SOME SOLUBILITY ISOTHERMS
OF SYSTEMS OF THE TYPE $R_2SO_4 - Al_2(SO_4)_3 - H_2O$
WHERE R = Li, Na, K, NH_4 or Tl.

and

SOME REACTIONS OF PROPENYLPHENYL KETONE
WITH SEMICARBAZIDES AND THIOSEMICARBAZIDES

BEING THESES SUBMITTED TO THE SENATE
OF GLASGOW UNIVERSITY IN COMPLIANCE
WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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The [illegible]

Governors [illegible] Royal [illegible] College [illegible]

Assistant[illegible] Industrial [illegible]

scholarship [illegible]

he has pleasure in recording his best thanks.

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INTRODUCTION

This thesis gives an account of the equilibrium conditions of the following systems:

Na_2SO_4 -$Al_2(SO_4)_3$ -H_2O at 0°C and 25° C
K_2SO_4 " " " " " "
$(NH_4)_2SO_4$ " " " " " "
Tl_2SO_4 " " " " " "
Li_2SO_4 " " " " " 30° C

The work has been described under four general headings:- Theoretical, The Systems, a General Discussion of Results, and an Appendix.

In the Theoretical portion the theories of double salt formation are reviewed.

The Systems, under that heading, are then treated separately and the results obtained in each system dealt with briefly.

Under the section described: General Discussion of Results, the experimental results are discussed in relation to one another, and their bearing on the theory of practically complete dissociation of electrolytes in solution.

In the Appendix is given a description of the analytical methods employed, a development of the Debye theory of the solubility of strong electrolytes, and a bibliography.

THEORETICAL.

When two salts with a common ion are dissolved in water and crystallisation occurs from the solution, the product obtained may be

(1) mixed crystals,
(2) a solid solution,
(3) a double salt, or
(4) a complex salt.

These types are distinguishable from one another.

In the case of mixed crystals the independent crystals may be separated mechanically. When a solid solution is formed there can be no mechanical separation, and the composition of the crystalline mass is dependent on the concentrations of the component salts. Further, when recrystallised the composition of the product changes.

When a double salt is formed the crystals may be recrystallised at the same temperature without change of composition. They may be crystallised from solutions containing one or other component in excess, without altering the composition of the crystals in any way. Solutions of double salts give the reactions of the component salts.

A complex salt formation can be distinguished from the former cases in that the crystals can be recrystallised without change of composition, but solutions of the crystals do not give the reactions of the original solutes.

It is with double salt formation that we have to deal.

Double salts have long been known. Berzelius in 1812 cited potassium alum in support of his dualistic theory, whilst Graham used alkali double sulphates in his investigation on water of crystallisation.

The conditions governing the formation of this class of salts, however, were very little understood. It was known, for example, that if certain salts were dissolved in water in equimolar proportions double salts were formed. That double salts could be formed by using other than equimolar proportions, whilst reported by Schreinemakers (1),was not generally known, and even today there seems to be some ignorance on this point.

Up to the time of van't Hoff there had been no outstanding attempt to explain the formation of these compounds; but van't Hoff, using the technique of the ionic theory of Arrhenius, offered in his "Doppelsalz Bildung and Spaltung" rational explanations of many of the phenomena associated with this type of compound.

Influence of the Ionic Groups.

At the outset it is apparent that the metals forming the salts as well as the acidic radicles have a large influence in the formation of the double salts. For example, sodium chloride forms no double salt with sodium nitrate, yet, sodium nitrate forms a double salt with sodium sulphate, thus shewing that the character of the acidic radicle has some bearing on double salt formation.

The influence of the metallic radicle is evident in the case of ferrous sulphate, magnesium sulphate and ammonium sulphate. Ferrous sulphate does not form a double salt with magnesium sulphate, yet forms one with ammonium sulphate, i.e. Mohr's salt. Also ferric chloride and sodium chloride form no double salt, whilst ferric chloride and potassium chloride do so. Thus it may be assumed that there must be a definite affinity between the two metallic ions for double salt formation to take place.

Difference in affinity between various substances was explained by Berzelius as due to the substances being charged with varying quantities of electricity, and on such a basis, he arranged the then known elements in a series in which the gradation, with respect to the electric character, was from positive to negative. This really showed a transition from metal to non-metal.

This method culminated in the electro-chemical series, in which the metals are arranged in the order of magnitude of the potentials developed when they are placed in solutions of their salts. The series may be written:

Cs Rb K Na Li 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 also represents for the metals the power of displacing other metals from salt solutions, so that any chosen metal can displace from solutions of a metal which follows it in the list, an equivalent weight of that metal.

It is also probable that combination is most likely to occur between elements widely separated in the above series; - and this may apply, to a limited extent, to compounds of these metals - particularly compounds of the same type, e.g. K_2SO_4 $FeSO_4$ etc.

Formation of Ionic complexes in solution.

Kendall and his co-workers (2) in U.S.A. have developed this point of view to a great extent. They have applied this generalisation to compound formation between elements, between molecular complexes formed between solutes and solvents, and to dissociation and order of solubility. These contentions are, in the main, well upheld by published data, but, as might be expected, there are numerous exceptions.

Support of the generalisation is furnished by work of Forbes (3) who determined the solubility of silver chloride in aqueous solutions of various chlorides.

It would be expected, if by this generalisation complex ions tend to be formed according to the difference of positions of the metals in the electro chemical series, that variations in solubility of a salt in the presence of another with a common acidic radicle would bear some relation to these differences. This was found to be the case to a great extent, and the experimental results showed that the order of the increase of solubility of silver chloride with the various influencing salts was H $<$ Ca $<$ Na $<$ Sr $<$ Ba $<$ K or NH_4.

With respect to the sulphates of the alkali metals, it is suggested by Caven, Ferguson and Mitchell (4) that a definite order of the power of forming double sulphates exists. According to their view the chemical affinities of the salts are associated with, or may be interpreted in terms of their degrees of electrolytic dissociation at equivalent dilution.

When the degrees of dissociation are plotted as ordinates against the concentrations in molecular equivalents from data given in Kohlrausch's "Electrical Conductivity", it is seen Fig. 1 that there is a different order of dissociation for each metallic sulphate.

Dissociation Figures.

(Kohlrausch's Electrical Conductivity)

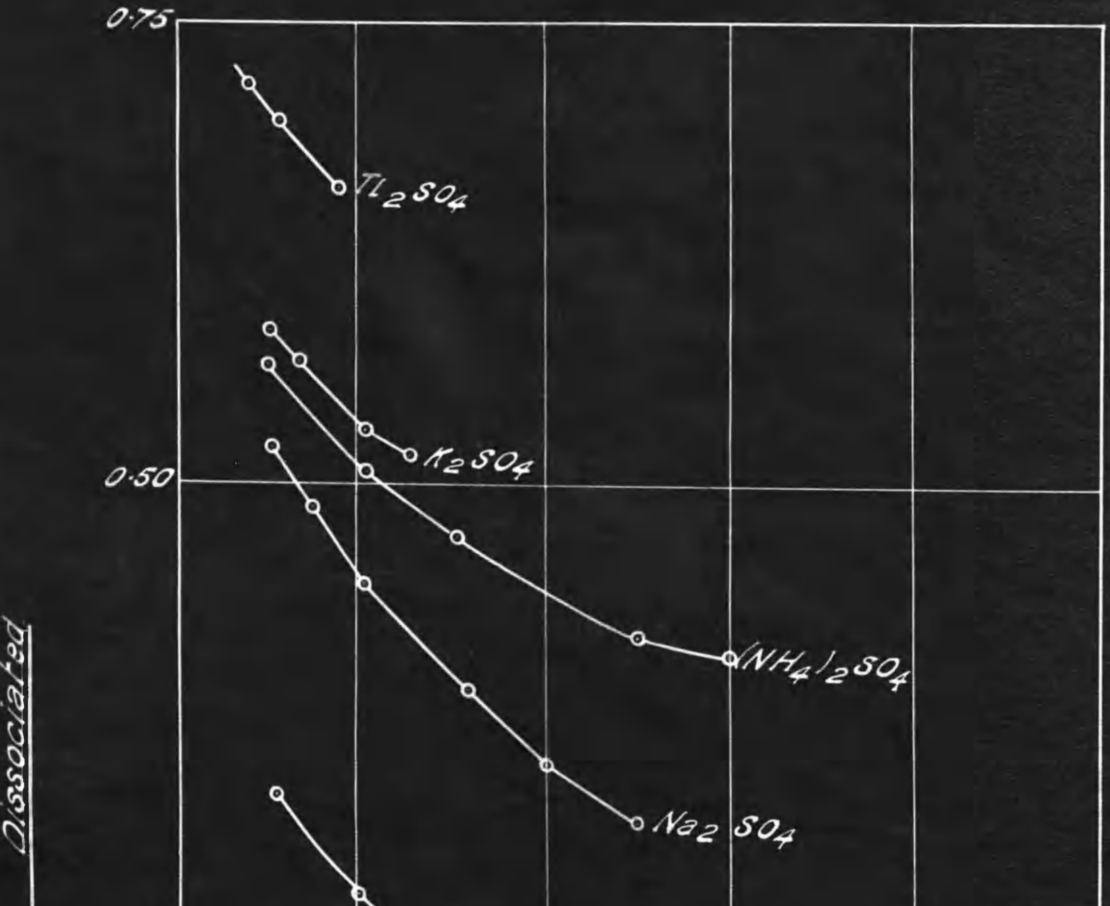

Fig. I.

According to these data, the order of decreasing affinity would be Tl, K, NH_4, Na, Li.

As regards the bearing of these results on double salt formation it is argued that whilst thallium, potassium, ammonium and sodium sulphates provide sufficient SO_4'' ions, in varied states of dilution, to bring about union with the sulphate of a bivalent or trivalent metal, to form metallic complexes which can combine with say alkali cations to form double salts,

$$\text{e.g.}\quad Cu\ SO_4 + ''SO_4 \rightarrow [Cu\ (SO_4)_2]''$$

$$Al_2(SO_4)_3 + ''SO_4 \rightarrow [Al_2(SO_4)_4]''$$

lithium sulphate, by reason of its inferior dissociation, does not produce SO_4'' ions in sufficient quantity for such a union.

Koppel (5) 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 sulphates, e.g. those of Zn, Co, Ni, ferrous iron, Mg, Cu and Cd. He found that the solubility of the sodium sulphate was always increased by the addition of the bivalent sulphate, but the solubility of the bivalent sulphate decreased with the addition of the sodium sulphate. These double sulphates differ greatly from those formed by the other alkali metals.

Lithium sulphate forms no double sulphates, and considering the alkali group, it appears that double salt formation first occurs with sodium.

In the case of the alums, there is an increase in stability and decrease in solubility with increase in basigenic properties of the alkali metals. Lithium forms no alum. Sodium alum is very soluble and 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, but nearly four times as soluble as caesium alum.

Atomic Structure and Dielectic Constant of Medium.

The question why lithium sulphate forms no double salts, may be connected closely with the structure of the lithium atom.

It has been shewn (6) regarding the 'salting out' coefficient of a series of alkali salts, which have the same anion, that the series goes

$$\begin{array}{ccccc} Li & Na & K & Rb. & Cs \end{array}$$

$$\xleftarrow{\qquad\qquad\qquad\qquad} K_{(s)}$$

i.e. there is increase from caesium to lithium. Lithium salts shew the greatest power of precipitating from aqueous solutions, neutral substances like ether, etc., or positive ions, and caesium the least.

The connexion between the salting out effect and atomic structure is made by Hückel, who points out (7) that from an atomistic standpoint, it is clear that the electrical properties of ions cannot be expressed entirely by the assumption that ions are simple spheres, upon which electricity is uniformly distributed - indeed the Bohr theory must be considered for an explanation of the actions of ions on one another in salt solutions. From the Bohr theory, it is evident that the orbits, which electrons describe in an atom, may be deformed to a greater or a less extent when the ion is exposed to intense electrical fields set up by the surrounding ions. In a medium of high dielectric constant such as water (D = 81) this phenomenon will result as a rule in a repulsive, as well as the attractive Coulomb forces between the ions.

As an example (6), consider a charged metallic sphere suspended in air or a vacuum where D = 1. This body will attract another uncharged sphere if brought near, as it will pieces of paper, etc., because it induces opposite charges in these bodies. Thus the neutral bodies on approaching the charged sphere become subject to forces which tend to drive them to the point where the absolute value of the electric field is the greatest. It will be observed that the neutral body becomes polarised and this polarisation always results in an attractive force.

Now if the same experiment were carried out in a medium, the dielectric constant of which was greater than that of the neutral body, it would be found that a repulsive force was exerted between the charged sphere and the neutral body. This would come about by the medium, as well as the neutral body, becoming polarised; but since the medium has a much greater dielectric constant than the neutral body it will be more easily polarised and attracted. Hence molecules of the medium would congregate in the neighbourhood of the charged sphere at the expense of those of the neutral body, thus causing the charged sphere and the neutral body to be forced apart.

According to Hückel a somewhat similar state will hold in an aqueous solution of ions in addition to the primary effects, and he argues that the dielectric constant of the ions depends on the ease with which the outer electronic orbits can be deformed by an electric field. The optical data by Heydweiler, shew that the electron orbits of Cs, for example (8), are more easily deformed than the smaller orbits of lithium ions, and those of lithium less easily than those of sodium, i.e. the lithium ion has the least polarisability of the series.

It may be suggested that this low polarisability of the lithium ion is closely associated with its deficiency in double salt forming properties.

It will be noted that with increase in polarisability, there is increase in the tendency for double salt formation, and this suggests that double salt formation is

(a) a function of size of the electronic orbits of the ion

(b) a function of the dielectric constant of the medium.

The evidence in support of (a) lies in the similarity of the order of the salting out properties, and the double salt forming properties of the metallic ions.

Unfortunately, no experimental evidence can be given in direct support of (b). If we consider that double salts consist of simple ions held together by static influence, it is feasible to believe that formation will commence in solution, i.e. molecular complexes will be formed, and it is evident that the formation of these complexes will depend on the dielectric constant of the solution.

This conception of formation of double salt ions in solution is dealt with later in this paper (page 109) in terms of relative probabilities.

W. Johnston and R. M. Caven have shown that at 25° C, $ZnSO_4$ and $MnSO_4$ form double salts with Na_2SO_4, (9), but not at 0° C. The formation at 25°, is explained on the relative solubility of the double salt, as will be dealt with later, but it is suggested here that the alteration of the dielectric constant of the medium, influences the formation. Further arguments in support of this idea will be presented later.

