The Conditions of Formation
of
Certain Double Sulphates.

A thesis submitted to the Senate of Glasgow University
in compliance with the requirements for the Degree of
Doctor of Philosophy,
by
William Johnston, B.Sc.

The work embodied in this thesis was carried out in the Research Laboratory of the Royal Technical College, Glasgow, and in submitting it the author wishes to record his deep sense of gratitude and indebtedness to Professor R. M. Caven, D.Sc. under whose supervision the work was carried out. Dr. Caven's help and advice was at all times freely and gladly forthcoming.

The author also desires to acknowledge his debt to the Governors of the Royal Technical College for a Research Assistantship, and to the Carnegie Trustees for a Scholarship, which enabled him to carry out the work embodied in this thesis. He takes this opportunity of laying on record his sincerest thanks.

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General Introduction.

While the fact that two single salts can combine to form a third salt with an individuality of its own had long been known to students of chemistry, yet it was only in comparatively recent years that this question received any particular attention.

It is not known with any certainty who first drew attention to the above fact, for, like many other interesting cases, we first come across it in the literature as an accepted fact. Berzelius as far back as 1812 cited potassium alum as an example in support of his Dualistic Theory, and Thomas Graham made extensive use of the alkali double sulphates in his investigation of "Water of Crystallization".

These, and other cases, go to show that double salts were well known, though there seems to have been little or nothing known about the conditions of their formation. The prevalent idea seems to have been that which still commonly holds, that these conditions are completely summed up in the following statement:- equimolecular quantities of the two single salts are dissolved in hot water, and on cooling the double salt crystallizes from the mixed solution. It is seen in the sequel that these conditions are totally inadequate.

It was left to such investigators as Arrhenius and van't Hoff to supply a theory of double salt formation.. The approach was first made by investigations and suggestions on the problem of the solution of single electrolytes, a very necessary procedure before any idea as to the formation of double salts could be evolved. The immense amount of both theoretical and practical work put forward in the past decade has left the problem of solution still unsolved, but on the other hand as regards the conditions of formation of double salts the work done has been of the utmost value, especially when considered in the light of the Phase Rule. This aspect of the problem will be dealt with later.

The first point that emerges is that there appear to be two kinds of salts formed by the chemical union of two single salts, double salts and complex salts. A double salt is distinguished by having an individual constitution in the solid state only, decomposing in solution into its component salts. A complex salt maintains its individuality in solution.

It would appear, however, that this difference is more apparent than real, and a consideration of known facts would suggest that the distinction is one rather of degree than of kind. Thus complex salts show varying degrees of stability among themselves, and can be arranged in the order of their stability. The complex cyanides supply a very good example. They can be arranged in a table showing several stages of stability. The least stable are those which, although they can be isolated in the solid state, are decomposed by dilute acids with separation of the simple cyanide. The most stable are those from which the complex acid itself may be isolated.

To the first class belong potassium nickel cyanide and potassium palladium cyanide, and to the second potassium ferrocyanide. Yet it is interesting to note that even potassium ferrocyanide, the most stable of the complex cyanides, is decomposed in solution into the simple cyanides to a measurable degree. It should be possible to arrange the double sulphates in a similar manner, and thus throw some light on the mechanism of their formation.

However, in spite of the large amount of experimental work that has been done, very little correlation between the work of different investigators is to be found. Koppel (1) investigated a series of the double salts of sodium sulphate with the sulphates of the bivalent metals. Benrath (2) has investigated the thallium double sulphates. Schreinemakers (3) and his co-workers have published a large number of papers on various double salts, and he has correlated these results in several books, considering them, however, mainly from the point of view of the Phase Rule. Caven and Mitchell (4,5,6) have published several papers on various double sulphates, and have suggested that the double sulphates of the alkali metal type should be thoroughly studied. By this means the effect of alteration of alkali metal and of heavy metal could be investigated.

Caven, Ferguson, and Mitchell (6) have elaborated this view, and have put forward a general hypothesis regarding the formation of double and complex salts in solution. Moreover, evidence is submitted which indicates the presence of complex ions in solution and demonstrates the existence and persistence of double sulphates in solution.

The work submitted in the present thesis is a continuation and extension of the work of Caven, Ferguson, and Mitchell. From investigation of still more of the alkali-heavy metal sulphates further light is thrown on the above points. Moreover, the double salts are considered from a general point of view, that is their formation from solution is studied as regards relative concentration of the component salts, change of temperature, and isothermal evaporation.

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Theoretical.

Van't Hoff in his classical work "Vorlesungen über Bildung und Spaltung von Doppelsalzen" (Liepzig,1897) developed his theory of double salt formation from the point of view of "solubility product". He recognized that two kinds of salts can be formed by the chemical combination of two single salts, double salts and complex salts. A double salt is distinguished by having an individual constitution in the solid state only, decomposing in solution into its component salts; a complex salt maintains its individuality in solution. Or expressed from the point of view of the ionic theory:-

The ions of complex salts in solution are different, and the ions of double salts are similar to the ions of the simple salts from which they are derived.

The mode of formation of the two classes of compounds brings out a definite distinction between them. The double salt potassium ferrous sulphate ($K_2SO_4.FeSO_4.6H_2O$) is deposited in the form of crystals from a mixed solution of the two sulphates, which are both soluble in water. The complex salt potassium ferrocyanide ($K_4Fe(CN)_6$) is formed by the addition of potassium cyanide to a ferrous salt solution. Ferrous cyanide is first precipitated, but is dissolved on addition of excess potassium cyanide forming potassium ferrocyanide, which in sharp contradistinction to ferrous cyanide is readily soluble in water. This sudden increase in solubility is peculiar to the formation of complex salts.

These facts can be studied from the view point of "solubility product". Thus consider a saturated solution of a salt (an electrolyte). In such a case there is equilibrium between the solid salt and the non-ionized salt in the solution, so that the concentration of the non-ionized salt remains constant at constant temperature. Further, there is equilibrium in the solution between the non-ionized salt and its ions. This can be represented by the equation,

$$A^{\cdot} + B^{\prime} \rightleftharpoons AB$$

where AB represents the salt, and A and B the ions. Applying the "law of mass action" it follows, for the latter equilibrium, that,

$$[A^{\cdot}]\,[B^{\prime}] = K[AB] = S,$$

where S is the product of the concentration of the two ions --- the so-called solubility product --- and is constant, since the right-hand side of the above equation is constant. The equilibria in the heterogeneous system may be represented as follows:-

$$\begin{array}{ccl} A^{\cdot} + B^{\prime} & \rightleftharpoons & AB \text{ (in solution)} \\ & & \downarrow\uparrow \\ & & AB \text{ (solid)} \end{array}$$

If by any means the solubility product is exceeded, for example by adding a salt with an ion in common with the salt already present, the ions unite to form undissociated salt, which falls out of solution, and this goes on till the normal value of the solubility product is reached. A well-known illustration of this is the precipitation of sodium chloride from its saturated solution by passing in gaseous hydrogen chloride. In this case the original equilibrium between equivalent amounts of $Na^{\cdot}$ and Cl' ions is disturbed by the addition of a large excess of Cl' ions, and sodium chloride is precipitated till the original solubility product is reached, when the solution contains an excess of Cl' ions and relatively few $Na^{\cdot}$ ions.

When the case of complex salts is considered, however, this "principle of solubility product" breaks down, or at least appears to do so. If potassium cyanide is added to a solution of a ferrous salt, ferrous cyanide is immediately precipitated, showing that it is very insoluble in water. On the addition of a further (excess) quantity of potassium cyanide the ferrous cyanide is completely dissolved. Thus the addition of the common ion $(CN)'$ seems to increase greatly the solubility of ferrous cyanide, in sharp contrast to the case of sodium chloride. The "principle of solubility product" seems, therefore, to break down, but the increase of solubility is really due to the formation of the complex ion $[Fe(CN)_6]''''$. That is why the "principle of solubility product" no longer holds for the original CN' ions.

This apparent breakdown of the "principle of solubility product" is peculiar to the formation of many complex salts, and was taken by van't Hoff to form a distinguishing feature between complex and double salts. In his opinion the crystallization of double salts from solution is not preceded by any increase in solubility of one single salt by the addition of the other. He believed that the addition of a salt with a common ion diminished the solubility of the other salt whether

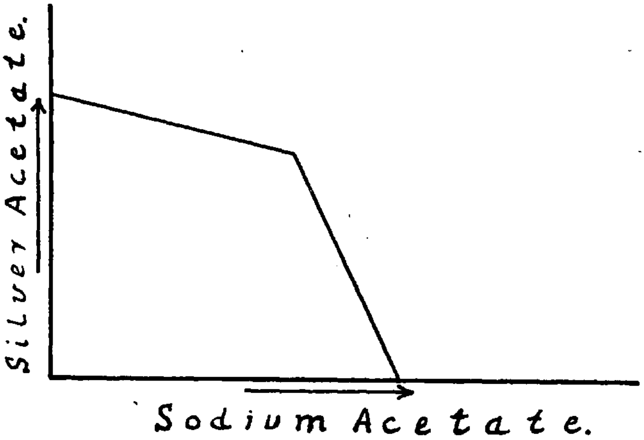


FIGURE 1.

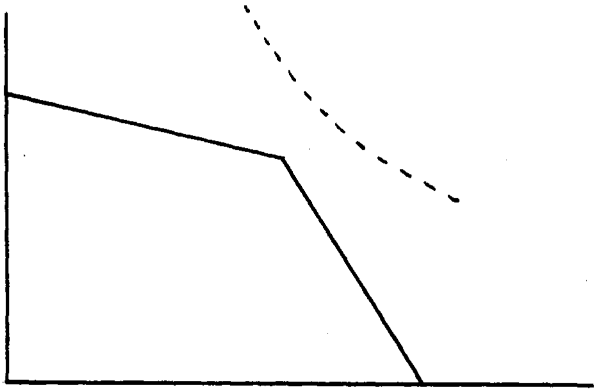


FIGURE 2.

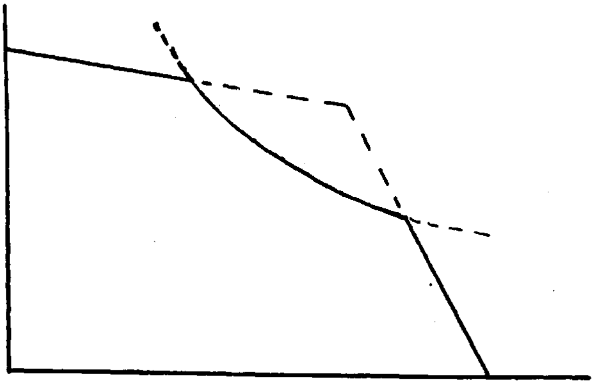


FIGURE 3.

double salt ultimately crystallized from the solution or not. Thus van't Hoff places the case where there are two salts with a common ion and double salt formation on the same level as the case of two salts with a common ion and no double salt formation.

A convenient example of the latter case is given by sodium acetate and silver acetate. In this case the "principle of solubility product" holds good, as each salt mutually diminishes the solubility of the other. When the effect of this reciprocal influence is plotted a curve of the type shown in Figure 1 is obtained.

Consider now the case of two salts with a common ion and with double salt formation, such as is given by the sulphates of potassium and ferrous iron. In this case two states of affairs must be considered. The first case is where the conditions are such that no double salt can exist in equilibrium with the solution, the double salt being more soluble than either of the single salts. It decomposes in solution, and gives crystals of that single salt with which the solution first becomes saturated. The second case is where the conditions are such that double salt can exist. These two cases are represented according to van't Hoff by Figure 2 and Figure 3.

Thus according to van't Hoff double salt formation is supposed to take place in accordance with the "principle of solubility product", being dependent on solubility only, crystallization of double salt not being preceded by its formation in solution. The salts are assumed for the sake of argument to be wholly ionized in solutions which nevertheless are saturated.

This view has not been supported by experimental investigation. Indeed the facts recorded by various observers have given rise to a different view of the origin of double salts:-

Double salts appear to exist in solution previous to crystallization; or, in other words, unstable complex ions are formed as the result of the contiguity of molecules of the single salts when a solution of these salts becomes concentrated. These complex ions are analogous to the ions of complex salts, and may thus be expected to increase the solubility of the single salts. The case of potassium and ferrous sulphates may be studied from this point of view. In dilute solution these salts are almost completely dissociated into $K^{\cdot}$, $Fe^{\cdot\cdot}$, and $SO_4^{''}$ ions. As the solution is concentrated dissociation is reduced and molecules of the salts are formed, those of $FeSO_4$ being formed earlier than those of K_2SO_4. The $FeSO_4$ molecules then combine with $SO_4^{''}$ ions, to a certain extent, to form ferrosulphate ions as follows:-

$$2K^{\cdot} + SO_4^{''} + FeSO_4 \rightarrow 2K^{\cdot} + [Fe(SO_4)_2]^{''}.$$

The formation of $[Fe(SO_4)_2]^{''}$ ions may be expected to increase the solubility of ferrous sulphate as in the case of the formation of a complex salt such as potassium ferrocyanide, where the greatly increased solubility of ferrous cyanide is due to the formation of the complex ions $[Fe(CN)_6]^{''''}$. Thus, on this assumption, when two sulphates are known to form a double

SYSTEM – $FeSO_4$ – $(NH_4)_2SO_4$ – H_2O at 30° C.

(Schreinemakers.)

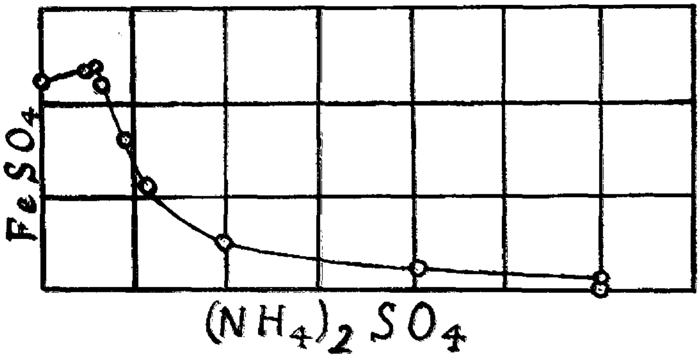


FIGURE 4.

SYSTEM – $FeSO_4$ – Li_2SO_4 – H_2O at 30°C.

(Schreinemakers.)

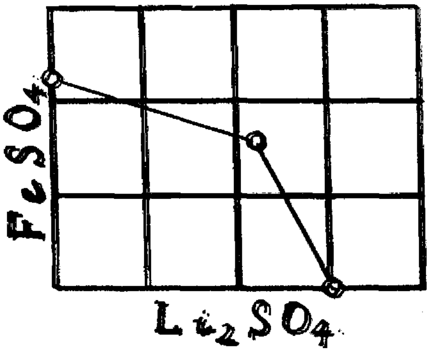


FIGURE 5.

salt the solubility of one sulphate will be found to be increased by the presence of the other, due to formation of complex ions in solution. If no double salt is formed, then there will be no increase. Recorded observations confirm this view.

Hittorf (7) was the first to make the suggestion that the abnormal behaviour of certain electrolytes might be accounted for by assuming the formation of complex ions in them. In the course of his study of migration he made the classical discovery that the migration ratio for the anion in solutions of many double salts and certain single ones increased rapidly with increase in the concentration of the solution and at high concentrations became greater than unity. Hittorf suggested that this was due to the formation of a "double salt" in the solution, which gradually dissociated on dilution.

Schreinemakers (8) investigated the influence of ammonium and lithium sulphates on the solubility of ferrous sulphate at 30°, with the result illustrated in Figure 4 and Figure 5. In the case of ammonium sulphate the solubility of ferrous sulphate is increased, and in the case of lithium sulphate the solubility of ferrous sulphate is decreased. It is a well known fact that ammonium sulphate forms a double salt with ferrous sulphate while lithium sulphate does not.

E. Klein (9) reached a similar conclusion regarding the existence of complex ions in mixed solutions of sulphates. He investigated the electrical conductivities of copper potassium sulphate and similar double salt solutions. He found that, in the case of concentrated solutions, there was a departure from the mean of the sum of the conductivities of equimolecular solutions on mixing the components, while with dilute solutions the equimolecular conductivity became practically the mean of the conductivities of the components. He also showed, by means of electrical conductivity experiments, that the double salt in solution was dissociated by diluting, or by raising the temperature.

The conductivity of copper potassium sulphate was determined at 18°C by MacGregor and Archibald (10). The conductivity was calculated assuming non-formation of double salt by a method due to MacGregor (11). They found a discrepancy between observed and calculated values, and concluded that the difference could be accounted for by the presence of double salt in solution.

Magnesium potassium sulphate was examined at 18°C by MacGregor and McKay (12), and they concluded that there was sufficient evidence to show that in strong solutions the salts are partly united.

W. Pfanhauser (13) investigated the double salt nickel ammonium sulphate, and showed that in saturated solutions at ordinary temperatures the ions are mostly $NH_4^{\cdot}$ and $[Ni(SO_4)_2]''$.

Reiger (14) has also shown that in solutions of copper potassium sulphate the copper migrates partly to the anode, thus indicating the presence of complex ions.

Jones and Caldwell (15) showed that the double sulphates of ammonium with cadmium, copper, magnesium, ferrous iron, and nickel, and the double sulphate of potassium and nickel remain partly undissociated in concentrated solution, and even in dilute solution are not entirely broken into their constituents.

Support for this view is also forthcoming as a result of solubility measurements by a large number of investigators.

Schreinemakers (8) showed that ammonium sulphate increases thr solubility of ferrous sulphate. He also showed (16) that at 25° C the solubility of manganese sulphate is increased by the addition of ammonium sulphate.

Roozeboom (17) observed an increase of solubility when ammonium chloride was added to ferrous chloride.

Schreinemakers (18) found that potassium iodide increased the solubility of lead iodide, and Lipscombe and Hulett showed (19) that the solubilities of both zinc chloride and cadmium chloride were increased by addition of potassium chloride.

Britton and Allmand (20) as a result of investigation of the system potassium sulphate - glucinum sulphate - water, and Britton (21) as a result of investigation of the system aluminium sulphate - ammonium sulphate - water obtained similar results to the above.

Caven and Mitchell (4), in an attempt to discover further evidence of the existence of double salts in solution, investigated the systems cupric sulphate - potassium sulphate - water and cupric sulphate - ammonium sulphate - water at 25°, 51°, and 61° C. They found that "the solubility of each of the three simple salts is continuously increased up to the triple point, at which point the double salt separates". They conclude that this "increase is an indication of the presence of a considerable amount of the double salt (or its ions) in solution".

Cameron and Breazeale (22) studied the conditions of formation of the double salt $CaSO_4.K_2SO_4.H_2O$ at 25°, and Caven and Miss Rooney (23) at 0°. At both temperatures the influence of potassium sulphate upon the solubility of calcium sulphate is most peculiar. At first there is rapid diminution in solubility of calcium sulphate with addition of potassium sulphate, but with continued addition of potassium sulphate this diminution is arrested and is turned into an increase up to the triple point where double salt separates. Caven and Miss Rooney interpret this result as follows:- The solubility of calcium sulphate is very small. Therefore, at first "when both salts are present in a highly diluted state so as to be greatly ionized the law of solubility product holds". As the concentration of potassium sulphate is increased, however, complex ions of the double salt are formed in increasing numbers until the diminution is overcome and converted into an increase.

In this connection it is interesting to note that Sabatier (24) showed that the solubility of cobalt chloride in water is first diminished and then increased by continuous addition of hydrochloric acid.

Caven, Ferguson, and Mitchell (6), while bringing forward evidence for the existence of double salt molecules or complex ions in solution, have also suggested a general hypothesis regarding double salt formation.

Cupric sulphate forms well known double sulphates with ammonium and potassium sulphates, and the solubility of each alkali salt is increased by cupric sulphate, and that of cupric sulphate by alkali sulphate. On the other hand Schreinemakers (8) has shown that cupric sulphate does not form a double salt with lithium sulphate, and the solubility of each salt is diminished by addition of the other. In the earlier days of chemistry this difference between potassium and lithium sulphates might simply have been referred to as a question of affinity. Chemical union is effected between potassium and cupric sulphates because there is sufficient chemical affinity between the two salts. The affinity between lithium and cupric sulphates is insufficient because of the less intensely metallic properties of lithium as compared with potassium. Van't Hoff considered the formation of double salts only from the point of view of solubility and the operation of the phase rule. He ignored this view completely, though it is fundamentally true.

Before proceeding to study this point more closely it may be of interest to glance briefly at the attempts to classify the elements as regards affinity.

The electro-chemical classification of Berzelius was the first, and he used it as the basis of his "dualistic theory" of chemical compounds. This theory stated that "electricity is the first cause of all chemical activity", and the varying degrees of chemical affinity were supposed to imply that the different substances were charged with varying quantities of electricity. By this means Berzelius was able to classify the elements in a series in which the graduation with respect to electric character was from positive to negative. This in reality formed a transition from metal to non-metal.

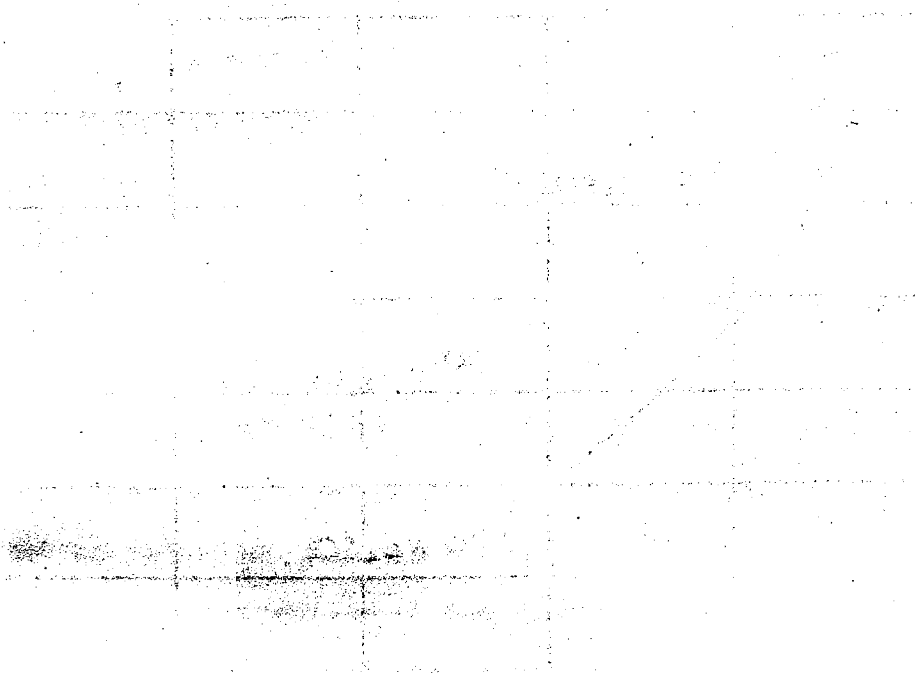
This method of classification culminated in the Electrochemical Series of the elements, in which the elements are arranged in a series representing the potential difference in volts which is developed between the metals and solutions of their salts. The series is as follows:-

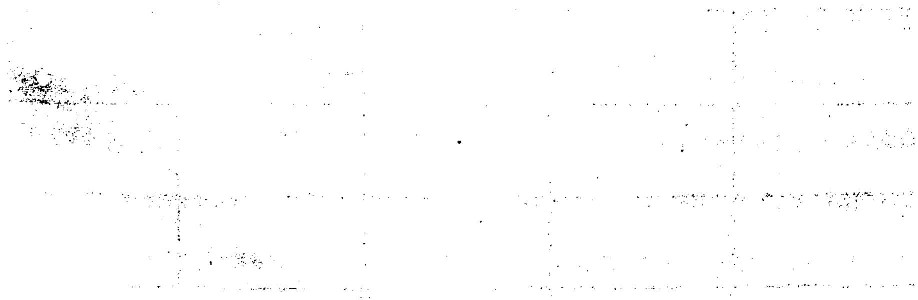
Metals:- Cs, Rb, K, Na, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Cd,
Tl, Fe, Co, Ni, Sn, Pb, H, Sb, As, Cu, Hg, Ag, Pd,
Pt, Au, Ir, Rh, Os.

Non-metals:- Si, C, B, N, Se, P, S, I, Br, Cl, O, F.

This order represents also, as regards the metals, the relative power of displacing other metals from salt solutions, so that any chosen metal can precipitate from solutions of equivalent strength any metal that follows it in the list. Moreover, combination is most likely to occur between elements widely separated in the above series, and this to a limited extent may apply to compounds of these metals.

This is the point of view taken up by Kendall (25) and his co-workers. Indeed they have extended this generalization to include compound formation between elements, compound formation between molecules of solute and solvent, formation of molecular compounds, dissociation, and order of solubility. In the main their contentions are shown to hold, though, as is to be expected, there are a number of exceptions. Kendall (26) also draws a parallelism between the electro-potential series





DISSOCIATION FIGURES.

(KOHLRAUSCH'S ELECTRICAL CONDUCTIVITY.)

