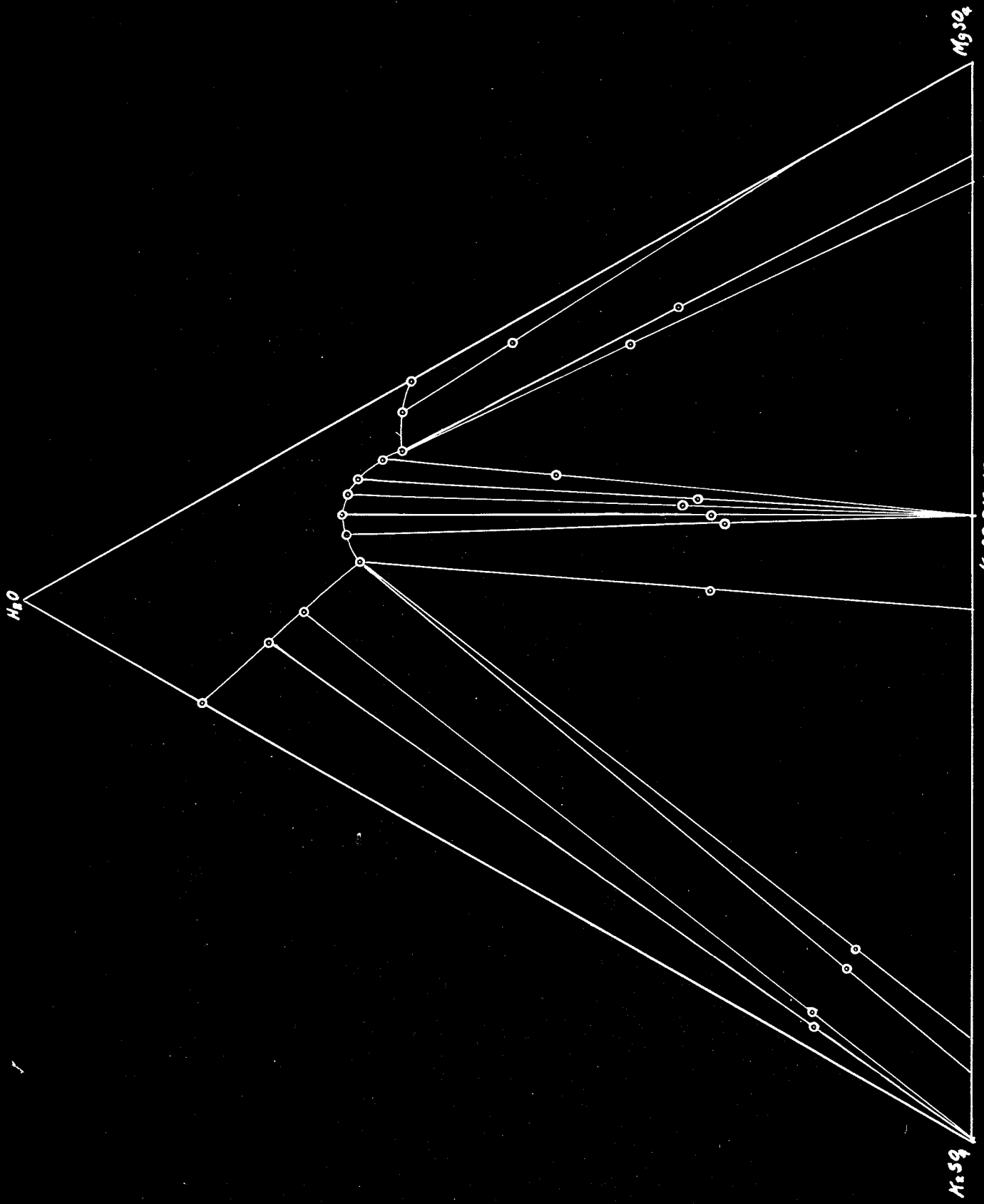
The most suitable langbeinite for dilatometric experiments is that obtained in the wet way. This can best be prepared from magnesium and potassium sulphates and magnesium chloride by digestion on the water bath. Its formation from blodite K<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O takes place at 89<sup>0</sup>, as has been found by the dilatometer and this is confirmed by observing the characteristic tetrahedral crystals when blodite was stirred in its saturated solution at 90<sup>0</sup>. The presence of magnesium sulphate hexahydrate depresses the temperature of formation from blodite, and langbeinite is produced at 61<sup>0</sup>. This temperature may be easily passed without the change taking place and then at 72<sup>0</sup> the compound K<sub>2</sub>Mg(SO<sub>4</sub>)<sub>4</sub>·5H<sub>2</sub>O<sup>36</sup> is formed. This compound is unstable, for when langbeinite is added it is slowly converted into this. In the presence of NaCl the formation temperature may be still further depressed. The naturally accompanying minerals are magnesium sulphate hexahydrate, kainite, blodite, sylvite, and langbeinite is formed at about 37<sup>0</sup>. Its occurrence along with sylvite indicates that it has been formed at a higher temperature than this.