Further, if the supposition of Kendall (2) holds, that molecular complexes are more likely to be formed between salts of two elements with a common ion placed far apart in the electro-chemical series, it is feasible that the dielectric constant of the medium as well as the concentration of the ions will be of primary importance.

The Influence of the Solubility of the Component Salts and the Double Salt, on Double Salt Formation.

In the majority of text books double salt formation from two component salts in solution is described as if it were necessary that each of the components should be present in equimolar proportions. The fact that double salts may be formed when the component salts are present in other than equimolar proportions does not seem to have been given sufficient prominence though Schreinemakers(1) and van't Hoff (11), by studying the influence of each component on the solubility of the other and the double salt, at specific temperatures, clearly demonstrated that double salt could be formed from varying proportions of component salts.

The influence of a salt on the solubility of another has been the subject of much work and thought; and van't Hoff using the mechanism of the ionic theory as propounded by Arrhenius provided laws by which the solubilities of single salts and double salt formation could be in many cases qualitatively foretold.

Van't Hoff applied the theory of the solubility product to double salt formation. He assumed that in the case of a salt in equilibrium with its solution in water at a certain temperature, reversible reactions, such as the following, took place.

$$\underset{\text{solid}}{A\,B} \rightleftharpoons \underset{\text{unionised salt}}{(A\ B)} + \underset{\text{ionised}}{[A] + [B]}$$

where A B is the salt composed of the radicles A and B. Applying the law of mass action, the equilibrium constant K is connected with the concentration of the un-ionised and ionised salt, by

$$[A]\ [B] = (A\ B)\ K.$$

Since at constant temperature the quantity of un-ionised salt in equilibrium with solid salt will be constant, the expression (AB) K may be written equal to a constant S, referred to as the solubility product. This postulates that the product of the concentrations of the individual ions at constant temperature is constant. Hence, if to such a solution under these conditions, a small quantity, let us say, of salt BC was added, the concentration of A in solution would be diminished, as the concentration of B was increased - i.e. the solubility of the salt AB would be decreased by the presence of another salt BC with a common ion. A well known example of this phenomenon is the precipitation of sodium chloride, from its saturated solution by the addition of sufficient hydrochloric acid.

Van't Hoff suggested (11) that where two salts with a common

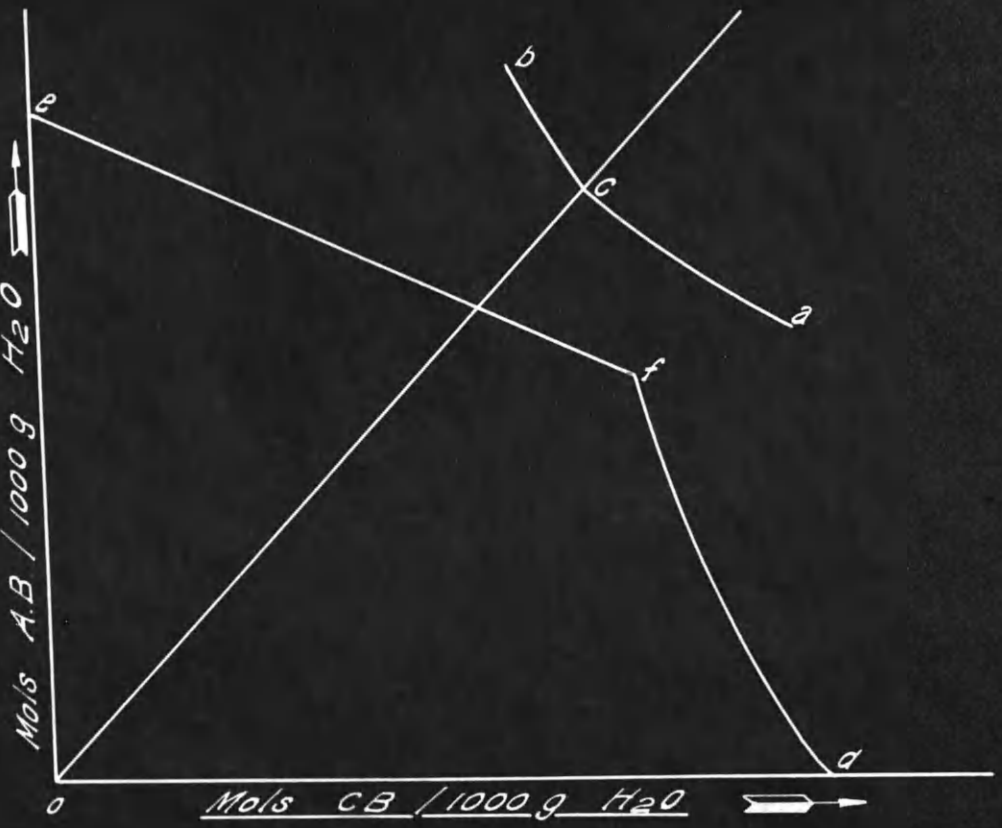
e
b
c
a
f
d
0
Mols A.B. / 1000 g H₂O
Mols CB / 1000 g H₂O

Fig. 2

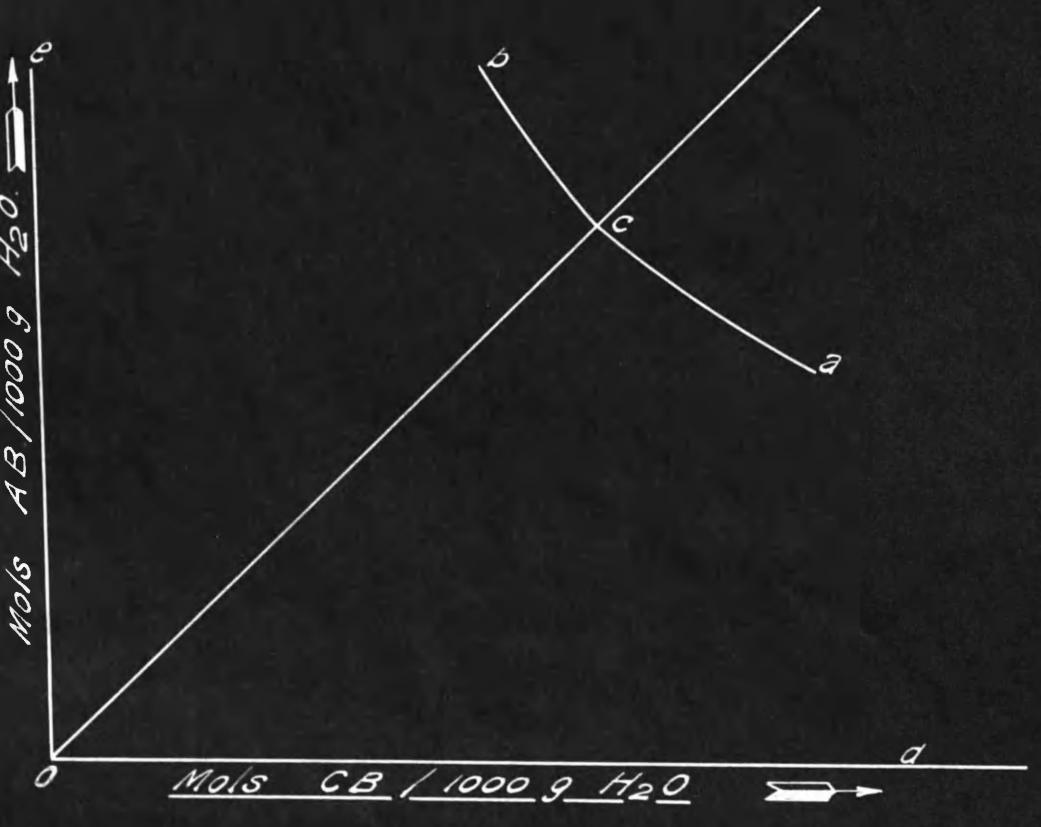
e
b
c
a
d
0
Mols AB/1000 g H₂O.
Mols CB / 1000 g H₂O

Fig. 3.

ion formed a double salt, at a certain temperature, this was a function of the relative solubility of the double salt, and of the component salts, at that temperature.

For example, consider a salt AB, the solubility of which is decreased by the addition of CB - just as the solubility of CB is decreased by the addition of AB, and let these solubilities at a certain temperature, be represented in Figure 2.

The line e f represents the change in solubility of the salt AB with increasing concentration of CB. Thus the ordinate Oe represents the constitution of the solution in equilibrium with solid AB at a specific temperature. With addition of CB, this value changes along the curve ef, with AB as solid phase, till the point f is reached. At this point, the solid phase is a mixture of CB and AB. Similarly, the curve df represents the change in solubility of CB with increased concentration of AB. At f solid AB and CB are in equilibrium with a solution of composition represented by the co-ordinates of the point f.

The curve efd is the boundary curve for saturated solutions. The area eOdf represents unsaturated solutions, whilst points lying outside this area represent either super-saturated solutions, or mixtures of saturated solutions and solid salt.

Now consider the solubility of a double salt AB.CB at the given temperature. Since the double salt is composed, let us say, of one molecule of each of the component salts, its saturated solution must be represented by a point which will lie on the bisector of the angle eOd, e.g. 'c'. (Fig. 3.)

Now double salts are not stable at all temperatures. For each double salt there is a transition temperature - i.e. a temperature at which the double salt decomposes. Further, the double salt may be stable either above or below the transition temperature.

Let us suppose that the double salt AB . CB is stable above the transition point, i.e. it can be formed from the single salts at temperatures above the transition point. (10)

At temperatures below the transition point the solubility of the double salt is greater than that of a mixture of the two salts, so that a curve representing its solubility with solutions of varying composition would lie above the point 'f' in the region representing solutions supersaturated with respect to the single salts. (See Fig. 2.)

Such solutions would be metastable, and on coming into contact with one or other of the single salts would deposit this, and finally give a solution represented by the point f. Thus at this given temperature below the transition point, a solubility curve of the two salts will be of the type efd. (Fig. 2)

At the transition point, the double salt can remain in equilibrium with its component salts and solution, thus the curve of its solubility will pass through the point f as in Figure 4.

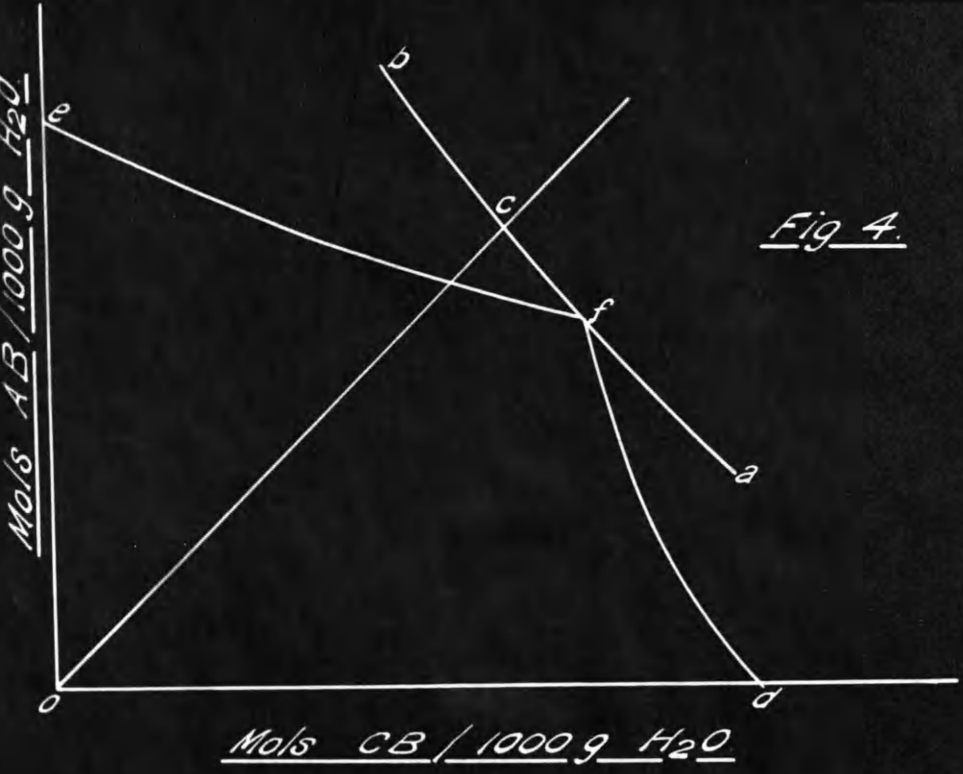
b
e
c
f
a
o
d
Mols AB / 1000 g H$_2$O
Mols CB / 1000 g H$_2$O

Fig 4.

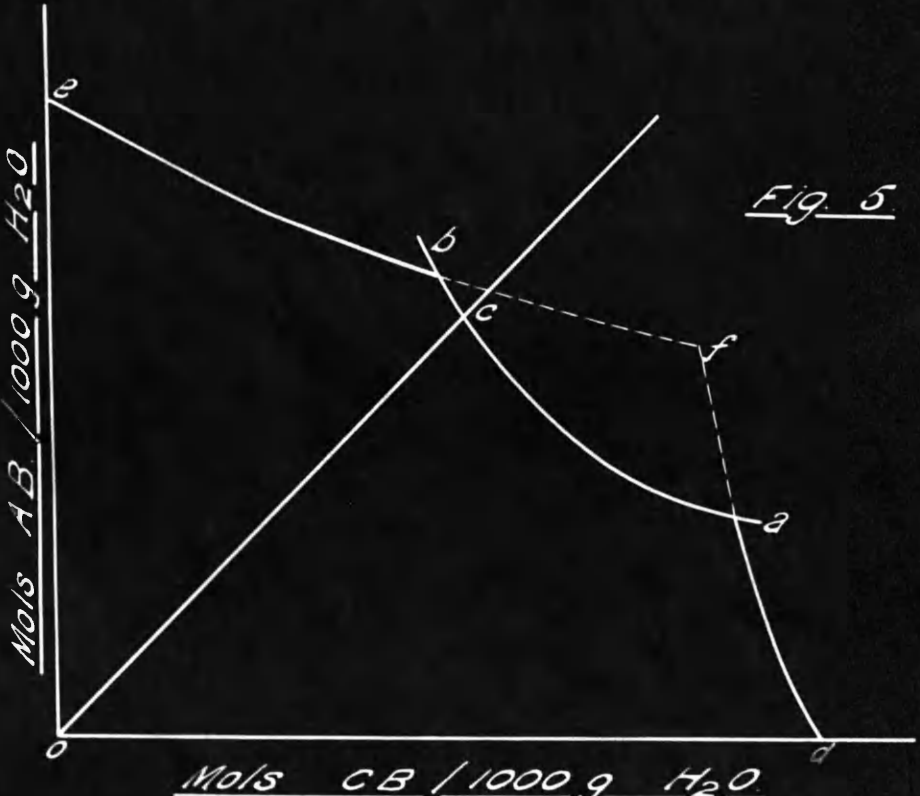
e
b
c
f
a
o
d
Mols AB / 1000 g H$_2$O
Mols CB / 1000 g H$_2$O

Fig. 5

Now if one component, at the transition temperature is more soluble than the other, the point f will lie either to the left, or right of the bisector of eOd as in Figure 4.