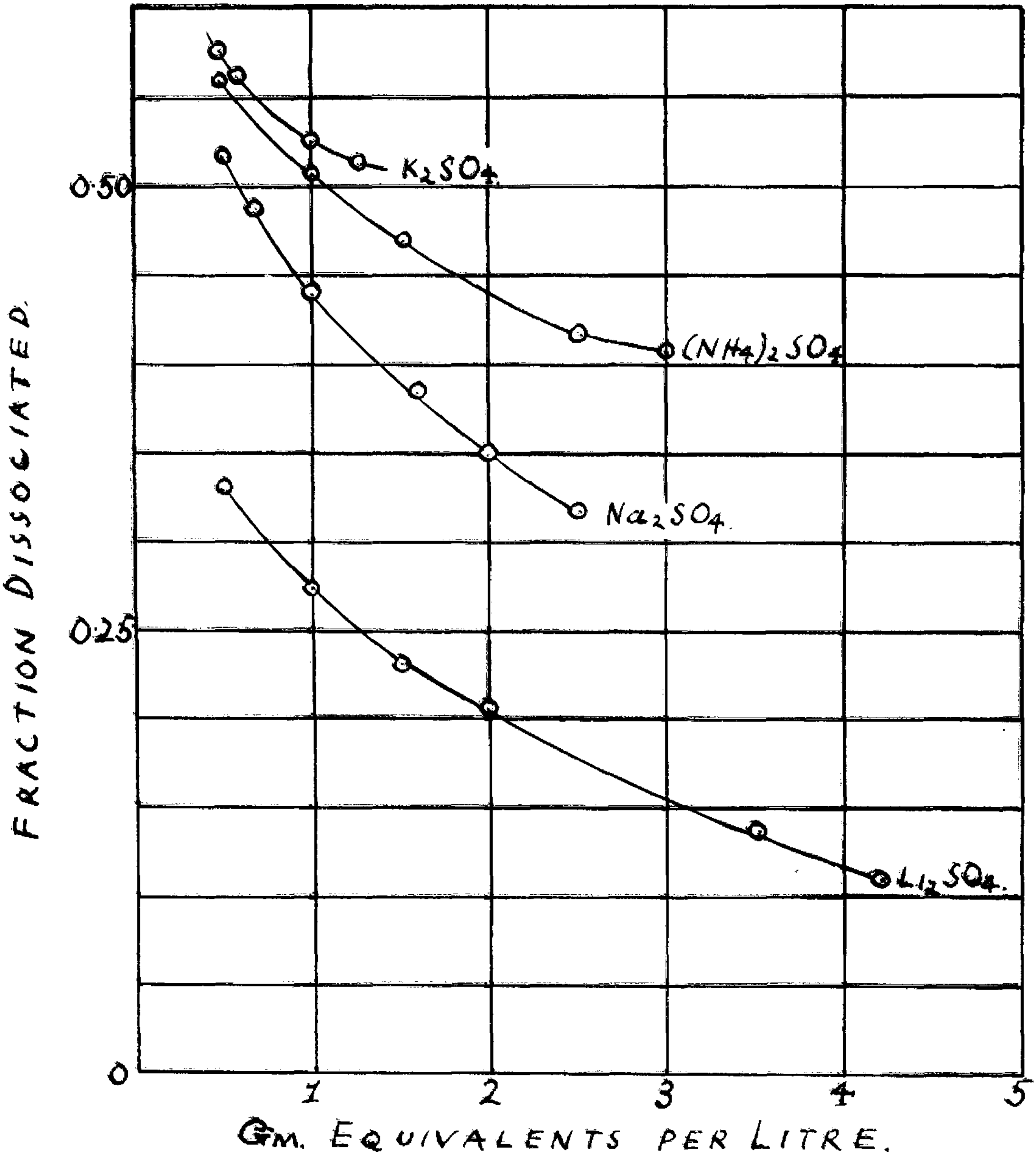


FIGURE 6.

their bearing on double salt formation is that whilst potassium, ammonium, and sodium sulphates provide sufficient concentrations of SO_4'' ions in varied states of dilution to bring about union with the sulphate of a bivalent metal, as for example:-

$$CuSO_4 + SO_4'' \rightarrow [Cu(SO_4)_2]'',$$

lithium sulphate, by reason of its inferior dissociation, does not produce SO_4'' ions in sufficient quantity for such union to take place; so that double salt is not formed.

Koppel (1) has thrown further light on the question of double salt formation by his investigation of the double salts formed by sodium sulphate with a series of bivalent metal sulphates. These double sulphates differ greatly from those formed by the sulphates of other alkali metals. Those of zinc, cobalt, nickel, ferrous iron, and magnesium crystallize with four molecules of water, while those of copper and cadmium crystallize with only two molecules of water. Moreover, none of these double salts are formed at 0° from solutions of the component salts; the transition point in all cases is considerably above this temperature. He also found, with the exception of the ferrous double salt, where an increase occurs at both ends, that an increase of solubility of sodium sulphate was caused by the bivalent metal sulphate, but a decrease in the solubility of the bivalent metal sulphate by sodium sulphate.

Since lithium forms no double sulphates it seems justifiable to infer that a beginning of double salt formation is being witnessed with sodium sulphate. Further support is given to this idea when the alums are considered. These show an increase in stability and insolubility with increase in basigenic properties of the alkali metal.. Schreinemakers and De Waal (28) have shown that lithium alum is not formed at 30°, and Caven and Livingstone (29) have found that it is not formed at 0°. Sodium alum is very soluble in water and is difficult to obtain in a pure crystalline state. Potassium alum is well known, ammonium alum is less soluble than the potassium compound; rubidium alum is much less soluble than either, and nearly four times as soluble as caesium alum..

Moreover,. it would appear that when a double sulphate begins to be formed, its formation is first shown by an increase in solubility of the alkali sulphate, caused by the presence in solution of the sulphate of the bivalent metal. This means that "the formation of double salt begins when the undissociated molecules of the bivalent metallic sulphate take to themselves sulphate ions from the alkali sulphate in solution". Thus more of the alkali sulphate dissolves than would dissolve in the absence of bivalent sulphate.

Under certain conditions the double salt might be formed in solution but in a quantity insufficient to saturate the solution. Thus it would not crystallize but its presence would be indicated by the alteration of the gradients of the two solubility curves in the direction of increased solubility. In this connection, however, one point must be noted. Van't Hoff's curves were calculated from the law of solubility product on the assumption of complete ionization, although they referred to saturated solutions. If the actual ionization is taken into account the mutual reduction in solubility is less, and the curves would meet in an angle nearer to a right angle. Thus it might be difficult to find evidence of the formation of double salt apart from its actual crystallization.

Caven, Ferguson, and Mitchell (6) postulate the following hypothesis of double or complex salt formation based on the above evidence:-

"A double or complex salt is formed in solution from two salts with a common ion when there is sufficient difference in basigenic character between the two metals forming the cations to yield simultaneously sufficient concentrations of the common anion and the undissociated salt of the weaker cation to cause their union".

They are careful to point out, however, that the nature of the common anion as well as of the cations must necessarily influence the result of bringing the two salts together in solution. Thus, although lithium and ferrous sulphates do not combine to form a double salt, the cyanides of these metals unite to form lithium ferrocyanide. Indeed the power to cause union must primarily reside in the common ion, and this is particularly the case with the complex cyanides, whose formation is due largely to the qualitative nature of the cyanide ion.

Tutton (30) has examined the physical properties of double salts of the type $M_2^{\cdot}[\ddot{M}(SO_4)_2].6H_2O$. The crystals are monoclinic, and the author has come to the conclusion regarding them that "the structural unit of the space lattice will more probably prove to be simply the chemical molecule, or at most two molecules". The same author (31) has analysed potassium alums by means of X-rays, and he has shown that the 24 molecules of water in the molecule $K_2Al_2(SO_4)_4.24H_2O$ are divided into six groups of $4H_2O$. These groups are situated with regard to the rest of the molecule at the angular points of a regular octahedron. It is to be expected that the six molecules of water in the double sulphates are similarly disposed except for the modification necessary because of the monoclinic structure of the crystal.

If the water of crystallization of a hydrated salt be removed by heat or other dehydrating agency it can be restored again so that the original crystallohydrate is produced; for instance in the case of $K_2SO_4.CuSO_4.6H_2O$ by absorption of water vapour from the air. Moreover, it is a well known fact that the chemical union of the anhydrous salts persists, although the removal of water destroys the crystal structure of the hydrate. If the salt $K_2[Cu(SO_4)_2].6H_2O$ is fused at a red heat and cooled, it is found to retain its blue colour in contradistinction to copper sulphate. This fact was first observed by Graham, and proves that the double salt maintains its identity when deprived of its water.

Graham (32) also showed that this salt when dried at 100°C. retained 2 molecules of water. Caven and Ferguson (33) have studied the course of dehydration of alkali cupric sulphates of the type $M'_2[Cu(SO_4)_2].6H_2O$. They have done so by determining the relative vapour pressures of the hydrated salts at common temperatures. By this means they have been enabled to compare the relative strengths in analogous compounds of the forces of attraction for water. The reactions studied are those represented by the equation,

$$M'_2[M''(SO_4)_2].6H_2O \rightleftharpoons M'_2[M''(SO_4)_2].2H_2O + 4H_2O.$$

They found "that the order of increasing strength of alkali metals, including thallium and ammonium, as regards the power they confer on the rest of the molecule to retain $6H_2O$ is K, Rb, Tl, NH_4, Cs." This is the same order as that found by Tutton through observations of the physical properties of the same salts. It is also pointed out "that the specific influence of the alkali sulphate in the cupric double salts is to cause more water to be retained in the molecule than can be retained by cupric sulphate alone."

The water of crystallization of the single salts seems to have a specific influence on the degree of hydration of the double salt. This fact is apparent even on superficial examination, when it is considered that the double sulphates of potassium and ammonium crystallize with 6 molecules of water, while those of sodium crystallize with a maximum of 4 molecules, and some with only 2 molecules. Potassium and ammonium sulphates are anhydrous; that of sodium is decahydrated.

Koppel's (1) work brings this fact out still more clearly. He concludes, as a result of his investigations, that in the formation of a sodium double sulphate 13 molecules of water are split off in every case, the general equation being,

$$M''SO_4.xH_2O + Na_2SO_4.10H_2O = M''SO_4.Na_2SO_4.(x-3)H_2O + 13H_2O.$$

Thus the formation of the zinc salt, which is tetrahydrated, is represented as follows:-

$$ZnSO_4.7H_2O + Na_2SO_4.10H_2O = ZnSO_4.Na_2SO_4.\underline{4H_2O} + 13H_2O,$$

and that of the copper salt, which is dihydrated,

$$CuSO_4.5H_2O + Na_2SO_4.10H_2O = CuSO_4.Na_2SO_4.\underline{2H_2O} + 13H_2O.$$

The total water of crystallization of the two single salts has considerable influence on the conditions of formation of the double salt, and may even determine, whether, at a specific temperature, the double salt is formed or not. Thus, Findlay (34) gives the following general rule; "In those cases where the change at the transition point is accompanied by the taking up or the splitting off of water then, if the water of crystallization of the two constituent salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature (e.g. astracanite from sodium and magnesium sulphates thus:-

$$Na_2SO_4.10H_2O + MgSO_4.7H_2O = MgSO_4.Na_2SO_4.4H_2O + 13H_2O.),$$

but if the double salt contains more water of crystallization than the two single salts, raising the temperature will effect the decomposition of the double salt." This rule is connected with van't Hoff's law of Movable Equilibrium which states that, the change which takes place at the higher temperature is that which is accompanied by an absorption of heat.

The connection lies "in the fact that the heat effect involved in the hydration or dehydration of the salts is much greater than that of the other changes which occur, and determines, therefore, the sign of the total heat effect."

The above fact applies with the greatest interest to the sodium double sulphates, whose transition points all occur at ordinary temperatures.

Sidgwick (35) under the heading "Solvation" deals with several points pertinent to the formation of double salts.

Thus he states that "there are numerous double salts forming solid phases of definite formula, which nevertheless give no indication of their existence in solution, and it is doubtful if they have any existence as single molecules. Rather they consist of two or more molecules packed together in the crystals." These molecules are presumed to be held together by the weak external fields which surround every atom. On this assumption can be explained the existence of such salts as $K_{15}TaF_{20}$, "which if represented as a true complex salt $K_{15}[TaF_{20}]$ gives Ta a co-valency of twenty against a normal maximum of eight". It may, however, be considered to consist of one molecule of $K_3[TaF_8]$, and twelve of KF. These form separate molecules but a single crystal unit. The alums $M^{\cdot}M^{\cdot\cdot}(SO_4)_2.12H_2O$ can be explained on the same basis. It is to be noted, however, that even the above point of view postulates the formation of complex ions.

He also introduces the question of hydration in solution, and the relation of the hydrated compounds in solution to those obtained in the solid state.

It is doubtful in the case of hydrated compounds "whether all the solvent molecules which appear in the formula really form part of the molecular complex", as is also the common assumption that if a solid hydrate of a particular formula separates this hydrate also exists as a molecule (or as its ions) in solution.

Cations are hydrated more easily than anions both in solution and in the solid state, but the water of crystallization of a salt is not determined solely by the tendency of the individual ions to combine with water, though it is an important factor.. In solution the hydration of each ion is independent of the others, "but in the crystal the number of water molecules may be the sum of those combined with the two ions in solution, or a smaller number, and whether it is less, and if so how much less, will depend on both the ions of the salt." The degree of hydration, however, depends more on the cation than the anion.

The sulphate ion is hydrated thus, $SO_4.H_2O$, and the bivalent metal sulphates may be represented, $M(H_2O)_6.(SO_4.H_2O)$. The hexahydrated double sulphates given by these bivalent metal sulphates, where one molecule of water appears to be replaced by one of alkali sulphate, are remarkable, as it is not easy to explain this type.

When the hydrated ions separate from solution it is suggested that there is a kind of competion between the ions for the water, which is more likely to be retained if the hydration of one ion greatly exceeds that of the other. Contrary to expections the power of forming hydrates, while dependent on the extent of hydration in solution, does not depend on the solubility of the hydrate.

* * *

Summary.

A number of systems of the type, bivalent metallic sulphate - alkali sulphate - water, have been investigated at various temperatures, and from the results conclusions regarding the conditions of formation of the corresponding double sulphates are drawn.. Evidence is also adduced for the existence of complex ions in solution.

Three alkali sulphates were chosen:- potassium sulphate, ammonium sulphate, and sodium sulphate. It was expected that a study of the double sulphates of these compounds would prove of particular interest, especially in view of the following facts.

Potassium may be regarded as a typical alkali metal. Ammonium is of peculiar interest as regards its remarkable position in the series of alkali metals. Sodium is noteworthy when the anomalous properties of its compounds are taken into consideration..

Various bivalent metallic sulphates have been investigated with each of the alkali sulphates, and by this means, and by reference to the work of other investigators, not only have the alkali sulphates been compared as regards the formation of double salts, but some light has been thrown on the specific influence of the different bivalent metallic sulphates..

These double salts have also been studied from the general point of view of range of formation as regards change in temperature and relative concentration of the constituent

salts, and also from the point of view of isothermal evaporation.

The following potassium systems have been studied:-

Potassium sulphate - nickel sulphate - water at 0° and 25° C.
Potassium sulphate - cobalt sulphate - water at 25° C.
Potassium sulphate - zinc sulphate - water at 25° C.
Potassium sulphate - manganese sulphate - water at 0° and 25° C.

Ammonium system:-

Ammonium sulphate - manganese sulphate - water at 0° C.

Sodium systems:-

Sodium sulphate - copper sulphate - water at 0°, 25°, and 37.5° C.
Sodium sulphate - zinc sulphate - water at 0° and 25° C.
SOdium sulphate - manganese sulphate - water at 0°, 25°, and 35° C.

As aresult of these investigations it has been shown that manganese potassium sulphate is tetrahydrated, and that manganese sodium sulphate is dihydrated.

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Note on the Method Employed in Setting out Results.

For convenience and for the sake of clearness the following method in setting out results has been employed.

Each system is dealt with individually and in detail. The potassium systems are taken first, followed by the ammonium systems, and finally the sodium systems, conclusions being drawn for each particular system.

This is followed by a general discussion of the results, the whole field of the investigation being reviewed. General conclusions are drawn, and their bearing on the various points of double salt formation discussed.

Those experimental points, such as apparatus, method of abstracting phases, etc., which apply throughout the investigation, are dealt with in the appendices, as are also the Analytical Methods and the Graphical Representation of Results.

-:-:-:-:-:-:-:-:-:-:-:-:-:-:-

The Systems.

Nickel Sulphate - Potassium Sulphate - Water at 0° and 25° C.

The investigation of the system nickel sulphate - potassium sulphate - water was carried out primarily as a continuation of the work of Caven and Mitchell (4) to determine the limits of existence of double salts of the type $M''SO_4.M'_2SO_4.6H_2O$ in equilibrium with solutions containing their component salts, and to obtain evidence of the existence of the double salts in these solutions.

Caven and Mitchell (4) have shown that the double salts $CuSO_4.M'_2SO_4.6H_2O$ ($M = K'$ or NH'_4) are stable over wide ranges of temperature and relative concentrations of the component salts. Moreover, the continuous increase in solubility of each of the three simple salts caused by the addition of the second component up to each triple point, at which double salt separates, is believed to indicate the presence of a considerable amount of the double salt, or its ions, in solution.

Nickel is well known to form the double salt $NiSO_4.K_2SO_4.6H_2O$, and its physical properties have been examined by Tutton (36), who states that the crystals vary between the prismatic and the tabular form. Locke (37) determined the solubility of the double salt at various temperatures. Jones and Caldwell (15) showed that nickel potassium sulphate remains partly undissociated in concentrated solution, and even in dilute solution is not entirely broken into its constituents.

Experimental.

For the system at 0°C. saturated solutions of the two salts were made at room temperature, and various proportions of the two solutions placed successively in a reaction flask, fitted with a stirrer, and immersed in ice and water. The mixtures were stirred for 3 days, and then portions of the solutions were separated and analysed.

The same procedure was carried out for the system at 25°C. except that saturated solutions of the two single salts were made at 40°, and the flask was immersed in a thermostat at 25± .01°C.

The nickel was estimated by a method suggested by Kelly and Conant (38). This consists in adding an excess of potassium cyanide to the nickel solution and titrating back with standard nickel sulphate solution in presence of ammonia, diphenylglyoxime being used as indicator. Potassium sulphate was calculated after determination of total sulphate.

Table I.

System $NiSO_4$ - K_2SO_4 - H_2O at 0° C.

Moles of $NiSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
------	0.463	K_2SO_4.
0.008	0.466	K_2SO_4 & $NiSO_4.K_2SO_4.6H_2O$.
0.035	0.214	$NiSO_4.K_2SO_4.6H_2O$.
0.346	0.138	"
0.821	0.214	"
1.367	0.307	"
1.668	0.398	"
1.869	0.467	$NiSO_4.K_2SO_4.6H_2O$ & $NiSO_4.7H_2O$.
1.754	0.277	$NiSO_4.7H_2O$.
1.734	0.227	"
1.632	------	"

Table II.

System $NiSO_4 - K_2SO_4 - H_2O$ at 25° C.		
Moles of $NiSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
------	0.680	K_2SO_4.
0.024	0.724	K_2SO_4 & $NiSO_4.K_2SO_4.6H_2O$.
0.093	0.302	$NiSO_4.K_2SO_4.6H_2O$.
0.274	0.259	"
0.765	0.275	"
1.272	0.343	"
1.364	0.430	"
2.128	0.559	"
2.824	0.743	$NiSO_4.K_2SO_4.6H_2O$ & $NiSO_4.7H_2O$.
2.743	0.550	$NiSO_4.7H_2O$.
2.638	0.321	"
2.505	------	"

SYSTEM ~ $NiSO_4$ - K_2SO_4 - H_2O
at 0° and 25°

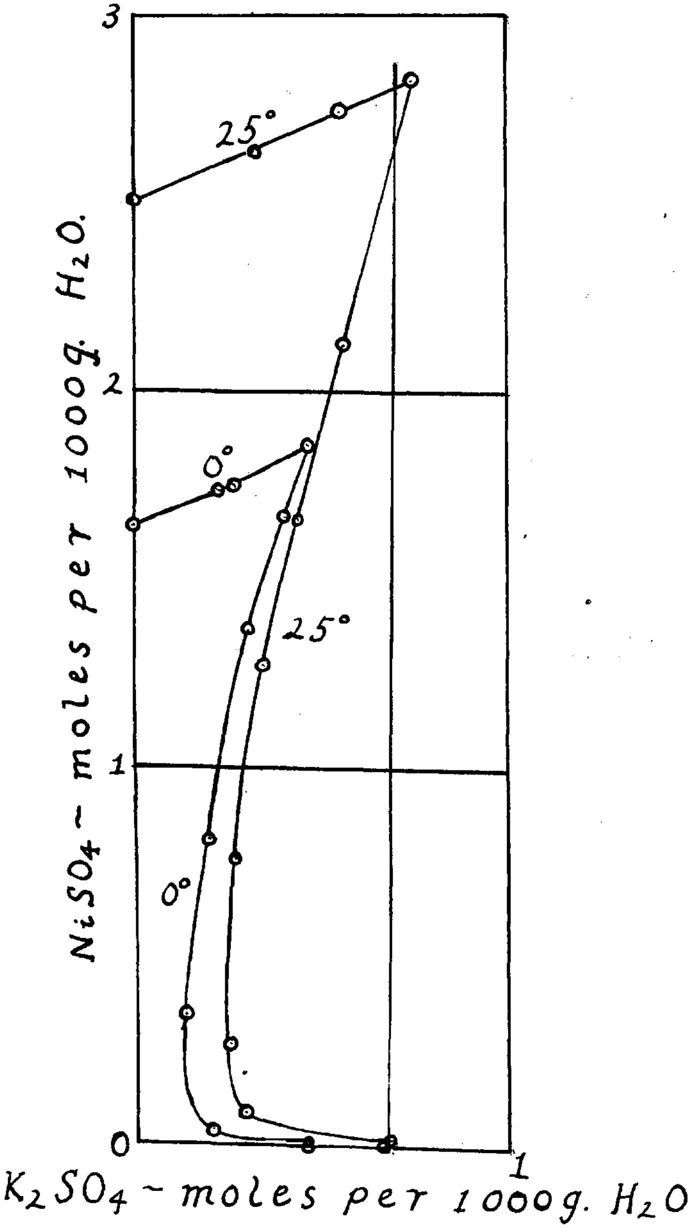


FIGURE 7.

Conclusions.

(Tables I and II and Figure 7.)

The double salt $NiSO_4.K_2SO_4.6H_2O$ is formed over a wide range of relative concentrations of the component salts at both 0° and 25° C. The range of existence at 0° is

from 0.018 to 4.00 moles of $NiSO_4$ to 1 mole of K_2SO_4,

and at 25° is

from 0.031 to 3.80 moles of $NiSO_4$ to 1 mole of K_2SO_4.

At both temperatures increase of solubility of each salt occurs previous to the separation of the double salt, and it is inferred that this is due to the formation of complex ions in solution.

A remarkable characteristic of the isotherms is their indented shape, in consequence of which the solubility of potassium sulphate repeats itself as the curve is traversed. Consider, for example, a concentration of potassium sulphate of 0.7 moles per 1000 grams of water at 25 C. This quantity may be in equilibrium once with potassium sulphate, twice with the double salt, and once with nickel sulphate, as the solid phase, according to the amount of nickel sulphate present in solution. This is shown by erecting a perpendicular from the point on the base line representing 0.7 moles of potassium sulphate.(See Figure 7).

This isotherm indeed differs considerably from the general form obtained for double salts of the type, $M^{\cdot\cdot}SO_4.M^{\cdot}_2SO_4.6H_2O$, as for example the systems $CuSO_4 - M_2SO_4 - H_2O$. ($M = K^{\cdot}$ or $NH_4^{\cdot}$).

Cobalt Sulphate - Potassium Sulphate - Water at 25°C.

This system was investigated as a continuation of the scheme outlined under the system nickel sulphate - potassium sulphate - water, and also, since the results for the nickel system seemed somewhat anomalous, as an unique method of comparing the two metals, nickel and cobalt.

Tutton (39) investigated the crystalline properties of $CoSO_4.K_2SO_4.6H_2O$, and Locke (40) determined its solubility at various temperatures. Locke observed that the solubility of the double salt was less than that of cobalt sulphate.

Experimental.

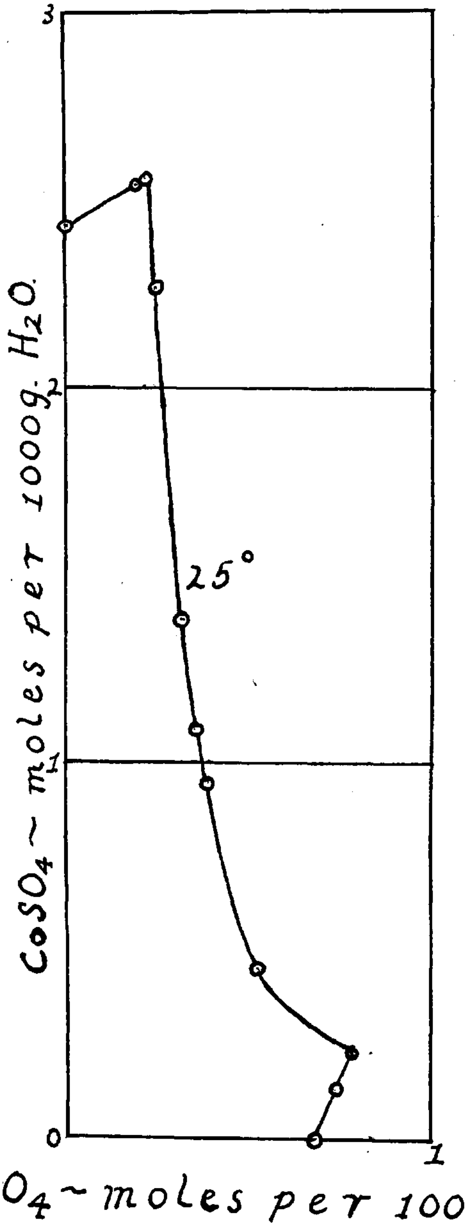
Saturated solutions of potassium sulphate and cobalt sulphate were made at 40°, and various proportions placed in a flask, fitted with a stirrer, and immersed in a thermostat at 25 ± .01°.

The mixtures were stirred for 3 days, and only liquid phases analysed. Cobalt was estimated by precipitation as cobalt ammonium phosphate, and ignition to pyrophosphate. Potassium sulphate was calculated after determination of total sulphate.

Table III.

System $CoSO_4$ - K_2SO_4 - H_2O at 25° C.		
Moles of $CoSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
——	0.680	K_2SO_4.
0.150	0.737	"
0.239	0.780	K_2SO_4 & $CoSO_4.K_2SO_4.6H_2O$.
0.458	0.531	$CoSO_4.K_2SO_4.6H_2O$.
0.950	0.388	"
1.095	0.361	"
1.372	0.321	"
2.205	0.240	"
2.557	0.212	$CoSO_4.K_2SO_4.6H_2O$ & $CoSO_4.7H_2O$.
2.536	0.190	$CoSO_4.7H_2O$.
2.433	——	"

SYSTEM ~ $CoSO_4$ - K_2SO_4 - H_2O at 25°



K_2SO_4 ~ moles per 1000g. H_2O.

FIGURE 8.

Conclusions.

The double salt $CoSO_4.K_2SO_4.6H_2O$ is formed over a wide range of relative concentrations of its component salts at 25°C. The limits are

from 0.30 to 12.06 moles of $CoSO_4$ to 1 mole of K_2SO_4.

The solubility of each single salt is increased by the addition of the other.

The isotherm conforms to the general type, and differs considerably from that for the nickel system. That some such difference is to be expected is seen when the following points are considered. The solubility of potassium sulphate is the same in both cases, the solubility of nickel sulphate is only slightly greater than that of cobalt sulphate, but the solubility of nickel potassium sulphate is only about half that of cobalt potassium sulphate.

....

Zinc Sulphate - Potassium Sulphate - Water at 25°C.

Zinc sulphate and potassium sulphate are well known to form the double salt $ZnSO_4.K_2SO_4.6H_2O$. Its preparation has been described as follows:- $ZnSO_4$ is very rapidly soluble in saturated K_2SO_4+ Aq. with separation of a double salt." (41).

Tutton (42) examined the crystals and found them to be of the short prismatic form.