Kassalkin in his study of the formation of langbeinite states that above - 3<sup>0</sup> the first molecule of water is split off, with the

formation of shoenite. At 41<sup>0</sup>, leonite is formed with the loss of two molecules of water, while at 47.2<sup>0</sup>, the magnesium sulphate loses water and we get a mixture of magnesium sulphate hexahydrate and tetrahydrate in solution, from these stages of hydration he followed the path up to the formation of langbeinite and met with a hitherto unknown product, which he immediately investigated. It appeared to be a peculiar double salt of the composition  $(SO_4)_5Mg_2K_2 \cdot 5H_2O$ , which can be compared with the magnesium sulphate penta tetra hydrate on the way to keiserite formation. The formation of the new double salt takes place on warming a mixture of magnesium sulphate hexahydrate and leonite and shows itself in a dilatometer by a marked expansion above 72.5<sup>0</sup>, which is reversed below this temperature. The change in question is one that is easy to follow, since it takes place quickly. Easy as it is to determine the temperature of formation, it is just as difficult to determine the composition of the new compound. It is obvious that it is not produced simply from one of the salts present in the mixture, because on heating  $MgSO_4 \cdot 6H_2O$  or leonite the change does not take place. If 4 mols of  $MgSO_4$  are present in the solution for every mol of  $K_2SO_4$ , leonite just forms, then the new substance in well shaped crystals, after which, with slow concentration, the leonite dissolves up and the whole solidifies. When this compound is analysed we get  $(SO_4)_5Mg_2K_2 \cdot 5H_2O$ . This formula may be due to the mother liquor which it contains or may be analogous to the before mentioned penta tetra hydrate of magnesium sulphate.

## Solubility Data.

Solubility per 100 grams of water.		Percentage solubility.		Percentage solid phase analysis.	
Grams MgSO <sub>4</sub>	Grams K <sub>2</sub> SO <sub>4</sub>	% MgSO <sub>4</sub>	% K <sub>2</sub> SO <sub>4</sub>	% MgSO <sub>4</sub>	% K <sub>2</sub> SO <sub>4</sub>
12.63	24.2	9.25	17.7	2.2	80.2
25.00	22.7	16.9	15.4	3.9	80.00
34.2	21.85	21.9	14.00	37.00	35.1
55.5	10.5	33.5	6.32	54.00	8.00
43.1	12.3	27.6	8.00	44.8	25.2
37.5	18.3	24.00	11.7	44.5	30.00
53.00	9.1	32.7	5.6	44.95	24.5
53.8	9.5	33.1	6.00	40.1	16.2
57.25	9.7	34.4	5.8	54.00	8.45
51.5	9.45	32.00	5.87	47.8	28.00
44.00	10.45	28.5	6.755	44.5	25.5
32.3	21.00	21.00	13.7	9.8	77.4
45.7	11.00	29.00	7.1	40.1	20.00
68.00	6.5	39.00	3.7	49.1	2.5
00.00	24.5	00.00	19.00	00.00	00.00
50.5	00.00	33.5	00.00	00.00	00.00



K<sub>2</sub>SO<sub>4</sub> & MgSO<sub>4</sub>  
Congruent

### Conclusions.

The isothermal at  $100^{\circ}$  for the system  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  has been completed. At this temperature double salt formation takes place. That is the solubility isothermal at this temperature consists of three intersecting curves, representing isothermally univariant equilibrium between the solution and one solid phase and two isothermally invariant points, where two solid phases are in equilibrium with the solution.

The left hand of the isothermal solubility curve on the triangular diagram represents the equilibrium between the saturated solution and  $\text{K}_2\text{SO}_4$  as solid phase. This curve starts at the solubility of pure  $\text{K}_2\text{SO}_4$  19 per cent and on the addition of  $\text{MgSO}_4$ , the solubility increases and a curve runs down to the first invariant point at 21 per cent  $\text{MgSO}_4$  and 13.7 per cent  $\text{K}_2\text{SO}_4$ . The tie lines on this solubility curve intersect at  $\text{K}_2\text{SO}_4$  100 per cent, showing that  $\text{K}_2\text{SO}_4$  is the solid phase in equilibrium with the solution up to the invariant point. The right hand curve on this diagram is at the present time questionable. The conditions represented on this graph were obtained by using heptahydrated magnesium sulphate and allowing the solution to come to equilibrium, but was found by myself and the before mentioned workers in this field, that  $\text{MgSO}_4\text{H}_2\text{O}$  at  $100^{\circ}$  is very difficult to obtain in equilibrium with the solution, due to the presence of the metastable penta and tetra hydrates of  $\text{MgSO}_4$  being present, this results in a high solubility for  $\text{MgSO}_4\text{H}_2\text{O}$  and a tie line that does not intersect at  $\text{MgSO}_4\text{H}_2\text{O}$ . The invariant point on this curve will also be in question, since at this point the solid phase  $\text{MgSO}_4\text{H}_2\text{O}$  makes its