Thus the point c representing the composition of a saturated solution of the double salt lies in the area representing supersaturated solution; and such a solution, being metastable, would change its composition with deposition of the single salts until f was reached. In other words, if excess of double salt was stirred with water at the transition temperature, decomposition would take place with deposition of AB, and the concentration of CB in the solution would increase, till the point f was reached.

Of course, if the solubilities of the component salts are identical, as in the case of optical isomerides, the point f will be on the bisector of the angle eOd, and the pure saturated solution of the double salt would not be supersaturated with respect to either of the component salts, so that the double salt would, therefore, not be decomposed by water.

The isothermal curve at the transition temperature, therefore, consists of two branches ef and fd.

At a temperature above the transition point the solubility of the double salt will be less than that of a mixture of the two salts, and consequently the point f will lie outside the boundary of the double salt curve as represented by Figure 5, 'f' will represent a condition of metastability, i.e. a supersaturated solution as represented by 'f', in contact with a mixture of the two component salts, would change in composition with formation of the double salt, until the solution reached a composition represented by some point on the curve bca, when the solid phase would consist of double salt only. The points 'b' and 'a' represent double salt in equilibrium with solution of composition as given by the co-ordinates of b and with solid salt AB, in the case of 'b', and of solution represented by the co-ordinates of the point 'a' and solid salt CB, in the case of 'a'.

In connexion with the above figure it should be noted that, at a certain temperature above the transition point, and below the temperature of the diagram, the points b and f will coincide, and at such a temperature, and temperatures above it, the double salt will not be decomposed by water. A similar case could occur with the point a.

According to this theory then, the formation of the double salt is contingent on solubility alone, it being supposed that the addition of one salt reduces the solubility of the other in accordance with the solubility product law. In other words this postulates that the separation of the double salt at b is not preceded by its formation in solution, the salt being held to be completely dissociated in solution although these solutions are saturated.

Such a theory determines that, if to a salt in equilibrium with its saturated solution at a given temperature, another salt with an ion common to that of the first salt be added, equilibrium will be disturbed in such a way that the solubility of the solid phase salt will be decreased. Experimental evidence does not support this view entirely. In fact, in the majority of cases, the solubility of the solid phase salt is increased.

This phenomena may be capable of two explanations, one on the basis of complex ion formation, the other on the basis of the Debye-Hückel theory.

Complex Ion Formation and Solubility.

It has been general to differentiate double salts from complex salts, by the fact that double salts have individuality in the solid state only, whereas complex salts have characteristics in the solid state and in solution, i.e. double salts when dissolved show the reactions of their component radicles and exhibit no properties not associated with these components, whilst a solution of complex salts exhibits new chemical properties, and does not give the chemical reactions of its component salts.

Typical examples of double and complex salts are potassium iron sulphate, and potassium ferrocyanide, respectively. The formation of these salts may be represented

$$K_2\,SO_4 + Fe\,SO_4 + 6\,H_2O, = K_2\,SO_4\,Fe\,SO_4\,6\,H_2O.$$

$$4\,K\,C\,N + Fe\,(CN)_2 = K_4\left[Fe\,(CN)_6\right]$$

A solution of potassium ferrous sulphate exhibits all the reactions associated with ferrous, potassium and sulphate ions, but a solution of potassium ferrocyanide does not show reactions indicating the presence of ferrous or cyanide ions - but those indicating the presence of a new ion - the ferrocyanide ion.

An examination of the methods of preparation of the above salts shows a further distinction between the two classes. Potassium and ferrous sulphates are both soluble in water and the double salt is formed by crystallisation from their mixed solution; i.e. the double salt is less soluble than either of its component salts. Potassium ferrocyanide is formed by adding potassium cyanide to a ferrous salt solution. At first ferrous cyanide is precipitated, but when excess of potassium cyanide has been added, the precipitate is dissolved owing to the formation of the complex salt, potassium ferrocyanide, which is much more soluble in water than ferrous cyanide. Thus there is a very sharp break in the continuity of properties in the formation of the complex salt, but not with the formation of the double salt (Caven (4)).

Further, formation of the complex salt, i.e. formation of complex ions in solution, is associated with increase in solubility, whilst according to van't Hoff, but not as a matter of fact, the reverse is the case with the double salt.

Now when complex ions are formed, as in the above case, the principle of the solubility product cannot be applied to the original cyanide ions since they are no longer present, for when potassium cyanide is added to a suspension of ferrous cyanide, the solubility of the ferrous cyanide appears to be increased by the addition of the common ion due to the formation of the complex ion $''''[Fe(CN)_6]$.

Thus the formation of complex ions reasonably explains the sudden increase of solubility in the above case; and conversely, in similar cases of the influence of a salt on the solubility of another where an increase in solubility is observed, contrary to the law of solubility product, this increase in solubility may be taken as a sign of complex ion formation.

R. M. Caven and his collaborators (4), on extensive experimental data, offer a convincing theory of double salt formation, involving the formation of complex ions. In the theory of van't Hoff, separation of the double salt is not supposed to have been preceded by its formation in solution; whilst in the Caven theory, formation of double salt in solution is assumed to take place previous to its crystallisation.

Consider the case of potassium and ferrous sulphates. In dilute solution there will be present the ions K, Fe'', and SO_4''. If the concentration is increased there will be present un-ionised ferrous sulphate - $Fe\ SO_4$. This will be formed before un-ionised potassium sulphate K_2SO_4, on account of the lesser polarisability - or degree of dissociation of ferrous sulphate. If the concentration of sulphate radicle ions - SO_4'' is great enough there will be formed ferrosdisulphate ions, i.e.

$$2\,K^{\cdot} + SO_4'' + Fe\,SO_4 \rightleftharpoons 2\,K^{\cdot} + [Fe\,(SO_4)_2]''$$

just as in the case of ferrous cyanide and potassium cyanide. When the concentration of these ions becomes great enough, double salt crystallises from solution.

In the case of lithium sulphate and ferrous sulphate where no double salt is formed, the concentration of SO_4'' ions from the lithium sulphate is too small to cause the formation of the $[Fe\,(SO_4)_2]''$ ions. (See Fig. 1).

Similarly the formation of potassium alum would take place:-

$$2K^{\cdot} + SO_4'' + Al_2(SO_4)_3 \rightleftharpoons 2\,K^{\cdot} + [Al_2(SO_4)_4]''$$

With lithium sulphate there would not be enough lithium and sulphate ions to bring about complex ion formation.

It must be pointed out, however, that analytical tests shew no indication of complex ions being formed in solutions of the alums. A solution of potassium alum for example shows the reactions of potassium, aluminium and sulphate ions, but no analytical tests indicate the presence of ions of the type $[Al_2(SO_4)_4]''$.

This explanation of double salt formation as a function of the concentration of certain ions is in agreement, and is the complement of the view of Kendall (2) outlined earlier.

It follows, then, from this theory, that double salt

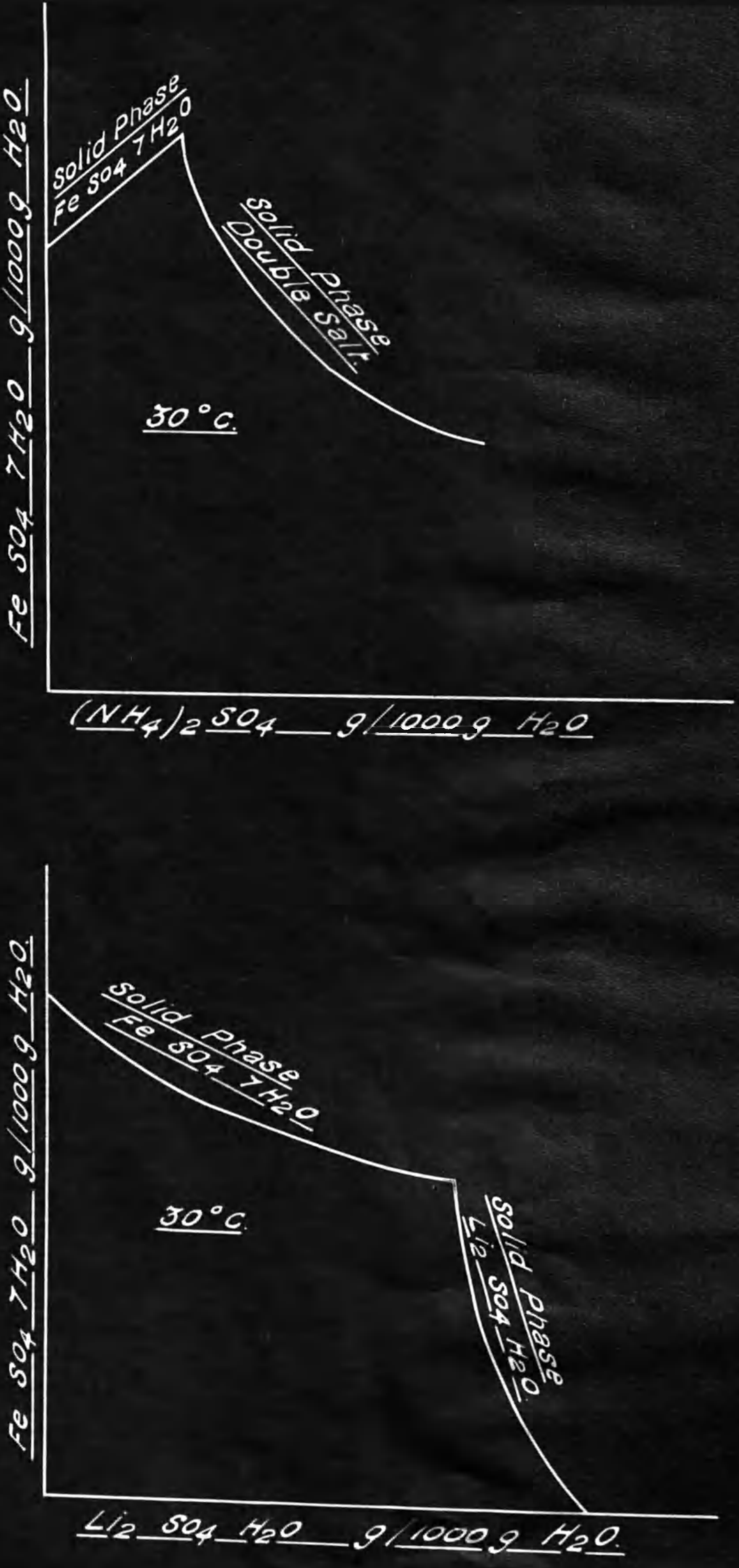
Fe SO4 7H2O g/1000 g H2O
Solid Phase
Fe SO4 7H2O
Solid Phase
Double Salt.
30 °c.
(NH4)2 SO4 g/1000 g H2O
Fe SO4 7H2O g/1000 g H2O
Solid Phase
Fe SO4 7H2O
30 °c.
Solid Phase
Li2 SO4 H2O.
Li2 SO4 H2O g/1000 g H2O.

Fig. 6.

separation is preceded by the formation of double salt ions in solution, and consequently in cases where double salt formation takes place, the presence of one component salt will produce an increase in solubility above what the law of solubility product would allow. In cases where no double salt is formed a decrease in solubility of one salt by the presence of the other is predicted.

Many experimental data support the theory. For example, Schreinemakers (12) found the solubility of ferrous sulphate at 30° C to be influenced by ammonium sulphate and lithium sulphate respectively, as shown in Figure 6.

It will be seen from the above figure that with ammonium sulphate there is an increase of the solubility of ferrous sulphate up to the formation of the double salt, as would be expected from the theory, while the solubility of ferrous sulphate is decreased by the addition of lithium sulphate. Further, at 35° C, the solubility of manganese sulphate is decreased by the addition of sodium sulphate, but the decrease in solubility is less than the solubility product law would allow; the double salt $Mn SO_4 Na_2 SO_4 4 H_2O$ is formed at this temperature. (13).

Thus in cases of an increase in solubility of a salt caused by the presence of another, this theory favours the explanation of complex ion formation as the cause of the increase.

An examination of the solubility of data in the light of the Debye Hückel theory shows, however, that increase in solubility of a substance by the addition of another is not necessarily due to complex ion formation.

The Debye-Hückel Theory of Solution of Electrolytes.

Before dealing with these points from the modern standpoint, it is convenient to describe briefly the development of the theories of solution leading up to the Debye-Hückel Theory and to give an outline of this theory of solubility from the aspect of the solubility of mixed electrolytes.

The classical ionization theory of solution was developed to account for three properties common to acids, bases,and salts. These properties were

(1) the almost instantaneous reactions of inorganic chemistry in which radicles were interchanged at rates infinitely quicker than in organic chemistry reactions;

(2) the alteration in value of equivalent conductivities with dilution to a finite limit;

(3) van't Hoff's observation, that the osmotic properties of this class of substance always exceeded that predicted by his gas law equation, which he had demonstrated to be valid for non-electrolytes in dilute solution.

To account for the first property, it was suggested by B. Clausius and Grotthus (1807 to 1860) that the type of substances which we now term electrolytes were partially dissociated at the moment of decomposition.

In connexion with equivalent conductivities many data were obtained by Kohlrausch, and the values of osmotic pressures of many electrolytes in solution were obtained by van't Hoff. It remained for Arrhenius to propose his famous 'ionic hypothesis' which seemed to account for many of the results of Kohlrausch and van't Hoff. Arrhenius put forward the view that the electrolytes, when dissolved in water, were, partially or wholly, split up into particles which were electrically oppositely charged. Further, the amount of splitting up - or the degree of dissociation of the substance appeared dependent on the concentrations - at low concentrations salts seemed completely dissociated, and the dissociation decreased as the concentration was increased, up to a point. It was held that at definite temperatures an equilibrium was maintained between the un-ionised salt and the ions which were split off, to which the law of mass action could be applied.