Lipscomb and Hulett (43) examined the system $ZnSO_4$ - K_2SO_4 - H_2O at 25°C., and found that, while the solubility of potassium sulphate is increased by the addition of zinc sulphate, the solubility of zinc sulphate is decreased by the addition of potassium sulphate.

Experimental.

The procedure for this system was the same as that for the nickel and cobalt systems at 25°.

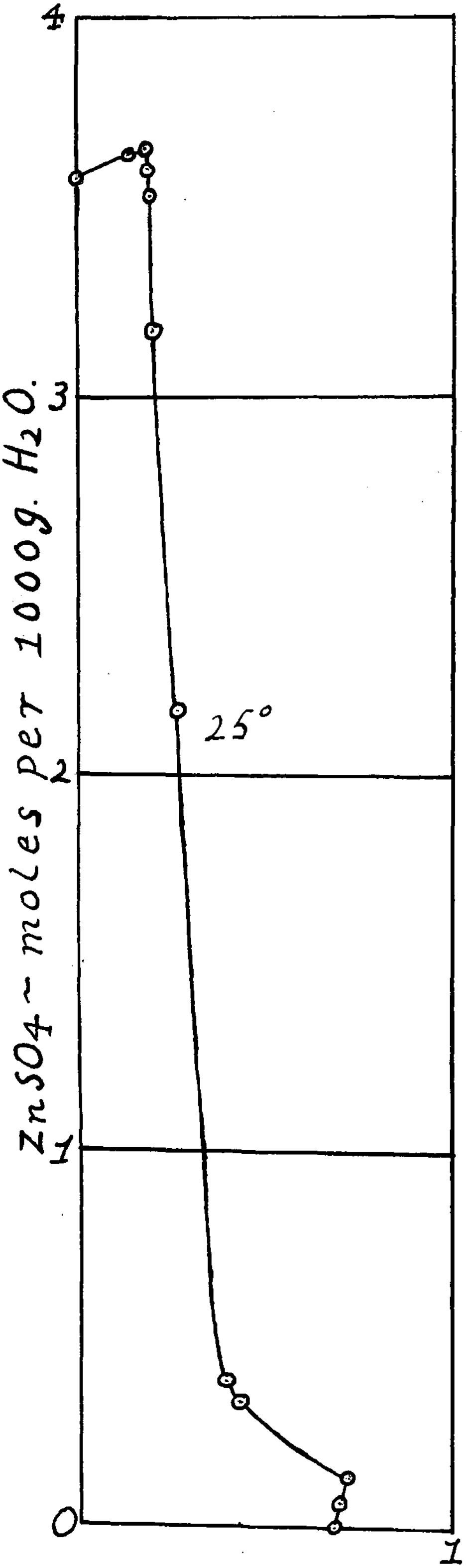
Zinc was estimated volumetrically by means of standard potassium ferrocyanide, and total sulphate determined.

Table IV

System $ZnSO_4$ - K_2SO_4 - H_2O at 25°C.

Moles of $ZnSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	0.680	K_2SO_4.
0.078	0.697	"
0.136	0.721	K_2SO_4 & $ZnSO_4.K_2SO_4.6H_2O$.
0.330	0.422	$ZnSO_4.K_2SO_4.6H_2O$.
0.378	0.388	"
2.170	0.256	"
3.171	0.202	"
3.529	0.179	"
3.587	0.168	"
3.651	0.172	$ZnSO_4.K_2SO_4.6H_2O$ & $ZnSO_4.7H_2O$.
3.632	0.133	$ZnSO_4.7H_2O$.
3.579	-----	"

SYSTEM - $ZnSO_4$ - K_2SO_4 - H_2O at 25°



K_2SO_4 - moles per 1000g. H_2O.

FIGURE 9.

Conclusions.

The range of existence of the double salt $ZnSO_4.K_2SO_4.6H_2O$ at 25° C. is

from 0.19 to 21.3 moles of $ZnSO_4$ to 1 mole of K_2SO_4.

The solubility of each single salt is increased by the addition of the other. This is in contradiction to the work of Lipscomb and Hulett (loc. cit.).

The isotherm is of the typical form.(see Figure 9).

……………………………

Manganese Sulphate - Potassium Sulphate - Water at 0° and 25°C.

It is a generally accepted fact that the sulphates of manganese and potassium form a double salt, but there seems to be some dubiety as to the degree of hydration of this salt.

Most text-books simply state that it conforms to the general type in being hexahydrated.

Other investigators (44) state that finely crystallized double sulphates are obtained from mixed solutions of manganese sulphate and the alkali sulphates; these double salts being of the type $MnSO_4.M_2SO_4.4H_2O$ and $MnSO_4.M_2SO_4.6H_2O$, where M = Na, K, Rb, Co, etc.

According to Pierre (45) this double salt exists in two hydrated forms, $MnSO_4.K_2SO_4.2H_2O$ and $MnSO_4.K_2SO_4.4H_2O$, the tetrahydrate being efflorescent.

By fusion of the component salts Mallet (46) obtained the double salt $2MnSO_4.K_2SO_4$.

Tutton (47), who wished to examine all double sulphates of the type $M\ SO_4.K_2SO_4.6H_2O$, was unable to prepare the double sulphate of potassium and manganese containing 6 molecules of water. The only crystals he obtained contained 4 molecules, the double salt being $MnSO_4.K_2SO_4.4H_2O$.

The system $MnSO_4 - K_2SO_4 - H_2O$ was therefore examined to see whether or not it was possible to obtain the hexahydrated form of the double salt. The system was examined first at 25°C. at which temperature it was expected that the tetrahydrate would be the stable form. Since manganese sulphate itself is tetrahydrated at 25°C. and heptahydrated at 0°C., it was also decided to investigate the hydration of the double salt at 0°C., in the expectation that it might then be hexahydrated, and thus conform to the general type $M''SO_4.M'_2SO_4.6H_2O$.

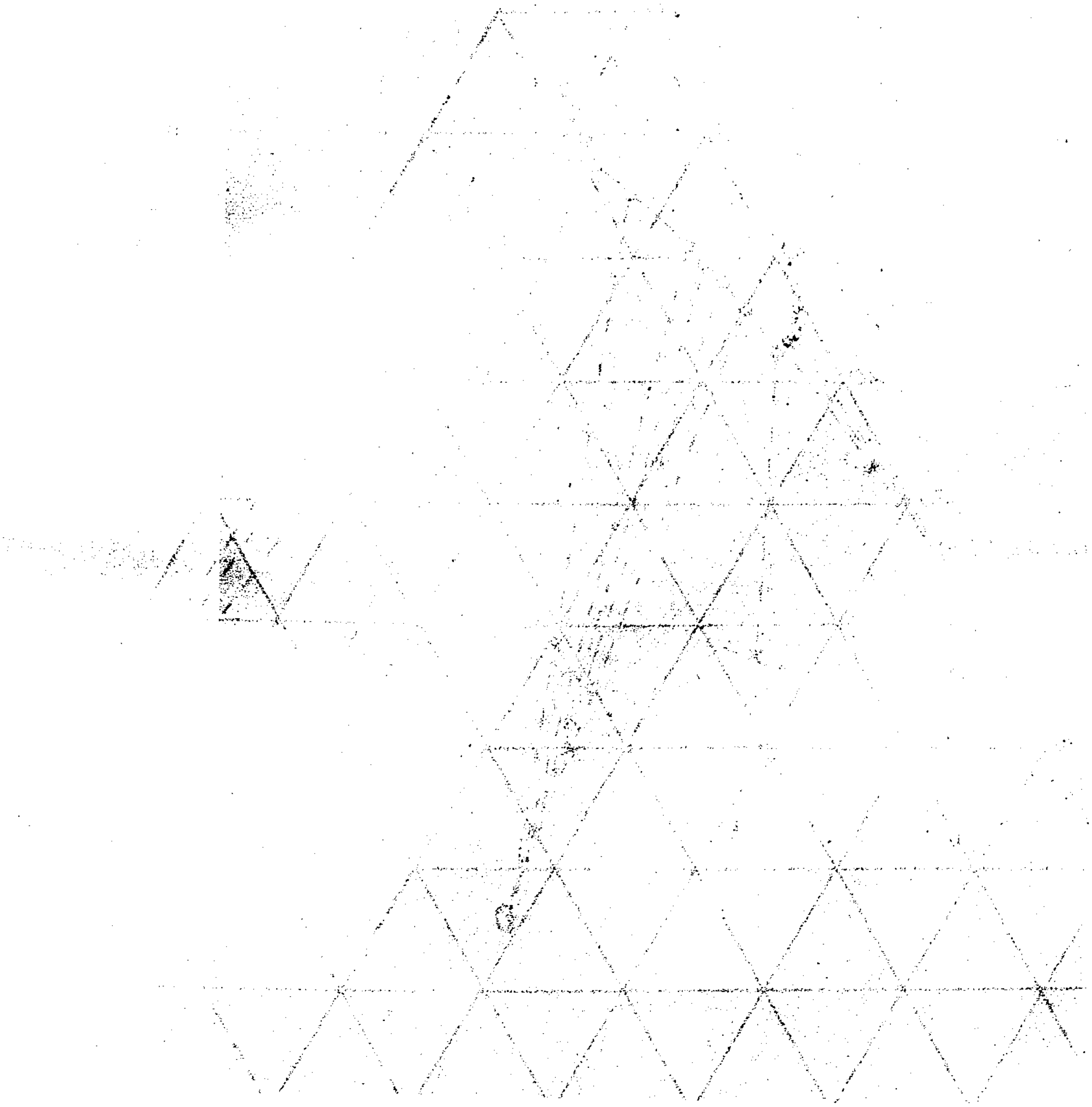
Experimental.

For the system at 0°C., solutions of the two salts were made at room temperature, and various proportions of these solutions were placed successively in a flask, and kept immersed in ice and water. The mixtures were stirred for 3 days before portions of the liquid and solid phases were separated and analysed.

As the system $MnSO_4 - H_2O$ shows a transition point at 26°C., whereafter the solubility decreases, there was no advantage in preparing solutions of manganese sulphate above this temperature. Saturated solutions of the two salts were therefore made at room temperature and mixed in various proportions. The mixtures were then evaporated isothermally at 25°C. by a filtered current of air (Appendix II). When sufficient solid phase had separated the solutions were transferred to the reaction-vessel and stirred for 3 days.

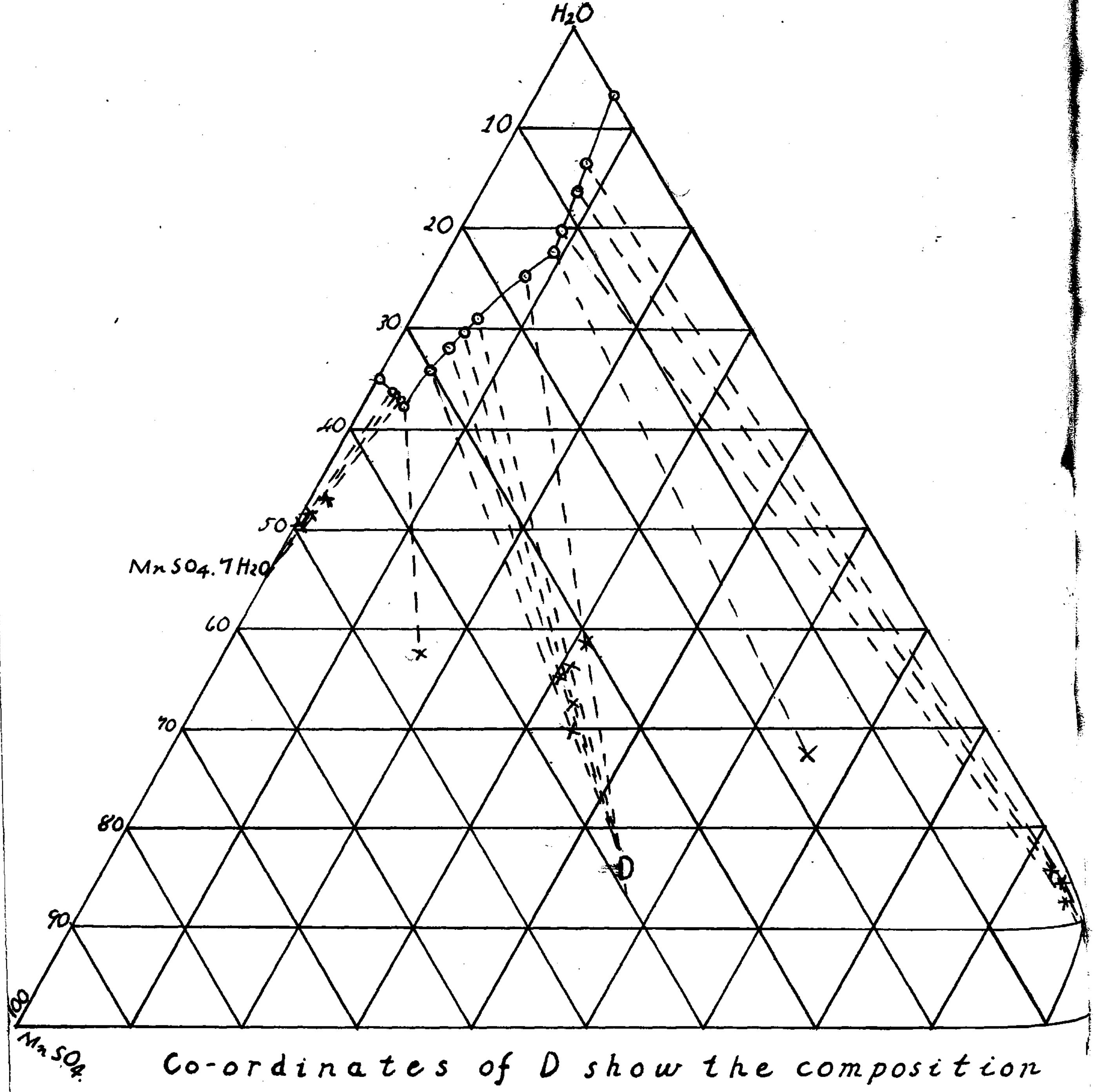
The manganese was estimated volumetrically with standard potassium permanganate by the Volhard method, the total sulphate determined, and the potassium sulphate calculated.

In Tables V and VI the results are expressed as "Grams per 100 grams of Solution", and these are used to plot on the triangular diagram, in order to determine the composition of the solid phase (Appendix I).



EQUILIBRIUM DIAGRAM.

K_2SO_4 - $MnSO_4$ - H_2O at 0° C.

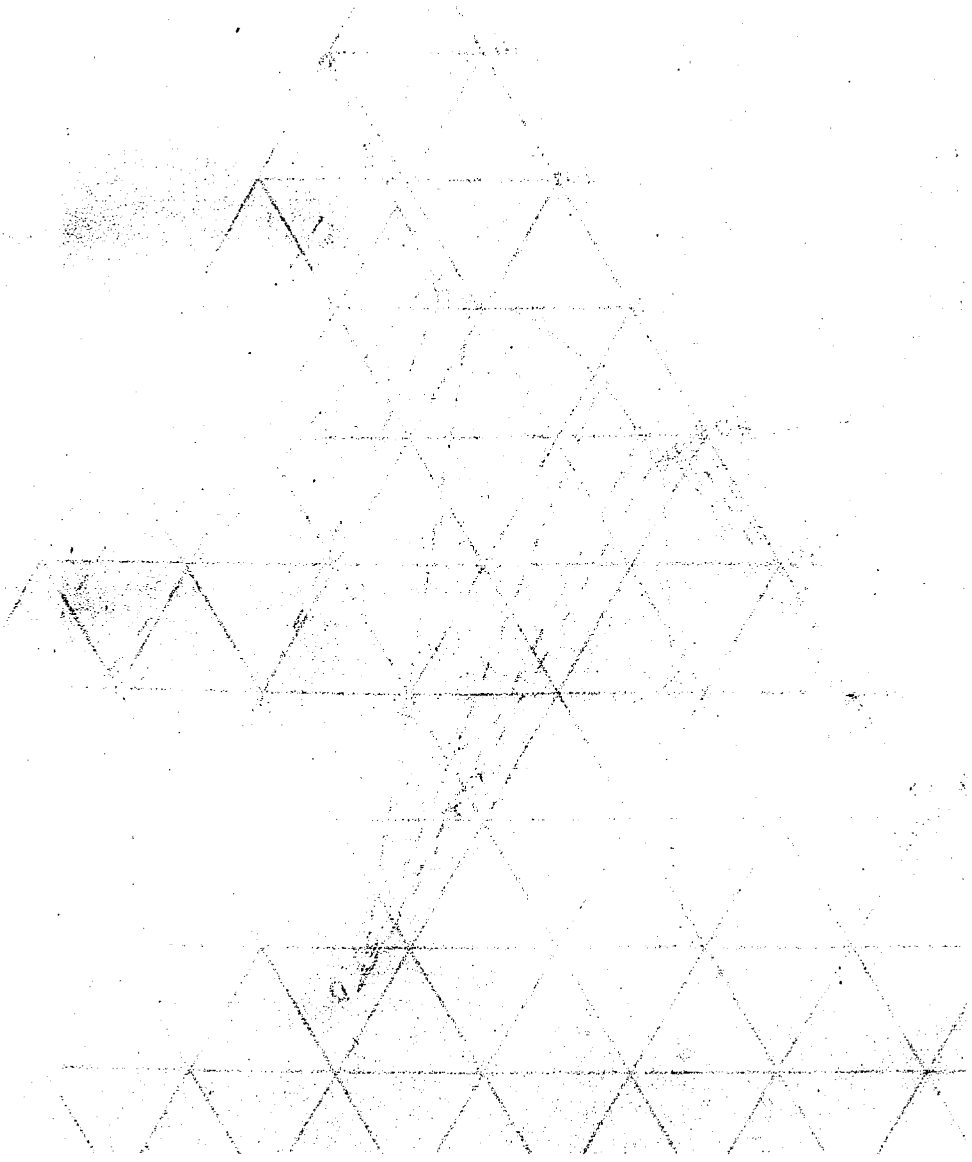


Co-ordinates of D show the composition of the double salt to be $MnSO_4.K_2SO_4.4H_2O$.

FIGURE 10.

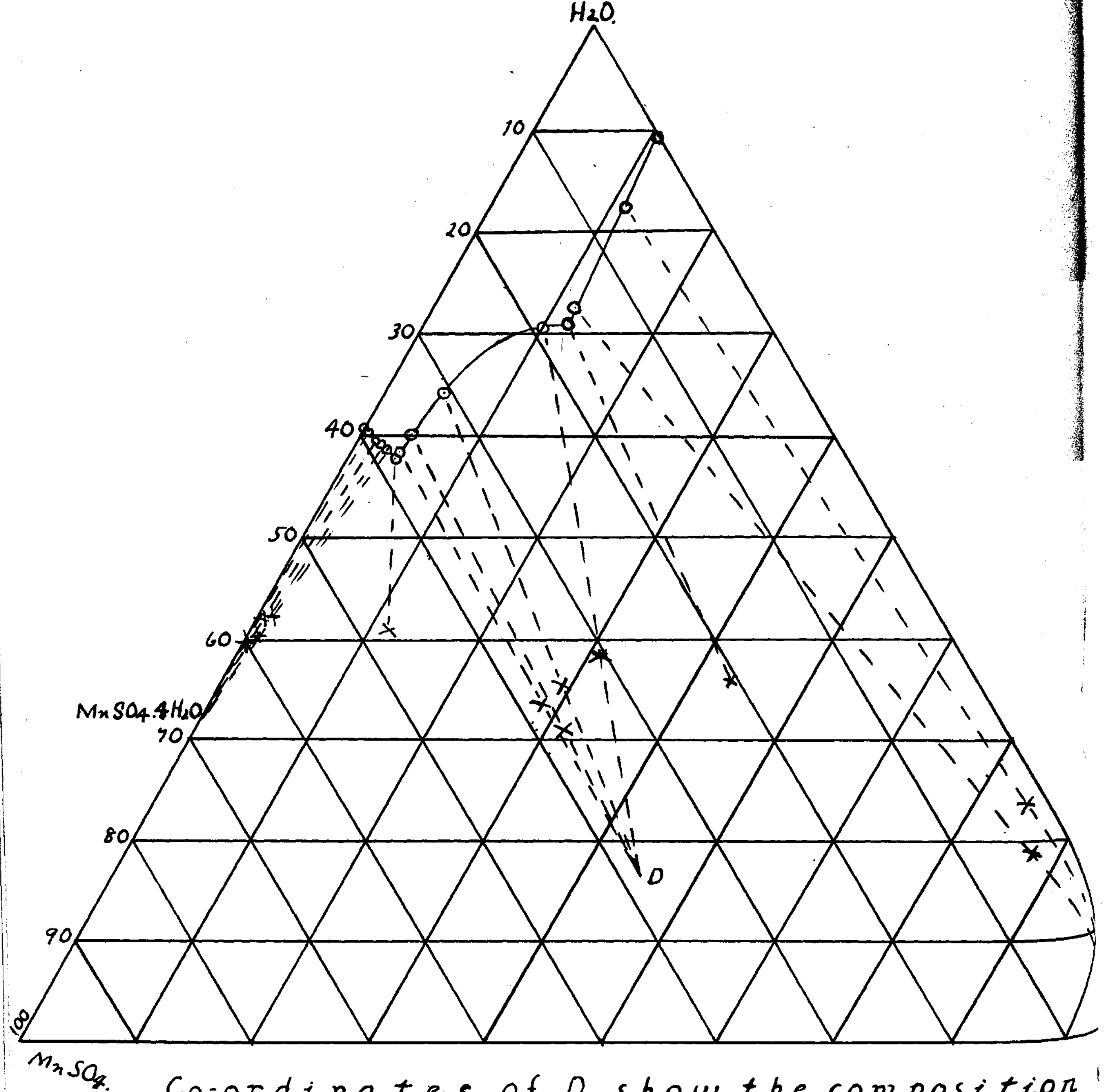
Table V.

System $MnSO_4$ - K_2SO_4 - H_2O at 0° C.						
Percentage Composition.						::::::::::::
Solutions.			Moist Solids.			Solid Phase.
$MnSO_4$	K_2SO_4	H_2O.	$MnSO_4$	K_2SO_4	H_2O.	::::::::::::
------	6.82	93.18	------	------	------	K_2SO_4.
6.21	7.75	86.04	1.11	84.55	14.34	"
8.21	7.97	83.82	1.52	82.81	15.67	"
11.80	8.48	79.72	1.82	86.00	12.18	"
13.68	8.88	77.44	16.90	55.60	27.50	K_2SO_4 & $MnSO_4.K_2SO_4.4H_2O$.
17.39	7.69	74.92	30.60	30.82	38.58	$MnSO_4.K_2SO_4.4H_2O$.
23.64	5.54	70.82	32.98	30.46	36.56	"
25.50	5.00	69.50	34.50	32.84	32.66	"
27.62	4.48	67.90	34.46	30.31	35.22	"
30.28	4.00	65.72	36.00	33.46	30.54	"
34.30	3.35	62.35	45.53	17.12	37.35	$MnSO_4.K_2SO_4.4H_2O$ & $MnSO_4.7H_2O$.
34.38	2.81	62.81	45.85	1.24	52.91	$MnSO_4.7H_2O$.
34.53	1.85	63.62	48.00	0.70	51.30	"
34.49	1.68	63.83	49.31	0.42	50.27	"
34.78	----	65.22	------	----	------	"



EQUILIBRIUM DIAGRAM.

$K_2SO_4 - MnSO_4 - H_2O$ at 25° C.



Co-ordinates of D show the composition of the double salt to be $MnSO_4 \cdot K_2SO_4 \cdot 4H_2O$

FIGURE 11.

Table VI.

System $MnSO_4 - K_2SO_4 - H_2O$ at 25°C.						
Percentage Composition.						::::::::::::
Solutions.			Moist Solids.			Solid Phase.
$MnSO_4$	K_2SO_4	H_2O.	$MnSO_4$	K_2SO_4	H_2O.	::::::::::::
-----	10.59	89.41	-----	-----	-----	K_2SO_4.
6.30	11.27	82.43	1.78	74.62	23.60	"
15.22	12.04	72.74	3.66	77.46	18.88	"
16.58	12.31	71.11	20.71	53.33	25.96	K_2SO_4 & $MnSO_4.K_2SO_4.4H_2O$.
19.27	10.06	70.67	30.83	30.91	38.26	$MnSO_4.K_2SO_4.4H_2O$.
30.47	5.27	64.26	35.01	29.02	35.97	"
35.58	4.30	60.12	37.23	31.42	31.35	"
37.28	4.20	58.52	37.75	28.42	33.83	"
37.92	4.15	57.93	47.42	11.88	40.70	$MnSO_4.K_2SO_4.4H_2O$ & $MnSO_4.4H_2O$.
38.21	3.03	58.76	56.66	1.25	42.09	$MnSO_4.4H_2O$.
33.42	2.46	59.12	58.42	0.83	41.75	"
38.54	1.87	59.59	57.35	0.66	42.99	"
39.03	0.43	60.55	60.01	0.17	39.82	"
39.10	-----	60.90	-----	-----	-----	"

Table VII.

System $MnSO_4$ - K_2SO_4 - H_2O at 0° C.

Moles of $MnSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	0.420	K_2SO_4.
0.478	0.517	"
0.649	0.546	"
0.978	0.611	"
1.169	0.659	K_2SO_4 & $MnSO_4.K_2SO_4.4H_2O$.
1.587	0.589	$MnSO_4.K_2SO_4.4H_2O$.
2.211	0.447	"
2.430	0.413	"
2.698	0.379	"
3.051	0.349	"
3.642	0.308	$MnSO_4.K_2SO_4.4H_2O$ & $MnSO_4.7H_2O$.
3.624	0.257	$MnSO_4.7H_2O$.
3.594	0.167	"
3.580	0.151	"
3.533	-----	"

Table VIII.

System $MnSO_4 - K_2SO_4 - H_2O$ at 25°C.		
Moles of $MnSO_4$ per 1000g. H_2O.	Moles of K_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	0.680	K_2SO_4.
0.506	0.785	"
1.386	0.951	"
1.544	0.994	K_2SO_4 & $MnSO_4.K_2SO_4.4H_2O$.
1.805	0.817	$MnSO_4.K_2SO_4.4H_2O$.
3.141	0.471	"
3.919	0.411	"
4.218	0.412	"
4.334	0.411	$MnSO_4.K_2SO_4.4H_2O$ & $MnSO_4.4H_2O$.
4.307	0.295	$MnSO_4.4H_2O$.
4.304	0.240	"
4.284	0.182	"
4.268	0.041	"
4.252	-----	"

SYSTEM ~ $MnSO_4 - K_2SO_4 - H_2O$

at 0° and 25° C.