appearance. At the time of publication of this work these points were doubted as to their integrity and will be redetermined using the monohydrate of  $\text{MgSO}_4$  in place of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and thus establishing equilibrium conditions with less trouble. It may be shown here the action of  $\text{MgCl}_2$  as dehydrating agent. In the systems, where it was present, the equilibrium was established at once, due to its dehydrating action, but in this system that dehydrating action is absent and we have therefore a condition of metastability of the hydrates of  $\text{MgSO}_4$  effecting the solubility of  $\text{MgSO}_4$  in the presence of  $\text{K}_2\text{SO}_4$  with keiserite as a solid phase. It is expected that the invariant point with keiserite present will vary very little from the one presented above at 34.4 per cent  $\text{MgSO}_4$  and 5.88 per cent  $\text{K}_2\text{SO}_4$  if any.

The solubility curve joining these two invariant points is a solution in equilibrium with the double salt, and the tie lines from this curve were found to intersect at 42 per cent  $\text{K}_2\text{SO}_4$  and 58 per cent  $\text{MgSO}_4$ , which corresponds to anhydrous  $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$  or the double salt known as langbeinite. This double salt appears as fine white tetrahedral crystals, which forms a very distinct powder that one can readily separate from the  $\text{MgSO}_4$  and the  $\text{K}_2\text{SO}_4$ . This was an important fact in dealing with the quaternary system, which we shall deal with shortly.

At the two invariant points on the curves we have present as solid phases (1)  $\text{K}_2\text{SO}_4$  and langbeinite at 21 per cent  $\text{MgSO}_4$  and 13.7 per cent  $\text{K}_2\text{SO}_4$  and (2)  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  and langbeinite at 34.4 per cent  $\text{MgSO}_4$  and 5.8 per cent  $\text{K}_2\text{SO}_4$ . This double salt is the same

as the one found by Starr and Storch in their work at  $100^{\circ}$ , although the invariant points vary, probably due to the metastable  $\text{MgSO}_4$  hydrates occurring, although it will be observed that these invariant points agree with those necessary for the four component system, where  $\text{MgCl}_2$  is present and removes these metastable forms of  $\text{MgSO}_4$  hydrates. Several wandering tie lines were obtained for each invariant point and they all agreed, which might suggest that all the invariant points were in equilibrium and only the  $\text{MgSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  curve was not in equilibrium with  $\text{MgSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  as a solid phase.

In the rectangular diagram representing the number of grams of magnesium sulphate and potassium sulphate per 100 grams of water, we find again the three curves and the two invariant points. The  $\text{MgSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  curve is again in question and is plotted in here as a dotted line, while the metastable points are left unjoined. The invariant points were found at (1)  $\text{K}_2\text{SO}_4$  and langbeinite, 21.85 grams of  $\text{K}_2\text{SO}_4$  and 34.2 grams of  $\text{MgSO}_4$  per 100 grams of  $\text{H}_2\text{O}$  and (2)  $\text{MgSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  and langbeinite at 57.25 per cent  $\text{MgSO}_4$  and 9.7 grams of  $\text{K}_2\text{SO}_4$  per 100 grams of  $\text{H}_2\text{O}$ .

THE QUATERNARY SYSTEM

MAGNESIUM SULPHATE - POTASSIUM CHLORIDE - MAGNESIUM CHLORIDE -

POTASSIUM SULPHATE - WATER

AT THE 100° ISOTHERMAL.

which he states is so great that the KCl can exist as solid phase in the form of carnallite  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$  at the invariant point of carnallite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  as the solid phase. He then considers the KCl and carnallite invariant point, where the  $\text{MgCl}_2$  is only present in solution and decreases to zero at the solubility of pure KCl.

The five invariant points in the four component system, representing solutions saturated with respect to three salts. The solid phases at each of the invariant points are as follows: -

- (1) Carnallite,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .
- (2) Carnallite,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and KCl.
- (3)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and KCl.
- (4)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , Shoenite and KCl.
- (5)  $\text{K}_2\text{SO}_4$ , Shoenite and KCl.

The limits of the fields of shoenite, KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , carnallite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  will be obvious upon an examination of the figure 5. The data for these points may be obtained from the original works of Lowenherz. He obtained his invariant points by saturating with two of the desired phases and then adding the third. His fields were determined by joining the invariant points with straight lines. Special notice should be taken of the peculiar solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , when they occur as solid phases, the latter is formed from water,  $\text{MgCl}_2$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .  $\text{MgCl}_2$  enters the solution and withdraws water of crystallization from  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  forming  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  until definite concentration is reached, if more  $\text{MgCl}_2$  is added this also dissolves and draws one molecule of water from  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , if sufficient

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is not present, it no longer occurs as the solid phase but only as  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , which latter coexists with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in the solid phase. Hence two different solutions can be prepared from the salts  $\text{MgSO}_4$  and  $\text{MgCl}_2$  each saturated with respect to the two salts.