Such a hypothesis explained the main features of conductivity and of the osmotic properties. With the passing of time, however, and with the accumulation of data, many discrepancies between observed and deduced values appeared. For example, in conductivity measurements cases were found where the degrees of dissociation apparently decreased with increase in concentration up to a point, and then began to increase with increase in concentration.

Also in solubility measurements the predictions by the classic theory were not generally fulfilled. By the theory, if to a saturated solution of salt

(1) another salt with no ion common to the first was added, the solubility of the first salt should be uninfluenced by the presence of the second

or (2) a salt with a common ion was added, the degree of dissociation of the first salt should be decreased with consequent decrease in solubility.

An examination of the data of solubilities proved that the cases which followed the theory were in a minority.

In 1904 Noyes (14) pointed out that N/30 solutions of the lithium, sodium, thallium, potassium, zinc, beryllium salts of α- bromocamphoronic acid had the same rotary power though conductivity measurements gave 84% dissociation in the case of univalent salts, and 70% in the case of divalent salts. He suggested that the salts were completely dissociated in solution.

Bjerrum (15) and Milner (16) were, however, the first to champion the view that strong electrolytes were a class completely dissociated - or at least practically so - even at moderate concentrations, and that the various discrepancies might be accounted for by the interionic forces arising from the strong electric fields set up by the charges on the ions.

The studies of the Braggs (17) and others, on the structure of crystals, furnished strong supporting evidence of the new point of view. It was shown that solid sodium chloride consists of ions arranged in a cubic lattice, in such a way that each ion is surrounded at equal distances by six chlorine ions, and similarly each chlorine ion with six sodium ions. In other words sodium chloride in the solid state is completely ionised. Further, the calculations of Born, Debye, Scherrer, Fajans, etc., on the magnitude of the space lattice energy (18) showed that the forces holding the ions together are electrostatic.

Since the suggestion, by Van Laar, (19), Sutherland (20), and Bjerrum (15), that the fields of the ions must be considered to account for the properties of solutions of strong electrolytes, many efforts have been made to calculate the magnitude of the effects of these fields, from purely physical considerations. Milner (21) was the first, but his method of calculation was so complex that he was restricted to uni-univalent salts. Ghosh, on the other hand, (22), made calculations which were shown to be theoretically unsound by Kraus (23), Chapman and George (24), and Kendall (49).

The calculations of Debye and Hückel are based on the principles of thermodynamics and electricity. The fundamental idea underlying the theory of Debye, as well as that of Milner, is, that owing to electrical attractions, an ion of given sign will, on the average, be surrounded by more ions of unlike sign than ions of like sign.

When such a solution is diluted in a large volume, the ions become separated to such an extent that the mutual electrostatic forces are no longer of significance, and uniform random distribution of the ions prevails - in other words, the gas laws become valid. If the excess of electrical work involved in this isothermal dilution, due to the rearrangement of the relative positions of the ions, can be calculated, the extent of the deviation from the gas laws, in terms of what is known as the activity coefficient of the ions, can be evaluated.

The activity coefficient f_i of the ith sort of ion in a solution containing ions of the ith --- sth sorts, has been expressed mathematically* by equation (11).

$$(11) \qquad \log f_i = -\sqrt{\pi}\left(\frac{\varepsilon^2}{DkT}\right)^{3/2} z_i^2 \cdot \sqrt{\sum_1^s n_i z_i^2} \; \frac{1}{1 + \bar{a}\sqrt{\frac{4\pi\varepsilon^2}{DkT}}\sqrt{\sum_i^s n_i z_i^2}}$$

where
ε - elementary quantum of electricity
D - dielectric constant of the medium (solvent)
T - absolute temperature
k - Boltzmann constant
z_i - valency of the ith sort of ion
n_i - the number of ions of the ith sort per cubic cm
$\bar{a}$ - the mean distance of closest approach of two ions measured from centre to centre

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* A development of the Debye theory as done by Schärer (25) up to this equation is given briefly in the appendix. For ease of reference the same equation numbers as employed in the appendix are used above.

This equation is developed by Schärer (25) somewhat as follows:-

From this equation, since $\sum_{1}^{s}$ is taken for all the ions present f_i depends on the total ionic concentration of the solution and the valency of the ions and not on the partial concentration of ions of the salt which is present in the solid phase and is therefore independent of the source of the ions, whether they are from the solid phase salt or the influencing salt.

Incidentally, f_i will be the same whether the influencing salt has an ion common to the solid phase salt or not.

Applying to a solution containing k sort of ions ($k < s$) of completely dissociated salts, the sum under the root in (11) may be split up into

$$\sum_{1}^{s} n_j z_j^2 = \sum n_i z_i^2 + \sum n'_i z'^2_i + \cdots\cdots \sum n_i^{(k)} z_i^{(k)2}$$

If $v_i^{(k)}$ is the number of ions of the i/th sort formed from a kth salt molecule, the concentration γ of the salt in mols/litre may be calculated from the value n_i of ions per cm^3.

$$n_i^{(k)} = 6 \cdot 06 \times 10^{20} v_i^{(k)} \gamma^{(k)}$$

Then we may write

$$\sum_{1}^{s} n_i z_i^2 = 6{\cdot}06 \times 10^{20} \left\{ \gamma \sum_{1} \nu_i z_i^2 + \gamma' \sum \nu_i' z_i'^2 + \cdots + \gamma^{(k)} \sum \nu_i^{(k)} z_i^{(k)2} \right\}$$

Then in expression (11) by writing

$$\sqrt{\pi} \left(\frac{\varepsilon^2}{DkT}\right)^{3/2} \sqrt{6{\cdot}06} \times 10^{10} = B$$

and

$$\sqrt{\frac{4\pi\varepsilon^2}{DkT}} \sqrt{6{\cdot}06 \times 10^{10}} = C$$

and putting $\sum \nu_i z_i^2$ for the kth salt with $\sum^{(k)}$ we finally get*

(11')
$$\lg f_i = -z_i^2 B \frac{\sqrt{\gamma\Sigma + \gamma'\Sigma' + \cdots + \gamma^{(k)}\Sigma^{(k)}}}{1 + C\bar{a}\sqrt{\gamma\Sigma + \cdots \gamma^{(k)}\Sigma^{(k)}}}$$

This is a general expression, and we have now to apply it to the case of one solid phase salt and one influencing salt.

If we let $\sum \nu_i z_i^2$ of the solid phase salt be expressed with Σ without the index, and the added salt as Σ', then for the activity coefficient of the ith ion,

$$\lg f_i = -z_i^2 B \frac{\sqrt{\gamma\Sigma + \gamma'\Sigma'}}{1 + C\bar{a}\sqrt{\gamma\Sigma + \gamma'\Sigma}} \qquad (11'')$$

---

*NOTE: For the variation of the dielectric constant with temperature of aqueous solutions the formula of P. Drude is applied (Ann. d. Phys. 59, 61, 1896).

$$D_t. = 88{\cdot}23 - 0{\cdot}4044t + 0{\cdot}00\,1035\,t^2.$$

For the temperatures of 0° and 25° B and C are as follows:

	B	C
0°	0·811	$2{\cdot}31 \times 10^7$
25°	0 843	$2{\cdot}35 \times 10^7$

Taking $\varepsilon = 4{\cdot}77 \times 10^{-10}$ and $k = 1{\cdot}37 \times 10^{-16}$

Now if we write equation (7) in the form[*]

$$\sum v_i \lg c_i = \lg K - \sum v_i \lg f_i$$

when the sum only extends to the ions of the solid phase salt (since only a change v_i in the number of molecules present takes place), $\sum v_i \lg f_i = \lg A$ where A is the activity product of all the dissolved salts, i.e. A is the multiple of all the activity coefficients of the single ions together.

Then let the solubility product $L = \sum v_i \lg c_1$ and from (7) (see appendix) we obtain

$$\lg L = \lg K - \lg A \qquad (12)$$

Then if these explicit values for f_i be put in expression (11), the activity product A of the solid phase salt is expressed through

$$\lg A = -B \sum \frac{\sqrt{\gamma \Sigma + \gamma' \Sigma'}}{1 + C\bar{a}\sqrt{\gamma \Sigma + \gamma' \Sigma}} \qquad (13)$$

It should be observed that the above expression has only taken this simple form through expressing '$\bar{a}$' as a mean value for the different ions.

Now when the solid phase salt is dissolved in pure water we have

$$\lg L^0 = \lg K - \lg A^0 \qquad (12')$$

where L^0 and A^0 are the solubility and activity products of the solid phase salt in pure water. Then to determine the

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[*] For equation (7) see appendix.

increase or decrease of solubility relative to that in pure water, due to the presence of an influencing salt, equation (12)' is subtracted from (12) so that

$$\lg \frac{L}{L^{o}} = -\lg \frac{A}{A^{o}} \tag{14}$$

in which lg A^{o} is evaluated from (13) through

$$\lg A^{o} = -B\sum \frac{\sqrt{y^{o}\Sigma}}{1 + C\bar{a}\sqrt{y^{o}\Sigma}} \tag{13)'$$

where y^{o} is the solubility in pure water, and $\bar{a}$ is given the same value as in the general case.

Two cases now exist

(1) The molecule of the dissolved salt splits up into v_1 ions of A, and v_2 ions of B, and the influencing salt splits up into v_1' ions A', and v_2' ions of B'. There are no ions common to both salts.

Then $$\lg \frac{L}{L^{o}} = \lg\left[\left(\frac{y}{y^{o}}\right)^{\nu_2+\nu_1}\right] \tag{15}$$

(2) When the ions, say, A and A', are identical

$$\lg \frac{L}{L^{o}} = \lg\left[\left(\frac{y}{y^{o}}\right)^{\nu_2}\left(\frac{\nu_1 y + \nu_1' y'}{\nu_1 y^{o}}\right)^{\nu_1}\right] \tag{15'}$$

or similarly when B and B' are identical.

$$\lg \frac{L}{L^{o}} = \lg\left[\left(\frac{y}{y^{o}}\right)^{\nu_1}\left(\frac{\nu_2 y + \nu_2' y'}{\nu_2 y^{o}}\right)^{\nu_2}\right] \tag{15)''$$

In the examples with which we shall deal the ions B, B' are identical, e.g. Tl_2SO_4 - $Al_2(SO_4)_3$ hence equation (15)''

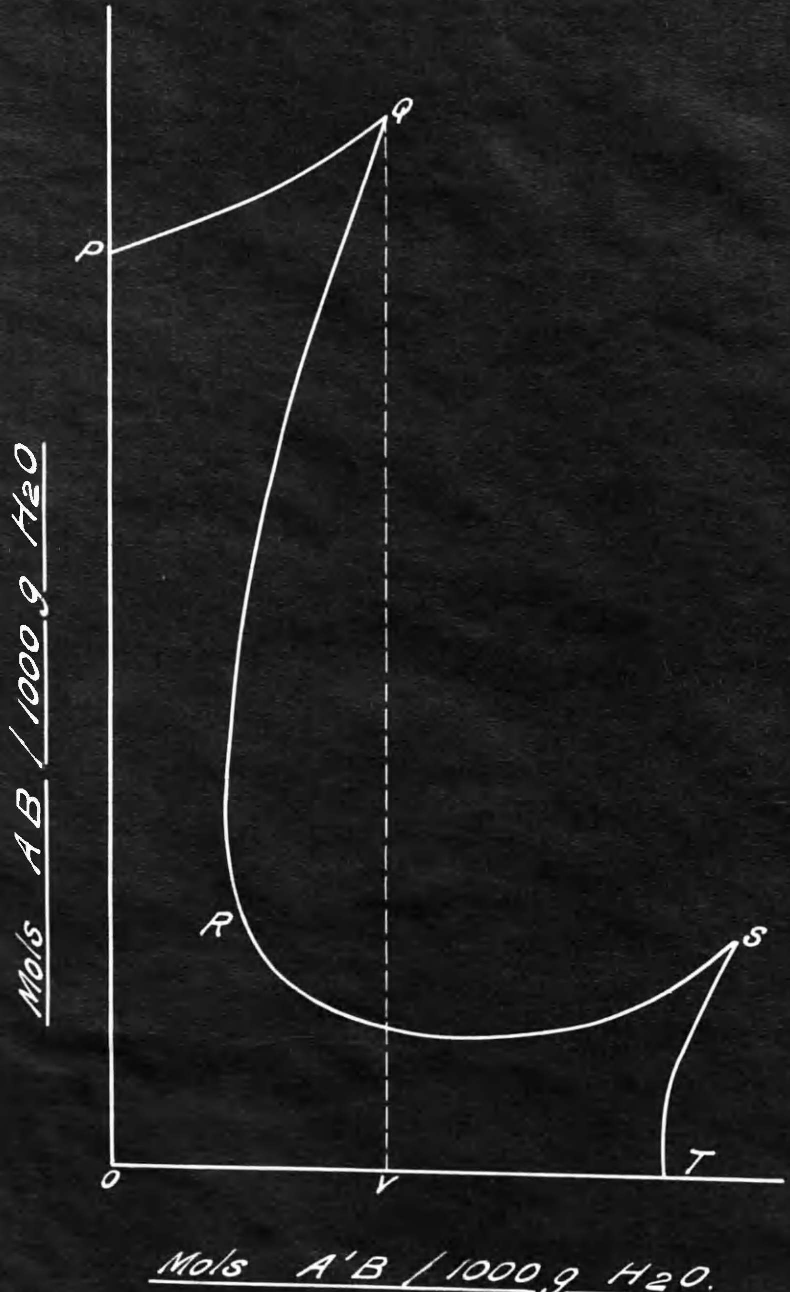


Fig. 7.

is that which is applicable.

Before these equations can be used, however, it is necessary to obtain, a value for '$\bar{a}$'. This cannot be obtained a priori but an approximate value may be obtained in the following way. Consider the isothermal solubility curve PQRST (figure 7) where PQ represents the change in solubility of AB with addition of A'B, the solid phase being AB. The curve QRS represents the double salt AB.A'B. in equilibrium with solutions containing varying quantities of AB and A'B, whilst the curve TS represents changes in the solubility of A'B with different proportions of AB in solution.

With reference to the curve PQ, consider the experimental values represented by the coordinates of P and Q. The ordinate O.P. represents the solubility of the salt AB in water, at the isotherm temperature. Now the point Q represents a mixture of solid AB, and double salt in equilibrium with a solution of the composition represented by the ordinate VQ, and the abscissa OV. The amount of the salt A'B represented by OV is the greatest amount of A'B that can at the temperature of the isotherm be contained in a saturated solution of AB when the solid phase still contains AB.