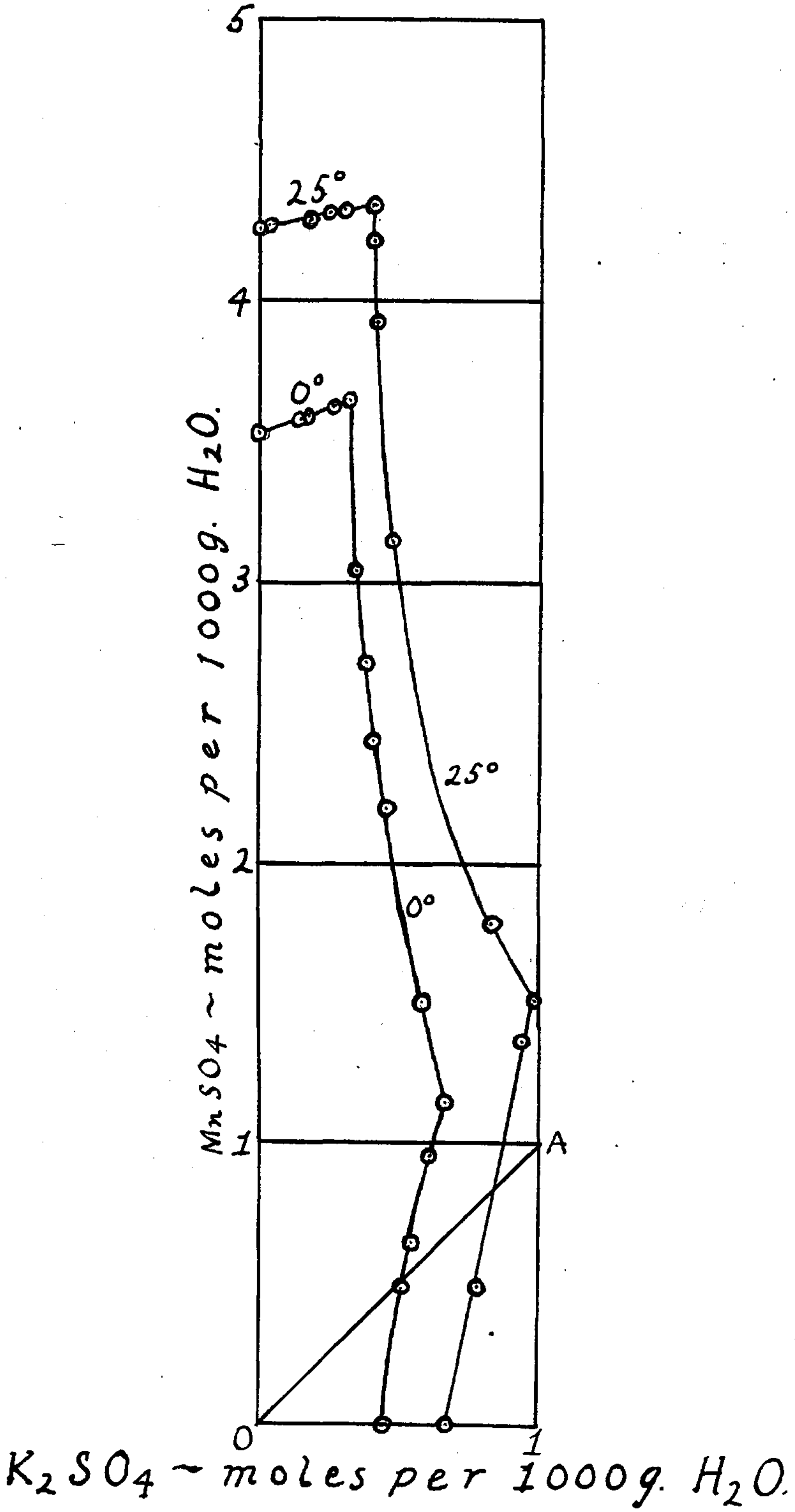


FIGURE 12.

Conclusions.

Manganese potassium sulphate crystallizes with 4 molecules of water at both 0° and 25° C. (Tutton, loc. cit.). (Figures 10 and 11. Tables V and VI).

The range of existence of the double salt $MnSO_4 \cdot K_2SO_4 \cdot 4H_2O$ at 0° C. is

from 1.77 to 11.82 moles of $MnSO_4$ to 1 mole of K_2SO_4,

and at 25° C. is

from 1.5 to 10.4 moles of $MnSO_4$ to 1 mole of K_2SO_4.

(Figure 12 and Tables VII and VIII).

The isotherms differ widely from those of analogous systems chiefly on account of the large quantity of manganous sulphate which must be present before the formation of double salt can begin. Moreover, a difference is to be expected in view of the different degree of hydration of this double salt, which points to the fact that the manganous ion differs from the bivalent ions of nickel, cobalt, copper, and zinc in a way that must ultimately be referred to the electronic constitutions of the metallic atoms concerned.

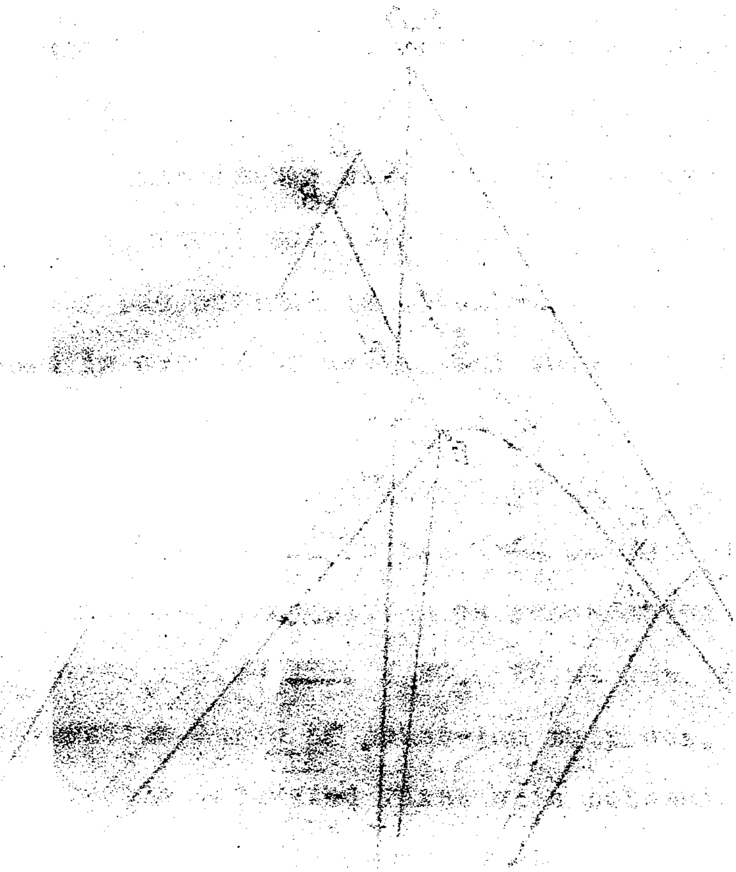
The solubility of potassium sulphate is increased at both temperatures by the addition of manganese sulphate, likewise addition of potassium sulphate increases the solubility of manganous sulphate at both temperatures. It is interesting to note, however, that there is a more rapid increase in this solubility at 0° C. than at 25° C. Some (such) difference would be expected, since at 0° C. the solid phase is $MnSO_4 \cdot 7H_2O$, whereas at 25° C. it is $MnSO_4 \cdot 4H_2O$.

The most interesting points arise, however, when the isotherms are considered from the point of view of equimolecular quantities of the two salts. The equimolecular line (Figure 12.) passes through the potassium sulphate portion of the isotherm (that is where potassium sulphate is the solid phase.) at 0°and 25°C. This means that the double salt cannot be in equilibrium with an equimolecular solution of its component salts at either temperature. Such a solution is in equilibrium with potassium sulphate.

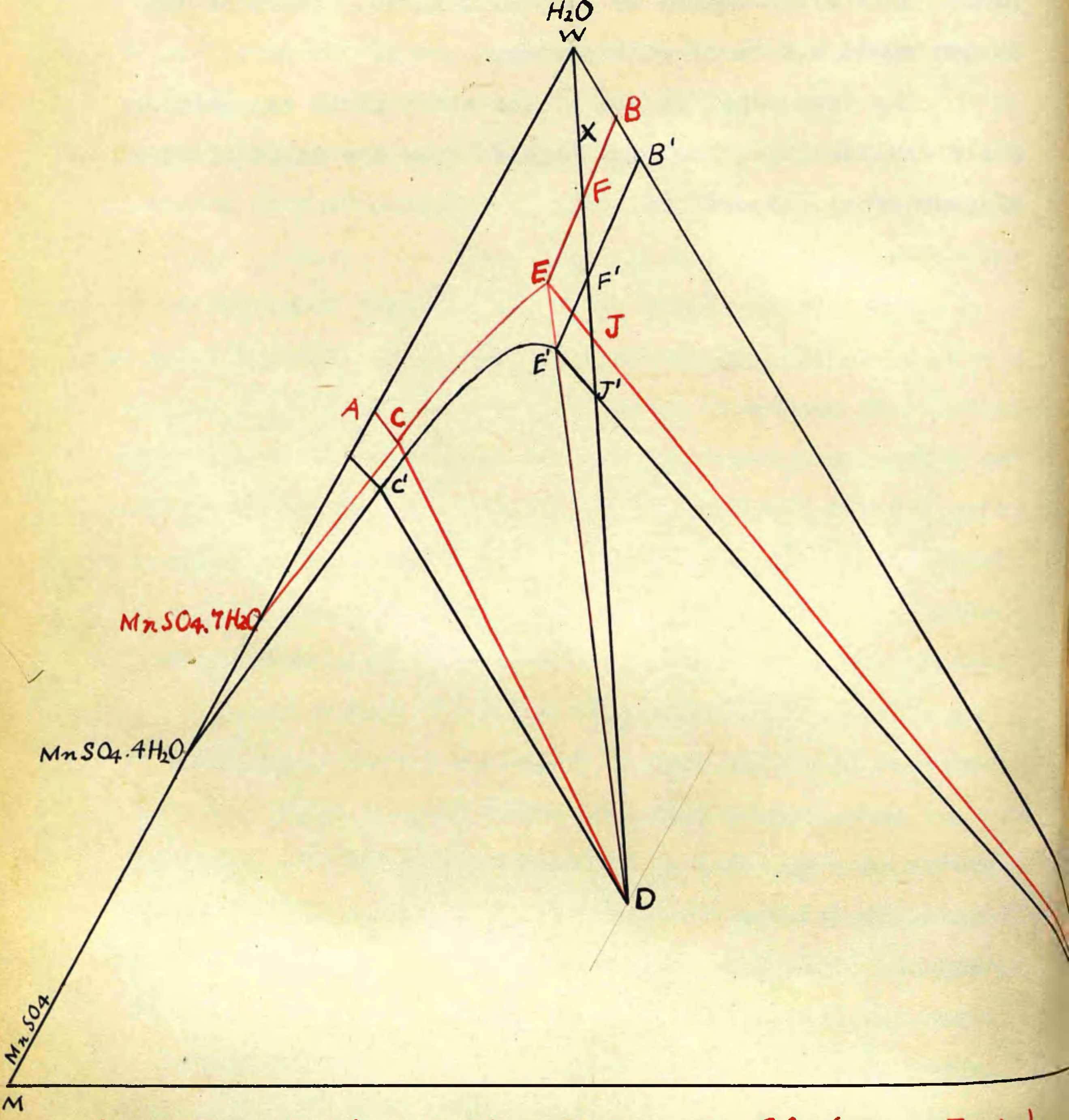
The temperatures 0° and 25°C. (and all temperatures between them), therefore, lie within the "Transition Interval" for the double salt manganese potassium sulphate, $MnSO_4.K_2SO_4.4H_2O$. The "Transition Interval" (48) is defined as the temperature range between the "Transition Point" (the temperature at which double salt is first formed) and the temperature at which a stable saturated solution of pure double salt just begins to be possible, (that is where it ceases to be decomposed by water).

Within this temperature range the double salt is decomposed by water. Thus if manganese potassium sulphate is brought into contact with less water than is sufficient to dissolve it completely it undergoes decomposition. This necessarily follows from the fact that a saturated solution containing equimolecular proportions of the salts is in equilibrium not with double salt but with potassium sulphate. So in order that equilibrium may be obtained more manganese sulphate than potassium sulphate must be dissolved; therefore, crystals of potassium sulphate will be deposited. When equilibrium *is* reached the solid phase must consist either of potassium sulphate and double salt or of potassium sulphate alone, according to the relative quantities of double salt and water. Double salt alone cannot be the solid phase, otherwise the system would not be in equilibrium.

The true significance of the above facts can only be fully realised when they are studied from the point of view of isothermal evaporation.



SYSTEM ~ $MnSO_4 - K_2SO_4 - H_2O$ at 0° and 25°C.



SYSTEM ~ $MnSO_4 - K_2SO_4 - H_2O$ at 0° (Red Ink).

SYSTEM ~ $MnSO_4 - K_2SO_4 - H_2O$ at 25° (Black Ink)

FIGURE 13.

Isothermal Evaporation and the System $MnSO_4 - K_2SO_4 - H_2O$.

In Figure 13 AC, A′C′ are the saturation curves of manganese sulphate; BE, B″E′ the saturation curves of potassium sulphate, and CE, C″E′ the saturation curves of the double salt $MnSO_4.K_2SO_4.4H_2O$ at 0° and 25° C. respectively. D represents the composition of the double salt, and WD the equimolecular line.

An unsaturated solution containing the single salts in equimolecular proportions is obtained by dissolving some pure double salt in excess of water. Let this solution be represented by the point X (3.78 gms. $MnSO_4$, 4.36 gms. K_2SO_4, 91.86 gms. H_2O) on the line WD, and let this solution be evaporated isothermally at 0° C. It will become saturated when so much water has been evaporated that its composition is represented by the point F (6.87 gms. $MnSO_4$. 7.92 gms. K_2SO_4. 85.21 gms. H_2O.) which lies on the saturation curve of potassium sulphate. The solution will, therefore, become saturated first with potassium sulphate, and not with double salt. If the evaporation is continued potassium sulphate will separate and the composition of the complex will be represented by a point between F and J in the area KBE the points of which represent complexes of potassium sulphate and a solution on the saturation curve BE. As the composition of the complex approaches that represented by the point J, the composition of the solution will be represented by a point which traverses the saturation curve from F towards E. When so much water has been evaporated that the composition of the complex is given by the point J (13.05 gms. $MnSO_4$. 15.06 gms.

K_2SO_4. 71.89 gms. H_2O.), formation of the solid double salt will begin, since points between J and D lie in the area KED and represent complexes of both potassium sulphate and manganese potassium sulphate in equilibrium with the invariant solution E. As evaporation is continued double salt will be deposited, and the composition of the solution will remain unchanged so long as the two solid phases are present. As can be seen from the diagram, however, the solution at E contains less of potassium sulphate than is contained in the double salt. Deposition of the double salt at E, therefore, would lead to a relative decrease in the concentration of potassium sulphate in the solution, and to counterbalance this, the potassium sulphate which separated out at the commencement must redissolve, and continue to redissolve as long as any liquid is present.

Since the salts were originally present in equimolecular proportions the final result of evaporation will be the pure double salt $MnSO_4.K_2SO_4.4H_2O$.

If now an unsaturated solution containing equimolecular proportions of manganese sulphate and potassium sulphate, represented by the point X, (3.78 gms. $MnSO_4$. 4.36 gms. K_2SO_4. 91.86 gms. H_2O.), be evaporated isothermally at 25° C., the following is the course of events.

The solution will become saturated when it reaches the composition represented by F′(10.50 gms. $MnSO_4$. 12.10 gms. K_2SO_4. 77.40 gms. H_2O.), on B′E′, the saturation curve of potassium sulphate. As evaporation is continued potassium sulphate will be deposited until the composition of the complex reaches the point whose composition is represented by J′ (15.70 gms. $MnSO_4$. 18.10 gms. K_2SO_4. 66.20 gms. H_2O.), when double salt will begin to be deposited, the composition of the solution being represented by E′, (16.58 gms. $MnSO_4$. 12.31 gms. K_2SO_4. 71.11 gms. H_2O.).

As at 0°C. the final result of evaporation will be pure double salt, $MnSO_4.K_2SO_4.4H_2O$.

In order that the first product of evaporation should be $MnSO_4.K_2SO_4.4H_2O$ it is necessary that the crystallization take place from a solution containing excess of manganese sulphate. Thus at 0°C. a solution containing more than 1.77 moles of $MnSO_4$ per 1 mole of K_2SO_4 would be necessary; for example a solution of the following percentage composition, 7.00 gms. $MnSO_4$. 4.30 gms. K_2SO_4. 88.70 gms. H_2O. At 25° C. the solution must contain more than 1.50 moles of $MnSO_4$ per 1 mole of K_2SO_4; for example:- 7.00 gms. $MnSO_4$. 5.00 gms. K_2SO_4. 88.00 gms. H_2O.

On evaporation of such solutions pure double salt, $MnSO_4.K_2SO_4.4H_2O$, will first be deposited. The separation of double salt will, however, cause a relative decrease in the concentration of potassium sulphate, and the composition of the solution will, therefore, alter in the direction EC (E′C′). If the evaporation is discontinued before the solution has attained the composition C (C′) only double salt will have separated out, otherwise complexes of double salt and manganese sulphate will be obtained.

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Manganese Sulphate - Ammonium Sulphate - Water at 0° C.

Since manganese ammonium sulphate conforms to the general type in being hexahydrated, it was decided to investigate the system $MnSO_4$ - $(NH_4)_2SO_4$ - H_2O, in order to compare it with the system $MnSO_4$ - K_2SO_4 - H_2O, manganese potassium sulphate being tetrahydrated. Schreinemakers (49) investigated the system $MnSO_4$ - $(NH_4)_2SO_4$ - H_2O at 25° C. so it was decided to investigate it at 0° C. Schreinemakers (49) also studied this system at 50° C., and while the double salt formed at 25° was $MnSO_4.(NH_4)_2SO_4.6H_2O$ that formed at 50° was $2MnSO_4.(NH_4)_2SO_4$.

Lepierre (50) found that the double salt $2MnSO_4.(NH_4)_2SO_4$ was easily decomposed by water, while Jahn (51) showed that $MnSO_4.(NH_4)_2SO_4.6H_2O$ was deliquescent and readily soluble in water.

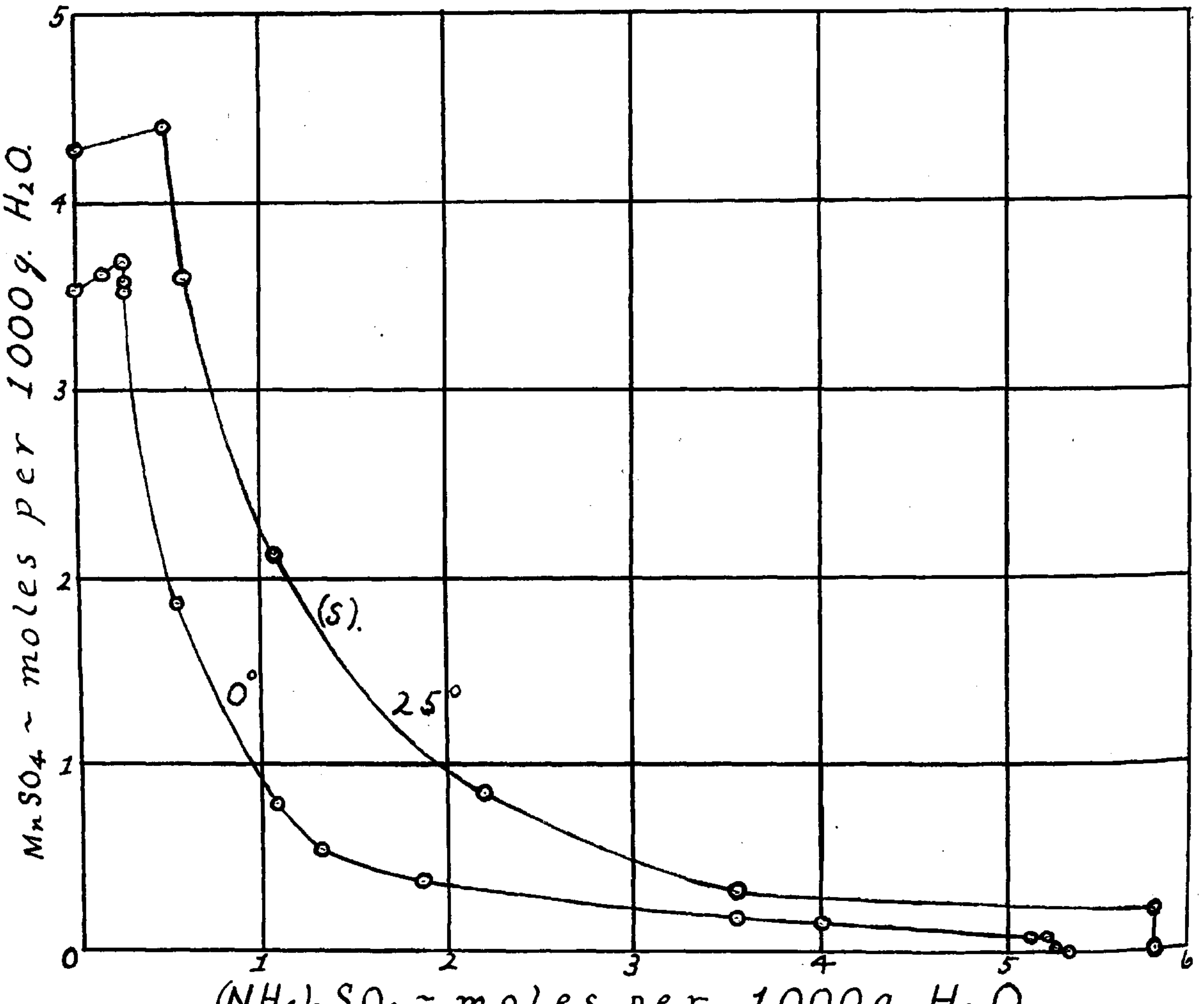
Locke (52) determined the solubility of the hexahydrated double sulphate at various temperatures.

Experimental.

Saturated solutions of the two salts were made at room temperature, and various proportions of these solutions were placed in a flask immersed in ice and water. The mixtures were stirred for 3 days before portions of the solutions were separated and analysed.

Ammonia was estimated by the distillation method, and total sulphate determined.

SYSTEM ~ $MnSO_4 - (NH_4)_2SO_4 - H_2O$ at 0° C.



(S). Schreinemakers.

FIGURE 14.

Table IX.

System $MnSO_4$ - $(NH_4)_2SO_4$ - H_2O at 0° C.

Moles of $MnSO_4$ per 1000g. H_2O.	Moles of $(NH_4)_2SO_4$ per 1000g. H_2O.	Solid Phase. ::::::::::::
-----	5.327	$(NH_4)_2SO_4$.
0.017	5.254	"
0.081	5.229	$(NH_4)_2SO_4$ & $MnSO_4.(NH_4)_2SO_4.6H_2O$.
0.075	5.135	$MnSO_4.(NH_4)_2SO_4.6H_2O$.
0.138	3.993	"
0.167	3.551	"
0.377	1.864	"
0.531	1.315	"
0.769	1.069	"
1.868	0.531	"
3.525	0.261	"
3.565	0.260	"
3.665	0.251	$MnSO_4.(NH_4)_2SO_4.6H_2O$ & $MnSO_4.7H_2O$.
3.623	0.168	$MnSO_4.7H_2O$.
3.533	------	"

Conclusions.

The limits of formation of the double salt manganese ammonium sulphate $MnSO_4.(NH_4)_2SO_4.6H_2O$ at 0° C. are

from 0.015 to 14.60 moles of $MnSO_4$ to 1 mole of $(NH_4)_2SO_4$, (Table IX and Figure 14.)

and at 25° C. are

from 0.036 to 9.25 moles of $MnSO_4$ to 1 mole of $(NH_4)_2SO_4$. (Schreinemakers, loc.cit. and Figure 14.).

The ammonium isotherms differ greatly from those of the potassium system, the range of double salt formation in the case of the former being much greater. This is traceable to two factors: (a) the much greater solubility of ammonium sulphate (b) the fact that manganese ammonium sulphate is hexahydrated, whereas manganese potassium sulphate is tetrahydrated.

The solubility of manganese sulphate is increased at both temperatures by addition of ammonium sulphate, but the increase is more accentuated at 0° C. (cf. manganese potassium system.).

The solubility of ammonium sulphate is decreased at both temperatures by addition of manganese sulphate. This decrease is more accentuated at 0° C. It is interesting to note that Caven and Mitchell (4) obtained a decrease in the solubility of ammonium sulphate at 25° C. on the addition of copper sulphate. A more remarkable fact, however, is that, at higher temperatures (51° and 61° C) there is an increase of solubility of ammonium with addition of copper sulphate. Thus, with increase in temperature, the decrease in solubility of ammonium sulphate on addition of copper sulphate gradually becomes less and is finally converted into an increase. The same appears to be the case for the manganese-ammonium system; for at 25°C. the decrease in solubility of ammonium sulphate caused by addition of manganese sulphate is much less than at 0° C. That this <u>is</u> the case is fully borne out by Schreinemakers results at 50°C.

Moles of $(NH_4)_2SO_4$ per 1000g. of H_2O.	Moles of $MnSO_4$ per 1000g. of H_2O.	Solid Phase.
6.375	----	$(NH_4)_2SO_4$.
6.415	0.739	$(NH_4)_2SO_4$ and Double salt.

It seems only fair to connect this fact with the increasing quantity of copper or manganese sulphate required at higher temperatures before the double salt begins to crystallize. The amount of bivalent metal sulphate, and, therefore, the amount of complex ions present is so small at the lower temperatures that it is insufficient to overcome the effect of "Solubility Product".

The fact that manganese potassium sulphate is tetrahydrated while manganese ammonium sulphate is hexahydrated accords with data concerning vapour pressures of hydrated double sulphates containing potassium and ammonium, for Caven and Ferguson (34) have shown that, when ammonium sulphate is a constituent of a double salt, the vapour pressure is always lower than the corresponding potassium salt. That is to say, ammonium sulphate confers upon the double salt containing it a greater power of retaining water of crystallization than does potassium sulphate.

This is now seen to apply, then, not only to the relative stabilities of similarly hydrated salts under the dissociating influence of heat, but also in the case of manganese even to the number of molecules of water which can enter into the composition of a double salt.

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Copper Sulphate - Sodium Sulphate - Water at 0°, 25°, and 37.5° C.

It is well known that the double sulphates of copper sulphate with potassium and ammonium sulphates conform to the general type in being hexahydrated, and the outstanding feature concerning them is the wide limits of their formation, both as regards temperature and proportions of the single salts which may be present in the solutions from which they crystallize.