Menge<sup>43</sup> worked on the system  $\text{K}_2\text{Cl}_2 - \text{K}_2\text{SO}_4 - \text{MgCl}_2 - \text{MgSO}_4$  above 500°. He points out that the double salt of  $\text{KCl}$  and  $\text{MgCl}_2$  was obtained.

Loewenhertz<sup>44</sup> published a later paper, in which he considers the variation in the solubility figures in his former paper to be due to unsaturation.

Janecke published a paper on a theoretical behaviour of the melting of the salt pairs  $\text{MgSO}_4 - \text{K}_2\text{Cl}_2 - \text{MgCl}_2 - \text{K}_2\text{SO}_4$ . Results have shown that besides the previously known salts langbeinite  $\text{K}_2\text{Mg}_2(\text{SO}_4)_4$  and  $\text{KClMgCl}_2$ , a third salt  $\text{KMgClSO}_4$  is present. The latter is of interest, since it is made up of four different radicals. He points out that  $\text{KMgCl}_2$  might be called anhydro kainite, since they are of the same composition as the hydrated salts, where the water content is neglected. All the compounds have congruent melting points, and cases occur, which were dealt with in former investigations, some of which have been referred to in this work. He uses a square as a method of representation and therefore the valency of the salt pairs must be considered as equivalents. He finds that he is dealing with seven different salts, which all possess a melting point maximum, that is a congruent melting point. Each has a definite zone of separation and the surfaces of the square must be broken up in such a manner that six different mixtures are obtained, which represents an equilibrium of the melts with three different salts. A number of these may correspond to eutectic mixtures, others may be transition temperatures.

The mixtures  $K_2SO_4$  and  $MgSO_4$  were investigated by Nachen<sup>35</sup>, The compound langbeinite forms two eutectics with  $K_2SO_4$  and  $MgSO_4$  above 595<sup>0</sup>. The more stable salt is alpha  $K_2SO_4$ , which forms mixed crystals.  $K_2SO_4$  and  $K_2Cl_2$  were investigated by Janecke. He finds it to have one eutectic, and the third system  $KCl$  and  $MgCl_2$  was investigated by Menge. He thought he had found beside the double salt  $KMgCl_3$ , the salt  $K_2MgCl_4$ . According to him the latter possesses a small melting point maximum. Janecke recalculated the results of Menge and found that he had no grounds for reporting  $MgK_2Cl_4$ . The system  $MgCl_2$  and  $MgSO_4$  was determined by Janecke. It appears that only one eutectic occurs. Besides the melting point of 1185<sup>0</sup> for  $MgSO_4$  others were found due to decomposition.

Janecke also points out that it would be very interesting, if this new salt were found in potash deposits. A possibility appears to exist for the appearance of shoenite, leonite occurs at a higher temperature and then finally langbeinite, then also in place of the hydrated salts the anhydrous kainite may occur. The name anhydro carnallite is due only to the loss of water caused by the ability of the crystallizing salts for removing water from one another.

According to Van't Hoff, kainite disappears at 83<sup>0</sup> as a solid phase in solution, by analogy to other salts, the anhydride may occur below this temperature due to the dehydrating action of the other salts. If it was not found by Van't Hoff, it may be that hysteresis may account for that; its complexity or mean valency of 1.5 may also be important factors. As salts crystalize in a regular system it would be found in the salt deposit. Moreover  $KMgCl_3$  also occurs at high temperature in place of carnallite as solid phase.

He suggests that the solubility diagrams of Van't Hoff and Meyerhoffer for salt mixtures  $KCl$  and  $MgCl_2$  may not be correct for high temperature.

Considerable work has been done on these salt pairs in the presence of the  $Na$  ion, which as we know occurs in great quantities and we will consider briefly the effect of this ion on the present system, remembering that we are really dealing with a five component system.

$K_2SO_4$  does not occur as such, but in the presence of an excess of  $NaCl$  as glasserite. Sodium sulphate occurs as anhydro thenardite. The areas for the different solid salts change and may entirely disappear, while new salts make their appearance. Thus shoenite which at  $25^{\circ}$  is stable, becomes at  $26^{\circ}$  unstable and the shoenite area entirely disappears from the isothermal diagram. The leonite and glasserite areas then become adjacent.