Since the activity (product of concentration and activity coefficient) of the ions of the salt AB remains constant from P to Q, and the activity coefficient changes as a result of the increase in total ionic concentration, the concentration will also change. Now it has been seen from the law of mass action that $\lg \frac{L}{L^0} = \lg \frac{A}{A^0}$ (14).

We can therefore obtain a mean value for the 'radius' of all the ions in solution by inserting the concentrations of all the ions present at the points P and Q respectively and solving the equation for $\bar{a}$.

Since in this case the ions B are identical, equation (15'') may be applied.

If γ_*^0 represents the solubility of AB in mols/1000gH_2O at, say, T°C corresponding to the point P in the diagram

If γ_* represents the solubility of AB in mols/1000gH_2O at T°C in presence of γ_*' mols/1000gH_2O of A'B (point Q in diagram)

the salt AB splits up into ν_1 ions of A and ν_2 ions of B,

the salt A'B splits up into ν_1' ions A' and ν_2' ions B.

From equations (15'') and (14) and substituting for logA and log A_0, from equations (13) and (13') we obtain[*]

$$B_T \Sigma \left[\frac{\sqrt{\gamma_* \Sigma + \gamma_*' \Sigma'}}{1 + C\bar{a}\sqrt{\gamma_* \Sigma + \gamma_*' \Sigma'}} - \frac{\sqrt{\gamma_*^0 \Sigma}}{1 + C\bar{a}\sqrt{\gamma_*^0 \Sigma}} \right]$$

$$= \lg \left[\left(\frac{\gamma_*}{\gamma_*^0}\right)^{\nu_1} \left(\frac{\nu_2 \gamma_* + \nu_2' \gamma_*'}{\nu_2 \gamma_*^0} \right)^{\nu_2} \right]$$

---

[*] For K_2SO_4 $\Sigma = 1 \times 2^2 + 2 \times 1^2 = 8$

" $Al_2(SO_4)_3$ $\Sigma' = 3 \times 2^2 + 2 \times 3^2 = 30$

Since everything except '$\bar{a}$' is known, the above equation may be solved for '$\bar{a}$'. In practice it is better to rearrange the above equation in quadratic form for '$C\bar{a}$', and solve for '$C\bar{a}$', and hence find '$\bar{a}$'.

It will be noted that the foregoing does not apply to that portion of the curve QRS where the solid phase is double salt AB A'B. This will be dealt with later, it being suitable to discuss, at this point, the phenomena of an increase or a decrease of solubility of AB in the curve PQ. According to Schärer (25) the effects which may take place in solution may be explained thus. When we have a solution of a salt in equilibrium with that salt at a definite temperature - i.e. a saturated solution, and to this we add another salt having no ion in common with the first, then the solubility always increases, contrary to the classical law. This is supposed to be due to the fact that, owing to the increase of the total ionic concentration, brought about by addition of the second salt, the work of bringing the ions from the solid phase into the solution is decreased - hence some of the solid phase passes into solution.

However, if the added salt has an ion in common with the first salt, there are two independent effects to be considered, firstly, an increase in solubility due to the increased ionic concentration as explained above, and secondly a greater probability that two oppositely charged ions may strike one another and fall out of solution. Whichever effect predominates will decide whether there is a resulting increase or decrease in solubility. The greater the concentration and the higher the valency, the more likely is it that an increase in solubility will result.

In the examples which will be dealt with it is apparent that because of the high valency of aluminium, an increase in solubility of aluminium sulphate, with addition of R_2SO_4 (where R is Na, K, or Tl) may be expected. Similarly, an increase in the solubility of R_2SO_4 where the aluminium sulphate is the influencing salt would be probable. Where $R = NH_4$, a decrease in solubility is obtained, but this also may be explained by the theory. Similarly, where aluminium sulphate ($Al_2(SO_4)_3$ $18\ H_2O$) is solid phase salt and R_2SO_4 the influencing salt, an increase in solubility of the aluminium sulphate may be expected.

The case of the system $Li_2SO_4 - Al_2(SO_4)_3 - H_2O$, where a decrease in solubility is experienced, at both ends of the curve, is dealt with under the experimental section.

We now come to consider the central curve QRS of figure 8. This curve represents double salt $AB\ A'B\ x\ H_2O$ in equilibrium with solutions containing various proportions of AB and A'B at the given temperature.

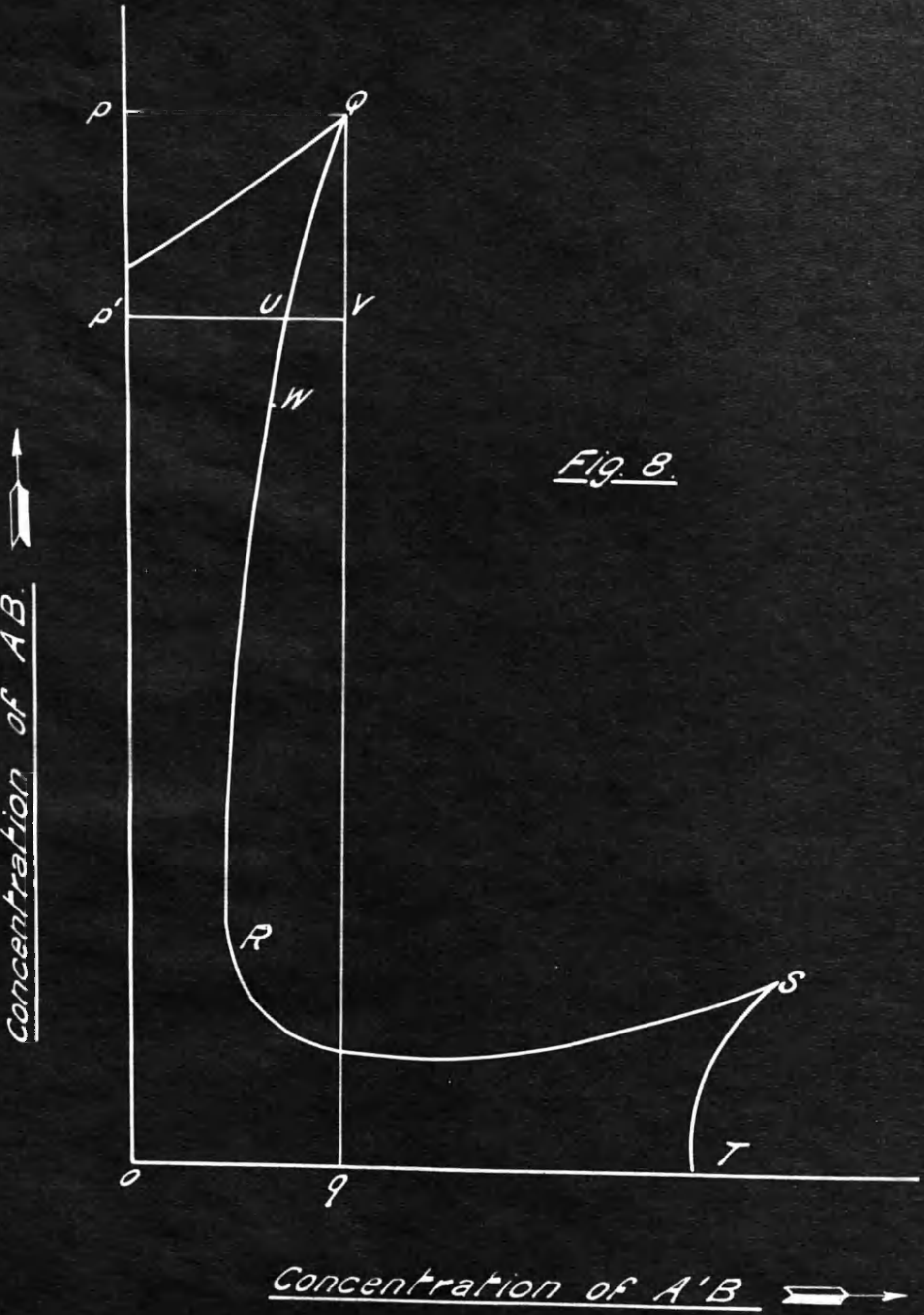


Fig. 8.

With reference to figure 8, where the curvesPQ, QRS, ST have the same significance as in figure 7:-

The concentration of the salt AB at Q is known
" " " " " A'B at Q " "

Then consider the concentration of the salt AB at any point U near to V. If there were no ionic effects U and V would fall together.

Thus at U we are dealing with 'unsaturated' solution of both AB and A'B. Now the activity of any ion in solution is a function of the total ions in solution (48). For the larger part of QR (of the curve QRS) the salt AB is in greater concentration, and we know its concentration, i.e. we can fix on any concentration of AB represented by any point U, and then proceed to calculate the effect of the reduction in concentration of the salt AB from Q to U on the amount of salt A'B which remains in a solution of AB with a solid phase AB A'B ($xH_2O\cdot$). By so reducing AB, the activity coefficient of the ion A' of A'B will be altered, and hence its concentration, since the activity remains unaltered, so that instead of the concentration of A'B remaining constant along Qq, it will fall along QR. With no ionic effect p'U should equal p'V, equal to pQ. So that we have now to calculate the ratio p'u/p'V representing the change in the concentration of the ions of A'B due to a fall in the total ionic strength of the solution.

Since AB is much greater than A'B in concentration, the effect of the reduction in concentration of the ions A'B is ignored and the ratio p'U/p'V considered as being due to the fall in concentration of ions of the salt AB from p to p'.

Starting then from Q we can calculate the position of U. Then from the known position of U, and the concentration of AB at another point W further down, we may calculate the concentration of A'B at W; and so on until the curve QR is calculated.

Thus

Activity of the ith ion of A'B at Q = $f_i^Q c_i^Q$

= activity of the ith ions at V

≑ " " " " " " U = $f_i^U c^U$

$$\frac{c_i^Q \text{ of salt } A'B}{c_i^U \text{ of salt } A'B} = \frac{f_i^U}{f_i^Q} \qquad (16)$$

The value of f_i is obtained from equation (11")

$$\lg f_i = -z_i^2 B \frac{\sqrt{\gamma\Sigma + \gamma'\Sigma'}}{1 + C\bar{a}\sqrt{\gamma\Sigma + \gamma'\Sigma'}}$$

Hence the concentration of the ith ion may be obtained. In each case the unlike ions are taken, e.g. in the case of system $(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$, the ions (NH_4) and (Al) which are not similar are taken. Then, γ for $(NH_4)_2SO_4$ and γ'

for $Al_2(SO_4)_3$ at Q is taken, and f_i for the ion of the salt A'B is calculated - in this case, say Al. The other end of the curve indicated by S R may be calculated in a similar way.

As the proportion A'B to AB increases, the influence of the change in concentration of A'B on the activity coefficient of the ions of salt A'B becomes appreciable, so that the central part of the calculated curve can only be regarded as very approximate.

It should be noted that the above calculation only applies to the case where a reduction in the concentration of AB produces a decrease in the concentration of A'B. In the case where a reduction in the concentration of AB gives an increase in the concentration of A'B the solution of the problem becomes slightly more complicated. Schärer (25) has shewn, however, that the theory also applies to such cases.

The value of '$\bar{a}$' used in the above calculation may be obtained approximately by taking mean values of solubility along QR, say near Q and R, and substituting in equation (16). Since every constant is then known, the equation can be solved for '$\bar{a}$'. This value may then be used along the entire part of the curve QR to calculate the variation in solubility of A'B from point to point of the curve.

A value for '$\bar{a}$' for the part of the curve RS is obtained in a similar fashion.

An explanation is necessary as to why the value of $\bar{a}$ used in calculating the curve PQ cannot be applied to the portion of the curve QR.

The value of $\bar{a}$ varies with change in concentration, and the average concentration between P and Q is very much greater than between Q and R. Hence, whilst that value of $\bar{a}$ used between P and Q, can be used to calculate points on QR near to Q with good agreement with the experimental values, the further from Q on QR, the greater the divergence between calculated and experimental results.

It should be noted here, that the value of $\bar{a}$ does not change the direction of the slope of QR - i.e either inwards or outwards from Q - it merely affects the gradient of the curve.

The Theories of van't Hoff and Caven on Double Salt Formation, in the Light of Modern Theories of Solution.

From the foregoing it is seen that according to van't Hoff's theory double salt formation was contingent on solubility alone. On the other hand, Caven explains double salt formation in a series, as a function of the difference in basicity between the cations of the component salts and the consequent formation of ions of the double salt in solution, from which the double salt crystallises, if these ions are formed in sufficient concentration. Further, the presence of these ions is indicated by an increase in the solubility of one component beyond what the solubility product law would allow, by the addition of the other.

It is evident, however, that such an increase in solubility of one salt by the addition of another cannot be regarded as a criterion of double salt ion formation.

Apart from the suggestion of double salt ion formation in solution, the theories differ only in two main points:-
van't Hoff's theory prescribes double salt formation as contingent on solubility of the double salt and component salts, and Caven's theory that double salt formation in a series is a function of the difference in basicity between the cations. Hence, if a direct connexion between solubility and the difference in basicity of the cations of double salts is established these theories would become very similar. In this connexion the theory of Fajans is of interest (28).

Fajans attempts to explain the different solubilities of inorganic salts by different degrees of deformation of their outer electronic shells. This hypothesis was shewn to be untenable by Urazovski (29), who has suggested that the solubilities of inorganic salts are related to the difference in the atomic numbers between the cation and the anion, and that the solubility is lowest when that difference is a minimum.

With particular reference to the alkali halides, the greater the solubility is, the further apart in the periodic system are the elements which constitute the salt.

Applying this hypothesis to the series Li, Na, K, Rb, Cs and Tl alums, very interesting and significant results are obtained. Since the anions are common to both metals of which the alum is composed, we might consider the solubility in relation to the atomic numbers and atomic weights of the alkali elements. Ammonium's alum cannot be dealt with in this way because neither an atomic weight nor an atomic number can be allocated to it.

The following table shews the atomic numbers of the alkali metals along with the solubilities of the respective alums at 25° C, whilst the graphs Figure 9 (A) and (B) shew these values, with solubility of the alum as ordinates, and atomic numbers and atomic weights of the alkali metals as abscissae.

Metal	Sol. of Alum per 1000g H_2O. at 25° C	Atomic Number	Atomic Weight approx.
Li	---	3	7
Na	0·9 mols	11	23
K	.139	19	39
Rb	.03	37	85.5
Cs	.02	55	132.8
Tl	.09 mols	81	204

Fig. 9 (A.)