Regarding the formation of a double salt of copper sulphate and sodium sulphate, however, very different conditions may be anticipated. For it is an important property of sodium to differ widely from potassium and ammonium in the solubilities and other properties of its single salts, as for example the sulphate and perchlorate, and of its double salts, as for example the platinichloride and cobaltinitrite. Moreover, sodium sulphate itself is decahydrated whilst potassium and ammonium sulphates are anhydrous. It may be on this account that the study of copper sodium sulphate has already claimed the attention of investigators.

Diacon (53) investigated the system $CuSO_4 - Na_2SO_4 - H_2O$ at 0° C., and found that no double salt exists at this temperature in contact with solutions of its component salts. Nevertheless the continuous increase in solubility of each of the two single salts caused by addition of the other salt up to the triple point indicates the presence of a considerable amount of the double salt or its ions in solution.

Koppel (54) showed that below 16.7° C. double salt does not crystallize from a solution of its component salts, but above this temperature the double salt $CuSO_4.Na_2SO_4.2H_2O$ is formed over a rapidly increasing range. Moreover, he showed that the solubility of the double salt is slightly decreased with rise in temperature. He also found that the solubility of copper sulphate is decreased at all temperatures between 0° C. and 40.15°C. by addition of sodium sulphate, whilst the solubility of sodium sulphate is increased up to the transition point - $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$ - by addition of copper sulphate. Above the temperature of this transition point the solubility is decreased.

Massink (55) investigated the system $CuSO_4 - Na_2SO_4 - H_2O$ at 20° C., and found that the double salt was formed over a short range at this temperature. However, he obtained only a single point within the double salt region, and this appears to make this isotherm convex, a condition which is highly improbable. He obtained a continuous increase in solubility of each of the single salts up to the triple point, on addition of the other.

In view, therefore, of the conflicting and inadequate results of previous workers it was decided to investigate the system at 0°, 25°, and 37.5° C. An investigation of this system was expected to throw much light on the conditions of formation of double sulphates from the point of view of the sodium salts, and also to prove extremely interesting in comparison with the potassium and ammonium copper sulphates.

Experimental.

For this system at 0° solutions of the two single salts were made at atmospheric temperature, and various proportions kept immersed in ice and water; for the system at 25° and 37.5° solutions of the two salts were made at temperatures about 15° above those required, and various proportions kept in a thermostat at 25 ± .01°. The solutions were stirred for 3 days before portions were separated and analysed. Copper was estimated iodometrically and total sulphate determined.

Table X.

System $CuSO_4 - Na_2SO_4 - H_2O$ at 0°C.

Moles of $CuSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	0.324	$Na_2SO_4.10H_2O$.
0.213	0.347	"
0.415	0.378	"
0.590	0.392	"
1.047	0.440	$Na_2SO_4.10H_2O$ & $CuSO_4.5H_2O$.
0.998	0.257	$CuSO_4.5H_2O$.
0.970	0.146	"
0.929	-----	"

Table XI.

System $CuSO_4 - Na_2SO_4 - H_2O$ at 25° C.

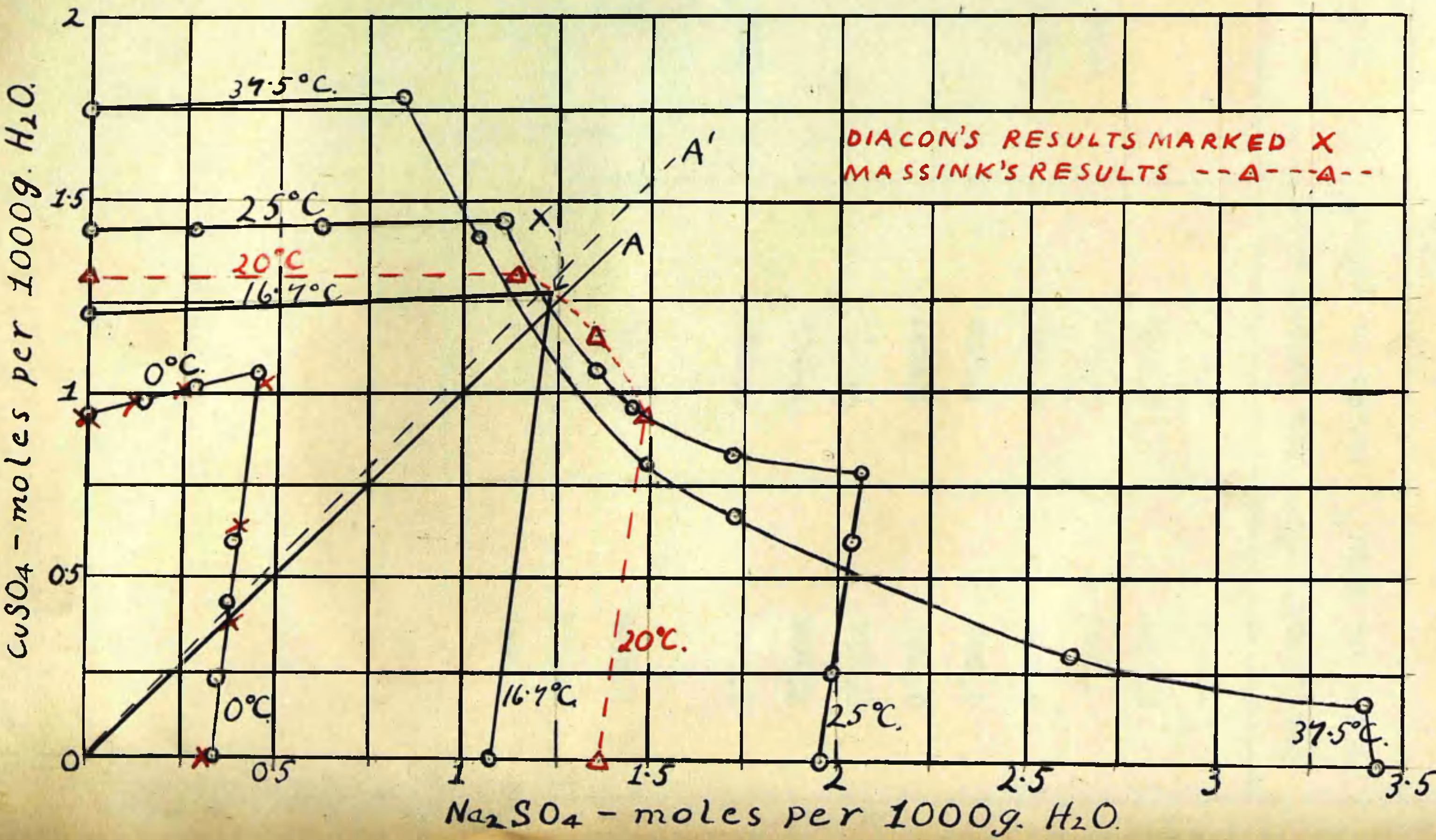
Moles of $CuSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. of H_2O.	Solid Phase.
------	1.972	$Na_2SO_4.10H_2O$.
0.254	2.006	"
0.593	2.038	"
0.781	2.063	$Na_2SO_4.10H_2O$ & $CuSO_4.Na_2SO_4.2H_2O$.
0.847	1.721	$CuSO_4.Na_2SO_4.2H_2O$.
0.979	1.439	"
1.068	1.343	"
1.457	1.109	$CuSO_4.Na_2SO_4.2H_2O$. & $CuSO_4.5H_2O$.
1.449	0.642	$CuSO_4.5H_2O$.
1.443	0.272	"
1.428	------	"

Table XII.

System $CuSO_4$ - Na_2SO_4 - H_2O at 37.5°C.

Moles of $CuSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	3.408	Na_2SO_4.
0.162	3.390	Na_2SO_4 & $CuSO_4.Na_2SO_4.2H_2O$.
0.230	2.668	$CuSO_4.Na_2SO_4.2H_2O$.
0.678	1.718	"
0.821	1.508	"
1.209	1.177	"
1.402	1.040	"
1.770	0.844	$CuSO_4.Na_2SO_4.2H_2O$ & $CuSO_4.5H_2O$.
1.754	-----	$CuSO_4.5H_2O$.

SYSTEM ~ $CuSO_4$-Na_2SO_4-H_2O at 0°, 25°, and 37·5° C.



Conclusions.

The results obtained at 0°C. agree closely with those published earlier by Diacon (loc.cit.), and they confirm the fact that no double salt is formed at this temperature, although a small increase in solubility of each salt is caused by the presence of the other. This differs from the conclusions of Koppel (loc.cit.) who found that the solubility of copper sulphate was decreased by addition of sodium sulphate.

At 25°C. the range of formation of the double salt $CuSO_4.Na_2SO_4.2H_2O$ is fairly wide being,

from 0.38 to 1.31 mole of $CuSO_4$ to 1 mole of Na_2SO_4.

The double salt isotherm, however, is not comparable with the isotherms for the double salts of copper sulphate with potassium and ammonium sulphates, which compounds are differently hydrated.

The addition of each component increases the solubility of the other up to the corresponding triple point where the double salt begins to crystallize. In the case of copper sulphate this increase is slight but definite, in agreement with Massink's results, but in contradiction to those of Koppel.

At 37.5°C. the range of double salt formation is greatly increased, the limits being,

from 0.041 to 2.097 moles of $CuSO_4$ to 1 mole of Na_2SO_4.

It is evident that this greatly increased range is connected with the large increase in solubility of sodium sulphate at this temperature.

It is to be noted that, although copper sulphate still shows a slight increase in solubility in presence of sodium sulphate, sodium sulphate now shows a decrease in solubility in presence of copper sulphate. A change in the form of the isotherm here is to be expected owing to the change of hydration of solid sodium sulphate.

The noteworthy fact, however, is the early appearance of the double salt, from whichever end approached, in consequence of which the isotherm of this salt lies throughout its whole length within the 25°C. isotherm. That is to say the solubility of copper sodium sulphate decreases with rise of temperature from 25°C. to 37.5°C., which is in agreement with the results of Koppel. (loc.cit.).

Since the solubility curve of the double salt diminishes in length from 37.5°C. to 25°C., it may be inferred that at some lower temperature it will disappear. It has already been stated that according to Koppel this temperature is 16.7°C., and it is not difficult to indicate on Figure 15 the point which marks this disappearance. This is done by drawing from the points representing the solubilities in water of copper sulphate and sodium sulphate respectively at 16.7°C., lines approximately parallel to the corresponding lines for say 25°C. Such lines intersect at the point X in the figure, and a curve drawn from this point in both directions through the pairs of triple points on the isotherms for higher temperatures would mark out the region of double salt formation as regards conditions of temperature and corresponding proportions between the single salts in solution.

Now the point X appears to lie on one side of the line OA, drawn at an angle of 45° from the origin, and representing equimolecular proportions of the two salts such as go to form the double salt; and it seems from the figure that for the double salt to be formed and exist in the solid state at 16.7° C. in equilibrium with a solution of its component salts a slightly larger molecular proportion of copper sulphate than of sodium sulphate must be present in that solution. From this it follows that the first product of isothermal evaporation of an equimolecular solution of the two salts at 16.7° C., or indeed for a few degrees above this temperature, is not double salt but sodium sulphate the less soluble of the two single salts. Sodium sulphate, then, will separate until the composition of the solution corresponds with the co-ordinates of the point X, or a triple point representing equilibrium with sodium sulphate and double salt, is reached.

The temperature at which double salt can first be crystallized from water without decomposition must lie between 16.7° C. and 20° C. (Massink, loc.cit.), that is the transition interval must be very small in contrast to that for the manganese sulphate - potassium sulphate - water system.

It is observed that the point X, if rightly placed, lies very close to the 25° C. isotherm, so that the region in which the isotherms between 16.7° C. and 25° C. appear must be very contracted, that is to say the solubility of the double salt between those temperatures, although diminishing, is very nearly constant. This accounts for the observations of Massink at 20° C., whose triple points appear to lie actually upon the 25°C. isotherm.

To test some of the foregoing theoretical conclusions the following experiments were performed:-

An equimolecular solution of copper and sodium sulphates was made and evaporated in the thermostat at 38°C. until crystallization of the double salt took place. The double salt and mother liquor were then available for the following tests:-

The equimolecular solution saturated at 38°C. was cooled rapidly to 0°C. Pure sodium sulphate crystallized to such an extent that the mass appeared to be solid. Thus from the same solution from which the double salt crystallized at 38°C., $Na_2SO_4.10H_2O$ crystallized at 0°C.

Some of the crystallized double salt was shaken with a little water at 0°C. Crystals of sodium sulphate appeared among those of the double salt, and there was a marked decrease in the amount of water present because $Na_2SO_4.\underline{10H_2}O$ had taken the place of $CuSO_4.Na_2SO_4.\underline{2H_2}O$.

Some of the crystallized double salt was dissolved in a little water at 10°C., and the solution cooled to 0°C. Sodium sulphate again crystallized.

These experiments all illustrate the non-formation of double salt at 0°C.

An equimolecular solution of the two salts was evaporated in a vacuum desiccator at 17.5°-18°C. Sodium sulphate crystallized first, showing that this temperature is within the transition interval.

A solution containing the two salts in the molecular ratio sodium sulphate:copper sulphate::1.00:1.05, shown in the figure by the line OA′, was evaporated in a vacuum desiccator at 17.5°-18°C. Double salt separated first. This proves that a point representing the above molecular ratio lies on the double salt isotherm of a temperature between 17.5° and 18°C., and confirms the conclusion that the point X, where the double salt begins to be formed, lies a little on the copper sulphate side of the line of equimolecular proportions OA, but very near to the line OA.

……

Zinc Sulphate - Sodium Sulphate - Water at 0° and 25° C.

The double salt zinc sodium sulphate was among those investigated by Graham (56), who states that the double salt $ZnSO_4.Na_2SO_4.4H_2O$ is deliquescent in moist air, and is decomposed into its constituents by water.

Against this latter statement is to be placed the following (57):- "Sodium sulphate is slowly but abundantly soluble in a saturated zinc sulphate solution with separation of a double salt after a few days." How these two apparently contradictory statements are reconciled will be seen in the sequel.

Koppel and Gumperz (58) have shown that the double salt $ZnSO_4.Na_2SO_4.4H_2O$ is formed from a solution of its component salts only above 8.7° C. They also found that the solubility of the double salt is constant at all temperatures at which it is not decomposed by water. As, however, they did not examine the system completely at any given temperature so as to establish the isotherm, it was decided to investigate the system at 0° and 25° C.

It is also to be noted that these investigators found that, while the solubility of sodium sulphate is increased by addition of zinc sulphate, that of zinc sulphate is decreased by addition of sodium sulphate.

Experimental.

For the system at 0° C. saturated solutions of the two salts were made at atmospheric temperature, and various proportions of these solutions were immersed in ice and water. The mixtures were stirred for 3 days before portions of the solutions were separated and analysed. For the system at 25°C. solutions of the two salts made up at 40 were used, and solutions as above stirred for 3 days at 25 ± .01°C.

Zinc was estimated by means of standard potassium ferrocyanide solution, and sodium sulphate calculated after determination of total sulphate.

Table XIII.

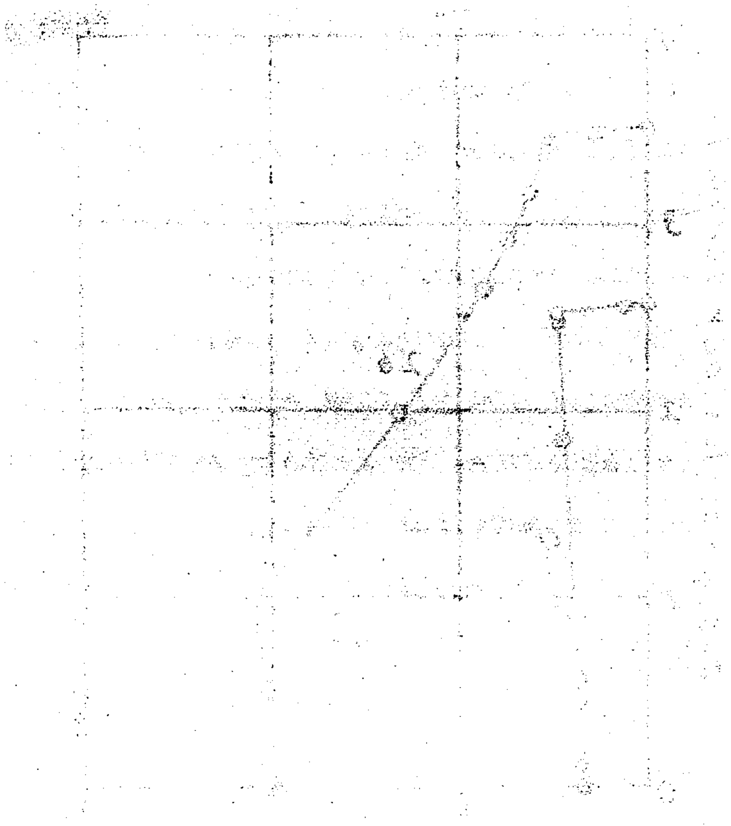
System $ZnSO_4$ - Na_2SO_4 - H_2O at 0°C.

Moles of $ZnSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
------	0.331	$Na_2SO_4.10H_2O$.
0.128	0.347	"
0.414	0.366	"
0.600	0.381	"
0.914	0.388	"
1.886	0.463	"
2.494	0.485	"
2.521	0.492	$Na_2SO_4.10H_2O$ & $ZnSO_4.7H_2O$.
2.568	0.122	$ZnSO_4.7H_2O$.
2.589	-----	"

Table XIV.

System $ZnSO_4$ - Na_2SO_4 - H_2O at 25° C.

Moles of $ZnSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase. ::::::::::::
-----	1.972	$Na_2SO_4.10H_2O$.
0.543	2.033	"
1.073	2.084	"
1.226	2.087	$Na_2SO_4.10H_2O$, & $ZnSO_4.Na_2SO_4.4H_2O$.
1.987	1.322	$ZnSO_4.Na_2SO_4.4H_2O$.
2.669	0.871	"
2.922	0.745	"
3.157	0.641	"
3.463	0.551	$ZnSO_4.Na_2SO_4.4H_2O$, & $ZnSO_4.7H_2O$.
3.504	0.255	$ZnSO_4.7H_2O$.
3.518	-----	"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SYSTEM ~ $ZnSO_4 - Na_2SO_4 - H_2O$ at 0° and 25°C.

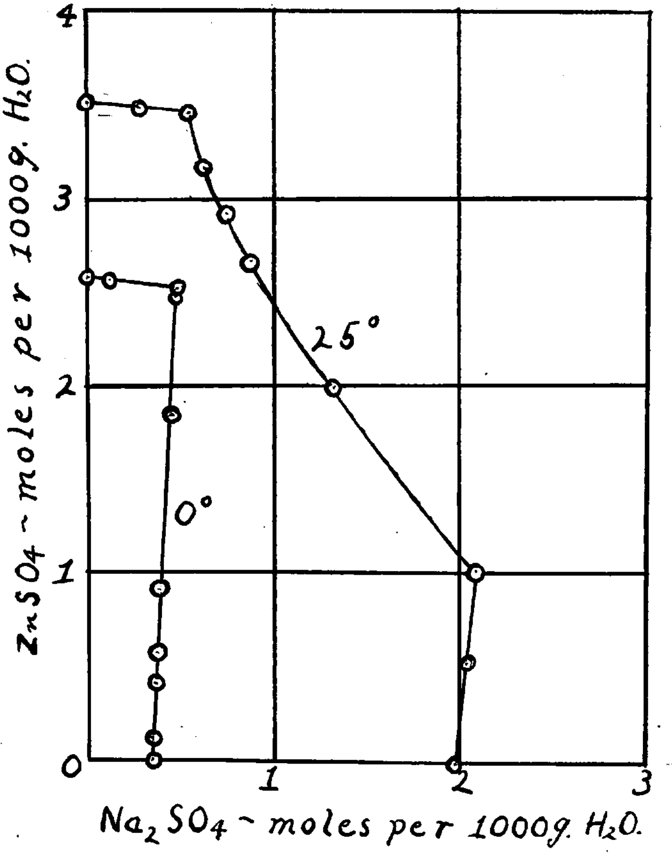


FIGURE 16.

Conclusions.

No double salt is formed at 0°C. This is in agreement with the work of Koppel and Gumperz.

The double salt $ZnSO_4.Na_2SO_4.4H_2O$ is formed over a considerable range at 25°C:-

from 0.59 to 6.28 moles of $ZnSO_4$ to 1 mole of Na_2SO_4.

The isotherm differs considerably from that of the copper sulphate - sodium sulphate system at the same temperature, the range being much wider. It is to be noted, however, that this increased range is mainly due to the much greater solubility of zinc sulphate as compared with copper sulphate. Indeed, at the sodium sulphate end of the isotherm, a much greater concentration of zinc sulphate as compared with copper sulphate must be present before double salt begins to appear.

At 25°C. the double salt is not decomposed by water, and consequently the first product of isothermal evaporation of an equimolecular solution of zinc and sodium sulphates at this temperature is the double salt $ZnSO_4.Na_2SO_4.4H_2O$.

According to Koppel and Gumperz, however, the transition interval for this double salt is 8.7° to 21°C. Therefore, ordinary (room) temperatures lie within this interval, and thus at these temperatures the double salt is decomposed by water. Herein lies the explanation of the apparently contradictory statements already quoted.

Thus, when the double salt is dissolved in water within this temperature range, it is decomposed into its constituents, with the probable separation of sodium sulphate. On the other hand if sodium sulphate is added to a saturated solution of zinc sulphate it is more than likely that the composition of the resulting solution will lie within the region of double salt formation (that is the solution will contain a greater molecular proportion of zinc sulphate than of sodium sulphate). Thus double salt will gradually be deposited from the solution.

At both 0° and 25° C. the solubility of sodium sulphate is increased by addition of zinc sulphate, and the solubility of zinc sulphate is decreased by addition of sodium sulphate. This is in agreement with the observations of Koppel and Gumperz.(loc.cit.).

……

Manganese Sulphate - Sodium Sulphate - Water at 0°, 25°, and 35° C.

Geiger (59), in a thesis submitted to Berlin University, alleged that the double salt of manganese and sodium sulphates exists in two hydrated forms, the tetrahydrate and the dihydrate: $MnSO_4.Na_2SO_4.4H_2O$ and $MnSO_4.Na_2SO_4.2H_2O$.

According to Marignac (60) the dihydrate of manganese sodium sulphate crystallizes from a solution of its component salts not below 36.5°C., and a tetrahydrate by free evaporation at ordinary temperature. Marignac's results were accepted by Koppel (1), although in default of a rapid and accurate method of estimating manganese he did not himself investigate the double salt.

Schreinemakers and Provije (61) have given the results of an investigation of the system $MnSO_4 - Na_2SO_4 - H_2O$ at 35°C., which show at this temperature two double salts, $9MnSO_4.10Na_2SO_4$ and $MnSO_4.3Na_2SO_4$, according to the composition of the mother liquor.

It was decided to investigate this system at 0° and 25°C., and also in view of the conclusions of Schreinemakers and Provije at 35° C.

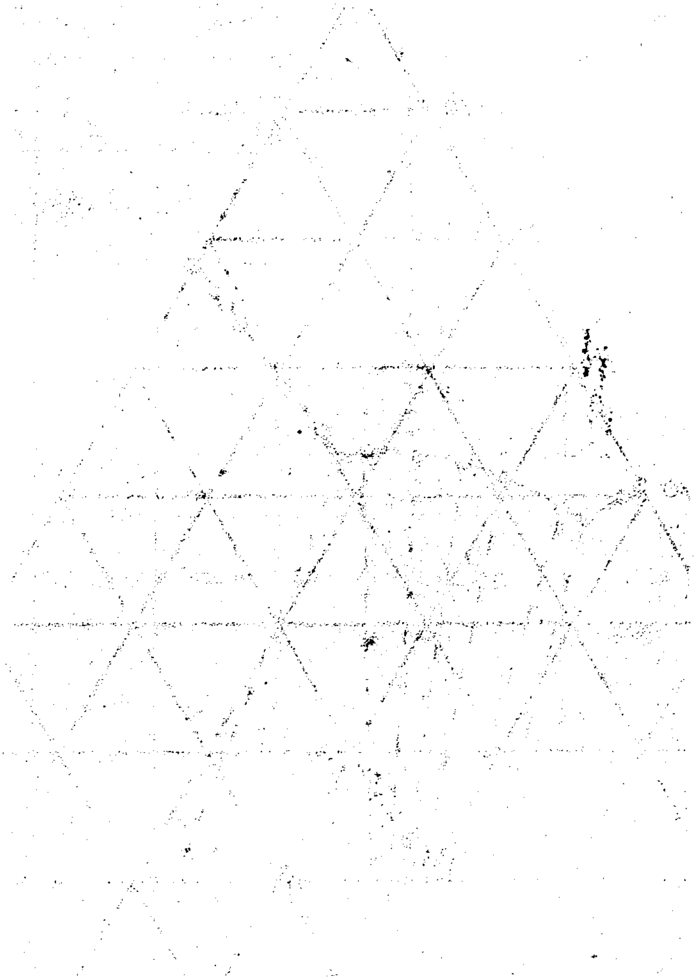
Experimental.

For this system at 0° the procedure was as usual, the mixtures being stirred for 3 days.

A slightly different procedure was necessary at 25° C. The solubility of manganese sulphate decreases above 26°C., therefore, there was no advantage in preparing solutions above this temperature. Consequently solutions of sodium sulphate saturated at 40°, and of manganese sulphate saturated at 25° were used. To ensure the presence of a solid phase on the manganese sulphate saturation curve, solid tetrahydrated manganese sulphate, the hydrate stable at 25° C., was added to different mixtures of the above solutions. These mixtures were immersed in a thermostat at 25 ± .01° C., and stirred for 4 days, after which it was found that equilibrium had been reached. At the sodium sulphate end of the isotherm different proportions of the above solutions were taken, and the mixtures stirred for 3 days. Both solid and liquid phases were analysed.