The important point to notice in this connection is the double salt kainite  $KMgSO_4Cl \cdot 3H_2O$ , which is a quaternary compound of the four radicals of the system we are considering and is stable only in the presence of  $Na$  ions and is not stable in the system we are considering. It is this hydrated quaternary salt that Janecke refers to in his melt.

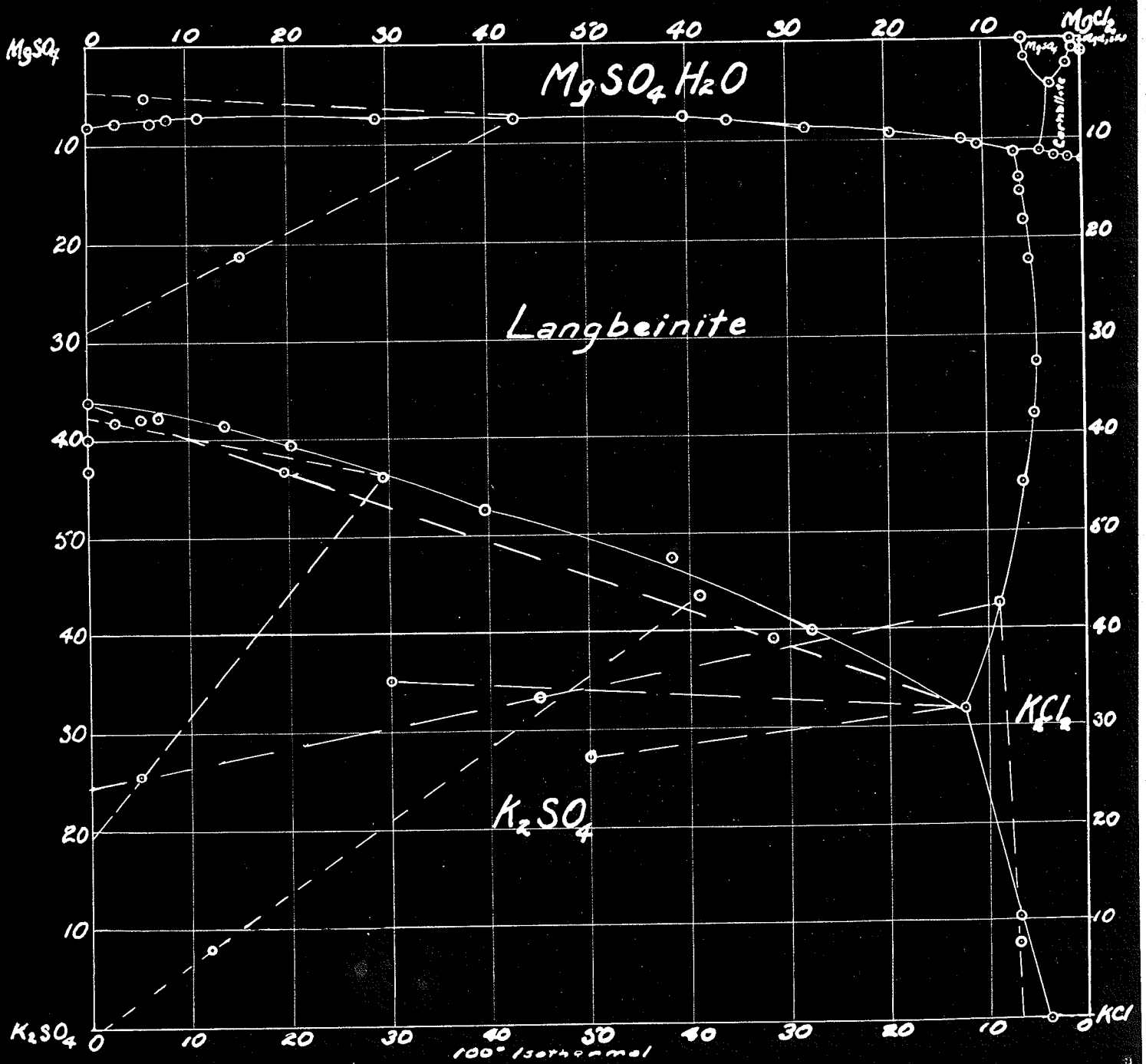
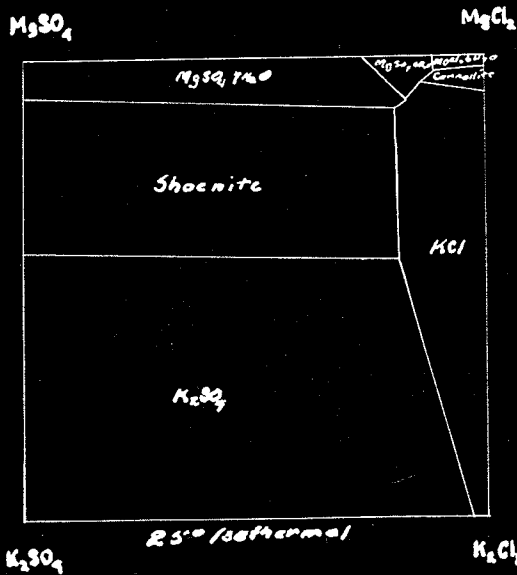
## Solubility Data