Graph showing Relation between Solubility of Alum & Atomic weight of Alkali Metal.

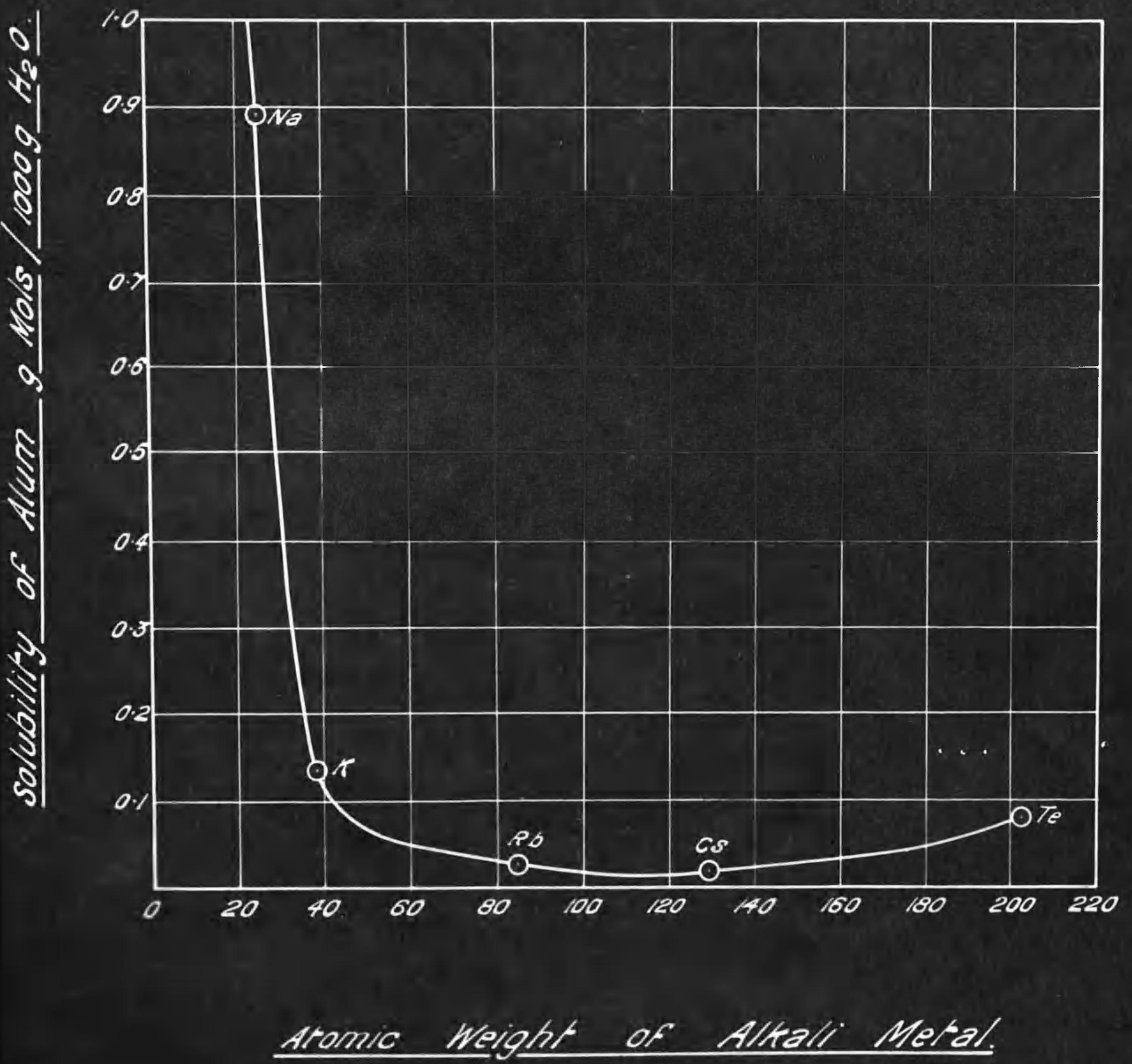
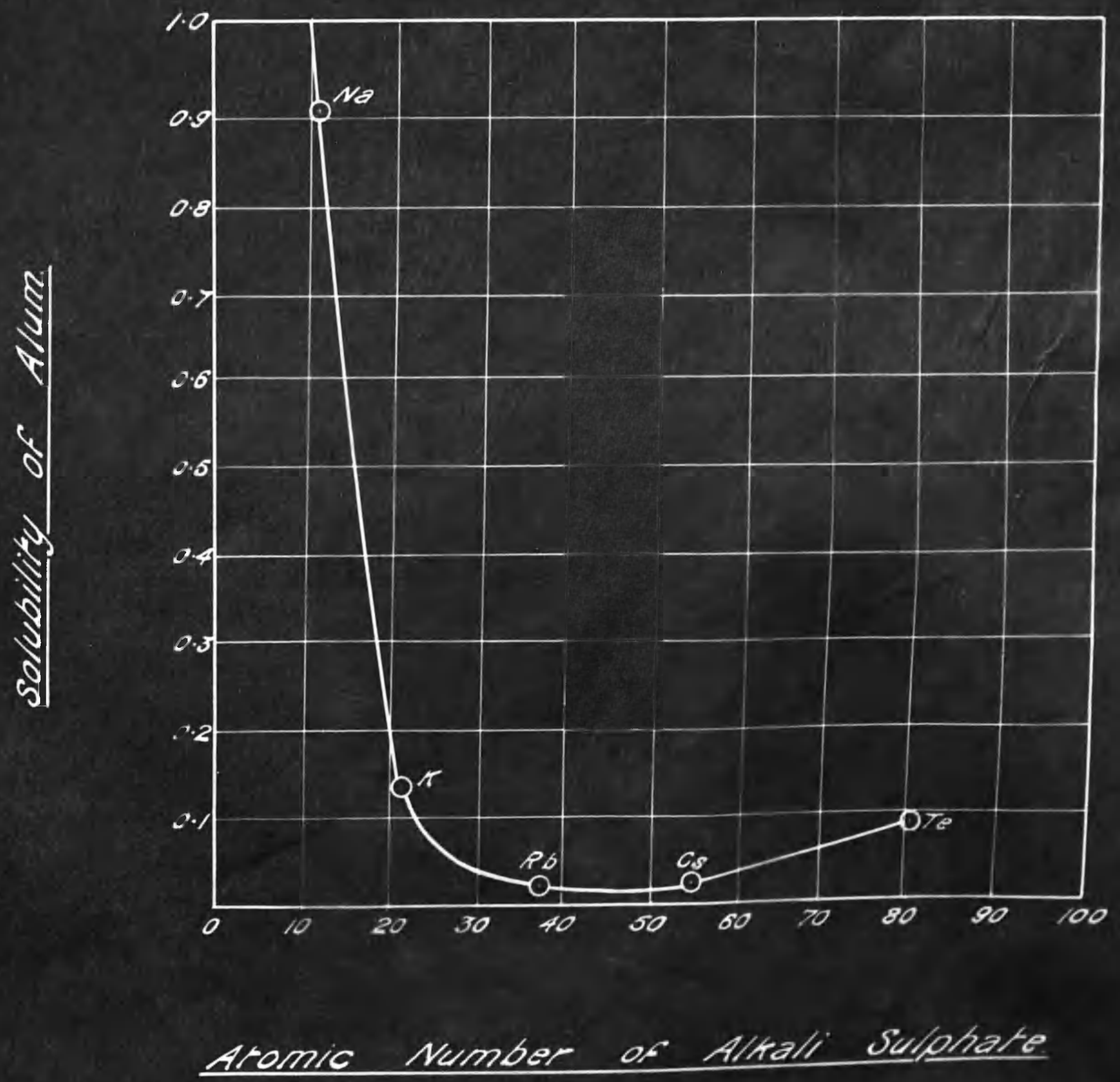


Fig. 9 (B)

Graph showing Relation between Solubility of Alum & Atomic number of Alkali Metal.



From these graphs the solubility of lithium alum would be infinite - i.e. its formation is impossible on account of solubility, thus providing evidence in favour of van't Hoff's theory. Also, since the difference in basicity will be approximately proportional to the atomic numbers as used in the graph, we have evidence that difference in basicity in this series influences the solubility.

It will be seen that the curves, in the direction Tl to Cs shew a decrease in solubility, but from Cs to Rb, K, to Na, there is increase in solubility. If the curve is continued it would appear that the solubility of lithium alum (atomic number 3) at 25^{o} would be infinite. Hence its formation could not be possible.

With reference to the connexion between the solubility and the structure of the ions, it will be noted that the lithium ion has an unsymmetrical structure (8) and it has been suggested by Urazovski, that unsymmetrical structure is associated with high solubility. (29)

Now $K_2SO_4\ Al_2(SO_4)\ 24\ H_2O$ has been shewn by Tutton (30) to consist of either one or two molecules with the 6 groups of 4 H_2O situated round the molecule or molecules as at the angular points of a regular tetrahedron. This symmetry of crystal structure may be associated with the regularity of the structure of the K and Al and SO_4'' ions, and in particular

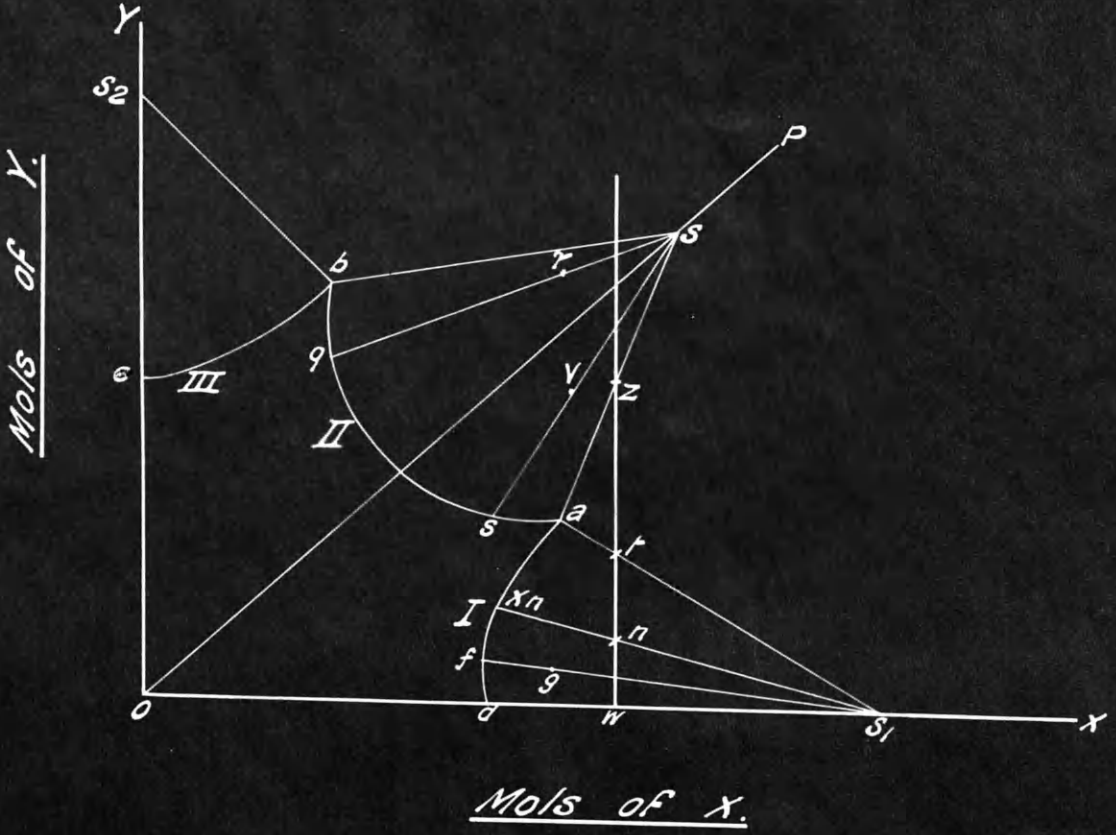


Fig. 10.

with the K ion. Crystals of sodium alum are more difficult to prepare than crystals of potassium alum and it is feasible that a crystal of sodium alum may be less regular in structure than a crystal of potassium alum. These differences may be due to the sodium ion being less symmetrical than the potassium ion, and since the lithium ion is even less symmetrical than the sodium ion, lithium alum may not be obtained in the crystalline or solid state.

It is thus seen that in the case of a simple salt the solubility is associated with the difference in atomic weights or numbers of the anions and cations. With double salts of the type of the alums, the solubility is related to the difference in atomic numbers of the cations, and this difference is, of course, associated with the basicity of the cations. We have, therefore, a definite relationship between the difference in basicity of the cations and the solubility of the double salt.

On this association, then, it may be said, that the theories of Caven and van't Hoff are very similar. Double salt formation is contingent on the solubilities of the component and double salts, but these solubilities in turn are dependent on the nature of the ions and the consequent forces between them, as indicated above.

Graphical Treatment of the Solubility Isotherms of a Double Salt and Its Components.

In the following a brief account, will be given of some deductions which may be made from a study of the solubility isotherms of double salts and their components by a treatment similar to that evolved by Schreinemakers (1). The matter will be treated in a general way, and then, in the section devoted to the various systems, the general observations will be applied in each particular system.

The cases which will be considered will be those changes which take place when

1. a saturated solution in presence of double salt or one of its components is heated or cooled
2. a double salt is mixed with water
3. one of the components is added at constant temperature.

A system composed of water and two electrolytes which yield a common ion is a three component system, and the components may be conveniently taken as the two electrolytes and water. The solid phases possible in such a system are, in addition to the simple salts and their hydrates, one or more double salts and one or more series of solid solutions. The liquid phase may contain variable proportions of all three components, hence if its composition is determined at a definite temperature and pressure, the entire system is defined.

The few variable factors in the system are, temperature, pressure, and the concentrations of the two salts. The experimental work was carried out under atmospheric pressure, it being assumed that the slight variations of pressure has no appreciable effect on the composition of the phases.
Thus with pressure fixed, the behaviour of the system may be expressed graphically in two dimensions at any definite temperature.

Under such conditions, the presence of three phases constitutes an invariant system.