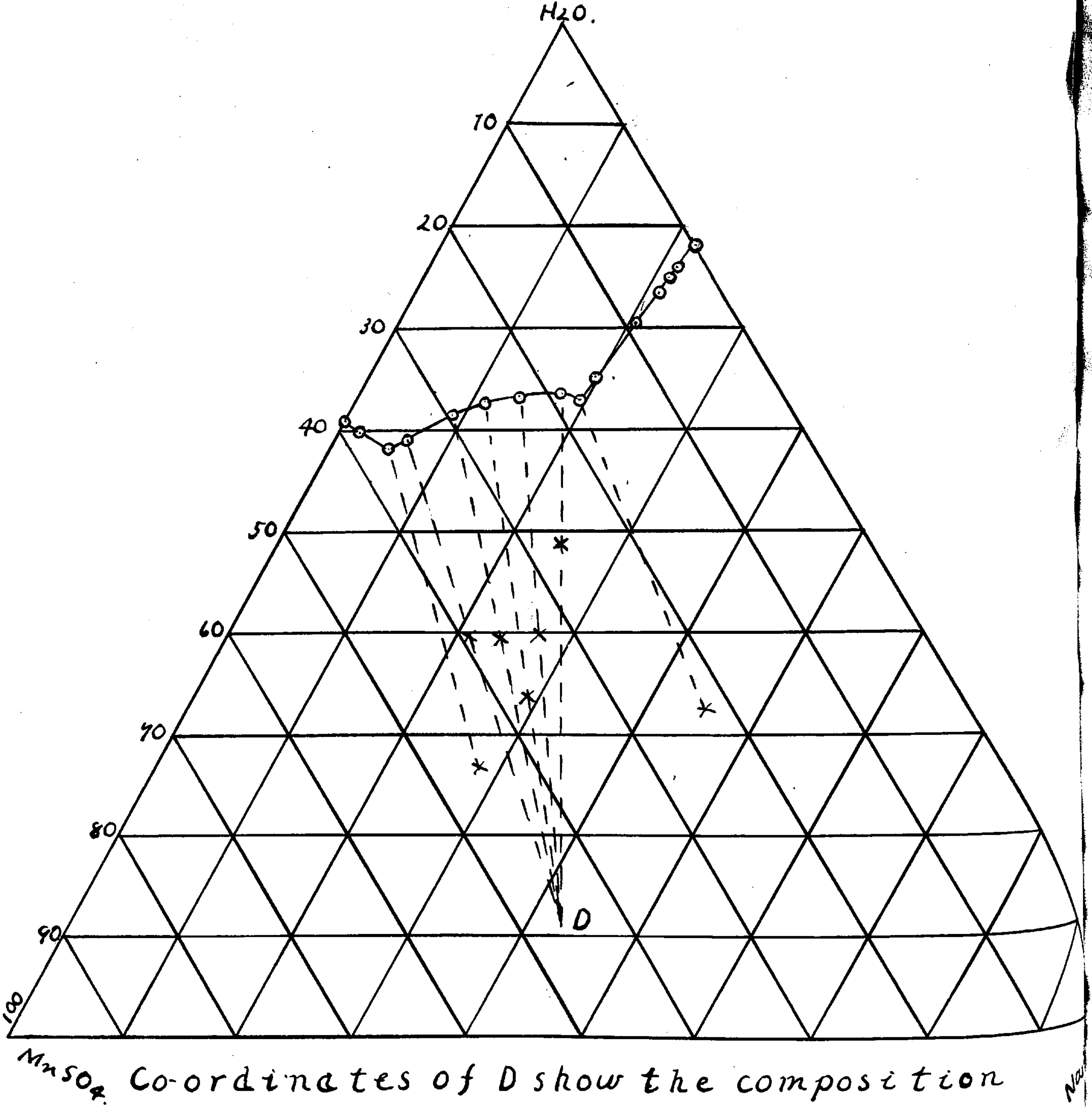
For the experiment at 35° various proportions of solutions of the two salts saturated at 40° were taken, while to ensure the presence of the appropriate solid phase anhydrous sodium sulphate was added at the sodium end of the isotherm, and monohydrated manganese sulphate at the manganese end. These mixtures were stirred for 4 days. Both solid and liquid phases were analysed.

Manganese was estimated volumetrically by the Volhard method, and sodium sulphate calculated after determination of total sulphate.



EQUILIBRIUM DIAGRAM.

$MnSO_4-Na_2SO_4-H_2O$ at 25°C.

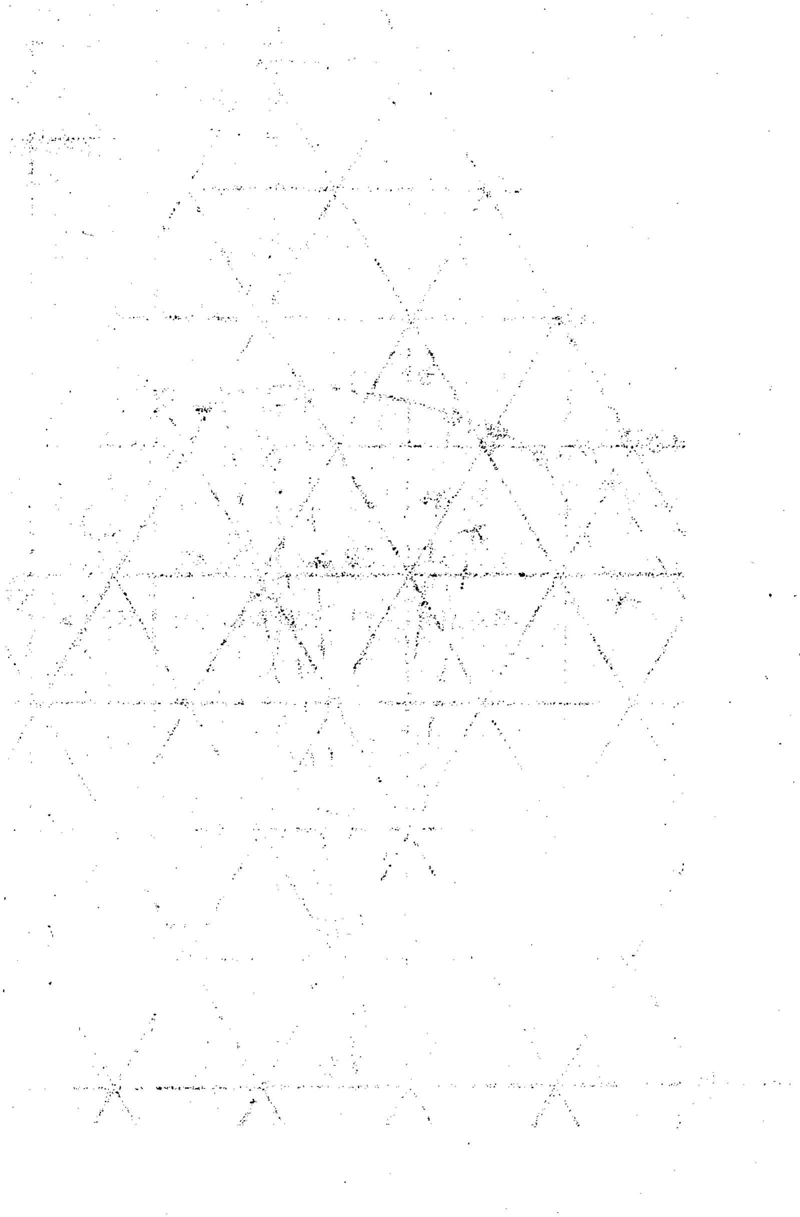


Co-ordinates of D show the composition of the double salt to be $MnSO_4.Na_2SO_4.2H_2O$

FIGURE 17.

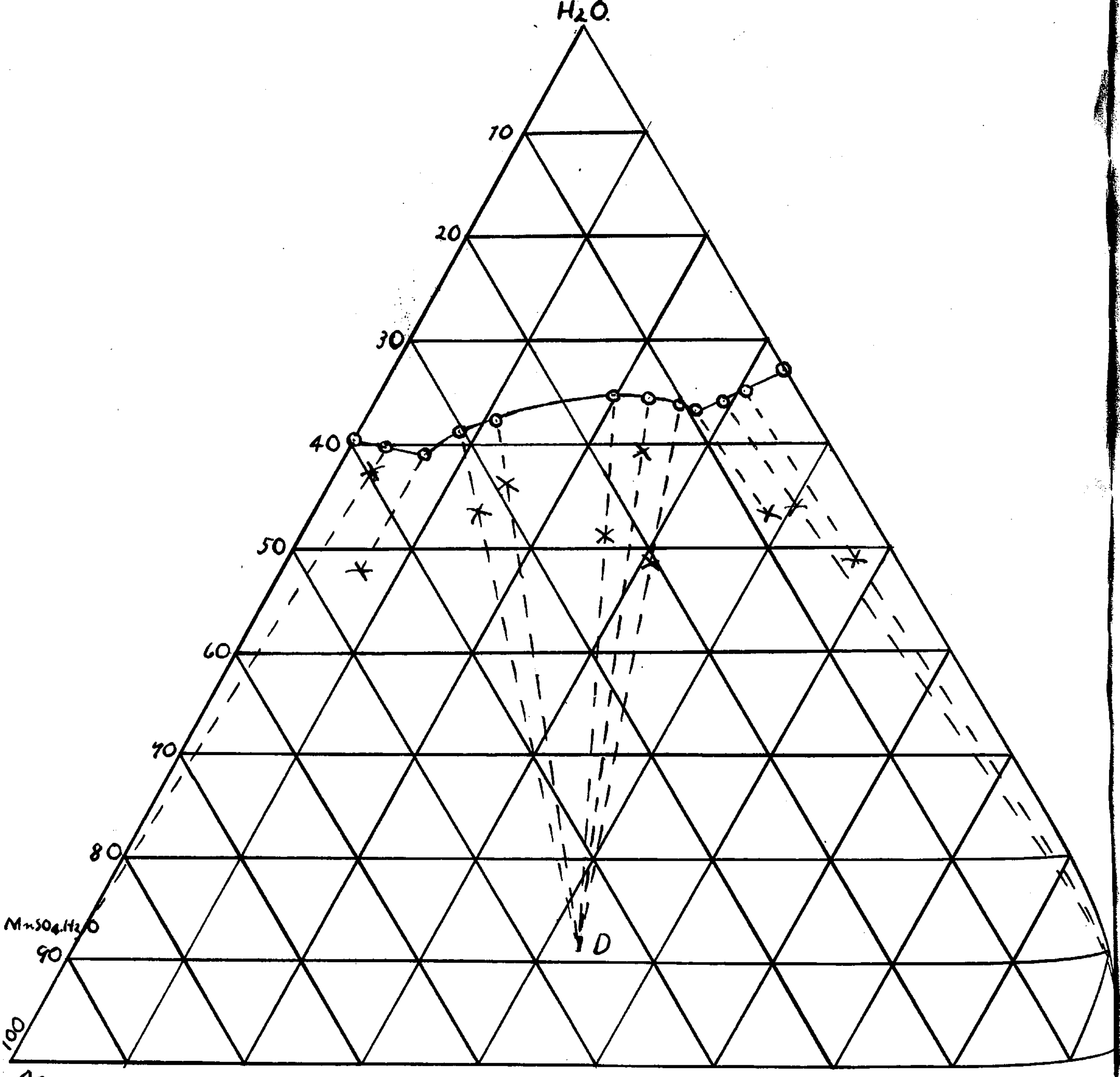
Table XV.

System $MnSO_4$ - Na_2SO_4 - H_2O at 25° C.						
Percentage Composition.						::::::::::::
Solutions.			Moist Solids.			Solid Phase.
$MnSO_4$	Na_2SO_4	H_2O.	$MnSO_4$	Na_2SO_4	H_2O.	::::::::::::
-----	21.89	78.11	-----	-----	-----	$Na_2SO_4.10H_2O$.
2.81	21.54	75.65	-----	-----	-----	"
3.94	21.28	74.78	-----	-----	-----	"
5.44	21.16	73.40	-----	-----	-----	"
9.14	20.53	70.33	-----	-----	-----	"
15.15	19.55	65.30	-----	-----	-----	"
17.15	19.26	63.59	24.50	44.95	30.55	$Na_2SO_4.10H_2O$ & $MnSO_4.Na_2SO_4.2H_2O$.
18.62	17.42	69.39	26.26	24.64	49.10	$MnSO_4.Na_2SO_4.2H_2O$.
22.88	13.51	63.61	33.24	26.87	39.89	"
26.23	11.00	62.77	37.26	28.81	33.93	"
29.52	8.78	61.70	36.58	23.97	39.45	"
34.69	6.23	59.08	39.20	20.94	39.86	"
36.94	5.09	57.97	45.01	28.10	26.89	$MnSO_4.Na_2SO_4.2H_2O$ & $MnSO_4.4H_2O$.
38.43	1.66	59.91	-----	-----	-----	$MnSO_4.4H_2O$.
39.10	-----	60.90	-----	-----	-----	"



EQUILIBRIUM DIAGRAM.

$MnSO_4 - Na_2SO_4 - H_2O$ at 35° C.



Co-ordinates of D show the composition of the double salt to be $MnSO_4 . Na_2SO_4 . 2H_2O$.

FIGURE 18.

Table XVI.

System $MnSO_4$ - Na_2SO_4 - H_2O at 35°C.						
Percentage Composition.						::::::::::::
Solutions.			Moist Solids.			Solid Phase.
$MnSO_4$	Na_2SO_4	H_2O.	$MnSO_4$	Na_2SO_4	H_2O.	::::::::::::
------	32.83	67.17	------	------	------	Na_2SO_4.
4.25	30.49	65.26	3.26	47.92	48.82	"
6.55	29.05	64.40	5.45	40.51	54.04	"
9.35	27.49	63.16	8.41	38.47	53.12	Na_2SO_4 & $MnSO_4.Na_2SO_4.2H_2O$.
10.21	25.75	64.04	20.43	31.06	48.51	$MnSO_4.Na_2SO_4.2H_2O$.
12.54	22.96	64.50	15.42	24.90	59.48	"
15.64	19.70	64.66	23.09	25.78	51.13	"
26.56	11.12	63.32	28.87	15.31	55.82	"
30.43	8.49	61.08	32.65	13.93	53.42	"
34.46	6.62	58.92	45.73	6.65	47.62	$MnSO_4.Na_2SO_4.2H_2O$, & $MnSO_4.H_2O$.
37.12	3.05	59.83	39.60	3.01	57.39	$MnSO_4.H_2O$.
39.56	-----	60.44	------	-----	------	"

Table XVII.

System $MnSO_4 - Na_2SO_4 - H_2O$ at 0° C.		
Moles of $MnSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	0.331	$Na_2SO_4.10H_2O$.
0.254	0.369	"
0.773	0.389	"
0.897	0.383	"
1.650	0.445	"
2.318	0.520	"
3.413	0.566	$Na_2SO_4.10H_2O$ & $MnSO_4.7H_2O$.
3.424	0.509	$MnSO_4.7H_2O$.
3.499	0.158	"
3.533	-----	"

Table XVIII.

System $MnSO_4$ - Na_2SO_4 - H_2O at 25° C.

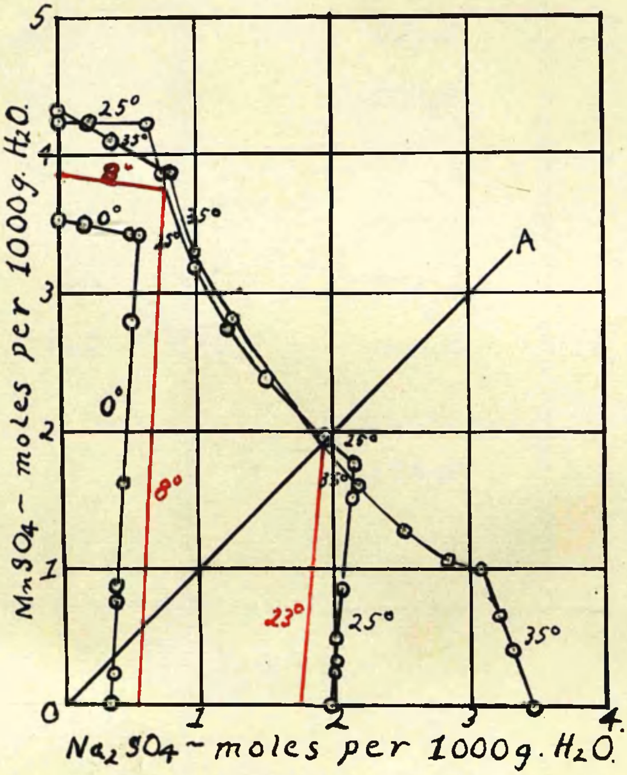
Moles of $MnSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
------	1.972	$Na_2SO_4.10H_2O$.
0.246	2.004	"
0.349	2.003	"
0.491	2.029	"
0.861	2.054	"
1.536	2.108	"
1.786	2.132	$Na_2SO_4.10H_2O$ & $MnSO_4.Na_2SO_4.2H_2O$.
1.928	1.917	$MnSO_4.Na_2SO_4.2H_2O$.
2.381	1.494	"
2.767	1.232	"
3.169	1.001	"
3.889	0.742	"
4.220	0.618	$MnSO_4.Na_2SO_4.2H_2O$ & $MnSO_4.4H_2O$.
4.248	0.195	$MnSO_4.4H_2O$.
4.252	------	"

Table XIX.

System $MnSO_4$ - Na_2SO_4 - H_2O at 35° C.		
Moles of $MnSO_4$ per 1000g. H_2O.	Moles of Na_2SO_4 per 1000g. H_2O.	Solid Phase.
-----	3.440	Na_2SO_4.
0.431	3.288	"
0.674	3.175	"
0.980	3.063	Na_2SO_4 & $MnSO_4.Na_2SO_4.2H_2O$.
1.055	2.830	$MnSO_4.Na_2SO_4.2H_2O$.
1.237	2.504	"
1.602	2.144	"
2.821	1.256	"
3.299	0.978	"
3.875	0.790	$MnSO_4.Na_2SO_4.2H_2O$ & $MnSO_4.H_2O$.
4.109	0.359	$MnSO_4.H_2O$.
4.334	-----	"

SYSTEM ~ $MnSO_4 - Na_2SO_4 - H_2O$ at

0°, 25° and 35° C.



SOLUBILITIES ARE INTERPOLATED AT 8°C AND AT 23°C TO INDICATE THE APPROXIMATE RANGE OF THE TRANSITION INTERVAL (8°C - 23°C

FIGURE 19.

Conclusions.

The 0°C. isotherm shows that no double salt is formed at this temperature. (Figure 19 and Table XVII.).

Double salt is formed at 25°C., the salt being the dihydrate $MnSO_4.Na_2SO_4.2H_2O$. (Figure 17 and Table XV.).

It is formed a considerable range at this temperature:-

from 0.84 to 6.83 moles of $MnSO_4$ to 1 mole of Na_2SO_4. (Figure 19 and Table XVIII.).

No evidence of the formation of the tetrahydrate at 25°C. was found.

The dihydrate $MnSO_4.Na_2SO_4.2H_2O$ is also formed a considerable range at 35°C., viz:

from 0.32 to 4.90 moles of $MnSO_4$ to 1 mole of Na_2SO_4. (Figures 18 and 19, and Tables XVI and XIX.).

NO evidence was found of the tetrahydrate nor of the double salts $8MnSO_4.10Na_2SO_4$ and $MnSO_4.3Na_2SO_4$.

A study of the isotherms at 25° and 35°C. shows the interesting fact that the double salt portion of the 25° isotherm is nearly coincident along all its length with the double salt portion of the 35° isotherm.(Figure 19.). This indicates that the solubility of the double salt at these two temperatures is almost identical. A closer inspection of the place where the equimolecular line OA cuts the isotherms shows that the solubility of the double salt $MnSO_4.Na_2SO_4.2H_2O$ is slightly less at 35°C. than at 25°C.

At all three temperatures the solubility of manganese sulphate is decreased by addition of sodium sulphate. This fact is of much greater interest on more particular examination, for the solid phases are all different at the different temperatures. The decrease is least at 25°C. where the solid phase is $MnSO_4.4H_2O$, and is greatest, being much accentuated, at 35°C. where the solid phase is $MnSO_4.H_2O$. An intermediate decrease is shown at 0° C. where the solid phase is $MnSO_4.7H_2O$. Thus the isotherms show the effect of addition of sodium sulphate on the solubilities of three hydrated forms of $MnSO_4$:- $MnSO_4.7H_2O$, $MnSO_4.4H_2O$, and $MnSO_4.H_2O$.

It is to be noted that the solubility of the monohydrate at 35°C. is slightly greater than that of the tetrahydrate at 25°C.

At 0° and 25° C. the solubility of sodium sulphate is increased by addition of manganese sulphate, and at 35°C. is much decreased. Here again there is a change of solid phase from the decahydrated to the anhydrous state.

The double salt is not decomposed by water at either 25° or 35° C. Thus the first product of isothermal evaporation of an equimolecular solution of the two single salts at these temperatures is the double salt.

By interpolation of the solubility of sodium sulphate at 23° C. it can be seen that this temperature is very probably just within the transition interval. Also by interpolation of the solubilities of sodium sulphate and manganese sulphate at 8° C. it is seen that the transition point lies very near this temperature. (Figure 19.).

Therefore, the approximate transition interval for the double salt manganese sodium sulphate is 8° to 23° C. Thus this salt is decomposed by water at ordinary (room) temperatures.

The results of [illegible] may now be discussed generally in the light of [illegible] theories [illegible] brought forward in the introductory part of this thesis.

A. Evidence for the Existence of Complex Ions in Solution.

The results of the investigation of the potassium sulphate – bivalent metallic sulphate – water systems give strong support to the view that considerable amounts of complex ions are formed in solution.

In all the four systems examined the solubility of each single salt is continuously increased up to the triple point, where double salt begins to appear, by addition of the other component. It has already been shown by Klein (8), Rieger (14), [illegible] and Archibald (10), and Caven and Mitchell (4), in the case of the analogous copper system, that this increase in solubility is due to the presence of complex ions in solution. For this reason and in view of the theoretical point already discussed it seems justifiable to conclude that this "increase is an indication of the presence of a considerable amount of the double salt or its ions in solution."

In the case of the manganese sulphate – ammonium sulphate – water system the increase in solubility of manganese sulphate by addition of ammonium sulphate indicates the presence of complex ions in solution. At first sight, however, the [illegible] sulphate by addition of [illegible]

Discussion of Results.

The results of this investigation may now be discussed generally in the light of the various theories and hypotheses brought forward in the introductory part of this thesis.

A. Evidence for the Existence of Complex Ions in Solution.

The results of the investigation of the potassium sulphate - bivalent metallic sulphate - water systems give strong support to the view that considerable amounts of complex ions are formed in solution.

In all the four systems examined the solubility of each single salt is continuously increased up to the triple point, where double salt begins to appear, by addition of the other component. It has already been shown by Klein (9), Reiger (14), MacGregor and Archibald (10), and Caven and Mitchell (4), in the case of the analogous copper system, that this increase in solubility is due to the presence of complex ions in solution. For this reason and in view of the theoretical points already discussed it seems justifiable to conclude that this "increase is an indication of the presence of a considerable amount of the double salt or its ions in solution."

In the case of the manganese sulphate - ammonium sulphate - water system the increase in solubility of manganese sulphate by addition of ammonium sulphate indicates the presence of complex ions in solution. At first sight, however, the decrease in solubility of ammonium sulphate by addition of manganese sulphate presents a difficulty, which disappears, as has already been pointed out, when all the facts are taken into consideration..

As the temperature is raised this decrease is overcome and converted into an increase. A similar state of affairs is found in the analogous copper system. It was suggested that this effect was due in each case to the relatively small amount of bivalent metallic sulphate required at lower temperatures before crystallization of double salt takes place. Indeed this effect might be regarded as due to the relatively greater insolubility of the double salts as compared with the single salt ammonium sulphate. Thus the amount of double salt or its ions is very small and insufficient to overcome the effect due to solubility product..

As the temperature is raised the solubility of the double salt increases relatively much more rapidly than that of the single salt; thus more of the bivalent metallic sulphate is required before the double salt begins to crystallize. Therefore, it follows that the amount of double salt (or its ions) in solution increases, and as the temperature is raised the effect of solubility product is gradually cancelled and finally overcome, the result being shown by an increase in solubility of ammonium sulphate with addition of the bivalent metallic sulphate

A study of the results for the sodium systems throws some very interesting light on this problem of the presence of complex ions in solution.

The copper sulphate - sodium sulphate - water system is of particular interest, and supplies strong evidence in support of the view of the presence of double salt ions in solution. Thus at 0°C., though no double salt is formed, the solubility of each single salt is increased by the addition of the other. On superficial consideration this would seem anomalous, and indeed in direct contradiction to the above view. On more particular examination, however, this apparent anomaly disappears. For the double salt, though not formed at 0°C., is formed at higher temperatures (above 16.7°C.), and the reason for its non-appearance at 0°C. (or 0°- 16.7°C.) is that its solubility is greater than that of the single salts. Indeed, while the solubility of the single salts is decreased by decrease in temperature, that of the double salt is increased.

At 16.7°C. the solubility of the double salt is just equal to that of the single salts, and therefore it can exist and crystallize along with them at this temperature. Thus it would seem fair to infer that below 16.7°C., though the double salt cannot exist in the solid state in contact with solutions containing its component salts, it is present in considerable amount in solution. Indeed it would be present in solution at temperatures considerably lower than this, and that this is so even at 0°C. is shown by the reciprocal increase in solubilities of the single salts at this temperature.

While the increase in solubility of copper sulphate is shown at all temperatures, it is to be noted that at 37.5°C. the solubility of sodium sulphate is decreased by addition of copper sulphate, though an increase is shown at 0° and 25°C.

Two factors are to be taken into consideration to account for this. The first is the early appearance of double salt, and the second is the change in hydration of sodium sulphate above 32.5° C.

As regards the sodium sulphate - zinc sulphate and sodium sulphate - manganese sulphate systems it is seen that, while the solubility of sodium sulphate is increased by the addition of the other component, the solubility of the bivalent metallic sulphates is decreased by addition of sodium sulphate. The increase in solubility of sodium sulphate in each case, even at 0° C. where no double salt is formed, seems to be clear evidence of the existence of considerable amounts of double salt in solution. The decrease in solubility of the bivalent metallic sulphates may be due to the amount of double salt ions in solution being insufficient to overcome the effect of solubility product.

Possibly, however, the explanation may be found in the suggestion of Caven, Ferguson, and Mitchell (6) "that the formation of double salt begins when the undissociated molecules of the bivalent metallic sulphate take to themselves sulphate ions from the alkali sulphate in solution; thus more of the sulphate dissolves than would dissolve if no bivalent sulphate were present."

From a consideration of all the facts it may be concluded, as far as the double salts examined in this investigation are concerned, that considerable amounts of the double salts (or their ions) exist in solution. Generally the presence of these double salts in solution is indicated by an increase in solubility of either or both single salts previous to crystallization of the double salt, though it may happen that this effect is masked by other influences.

B. Caven's General Hypothesis.

The results may now be considered in the light of Caven's general hypothesis regarding the formation of double and complex salts in solution (6) :-

"A double or complex salt is formed from two salts with a common ion when there is sufficient difference in basigenic character between the two metals forming the cations to yield simultaneously sufficient concentrations of the common anion and the undissociated salt of the weaker cation to cause their union."

It may first be considered as regards the alkali sulphates. It has already been seen, from the point of view of their electrolytic dissociation in equivalent states of dilution, that the order of the alkali sulphates is potassium sulphate, ammonium sulphate, sodium sulphate, and lithium sulphate. In the electrochemical series of the metals the order is potassium, sodium, and lithium in the direction of decreasing electronegativeness.