Percentage Composition.					Mol Percent.			
Mg.	K <sub>2</sub>	So <sub>4</sub>	Cl <sub>2</sub>	H <sub>2</sub> O	Mg	K <sub>2</sub>	SO <sub>4</sub>	Cl <sub>2</sub>
7.1	3.01	1.31	22.5	66.25	88.5	11.5	4.00	96.00
6.82	4.89	1.88	22.95	63.5	81.65	18.35	5.7	94.3
8.02	3.54	.70	26.1	62.00	88.00	22.00	1.8	98.2
7.09	3.51	2.09	22.4	64.9	86.6	13.4	6.45	93.55
8.78	1.743	1.02	26.08	62.5	95.5	4.5	2.8	97.2
7.75	5.5	1.99	21.6	63.21	97.9	2.1	6.27	93.75
6.66	2.24	5.69	17.3	68.11	90.5	9.5	19.5	80.5
5.58	8.9	1.44	23.42	60.65	66.5	33.5	4.5	95.5
9.7	1.1	.22	29.2	60.00	96.7	3.3	.5	99.5
8.62	8.53	.46	28.55	53.8	87.5	12.5	1.3	98.7
10.5	.35	.29	30.7	58.15	99.00	1.00	.8	99.2
9.25	.76	.57	27.2	62.2	97.5	2.5	1.5	98.5
1.88	14.00	3.07	16.14	64.91	29.8	70.2	12.2	87.2
.64	16.95	1.53	16.35	64.98	10.65	89.35	6.5	93.5
5.87	9.04	7.26	13.7	64.12	91.00	9.00	28.1	72.00
7.73	1.53	2.77	20.85	67.52	94.6	6.00	91.00	9.00
6.15	1.73	14.7	8.7	68.7	91.8	8.2	55.5	45.5
6.12	1.43	9.2	12.39	70.00	93.00	7.00	15.5	84.5
3.81	7.65	22.62	1.46	64.5	61.5	38.5	92.4	7.6
2.21	13.02	13.95	5.93	64.75	35.2	64.8	24.00	76.00
3.44	7.1	21.12	8.82	67.3	61.00	39.00	94.5	5.5
2.16	10.9	7.00	11.07	68.7	38.8	61.2	31.9	68.1
3.19	10.7	17.00	3.14	65.9	59.00	41.00	79.8	27.2
7.35	1.50	28.2	1.96	61.00	93.5	6.5	91.4	8.6
6.54	2.5	16.31	8.73	65.8	91.00	9.00	57.5	42.5
6.7	2.13	26.8	1.68	63.00	90.5	9.5	92.2	7.8
7.03	1.27	25.95	2.3	63.5	94.6	5.4	88.8	11.2
6.96	1.62	28.3	.82	62.5	93.5	6.5	96.4	3.6
7.45	.81	27.09	2.48	62.5	92.9	7.1	88.9	11.1
7.05	1.76	21.25	6.41	63.4	92.5	7.5	70.7	29.3
6.35	1.71	26.35	.66	65.00	92.4	7.6	96.65	3.35
7.03	1.95	28.42	1.2	61.5	92.4	7.6	94.6	5.4
6.64	1.88	26.25	1.64	63.5	92.00	8.00	92.2	7.8
7.25	1.53	28.25	1.96	61.00	93.9	6.1	91.4	8.6
6.72	1.76	26.4	1.69	63.4	92.5	7.5	92.00	8.00
3.87	7.72	21.4	2.47	65.2	61.7	38.3	86.4	13.6
3.32	10.45	18.39	6.62	62.5	50.5	49.5	70.7	29.3
3.22	9.1	14.52	6.93	66.2	53.2	46.8	60.7	39.3
3.76	7.95	21.05	2.56	64.5	60.3	39.6	85.8	14.2
3.39	7.28	20.7	1.19	65.7	60.2	39.8	92.8	7.2
3.74	7.92	22.8	2.13	64.8	60.4	39.6	87.5	12.5