In the case of two salts X and Y, (for simplicity X and Y may be taken as anhydrous) which may form a double salt $XY_\delta (H_2O)_\alpha$, and water, such a case of invariant equilibrium might be

(1) salt X with double salt $XY_\delta (H_2O)_\alpha$ and solution and vapour

(2) salt Y with double salt $XY_\delta (H_2O)_\alpha$ and solution and vapour

These are)(3) salt X, solution containing X only, and vapour
)
really two) (solubility of X at T°C)
)
component)(4) salt Y, solution containing Y only, and vapour
)
systems) (solubility of Y at T°C)

These will be represented by points on the diagram.

Cases of mono-variant, equilibrium, i.e. where a factor can be altered without the disappearance of a phase, will be

(I) salt X, solution and vapour
(II) " $XY_s(H_2O)_k$ " " "
(III) " Y " " "

These states will be represented by curves.

These states may be represented graphically as follows. Figure 10.

In Figure 10 the number of molecules of X and Y dissolved in 100 mols of water at the fixed temperature, are represented by the abscissae and ordinates respectively.

When the solution contains X only, the point representing this state will be on the axis OX, and when the solution contains Y only, the point will lie on OY.

The points a, b, d, e represent conditions described in (1) (2) (3) and (4), whilst the curves I, II, III represent the conditions referred to in I, II, III in the discussion.

The point S on the bisector through O represents the composition of the double salt hydrate (in the case where 1 mol of X combines with 1 mol of Y). The points S_1 and S_2 similarly represent the composition, i.e. degree of hydration, of the component salt hydrates. Should the double salt or the component salts, be anhydrous, the points S, S_1 or S_2 would lie, as before, on OP, OX and OY respectively, but at infinite distance from O.

The behaviour of the system under different conditions may now be dealt with.

Effect of Change of Temperature of Solution in Equilibrium with only one solid phase.

I. Where Double Salt is the Solid Phase.

The equilibrium in this case is monovariant, and the solution is represented by branch II of the isotherm in Figure 10. We have to find how the composition of the solution will change with lowering or raising the temperature.

Let the composition of the solution at any point q be represented by

a mols H_2O, x_1 mols X, and y_1 mols Y.

With a change of temperature only two things can take place.

1. Solution (or deposition) of n mols $XY_\delta (H_2O)_\alpha$.
2. Evaporation (or condensation) of n_1 mols H_2O.

If we consider that the quantity n_1 is very small, compared with a and n, then the constitution of the new solution is

$$(a + n\alpha)\ H_2O, \quad (x_1 + n)\ \text{Mols X}, \quad (y_1 + n\delta)\ \text{Mols Y}.$$

or in 'a' mols H_2O there are dissolved

$$\frac{a\ (x_1 + n)}{a + n\alpha} \text{ mols X , and } \frac{a\ (y_1 + n\delta)}{a + n\alpha} \text{ mols Y.}$$

The new solution will go through a point 'r', whose co-ordinates are such that

$$X_r = \frac{a\ (x_1 + n)}{a + n\alpha} \text{ and } Y_r = \frac{a\ (y_1 + n\delta)}{a + n\alpha}.$$

Then by eliminating n from the above equations we obtain

$$Y_r = \frac{a\delta - \alpha y}{a + \alpha x_1} X_r + \frac{a\ (y_1 - \delta x_1)}{a - \alpha x_1}, \tag{17}$$

This is the equation of a straight line, which passes through S, the co-ordinates of which represent the constitution of the double salt. Thus 'r' will lie on the line qS. It follows then that

1. if a solution, with double salt as solid phase, is warmed to a higher temperature, the composition of the solution will change in such a way as may be represented by a straight line which passes through a point, the co-ordinates of which represent the constitution of the double salt,
2. if the double salt is anhydrous, the point S in the limit will lie on OP, infinitely distant from O,

3. if the solution is cooled, 'r' will move towards 'q' along Sq, and double salt will be dissolved.

Incidentally, it might be pointed out that all points in the area abS represent solutions supersaturated at the temperature of the isotherm a b. If, at this temperature, a solution in presence of double salt has the constitution represented by r its constitution will slowly change along rq with deposition of double salt, till it reaches that of q, on ab,; oOr a solution represented by v, will change along vs, till s on ab is reached, at which point equilibrium will be attained. Similarly, for any point in abS.

Incidentally, all points within abS represent all the constitutions of all possible mixtures of solution and double salt, at the temperature of the isotherm.

It may be mentioned, in passing, that this may form the basis of a method of determining the constitution of the double salt, (31), where a solution and mixtures of double salt and that solution are analysed, and by projection the point S obtained.

II. One of the Components as the Solid Phase.

Let us consider the curves I and III. In I the solid phase is X $(H_2O)_\alpha$ and in III Y $(H_2O)_\beta$.

In curve I, let the point f represent solution in equilibrium with $X(H_2O)_\alpha$ at the temperature of the isotherm. The constitution of the solution is, say, a mols H_2O, x_2 mols X, and y_2 mols Y.

If the temperature is raised, suppose n mols of $X\,(H_2O)_\alpha$ to be dissolved. Then, if we take the quantity of solvent evaporated to be very small compared with a and α, the co-ordinates X_g and Y_g of a point 'g', which represent the new solution, are represented by

$$X_g = \frac{a\,(x_2 + n)}{a + n\alpha} \quad \text{and } Y_g = \frac{ay_2}{a + n\alpha}$$

from which, by eliminating n, we obtain

$$Y_g\,(a - \alpha x_2) + \alpha X_g = ay_2.$$

This is the expression of a straight line, which passes through the point S_1, which represents the constitution of the component $X\,(.H_2O)_\alpha$.

Then, as before, if we raise the temperature of the solution keeping $X\,(H_2O)_\alpha$ as the solid phase, the constitution of the solution will change so that its components may be represented by a straight line passing through a point, the co-ordinates of which represent the composition of the component salt.

Also, the triangle da S_1, represents solution supersaturated

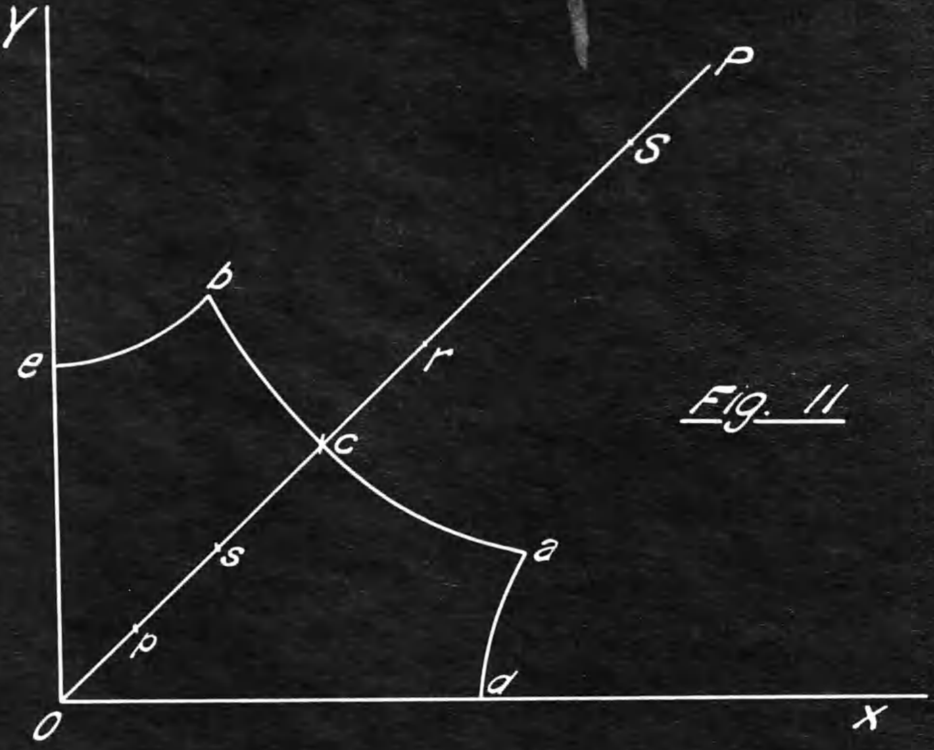


Fig. 11

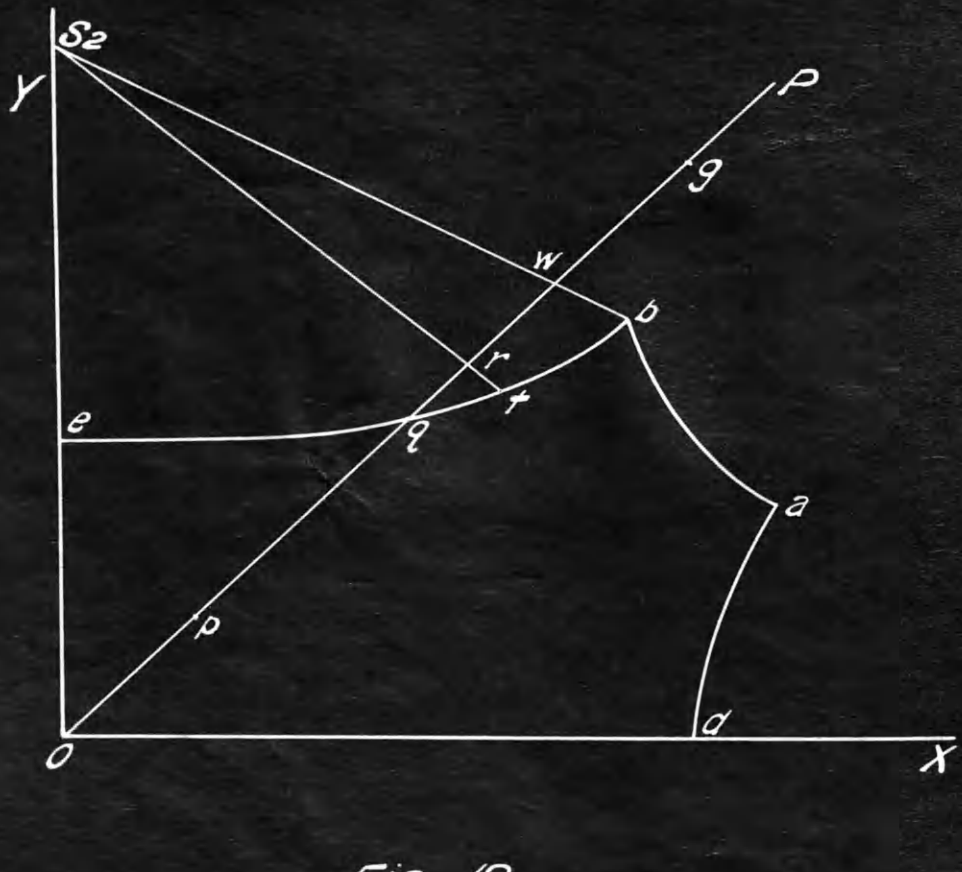


Fig. 12.

at the temperature of the isotherm; and also all possible stable mixtures of component and solution may be represented by points within the diagram, as in the case with the double salt.

All the foregoing may be applied to the curve III with $Y(H_2O)_3$ as solid phase.

Double Salt and Water at Constant Temperature.

There are three particular cases to be considered, according to the shape and position of the double salt isotherm relative to the equi-molecular line OP. The double salt is assumed to consist of equimolar proportions of its component salts.

Case I.

Let 'ebad' represent the isotherm (Figure 11) with the same significance as before.

If a little double salt is brought into contact with water, the double salt will dissolve to give solution, say 'p'. If more double salt is added, it will be dissolved, and the constitution of the solution will change to s, and finally to c. If more double salt is added when the solution has a constitution represented by 'c', it may dissolve to give solution represented by r. This solution, however, would be supersaturated and would attain stable equilibrium by depositing double salt, until its composition would become that represented by 'c'. If more double salt were added after this, it would simply remain unchanged.

'c' represents the solubility of the double salt at the temperature of the isotherm, and the solution contains equal molecular properties of X and Y.

Case II.

Let the isotherm have the form ebad Figure 12, where the line OP cuts the branch eb, where the solid phase is $Y(H_2O)_\beta$.

If we bring a little double salt into contact with water, the double salt would dissolve and we should obtain solution of composition represented by, say, p, and with more double salt the solution would finally have a composition represented by 'q'.

Now, from p to q there is no solid phase present, the solution dissolving the quantity of double salt added. At q the behaviour changes. If more double salt is added, sufficient to give solution equivalent to 'r', decomposition of the double salt takes place, and $Y(H_2O)_\beta$ is deposited and the solution attains the composition represented by t, at which composition it remains in equilibrium with the solid phase $Y(H_2O)_\beta$.

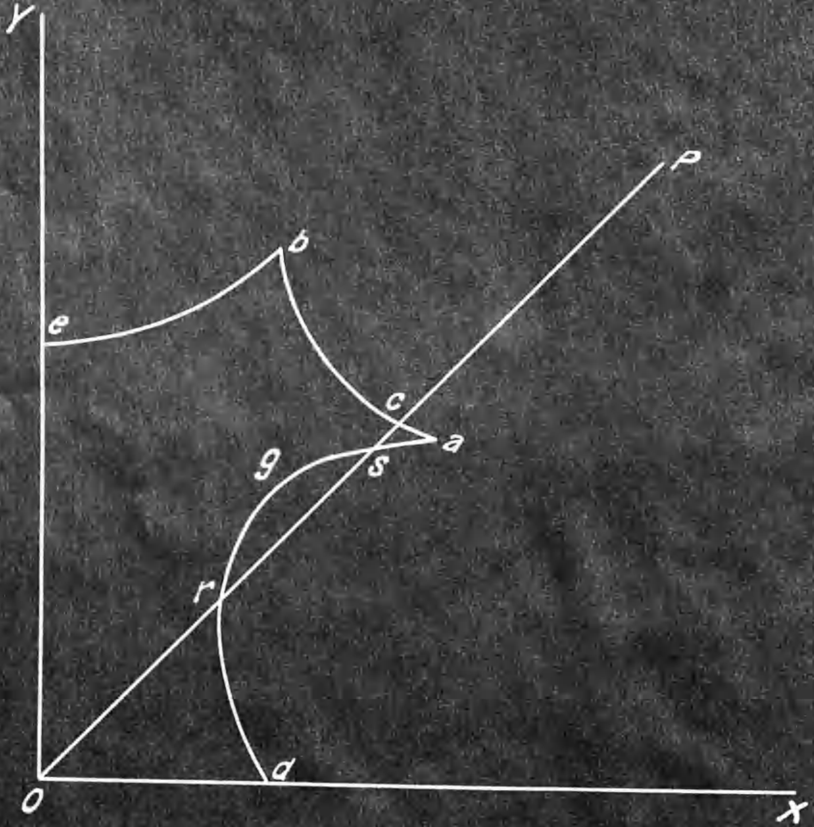


Fig. 13

If further double salt is added to give a mixture represented by w, decomposition again occurs to give solid $Y(H_2O)_\beta$ and solution represented by 'b'. If even more double salt were added to give a solution or mixture of the composition 'g', this solution would break up to give double salt, and component $Y(H_2O)_\beta$, and solution of composition 'b'.