As far as is known lithium sulphate forms no double sulphates. Potassium sulphate forms double sulphates with the sulphates of bivalent metals over a very wide range of temperature and relative concentration of the component salts.

Sodium sulphate does not form any double salts with the bivalent metallic sulphates at 0°C., but does so at higher temperatures, usually considerably above 0°C. It would appear, therefore, in the case of potassium, sodium, and lithium sulphates that the power of forming double sulphates is a function of affinity, the order of decreasing power being the same as decreasing affinity not only as shown by the sulphates but also by the metals themselves.

The fixing of the position of ammonium sulphate in the above series is not quite so simple. From the point of view of electrolytic dissociation ammonium sulphate should follow potassium sulphate. From other considerations, however, it would appear that it should come before potassium sulphate.

It is known that ammonium sulphate like potassium sulphate forms double sulphates over a wide range of temperature and relative concentration of the two single salts, and in both cases these are of the general type $M''SO_4.M_2SO_4.6H_2O$, ($M' = K'$ or NH_4').

Caven and Ferguson (34), however, as a result of an investigation of the dissociation pressures of Alkali Cupric Sulphates, found that the order of increasing strength of alkali metals, including thallium and ammonium, as regards the power they confer on the rest of the molecule to retain $6H_2O$ is K, Rb, Tl, NH_4, Cs.

Thus it is found that, while the double sulphates of potassium and ammonium with a large number of bivalent metallic sulphates such as those of copper, zinc, ferrous iron, and nickel all contain 6 molecules of water, the double sulphate of potassium and manganese only contains four molecules of water whereas the corresponding ammonium salt contains six.

Sodium sulphate has less power than potassium sulphate of forming double salts, and the maximum water of crystallization of sodium double sulphates is four molecules, as compared with six for those of potassium. It would appear, therefore, that the amount of water of crystallization of the double salt is an indication of the power of the component salts to form a double salt, or in other words the power of the double sulphate to retain water in the molecule is a measure of the power of the component salts to form a double salt.

Thus Caven and Ferguson (34) have shown that, from this point of view, ammonium sulphate is more powerful than potassium sulphate. Further support is forthcoming from the above mentioned fact that the double sulphate of ammonium and manganese is hexahydrated while that of potassium is tetrahydrated.

From a consideration of the above facts it seems only fair to conclude that the order of increasing power to form double sulphates is lithium sulphate $<$ sodium sulphate $<$ potassium sulphate $<$ ammonium sulphate.

This is more clearly brought out from a study of the following table which shows the double salts of the different alkali sulphates with the same bivalent metallic sulphates:-

Table XX.

Alkali Sulphate.	Zinc Double Sulphate.	Copper Double Sulphate.	Manganese Double Sulphate.
Lithium.	Not known.	Not known.	Not known.
Sodium. 0° C. 25° C.	::::::::::: Not formed. Zinc sodium sulphate formed. Tetrahydrated.	::::::::::: Not formed. Copper sodium sulphate formed. Dihydrated.	::::::::::: Not formed. Manganese sodium sulphate formed. Dihydrated.
Potassium. 0° C. 25° C.	::::::::::: Zinc potassium sulphate formed. Hexahydrated.	::::::::::: Copper potassium sulphate formed. Hexahydrated.	::::::::::: Manganese potassium sulphate formed. Tetrahydrated.
Ammonium. 0° C. 25° C.	::::::::::: Zinc ammonium sulphate formed. Hexahydrated.	::::::::::: Copper ammonium sulphate formed. Hexahydrated.	::::::::::: Manganese ammonium sulphate formed. Hexahydrated.

It is necessary for a fuller insight into this matter to study the effect of the bivalent metallic sulphate. This is done by studying the double salts of different bivalent metallic sulphates with the same alkali sulphate. Table XXI forms a summary of the various potassium double sulphates investigated.

Table XXI.

Double Salt.	Range of Formation at 25° C.	Solubility.
$NiSO_4.K_2SO_4.6H_2O$.	0.031 to 3.80 moles of $NiSO_4$ to 1 mole of K_2SO_4.	Least.
$CoSO_4.K_2SO_4.6H_2O$.	0.30 to 12.06 moles of $CoSO_4$ to 1 mole of K_2SO_4.	Greatest.
$ZnSO_4.K_2SO_4.3H_2O$.	0.19 to 21.30 moles of $ZnSO_4$ to 1 mole of K_2SO_4.	Intermediate.
$MnSO_4.K_2SO_4.4H_2O$.	1.50 to 10.40 moles of $MnSO_4$ to 1 mole of K_2SO_4.	Decomposed.

According to the electro-chemical series the order of the four metals in the direction of decreasing electronegativeness is Mn, Zn, Co, and Ni. A study of the above summary indicates that a classification according to Caven's Hypothesis would give a different order for the sulphates as regards power of forming double salts.

If the power of retaining water in the molecule is an indication of the power to form double salts, manganese sulphate has the least affinity since the double sulphate is only tetrahydrated. This is also supported by the fact of the relatively large amount of manganese sulphate (1.50 mole of $MnSO_4$ to 1 mole of K_2SO_4.) which must be present in solution before double salt begins to appear. From the basis on which the hypothesis is founded it follows that the greater the affinity between the component salts the earlier the double salt will make its appearance. A study of the data in this respect gives the order, in the direction of increasing affinity, manganese sulphate (1.50 moles to 1 mole of K_2SO_4.), cobalt sulphate (0.30 moles to 1 mole of K_2SO_4.), zinc sulphate (0.19 moles to 1 mole of K_2SO_4.) nickel sulphate (0.031 moles to 1 mole of K_2SO_4.). This order is confirmed by an examination of the solubilities of the double sulphates, these being a measure of the stabilities of the double salts, the least soluble being the most stable. Nickel potassium sulphate is least soluble, zinc potassium sulphate next, followed by cobalt potassium sulphate, manganese potassium sulphate being decomposed by water.

Thus, while the difference in electronegative character, and therefore of affinity, between the alkali metal potassium and the four bivalent metals is given by the electro-chemical series in the order manganese $<$ zinc $<$ cobalt $<$ nickel, the difference in basigenic character as shown by the double sulphates is in the order manganese $<$ cobalt $<$ zinc $<$ nickel.

As only one ammonium system was investigated no conclusions as regards the influence of the bivalent metallic sulphates can be reached.

The following (Table XXII) is a summary of the results for the sodium salts:-

Table XXII.

Double Salt. ::::::::::	Range of Formation. At 0° C.	 At 25° C.	Solubility. ::::::::::
$CuSO_4.Na_2SO_4.2H_2O$.	Not formed.	0.38 to 1.31 moles of $CuSO_4$ to 1 mole of Na_2SO_4.	Least.
$MnSO_4.Na_2SO_4.2H_2O$.	Not formed.	0.84 to 6.83 moles of $MnSO_4$ to 1 mole of Na_2SO_4.	Greatest.
$ZnSO_4.Na_2SO_4.4H_2O$.	Not formed.	0.59 to 6.28 moles of $ZnSO_4$ to 1 mole of Na_2SO_4.	Intermediate

According to the electro-chemical series the order of the metals in the direction of decreasing electronegativeness is manganese, zinc, copper. Other considerations, however, suggest a different order for the sulphates, for copper sulphate is only pentahydrated whereas zinc sulphate is heptahydrated. Thus the order of increasing power of forming double sulphates might be manganese sulphate, copper sulphate, zinc sulphate.

At first sight the evidence seems to confirm the order as given by the electro-chemical series. Zinc sodium sulphate is more soluble than copper sodium sulphate and makes its appearance later at 25°C. (0.59 moles $ZnSO_4$ to 1 mole Na_2SO_4 compared with 0.38 moles $CuSO_4$ to 1 mole Na_2SO_4.).

On more particular examination this evidence is discounted for the degree of hydration of the double sulphates is different. The zinc salt is tetrahydrated while the copper salt is dihydrated. This indicates that zinc sulphate has a greater power of forming a double sulphate than copper sulphate in spite of the fact that copper is much less electropositive than zinc.

Copper sodium sulphate and manganese sodium sulphate are both dihydrated, and the copper salt is less soluble than the manganese salt, and is therefore more stable. Thus the order of the three sulphates as regards increasing affinity or increasing power of forming double sulphates is manganese sulphate, copper sulphate, zinc sulphate.

To sum up it may be suggested that, while the bivalent metallic sulphates may influence the composition of the double salt, the determining factor as to whether double salt is formed or not is the alkali sulphate. Thus, while lithium sulphate does not form double sulphates even with the sulphates of metals widely separated from lithium in the electro-chemical series, sodium, which is next to lithium in the series, forms a series of double sulphates with the bivalent metallic sulphates. The difference between sodium and potassium sulphates is shown by the non-formation of the sodium double sulphates at 0° C., these making their appearance only at temperatures considerably above

0° C. Ammonium and potassium sulphates are distinguished mainly by the difference in the degree of hydration of certain of their analogous double sulphates.

The effect of the bivalent metallic sulphates is mainly seen in the earlier or later appearance and lesser or greater solubility of the double sulphates. Thus the greater the basigenic difference between the alkali sulphate and the bivalent metallic sulphate the earlier the appearance of the double salt and the greater its insolubility. Their effect may also be traceable in the degree of hydration of the double sulphate, and this aspect will now be considered.

C. The Influence of the Water of Crystallization of the Single Salts on the Degree of Hydration of the Double Sulphates.

This aspect must first be considered from the point of view of the alkali sulphates.

Caven and Ferguson (34) showed that "the order of increasing strength of alkali metals, including thallium and ammonium, as regards the power they confer on the rest of the molecule to retain $6H_2O$, is K, Rb, Tl, NH_4, Cs." Sodium was not included in the investigations.

The position of sodium can be fixed from a consideration of the water of crystallization of the double sulphates of the three alkali metals. (Table XXIII.).

Table XXIII..

Degree of Hydration of Alkali Double Sulphates.

::::	Zn..	Co.	Ni.	Cu.	Mn.
NH_4	$6H_2O$.	$6H_2O$.	$6H_2O$.	$6H_2O$.	$6H_2O$.
K.	$6H_2O$.	$6H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
Na.	$4H_2O$.	$4H_2O$.	$4H_2O$.	$2H_2O$.	$2H_2O$.

Thus it is seen that sodium has less power of retaining water in the molecule of the double sulphate than either potassium or ammonium. Therefore sodium comes before potassium in the above series.

Thus as far as the three alkali sulphates investigated are concerned, ammonium sulphate has most, potassium sulphate next, and sodium sulphate least power of retaining water in the molecule of the double sulphate. This power, as already suggested, is probably intimately connected with the power of forming double sulphates, otherwise it is difficult to explain why the double sulphates of sodium sulphate, which is decahydrated, should crystallize with a maximum of 4 molecules of water, while those of ammonium and potassium sulphates, both of which are anhydrous, crystallize with a maximum of 6 molecules of water.

Caven and Ferguson (62), as a result of an extended investigation of the dissociation pressures of double sulphates of the alkali metals with other bivalent metals, have come, among others, to the following conclusions:-

"In the case of the bivalent metals copper, cadmium, and manganese, which do not form heptahydrated sulphates, stable at the ordinary temperature, the order of the vapour pressures of the double salts formed with different alkali metals decreases with the alkali metals in the order, K, Rb, Cs."

"In the case of the bivalent metals cobalt, nickel, zinc, ferrous iron, and magnesium which form heptahydrated sulphates the order is K, Cs, Rb."

They conclude from these facts that "it is only in cases in which the alkali metal is instrumental in causing a larger proportion of water to be retained in the double salt than can be retained by the sulphate of the bivalent metal alone that the order of decreasing vapour pressure is the order of increasing metallic intensity of the alkali metals. In other cases the order of alkali metals instead of being K, Rb, Cs is K, Cs, Rb, that is to say there is not a complete reversal of the order, but reversal only as regards Rb and Cs."

In view of the above it is interesting to see if there is any difference between the double sulphates of copper, cadmium, manganese and those of the other bivalent metals.

The double sulphates of ammonium with copper, cadmium, manganese, cobalt, nickel, zinc, ferrous iron, and magnesium are all hexahydrated.

The potassium double sulphates of the following bivalent metals are hexahydrated, copper, cobalt, nickel, zinc, ferrous iron, and magnesium.

Potassium manganese sulphate is tetrahydrated, and Tutton (63) was unable to obtain potassium cadmium sulphate in the hexahydrated form.

Koppel and his collaborators (1) have shown that the sodium double sulphates of cobalt, nickel, zinc, ferrous iron, and magnesium are all tetrahydrated, while those of copper and cadmium are dihydrated; moreover, as a result of this investigation, it has been shown that manganese sodium sulphate is also dihydrated.

The above facts are summarized in Table XXIV.

[illegible]

[illegible] a study of the above summary it is seen, in confirmation of the conclusions of Caven and Ferguson, that there is a distinct difference between copper, cadmium, and manganese sulphates, and the sulphates of the other bivalent [illegible], cobalt, nickel, zinc, ferrous iron, and magnesium. [illegible] difference is first shown in the degree of hydration of [illegible] salts, and is also apparent in the degree of hydration [illegible] double salts. This influence is not apparent in the [illegible]

[illegible]

Table XXIV.

Single Salts.		Hydration of Double Salts.		
Salt.	Hydration.	NH_4.	K.	Na.
$CoSO_4$.	$7H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
$NiSO_4$.	$7H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
$ZnSO_4$.	$7H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
$FeSO_4$.	$7H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
$MgSO_4$.	$7H_2O$.	$6H_2O$.	$6H_2O$.	$4H_2O$.
$CuSO_4$.	$5H_2O$.	$6H_2O$.	$6H_2O$.	$2H_2O$.
$MnSO_4$.	$4H_2O$.	$6H_2O$.	$4H_2O$.	$2H_2O$.
$CdSO_4$.	$\frac{8}{3}H_2O$.	$6H_2O$.	?.	$2H_2O$.
:::	:::	:::	$6H_2O$,	:::
:::	:::	:::	(unknown).	:::

From a study of the above summary it is seen, in confirmation of the conclusions of Caven and Ferguson, that there is a distinct difference between copper, cadmium, and manganese sulphates, and the sulphates of the other bivalent metals, cobalt, nickel, zinc, ferrous iron, and magnesium. This difference is first shown in the degree of hydration of the single salts, and is made apparent in the degree of hydration of the double salts. This influence is not apparent in the ammonium double salts, but is first shown in the potassium double salts, and is brought out most sharply in the sodium double salts.

Thus it may be concluded that, while the degree of hydration of the bivalent metallic sulphates influences the degree of hydration of the double sulphates to a considerable extent, the alkali sulphate has the greater influence, and is indeed the deciding factor. This is to be expected as the power of forming double sulphates lies mainly with the alkali sulphates

D. Solvation.

Though the evidence adduced indicates the presence of complex ions in solution, there is nothing to show whether these ions are hydrated or not. In the solid state part of the water may be regarded as attached to the bivalent metallic radical, and part to the sulphate ion, thus, $M'_2[M''(4OH_2)][SO_4.OH_2]_2$. If the sulphate ion is hydrated in each case, then the single and double salts may be represented as follows,

$[Ni(6OH_2)][SO_4.OH_2]$.	$[Mn(3OH_2)][SO_4.OH_2]$.
$(NH_4)_2[Ni(4OH_2)][SO_4.OH_2]_2$.	$(NH_4)_2[Mn(4OH_2)][SO_4.OH_2]_2$.
$K_2[Ni(4OH_2)][SO_4.OH_2]_2$.	$K_2[Mn(2OH_2)][SO_4.OH_2]_2$.
$Na_2[Ni(2OH_2)][SO_4.OH_2]_2$.	$Na_2[Mn][SO_4.OH_2]_2$.

Thus the presence of the alkali ion causes the bivalent metallic radical to be hydrated to a less degree than in the single salt. The ammonium ion has least effect, potassium ion next, (as shown by the manganese double sulphate), and the sodium ion most. Indeed the effect of the sodium ion is so great that in certain of the double sulphates (those of manganese, copper, and cadmium.) the bivalent metallic radical is not hydrated at all.

E. General Considerations.

A discussion of the results from a general point of view raises several very interesting points.

A study of the potassium systems brings out several noteworthy facts. Thus it is found that the double sulphates of potassium with nickel, cobalt, and zinc all crystallize with 6 molecules of water, and are formed from solution over a very wide range as regards temperature and relative concentration of the constituent salts. Indeed it is particularly noteworthy that these double salts can be obtained from solutions containing an extraordinary small amount of the bivalent metallic sulphate. Moreover, these double salts are not decomposed by water, isothermal evaporation, not only of equimolecular solutions but of solutions whose composition is represented by points widely separated from the equimolecular line, resulting in the double salts as the first product.

The manganese system is sharply distinguished from the others. The double salt crystallizes with only 4 molecules of water, and the range of formation as regards relative concentration of the constituent salts is much smaller. The remarkable fact is the large amount of manganese sulphate which must be present before double salt makes its appearance. Thus the double salt is decomposed by water at both 0° and 25° C., the first product of isothermal evaporation of an equimolecular solution being potassium sulphate. It therefore follows that the transition interval for this system is very large.

In no case does the addition of one constituent salt displace the other from solution, the result of such an addition being an increase in solubility of the other component.

Manganese ammonium sulphate crystallizes with 6 molecules of water, and is also formed over a wide range of temperature and relative concentration of the constituent salts. It is not decomposed by water. While the addition of ammonium sulphate increases the solubility of manganese sulphate, manganese sulphate displaces ammonium sulphate from solution both at 0° and 25° C.

Of the series studied in this investigation the sodium double sulphates are of greatest interest. Manganese sodium sulphate and copper sodium sulphate crystallize with 2 molecules of water, while zinc sodium sulphate crystallizes with 4 molecules. They are all decomposed by water at 0° C., and even at ordinary air temperatures. All three are undecomposed by water at 25° C., being formed at this temperature over a comparatively small range as regards relative concentration of the constituent salts.

The transition point for copper sodium sulphate is 16.7° C. and the transition interval is very small possibly 16.7° C. to about 19° C. The transition point for zinc sodium sulphate is 8.7° C. and by interpolation of the solubilities of the single salts that of manganese sodium sulphate is about 8° C. The transition interval for the zinc sodium system is 8.7° C. to 21° C., and for the manganese sodium system, determined by the interpolation of the solubility of sodium sulphate, is about 8° C.

to about 23°C.

A noteworthy point about these double sulphates is the rapid increase in range of formation, as regards relative concentration of the constituent salts, with rise in temperature. This would seem to be partly connected with the corresponding rapid increase in solubility of sodium sulphate.

The solubility of sodium sulphate is increased by addition of each of the bivalent metallic sulphates up to the transition point for the following reaction:-

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O.$$

Above this temperature (32.5°C.) anhydrous sodium sulphate is displaced from solution. Addition of sodium sulphate increases the solubility of copper sulphate, but it displaces both zinc sulphate and manganese sulphate from solution.

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Appendix I.

Graphical Representation of Results.

Various methods can be employed for the graphical representation of isothermal relations in a ternary system. Indeed it is to be deplored that so many different methods have been employed, and therein lies the great difficulty of correlating the results of different investigators.

The results of different investigators have been recorded as,

Grams of salt per 100 grams of solution,
Grams of salt per 100 grams of water,
Grams of salt per 100 ccs. of water,
Gram-moles of salt per 100 gram-moles of water.

Jänecke (64) has also suggested the following method. The total salt is put equal to 100 and the amounts of the two salts, xA and (100 - x)B. A rectangular diagram is used. The amounts of the salts are measured off along the lower side of the rectangle, and of water in the solution associated with 100 parts of total salt, is measured upwards along the side of the rectangle. Britton (65) in an investigation of potassium alum makes use of this system.

In the present investigation two methods of representation are employed.

In the first the results are expressed as grams of salt per 100 grams of solution, and are expressed graphically on the triangular diagram. In the second they are expressed as moles of salt per 1000 grams of water, and are expressed graphically on the rectangular diagram; moles of alkali sulphate on the horizontal co-ordinates and moles of bivalent metallic sulphate on the vertical co-ordinates.

The triangular diagram is based upon the percentage compositions of the solutions, and therefore expresses amounts of the two salts in solution with reference to varying amounts of water; thus certain solubility relationships are not fully brought out. For instance consider the following results for the system manganese sulphate - potassium sulphate - water at 25°C. (Table VI.).

$MnSO_4$.	K_2SO_4.	H_2O.
39.10 gms.	----- gms.	60.90 gms.
39.03 "	0.43 "	60.55 "
38.54 "	1.87 "	59.59 "
38.42 "	2.46 "	59.12 "
38.21 "	3.03 "	58.76 "
37.92 "	4.15 "	57.93 "

It is almost impossible to tell from consideration of the above results or study of the triangular diagram (Figure 11.) whether the solubility of manganese sulphate is increased or decreased by addition of potassium sulphate. This difficulty is obviated when the results are expressed as moles per 1000 grams of water, thus:

$MnSO_4$.	K_2SO_4.
4.252 moles.	----- moles.
4.268 "	0.041 "
4.284 "	0.182 "
4.304 "	0.240 "
4.307 "	0.295 "
4.334 "	0.411 "

(Table VIII.)

A glance at the above, or at the rectangular diagram (Figure 12.), is sufficient to show that the solubility of manganese sulphate is increased by the addition of potassium sulphate.

For this reason the triangular diagram is only used when it is desired to determine the composition of the double salt or of the single salt. In this case the composition of both liquid and moist solid phases are determined, the results expressed as grams per 100 grams of solution, and plotted on the triangular diagram; for example the manganese potassium and manganese sodium systems.

Otherwise all results, including the above, are calculated as moles of salt per 1000 grams of water, and results plotted on the rectangular diagram. Thus the solubilities of the salts are referred to a fixed quantity of water, and all solubility relationships can be seen at a glance, for instance the effect of each single salt on the solubility of the other.

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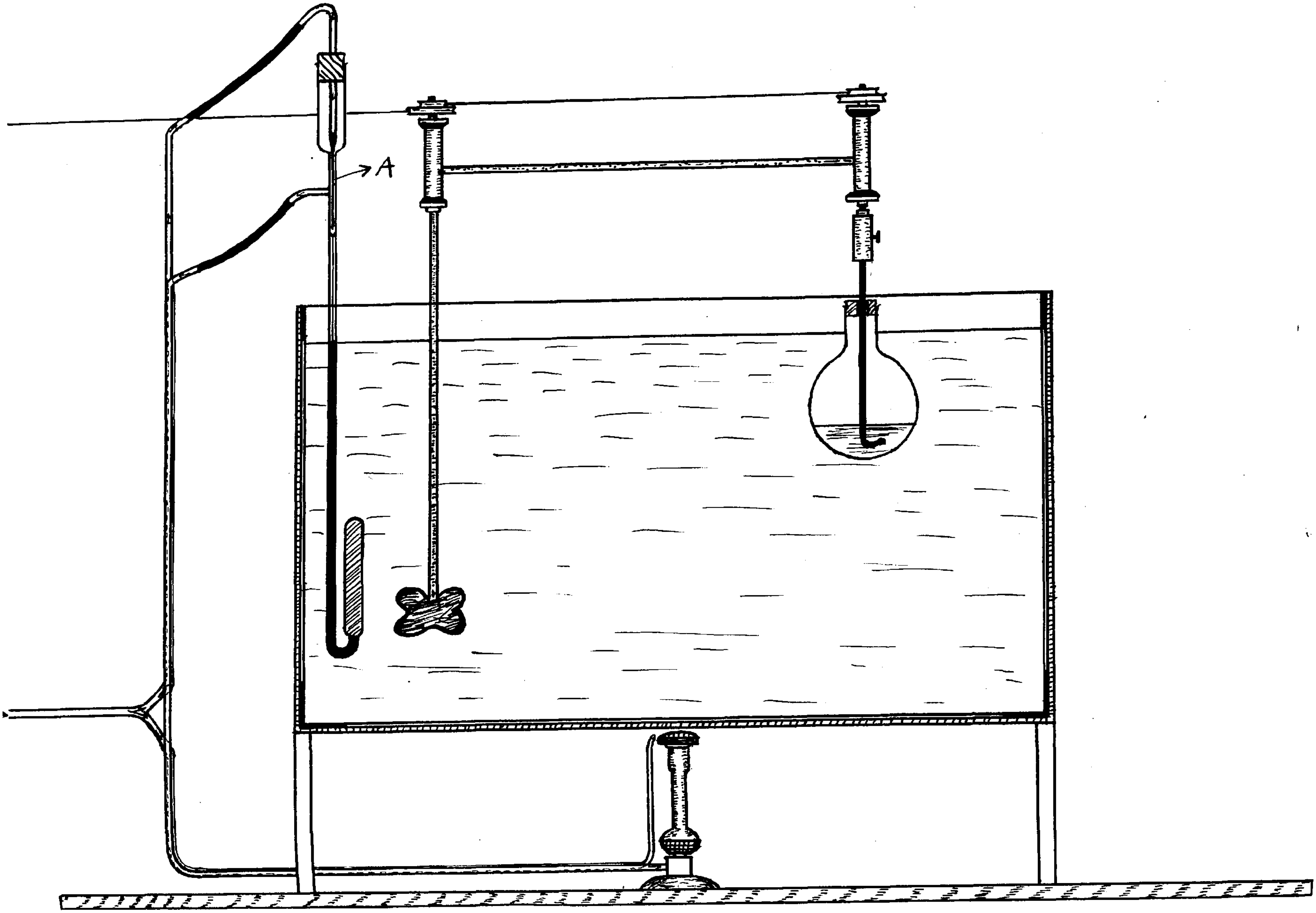


FIGURE 20

Appendix II.

Experimental Apparatus.

Figure 20 shows the thermostat and allied apparatus. The thermostat consists of a galvanized iron tank, externally lined with asbestos sheeting. The capacity of the tank is such that a very large mass of water is required to fill it, and thus temperature variation is reduced to a minimum. The water is kept in circulation by means of a stirrer of the propeller type driven by an electric motor. The source of heat is a gas burner, the supply of gas being controlled by the autoregulator A, which is very sensitive to change in temperature. The large bulb is filled with toluene and the tube with mercury. A by-pass supplies a pilot flame at the side of the burner. The temperature variation lies within the limit ±0.01° C.

The reaction vessel consists of a large wide-necked round bottomed flask. This is immersed in the water up to the neck, the contents being stirred by means of a glass stirrer.

For the abstraction of the liquid phases two types of filtering apparatus are used. The first one, Figure 21, is used for easily filtered liquids in conjunction with granular solid phases, the liquid being filtered through cotton wool. The second, Figure 22, is used for viscous liquids or where the solid phase is present in a very fine state; the buchner funnel gives a wide filtering surface.