## Solid Phase Analysis.

Percentage Composition					Mol. Percent			
Mg.	K <sub>2</sub>	SO <sub>4</sub>	Cl <sub>2</sub>	H <sub>2</sub> O	Mg	K <sub>2</sub>	SO <sub>4</sub>	Cl <sub>2</sub>
2.10	15.05	3.06	17.8	61.25	31.5	68.5	12.5	87.5
(I)	(A)	Mixed solid phase			26.0	74.00	50.00	50.00
	(B)	Langbeinite phase			57.00	43.00	80.5	19.5
(II)	(A)	Mixed solid phase			35.5	64.5	70.00	30.00
	(B)	Langbeinite phase			72.00	28.00	96.00	4.00
2.60	11.38	2.15	16.3	67.5	42.5	57.5	9.00	91.00
	(A)	Mixed solid phase			8.00	92.00	7.00	93.00
	(B)	Langbeinite phase			33.00	67.00	55.00	45.00
6.54	2.5	16.3	8.73	65.8	91.00	9.00	57.5	42.5
	(A)	Mixed solid phase			95.00	5.00	94.00	6.00
	(B)	Langbeinite phase			79.00	21.00	85.00	15.00
3.32	10.45	18.39	5.62	62.5	55.5	44.5	70.7	29.3
	(A)	Mixed solid phase			26.00	74.00	95.00	5.00
	(B)	Langbeinite phase			62.00	38.00	97.00	3.00
2.35	10.1	9.78	8.46	70.00	43.00	58.00	39.00	61.00
	(A)	Mixed solid phase			9.00	91.00	88.00	12.00
	(B)	Langbeinite phase			51.00	49.00	95.00	5.00



### Conclusions

The isothermal at  $100^{\circ}$  for the system  $\text{MgCl}_2 - \text{K}_2\text{SO}_4 - \text{MgSO}_4 - \text{KCl}$  has been completed. No quaternary salt occurs, that is no compound forms containing the four radicals of the system under consideration. In other words no divariant areas occur which are enclosed by three or more invariant points joined by univariant lines. Only the double salts that occurred in the four ternary systems appear in the quaternary system at  $100^{\circ}$  and the simple salts themselves. The relative divariant areas for the occurring salts was determined and the solubility variations with change in relative composition.

The method of Janecke was used to express the results obtained. The theory of which has been previously discussed. The invariant points of the four ternary systems were taken. The  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgSO}_4$ , langbeinite,  $\text{K}_2\text{SO}_4$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  invariant points were taken from this work and the carnallite,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$  invariant points were obtained from the data of my co-worker Dowens on his two ternary systems of this subject. These were calculated to mol percent and plotted on the sides of the square.

Seven areas were found to occur giving five points of complete invariance, that is, a saturated solution in equilibrium with three distinct solid phases. These are joined by curves representing equilibrium between saturated solutions and two solid phases. These seven divariant areas are saturated solutions in contact with  $\text{K}_2\text{SO}_4$ , langbeinite  $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ ,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KCl}$  and carnallite respectively as solid phases. The five invariant points were found to have (1)  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$  and langbeinite as solid phases in equilibrium

with saturated solution. (2) Langbeinite,  $\text{MgSO}_4\text{H}_2\text{O}$ , KCl as solid phases in equilibrium with saturated solution. (3)  $\text{MgSO}_4\text{H}_2\text{O}$ , carnallite, KCl as solid phases in equilibrium with saturated solution and (4)  $\text{MgSO}_4\text{H}_2\text{O}$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  as solid phases in contact with saturated solution.

The magnitude of these divariant areas represent saturated solution in equilibrium with one salt only as solid phase and vary inversely as the solubility of that solid phase. As the result of this fact we have a large  $\text{K}_2\text{SO}_4$  area, a large langbeinite area and  $\text{MgSO}_4\text{H}_2\text{O}$  and KCl area of almost equal size, while the carnallite and  $\text{MgSO}_4$  areas are small and of about equal magnitude. The  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  area is very small, as one would expect of a highly hydrated salt at this temperature.

The isothermal at  $100^\circ$  resembles markedly the isothermal at  $25^\circ$  completed by Lowenherz, except that his shoenite area is replaced by a langbeinite area and his  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  area is replaced by a  $\text{MgSO}_4\text{H}_2\text{O}$  area and his  $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$  area is replaced by  $\text{MgSO}_4$  area. The areas of the hydrated salts are much smaller and in his work at  $25^\circ$ .

In dealing with this system at  $100^\circ$  it was found that langbeinite occurs as a fine white powder of tetrahedral crystals, which can be readily distinguished and separated from the associating solid phases. We are able to utilize this, as a means of qualitatively determining whether langbeinite was present or not in the solid phase, and also of separating it from the mixed solid phases, when it was present. The dense well crystallized solid phases would settle to the bottom and the langbeinite would be deposited upon the top of this phase, forming a distinct line of