Both can be fitted with outer protective vessels so that

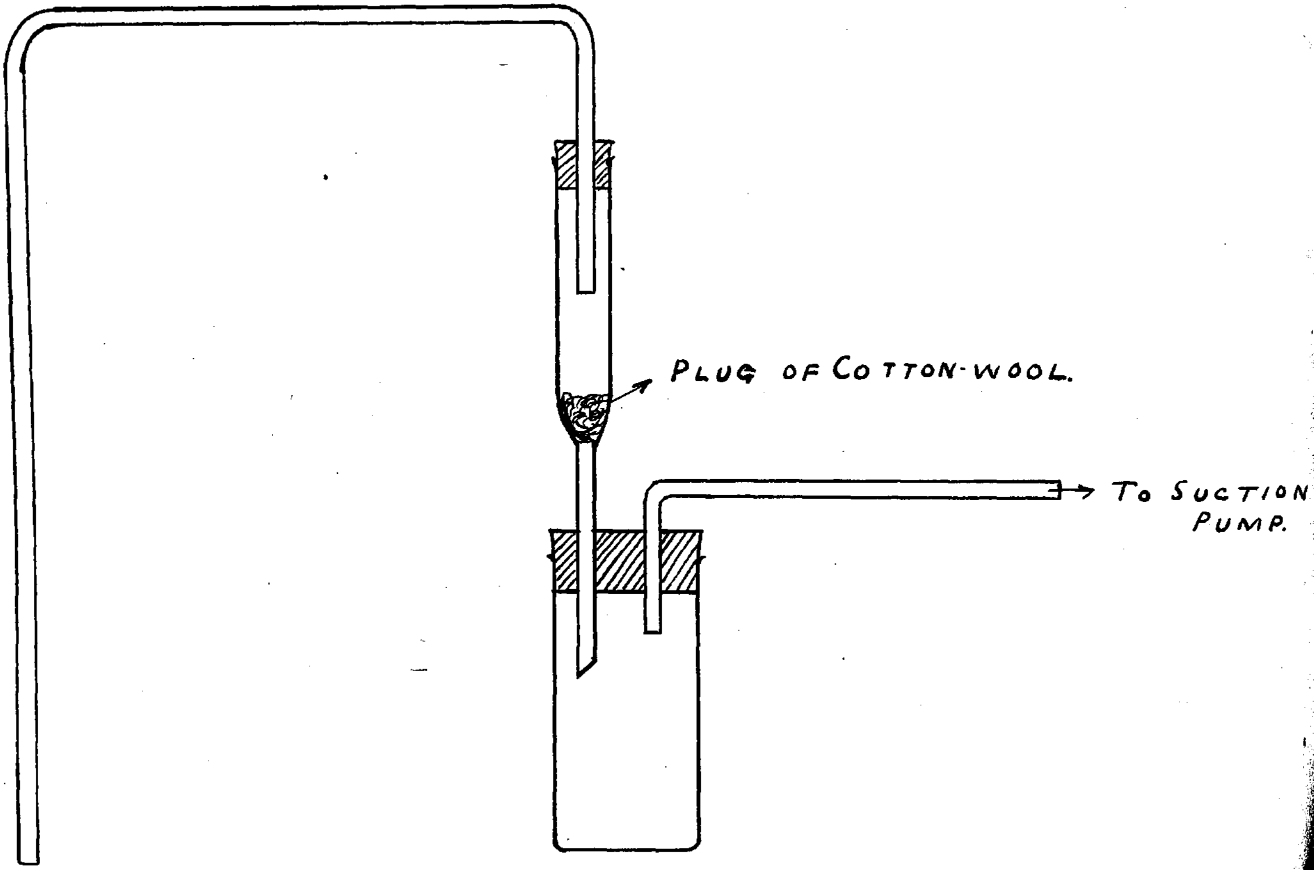


Figure 21.

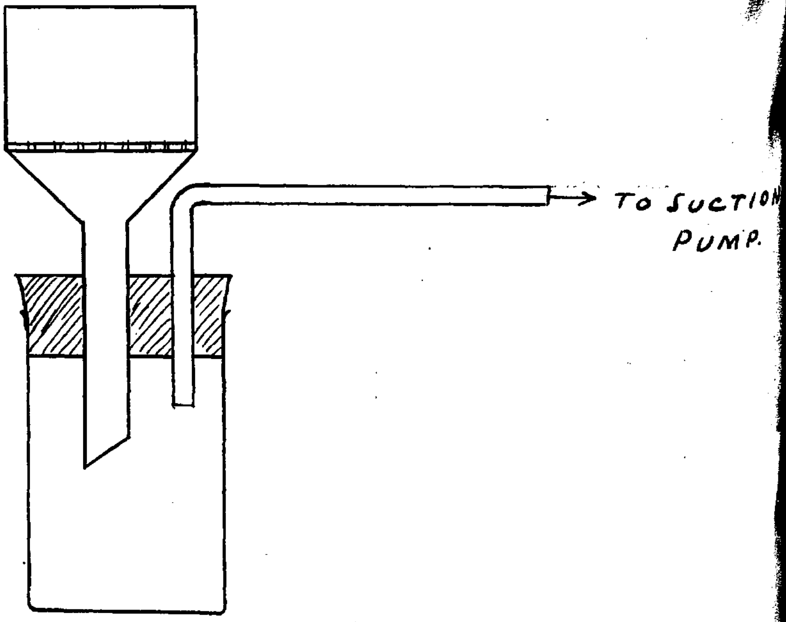
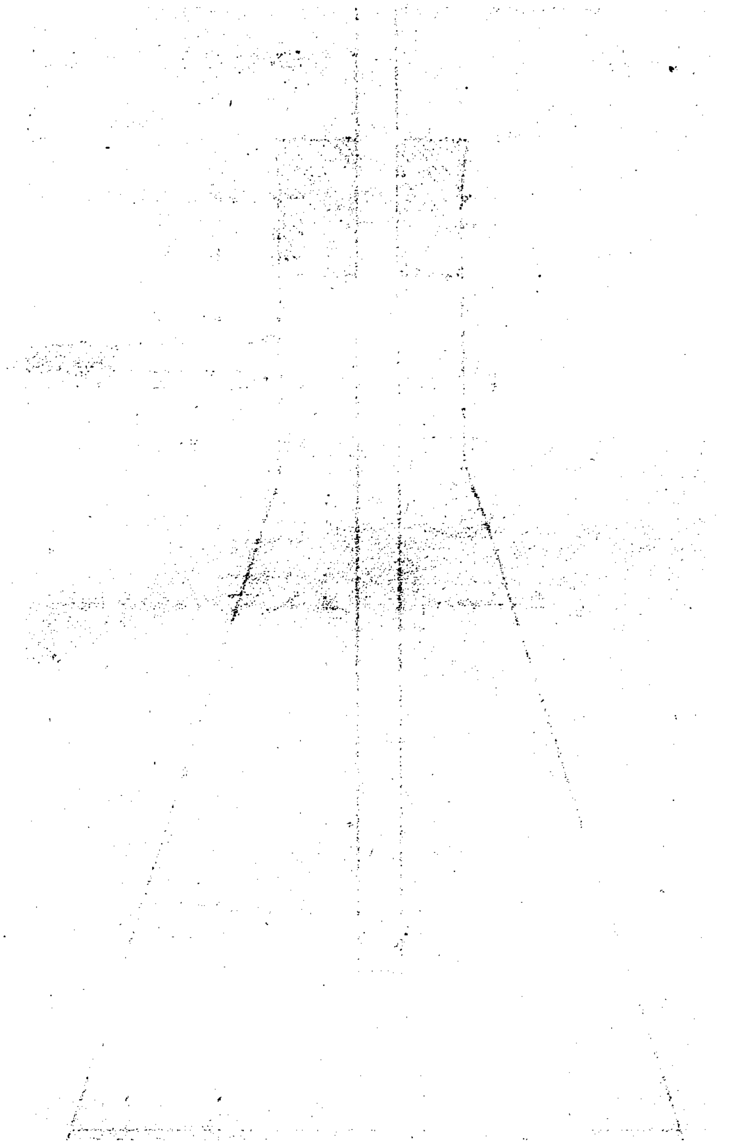


Figure 22.



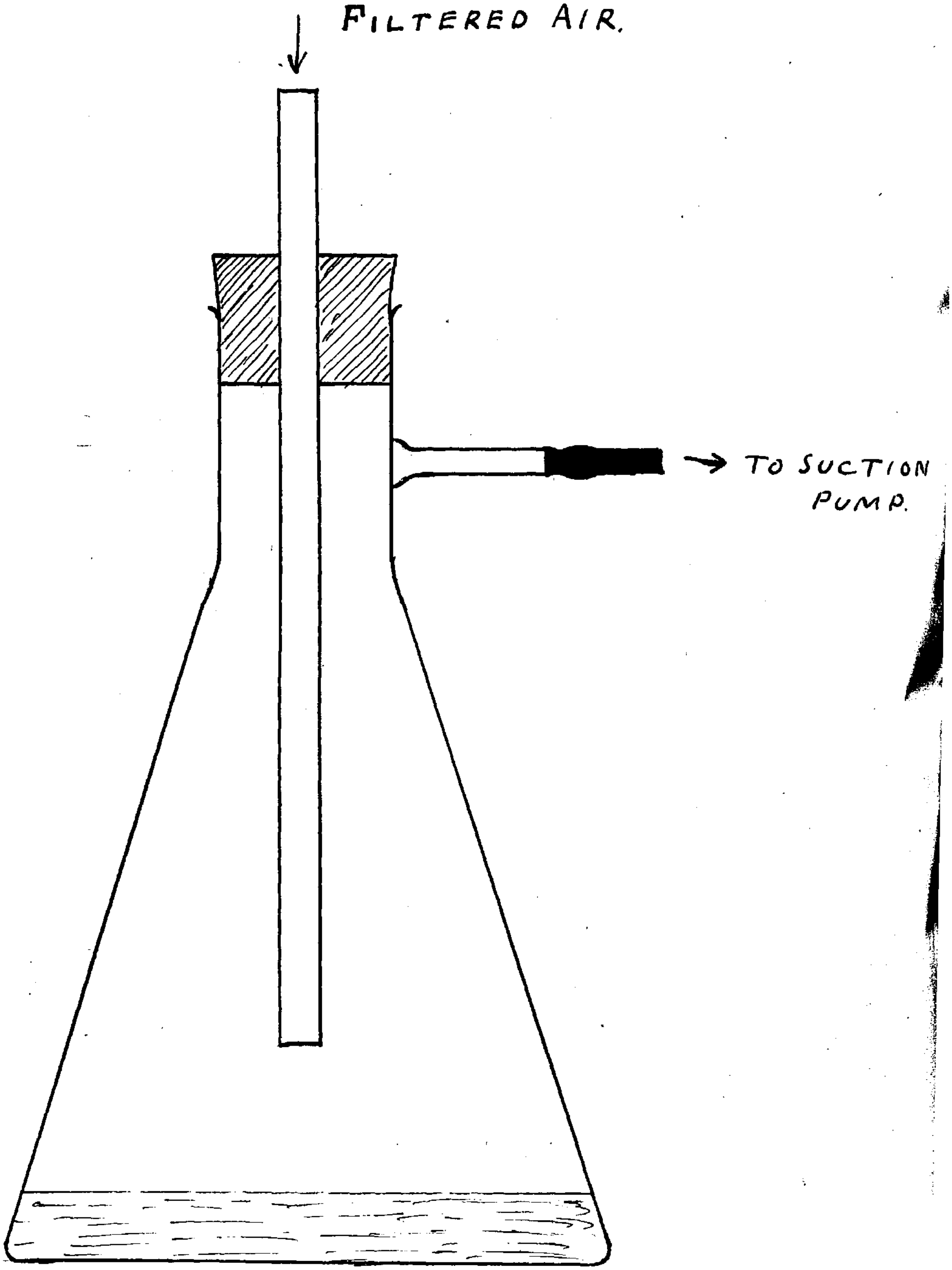


FIGURE 23.

they can be immersed in the thermostat, and allow filtering operations to be carried out at the experimental temperature.

Two methods are used for the abstraction of the solid phases In one case the reaction liquid is rapidly filtered, and a portion of the moist solid phase immediately transferred to a tared weighing bottle. In the other the reaction liquid is simply shaken up and a portion of the mixed liquid and solid phases poured into the tared weighing bottle.

The apparatus shown in Figure 23 is used for the isothermal evaporation of solutions. The air is drawn through cotton wool and bubbled through strong caustic potash solution and concentrated sulphuric acid in order to remove anything deleterious to the solution.

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Appendix III.

Analytical Methods.

To ensure the greatest possible accuracy in the analytical work all the apparatus used was standardized. All weighings were carried out on a sensitive balance with a box of standardized weights. Silica crucibles were used in the determination of total sulphate and other gravimetric estimations where ignition was necessary. The liquid and solid phases in every case were made up to 250 ccs. in accurately standardized flasks, and determinations made on aliquot portions, which were measured out by means of a standard 50 ccs. burette. This standard burette was used throughout for all volumetric work.

All chemicals used were either guaranteed analytical reagents (A.R.) or Merck's reagents.

Estimations.

In all cases total sulphate was determined, and in all but one - the ammonium-manganese system - bivalent metal was also estimated. Thence the amount of bivalent metallic sulphate was calculated, and by subtraction from total sulphate the amount as alkali sulphate was obtained. (In the above exception the only difference was that ammonia was estimated and ammonium sulphate calculated; bivalent metallic sulphate was then obtained by difference). The following is a typical calculation.

Typical Calculation.

Weight of solution. 17.67 gms.

Made up to 250 ccs.

Total Sulphate.

25 ccs. taken.

Weight of $BaSO_4$. (I) 0.3079 gms. (II) 0.3077 gms.

Average 0.3078 gms.

Determination of Zinc.

50 ccs. taken. 26.80 ccs. potassium ferrocyanide solution required.(1 cc. ≡ 0.001022 gms. of zinc.)

Calculation.

Total Zn. $= 0.001022 \times 26.80 \times 5 = 0.1370$ gms.

" $ZnSO_4$. $= 0.1370 \times 2.469 = 0.3381$ " .

" SO_4. $= 3.078 \times 0.4115 = 1.2660$ " .

SO_4 as $ZnSO_4$. $= (0.3381 - 0.1370) = 0.2011$ " .

SO_4 as K_2SO_4. $= (1.2260 - 0.2011) = 1.0649$ " .

K_2SO_4. $= 1.0649 \times 1.815 = 1.9330$ " .

(N.B. Factors:- $\frac{ZnSO_4}{Zn} = 2.469$; $\frac{SO_4}{BaSO_4} = 0.4115$; $\frac{K_2SO_4}{SO_4} = 1.815$)

From 17.67 gms. of solution 1.933 gms. K_2SO_4.

" 100 gms. " " $\frac{1.933 \quad 100}{17.67}$ gms. of K_2SO_4.

= 10.94 " " " .

From 17.67 gms. of solution 0.3381 gms. $ZnSO_4$.

" 100 gms. " " $\frac{0.3381 \quad 100}{17.67}$ gms. of $ZnSO_4$.

= 1.91 " " " .

Therefore, percentage composition of solution is as follows:-

K_2SO_4.	$ZnSO_4$.	H_2O.
10.94	1.91	87.15

$$\text{Moles of } K_2SO_4 \text{ per 1000 gms. of } H_2O = \frac{10.94 \times 1000}{174.2 \times 87.15}$$

$$= 0.721 \text{ moles.}$$

$$\text{Moles of } ZnSO_4 \text{ per 1000 gms. of } H_2O = \frac{1.91 \times 1000}{161.4 \times 87.15}$$

$$= 0.136 \text{ moles.}$$

-:-:-:-:-:-:-:-:-:-:-:-:-:-:-

Determination of Total Sulphate.

The determination of sulphate was carried out as follows:- An aliquot portion of the stock solution was diluted to about 250 ccs. with distilled water, and 2 or 3 drops of concentrated hydrochloric acid added. This solution was heated to boiling, and precipitation of sulphate effected with a boiling $\frac{N}{5}$ barium chloride solution. The barium chloride solution was added drop by drop with stirring. If barium chloride solution was added too quickly so as to be present in excess during the precipitation some barium chloride was carried down with the sulphate. Excess of barium chloride solution was added when precipitation was complete. The solution was allowed to settle on a hot plate until the supernatant liquid was perfectly clear. This liquid was then decanted through a Swiss filter paper, and the precipitate washed out of the beaker by means of a jet of hot water. The precipitate was washed thoroughly with hot water and ignited moist on the filter paper in a silica crucible. There was no reduction of sulphate in the above method as after-treatment with sulphuric acid failed to give any appreciable difference. All determinations were carried out in duplicate, and the following are representative results.

I	II	Difference.	% Difference.
0.4778 g.	0.4776 g.	0.0002 g.	0.04
1.4370 g.	1.4404 g.	0.0034 g.	0.23
1.7232 g.	1.7212 g.	0.0020 g.	0.12
0.2627 g.	0.2625 g.	0.0002 g.	0.08

Estimation of Nickel.

Nickel was estimated by a volumetric method due to Kelly and Conant (38), using diphenyl glyoxime as an indicator.

"In outline the method consists of adding a measured excess amount of standard potassium cyanide solution to an ammoniacal solution of the nickel salt. A quantity of the indicator is then added and the excess potassium cyanide titrated with standard nickel sulphate solution."

In practice the method was as follows:- All titrations were carried out on a volume of 250 ccs., an aliquot portion of the stock solution being taken and diluted to this amount. 5 ccs. of 0.88 ammonia were then added, followed by excess potassium cyanide solution (1 cc. equivalent to 0.001 gm. nickel) and then 5 ccs. of diphenyl glyoxime solution. This solution was obtained by dissolving 1 gm. of diphenyl glyoxime in a solution of 5 gms. NaOH in 100 ccs. of water and diluting to 1000 ccs. The excess cyanide was then titrated with standard nickel sulphate solution.(Approximately 0.001 gms. nickel per 1 cc.). This method was very accurate, results being usually duplicated to within about 0.3%.

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Estimation of Cobalt.

Cobalt was estimated gravimetrically as follows:- The neutral cobalt solution was diluted, if necessary, so that its concentration was 0.1 gm. cobalt to each 50-100 ccs. Precipitation was then brought about in the cold by adding a strong solution of ammonium phosphate in the proportion of 1 to 2 gm. $(NH_4)_2HPO_4$ for every 0.1 gm. of cobalt. At first the the precipitate of cobalt ammonium phosphate was flocculent and amorphous, but after heating at 70-80° C. for some time it became crystalline and settled well. The solution was then cooled to room temperature, filtered, and the precipitate washed with cold distilled water. It was then dried at 100° C., ignited on the filter paper in a silica crucible, and weighed as cobalt pyrophosphate $Co_2P_2O_7$. The following duplicates illustrate the accuracy of the method.

Weight of Pyrophosphate.

I	II
0.2854 g.	0.2850 g.
0.2332 g.	0.2338 g.
0.4954 g.	0.4966 g.
0.1128 g.	0.1130 g.
0.1093 g.	0.1089 g.

....

Estimation of Zinc.

Zinc was determined by means of standard potassium ferrocyanide solution using uranium acetate solution as external indicator.

An aliquot portion of the solution was placed in a 500 ccs conical flask, 10 ccs. of a 5% ammonium chloride solution and 10 ccs. of concentrated hydrochloric acid added, and this diluted to about 200 ccs. The resulting solution was then heated to about 80° C., and titrated with standard potassium ferrocyanide solution until a drop gave a permanent brown colour with uranium acetate solution. A blank experiment, in the absence of zinc, was performed under the above conditions to determine the volume of ferrocyanide solution required to give a standard brown colour with uranium acetate.

The ferrocyanide was standardized against a standard zinc sulphate solution.

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Estimation of Manganese.

Manganese was estimated volumetrically with potassium permanganate solution by the Volhard method. This method depends primarily upon the following reaction:-

$$2KMnO_4 + 3MnSO_4 + 2H_2O \quad = \quad 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Owing, however, to the acidic function of hydrated manganese dioxide, the reaction is variable, and therefore not quantitative If, however, a base is present to combine with the manganese dioxide all the manganese is precipitated in a form corresponding to this degree of oxidation, and the reaction is a quantitative one. A suitable base is provided by zinc sulphate.

The usual procedure is as follows: An aliquot portion of the manganese sulphate solution is placed in a large flask, and 50 ccs. of a 20% zinc sulphate solution added. A few drops of concentrated nitric acid are added; this is supposed to cause the precipitate to settle better. The solution is then diluted to about 250 ccs., heated to boiling, and titrated whilst hot with decinormal permanganate solution till a permanent pink tint developes.

Immediate difficulty was met with when the above method was tried out. A thin dark brown layer formed on the side of the flask, and some of the precipitate remained suspended in the liquid in a very fine state. This rendered it difficult to reach a definite end point, and impossible to obtain reasonable duplicates. After considerable experiment the following optimum conditions were evolved.

An aliquot portion of the manganese sulphate solution was diluted to about 250 ccs. in a glass beaker, and 4 grams of solid zinc sulphate added. The solution was then heated to boiling and titrated with decinormal permanganate solution, <u>without</u> addition of nitric acid. During titration the liquid was continuously stirred. A rough titration to within 1 cc. was first carried out, and then repeated very carefully in duplicate. Near the end point the precipitate settled very quickly and completely leaving a clear supernatant liquid, and thus the end point could be determined with great exactitude, a drop of permanganate being sufficient to give a definite pink tint. The accuracy of this method is shown by the following results of experiments carried out with manganese sulphate solutions of known strength:-

Manganese Sulphate ($MnSO_4$).

Present.	Found.
4.684	4.690
5.922	5.914
2.345	2.340
1.266	1.263
0.454	0.454

....

Estimation of Ammonia.

Ammonia was estimated by the well-known distillation method. An aliquot portion of the ammonia solution was heated with excess caustic soda solution, and the liberated ammonia absorbed in an excess of normal sulphuric acid. The excess sulphuric acid was then titrated with standard sodium hydroxide, using methyl red as an indicator.

……………………………

[illegible]

[illegible] of nitrogen. Finally a little urea was added and the solution boiled again to destroy nitrous acid,

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + 2N_2.$$

The solution was then diluted to 250 ccs. in a standard flask. An aliquot portion was placed in a conical flask, sodium carbonate added to give a faint permanent precipitate, and the precipitate dissolved with a little acetic acid. A few crystals of potassium iodide were then added, and the dark brown liquid titrated with the standard sodium thiosulphate solution, the titration being finished in the presence of starch solution.

For the estimation of copper aliquot portions of the [illegible] solutions were taken, [illegible] acetic acid, and the titration [illegible]

Estimation of Copper.

Copper was estimated iodometrically. The following was the procedure:-

A decinormal solution of sodium thiosulphate contains 24.82 gms. per litre, but its solution is decomposed by carbon dioxide dissolved in the water. So a solution slightly stronger than decinormal was prepared, and allowed to stand for several days before being standardized.. It was then standardized against pure copper, the copper solution being prepared as follows:

A weighed quantity of pure copper foil was dissolved in a little concentrated nitric acid, the solution boiled to expel oxides of nitrogen. Finally a little urea was added and the solution boiled again to destroy nitrous acid,

$$2HNO_2 + Co(NH_2)_2 = 3H_2O + CO_2 + 2N_2.$$

The solution was then diluted to 250 ccs. in a standard flask. An aliquot portion was placed in a conical flask, sodium carbonate added to give a faint permanent precipitate, and this precipitate dissolved with a little acetic acid. A few crystals of potassium iodide were then added, and the dark brown liquid titrated with the standard sodium thiosulphate solution, the titration being finished in the presence of starch solution.

In the estimation of copper aliquot portions of the copper sulphate solutions were taken, a little sodium carbonate added, followed by acetic acid, and the titration completed as above.

The following results indicate the accuracy of the method:-

Copper Sulphate ($CuSO_4$).

Present.	Found.
21.84 gms.	21.92 gms.
10.20 " .	10.17 " .
19.79 " .	19.71 " .
31.33 " .	31.40 " .
5.63 " .	5.60 " .

……

[illegible] } [illegible] moles.   0.5[illegible] } 0.748 } 0.7[illegible] moles.

K_2SO_4.

[illegible] [illegible]	[illegible] moles.	0.380 0.382	0.381 moles.

K_2SO_4.

[illegible] [illegible]	[illegible].378 moles.	0.388 0.380	0.38[illegible] moles.
[illegible] [illegible]	3.529 moles.	0.177 0.181	0.179 moles.

[illegible] [illegible]	[illegible].344 moles.	0.[illegible] 0.[illegible]	0.338 moles.
[illegible] [illegible]	[illegible] moles.	0.[illegible] 0.[illegible]	0.[illegible]
[illegible] [illegible]	[illegible] moles.	0.[illegible] 0.[illegible]89	0.[illegible]

Duplicates.

All estimations were done in duplicate and the following results taken at random from different systems are typical.

$NiSO_4$.

0.819 0.823	0.821 moles.
2.820 2.828	2.824 moles.

$CoSO_4$.

1.093 1.097	1.095 moles.

$ZnSO_4$.

0.377 0.379	0.378 moles.
3.524 3.534	3.529 moles.

$MnSO_4$.

1.541 1.547	1.544 moles.
3.620 3.627	3.624 moles.
0.504 0.508	0.506 moles.

K_2SO_4.

0.212 0.216	0.214 moles.
0.741 0.745	0.743 moles.

K_2SO_4.

0.360 0.362	0.361 moles.

K_2SO_4.

0.386 0.390	0.388 moles.
0.177 0.181	0.179 moles.

K_2SO_4.

0.990 0.998	0.994 moles.
0.255 0.259	0.257 moles.
0.781 0.789	0.785 moles.

$MnSO_4$.

1.861	1.868 moles.
1.875	

$CuSO_4$.

1.045	1.047 moles.
1.049	
1.454	1.457 moles.
1.460	
1.207	1.209 moles.
1.211	

$ZnSO_4$.

2.518	2.521 moles.
2.523	
1.224	1.226 moles.
1.228	

$MnSO_4$.

3.410	3.413 moles.
3.415	
1.536	1.536 moles.
1.536	
0.976	0.980 moles.
0.984	
1.600	1.602 moles.
1.604	

$(NH_4)_2SO_4$.

0.530	0.531 moles
0.532	

Na_2SO_4.

0.435	0.440 moles.
0.445	
1.105	1.109 moles.
1.113	
1.175	1.177 moles.
1.179	

Na_2SO_4.

0.490	0.492 moles.
0.493	
2.083	2.087 moles.
2.091	

Na_2SO_4.

0.56I	0.566 moles.
0.571	
2.102	2.108 moles.
2.114	
3.059	3.063 moles.
3.067	
2.140	2.144 moles'
2.148	

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Appendix IV.

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