separation between the two phases. When two distinct solid phases occurred, they were separated, and in some cases analysed separately. Two saturated solutions each in equilibrium with two solid phases, langbeinite and  $K_2SO_4$ , were analysed. The two solid phases were also analysed and the results shown on the diagram. One set of the tie lines intersect slightly below langbeinite, while the others run to  $K_2SO_4$ . These points tend to run toward one another, due to the presence of the other solid phase, mechanically contained in the solid phase under consideration. The two solid phase analysis show distinctly that two phases were present in equilibrium with the solution, therefore the two points must lie upon the univariant line between these two divariant areas. This method was utilized in determining the langbeinite,  $MgSO_4 \cdot H_2O$  boundary line or univariant line, and since results were obtained, as shown in the diagram, we conclude that  $MgSO_4 \cdot H_2O$  and langbeinite were present as two solid phases in equilibrium with the saturated solution. The KCl, langbeinite boundary was also determined in this manner and the invariant point langbeinite, KCl,  $K_2SO_4$  was determined, but in this case the  $K_2SO_4$  and KCl solid phases could not be separated mechanically, the result was that the solid phase analysis gave chloride 50% and sulphate 50%, which could occur, only if  $K_2SO_4$  and KCl were both present in the solid phase. The langbeinite tie line runs towards langbeinite as in the former cases, showing that three phases were present in equilibrium with the saturated solution, thus giving us an invariant point. This method was only made possible by the property of langbeinite for occurring in its characteristic powdery form. Therefore we were unable to determine the other di-

variant curves and invariant points, since their solid phases could not be mechanically separated, and the analysis of the solid phase in equilibrium with the saturated solution would mean nothing.

The curve from the invariant point langbeinite,  $K_2SO_4$  on the ternary diagram runs across the graph, and represents the univariant condition of a saturated solution in equilibrium with langbeinite and  $K_2SO_4$  as solid phase, to the invariant point, with langbeinite,  $K_2SO_4$ ,  $KCl$  as solid phase in equilibrium with the saturated solution, the mol percentage of which is Mg 31.5,  $K_2$  68.5,  $SO_4$  17.5,  $Cl_2$  87.5. From this invariant point two other univariant curves run out one to the invariant point on the  $K_2SO_4$ ,  $KCl$  ternary diagram and the other to the langbeinite,  $MgSO_4 \cdot H_2O$ ,  $KCl$  invariant point, where the three above mentioned compounds are in equilibrium with the saturated solution of mol percentage Mg 88,  $K_2$  12,  $Cl_2$  93.5,  $SO_4$  6.5. This point similarly has two univariant curves emitting from it, one to the langbeinite,  $MgSO_4 \cdot H_2O$  invariant on the ternary diagram and the other to the carnallite,  $MgSO_4 \cdot H_2O$ ,  $KCl$  invariant point where the above three compounds are the three solid phases present in equilibrium with the saturated solution of mol percent Mg 88.5,  $K_2$  11.5,  $Cl_2$  96. and  $SO_4$  4. Two other invariants occur at mol percentage Mg 98.1,  $K_2$  1.1,  $Cl_2$  99.1,  $SO_4$  .9 and Mg 95.75,  $K_2$  4.25,  $Cl_2$  97,  $SO_4$  3. The univariant curves meet this point as shown in the diagram giving us the areas of  $MgCl_2 \cdot 6H_2O$ , carnallite and  $MgSO_4$ .

The water content for the solubility determinations is contained in the data and was not represented on the diagram. It was found that the water content of the saturated solutions varied very little, dim-

inishing toward the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  area and at the invariant points as might be expected.

## Summary.

- I. (a) The isothermal at  $100^{\circ}$  for the system  $\text{MgSO}_4$ - $\text{MgCl}_2$ - $\text{H}_2\text{O}$  was completed.
- (b) No double salt occurs.
- (c) The three solubility curves were determined and their invariant points.
- (d)  $\text{MgSO}_4\cdot\text{H}_2\text{O}$ ,  $\text{MgSO}_4$  and  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  were the solid phases in equilibrium with the saturated solutions.
- II. (a) The isothermal at  $100^{\circ}$  for the system  $\text{K}_2\text{SO}_4$ - $\text{MgSO}_4$ - $\text{H}_2\text{O}$  was completed.
- (b) The double salt langbeinite  $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$  forms.
- (c) The three solubility curves were determined and their invariant points.
- (d)  $\text{MgSO}_4\cdot\text{H}_2\text{O}$ , langbeinite and  $\text{K}_2\text{SO}_4$  were the solid phases in equilibrium with the saturated solutions.
- III. (a) The isothermal at  $100^{\circ}$  for the system  $\text{KCl}$  -  $\text{MgSO}_4$  -  $\text{MgCl}_2$  -  $\text{K}_2\text{SO}_4$  -  $\text{H}_2\text{O}$  was completed.
- (b) No quaternary compounds occur.
- (c) Only the double salts and the simple salts, that occur in the ternary systems, were found in this isothermal.
- (d) The five invariant points and the univariant curves joining these points, forming the areas of divariance, in which one solid phase only is present in equilibrium with the saturated solutions, were determined.
- (e) The relative magnitude of the areas, in which  $\text{MgSO}_4\cdot\text{H}_2\text{O}$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ , langbeinite, carnallite are solid phases, were determined.



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