Case III.

Similar to this case is, where the line OP cuts the branch of the curve d a, where the solid phase is $X(H_2O)_\alpha$. Such a case is entirely analogous to the foregoing.

There is a special case of the second and third cases, namely, where the line OP cuts the branch, say, 'a d' of the curve in two places, then passes through the branch 'a b', as in Figure 13.

This case does not apply to any of the isotherms obtained for the alums, and is only mentioned as a possible case.

Addition of double salt in small quantities would first produce complete solution up to 'r', when the solid phase $X(H_2O)_\alpha$ would appear, and further addition of the double salt would cause the composition to change along rgs with solid phase $X(H_2O)_\alpha$ always present. Further double salt would give complete solution with no solid phase. With more double salt the composition of the solution would change till c was reached, at which composition, double salt would appear as solid phase, and double salt addition would not change the composition of the solution, the double salt remaining unchanged.

Addition of a Component at Constant Temperature.

Consider the isotherm of Figure 10 and suppose the point w to represent the composition of a mixture of component $X(H_2O)_\alpha$ and solution, in equilibrium at the temperature of the isotherm. Now let us suppose that to this mixture is added a quantity of Y, and that the new mixture in composition is represented by the point 'n'. This mixture will be unstable, and will, as explained previously, change into a solution of the composition represented by 'x_n and solid $X(H_2O)_\alpha$. If still more of Y is added, a mixture will be obtained represented by the point t, on the line 'a S_1', which will break up into solution 'a', and solid $X(H_2O)_\alpha$.

Should further amounts of Y be added, so as to give mixtures of composition represented by points between t and z, these mixtures would finally reach equilibrium by splitting up into solution 'a' and a mixture of double salt and $X('H_2O)_\alpha$. When a mixture represented by 'z' is reached, this would break up to give double salt only, and solution 'a'.

With further addition of Y, the composition of the solution will change along a b, with double salt as solid phase; and when finally, with addition of Y, a mixture is obtained which might be represented by a point above the line b S, this mixture would reach a state of equilibrium represented by a solution of composition 'b', and a mixture of double salt and $Y(H_2O)_\beta$.

Further addition of $Y(H_2O)_\beta$ would not produce a change in the composition of the solution, since any resulting mixture must be represented by a point between S_2 bS.

Starting from solution represented by 'e' in equilibrium with solid $Y(H_2O)_\beta$, it is possible to pass along, in a manner similar to that described above to solution of the composition 'a', in equilibrium with solid phase composed of $X(H_2O)_\alpha$ and double salt.

It will be observed that these general deductions do not decide whether the addition of one component, to a saturated solution of the other, causes solution, or deposition of that other, (or if double salt is the solid phase, deposition or solution of double salt). Such a point is determined by the gradient of the solubility isotherms, whether it is positive or negative, a negative gradient indicating that the solid phase salt is deposited by the addition of the other, and a positive gradient, that the solution of the solid phase salt takes place.

These general deductions will be applied in the discussion of the solubility isotherms of the systems dealt with hereinafter.

THE SYSTEMS.

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THE SYSTEMS.

The System Na_2SO_4 - $Al_2(SO_4)$ - H_2O at 0° and 25°C.

The existence of sodium alum was long the subject of dispute. It was reported to have been made by Zellner in 1816 (32) by the spontaneous evaporation of a solution containing sodium and aluminium sulphates. Ostwald doubted its existence, but Wadmore (34) and Smith (35) proved its existence and composition, beyond all doubt.

Smith (35), shewed that sodium alum could be represented by the formula $Na_2SO_4Al_2(SO_4)_3$ 2 4·H_2O, and that it was deposited from a hot solution of its components in molecular proportions, in the form of a pasty mass which became crystalline very slowly.

Its preparation on the manufacturing scale has been the subject of patents (36 and 37), in which its preparation is described by preparing a solution, of density of 1·35, of sodium sulphate and aluminium sulphate in molecular proportions at 50° - 60° and allowing to cool to about 15° C, when crystals of alum ($Na_2SO_4Al_2(SO_4)_3$ 24 H_2O) separate out.

The determination of the solubility isotherms of the system Na_2SO_4 - $Al_2(SO_4)_3$-H_2O at 0°C and 25°C is described below.

Experimental.

Equilibrium mixtures, in the case of the isotherm at 0°C, were obtained by preparing a saturated solution of one of the components at 15° - 20°C, and dissolving in it various quantities of the other component. The resulting solution was then placed in a flask in a thermostat at 0°C, and stirred continuously for four or five days. Stirring for shorter periods failed, with certain mixtures, to produce equilibrium, as a sample of the solution taken after a further day's stirring shewed a change in composition. (It may be mentioned here that for the other systems studied, three days' stirring was sufficient to attain equilibrium.)

At the end of the four or five days the resulting solution was, within a few seconds, filtered by suction into a tared weighing bottle at the temperature of the thermostat. The solution was then weighed and made up to a known volume.

A similar procedure was observed with the isotherm at 25°C except that the temperature of the saturated solutions was approximately about 30°C.

The aluminium was estimated volumetrically by the method used by Britton (38) in studying the isotherm of K_2SO_4-$Al_2(SO_4)_3$-H_2O at 25°C. Total sulphate was estimated by precipitation with barium sulphate, and the sodium sulphate estimated by difference.

It has been noted by Britton (38) that aluminium sulphate hydrolyses above 30°C. In the experiments carried out, the amount of hydrolysis of the aluminium sulphate in the solutions from which equilibrium mixtures were prepared was exceedingly small, and was neglected.

The solutions, where aluminium sulphate was the solid phase salt, were exceedingly viscous, and as reported by Britton, were in some cases cloudy.

Duplicate analyses were done for each point.

Results.

The results obtained are correlated in the following tables and Figure 14.

Table 1 gives the solubility data obtained for the isotherm at 0°C.

Table 2 gives the solubility data for the isotherm at 25·0° C.

Figure 14 shews graphs of these values, with solubility of the aluminium sulphate as abscissae and solubility of the sodium sulphate as ordinates.

TABLE I.

System $Na_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0°C.

Mols NA_2SO_4 per 1000_g H_2O.	Mols $Al_2(SO_4)_3$ per 1000_g H_2O	Solid Phase
0·352	0·000	$Na_2SO_4 10 H_2O$
0·373	0·099	"
0·395	0·163	"
0·409	0·239	"
0·414	0·309	"
0·489	0·565	"
0·541	0·763	"
0·560	0·793	"
0·635	0·807	"
0·689	0·824	($Na_2 SO_4$ 10 H_2O ($Na_2 SO_4 Al_2(SO_4)_3$ 24 H_2O
0·518	0·841	$Na_2 SO_4 Al_2(SO_4)_3$ 24 H_2O
0·297	0·999	"
0·292	1·052	"
0·341	1·090	($Na_2 SO_4 Al_2(SO_4)_3$ 24 H_2O ($Al_2(SO_4)_3$ 18 H_2O
0·317	1·095	$Al_2(SO_4)_3$ 18 H_2O
0·000	0·915	$Al_2(SO_4)_3$ 18 H_2O

TABLE 2.

The System Na_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 25·0° C.

Mols Na_2SO_4 per 1000_g H_2O	Mols $Al_2(SO_4)_3$ per 1000_g H_2O	Solid Phase
1·94	0·00	$Na_2SO_410\ H_2O$
1·97	0·139	" "
2·24	0·574	" "
3·01	0·678	($Na_2SO_410\ H_2O$ ($Na_2SO_4Al_2(SO_4)_3\ 24\ H_2O$
1·84	0·724	$Na_2SO_4Al_2(SO_4)_3\ 24\ H_2O$
1·45	0·734	" "
1·109	0·832	" "
0·90	0·90	" "
0·378	1·140	($Na_2SO_4Al_2(SO_4)\ 24\ H_2O$ ($Al_2(SO_4)_3\ 18\ H_2O$
0·347	1·073	$Al_2(SO_4)_3\ 18\ H_2O$
0·000	1·121	" "

Solubility of the Alum = 0·90 mols.

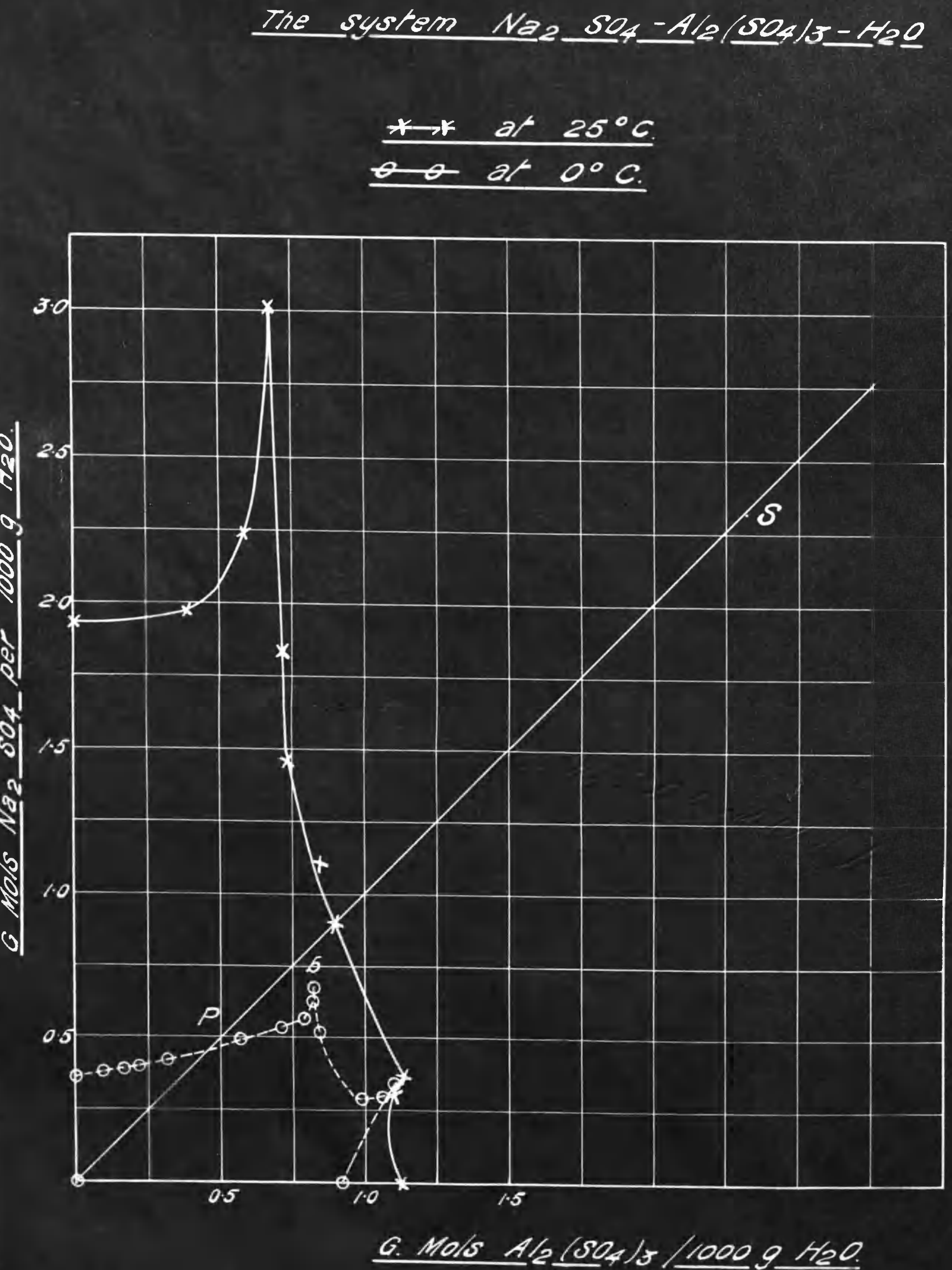
The system $Na_2SO_4 - Al_2(SO_4)_3 - H_2O$
×—× at 25° C.
o—o at 0° C.
3·0
2·5
2·0
1·5
1·0
0·5
0·5
1·0
1·5
S
P
b
G Mols Na_2SO_4 per 1000 g H_2O.
G. Mols $Al_2(SO_4)_3$ / 1000 g H_2O.

Fig. 14.

Discussion of Results.

Solubility of Isotherm at 25° : It will be observed that the addition of $Al_2(SO_4)_3$ to the saturated solution of Na_2SO_4 produces at first only a slight increase in the solubility of the solid phase salt. When, however, the concentration of the aluminium sulphate has reached 0·5 mols, the gradient of the solubility curve begins to increase, and a small increase in the concentration of the aluminium sulphate produces a very great increase in the solubility of the sodium sulphate. This holds, up to the triple point, where the concentration of the aluminium sulphate is approximately 0·69 mols.

Beyond this point, where the solid phase is double salt, an increase in concentration of the aluminium sulphate produces a great decrease in the concentration of the sodium sulphate. Between concentrations of aluminium sulphate of ·69 to ·75 mols the gradient of the curve is such that the addition of aluminium sulphate, to a solution at 25°C of the composition represented by a point on the double salt portion of the curve just beyond the triple point would result in a reduction in concentration of an amount of sodium sulphate, almost equivalent to the weight of aluminium sulphate added.

At the other end of the curve which represents the influence of sodium sulphate on the solubility of aluminium sulphate, it will be observed that while at first the addition of sodium sulphate produces a decrease in the solubility of the aluminium sulphate, the gradient of the curve changes and an increase in solubility is registered, up to the triple point. From this point onwards to the next triple point an increase in the concentration of sodium sulphate is associated with a decrease in the concentration of the aluminium sulphate.

Double salt is formed at concentrations of aluminium sulphate from 0·69 to 1·14 mols. [illegible] - a range of 0·46 mols aluminium sulphate.

Isotherm at 0°C.

This isotherm is similar in form to that at 25°C, though the range over which the double salt is formed is considerably less. It will also be noted that the equimolar line does not pass through the double salt curve, but passes through that section representing solid phase sodium sulphate decahydrate in equilibrium with its solution containing varying amounts of aluminium sulphate. This state of affairs is in agreement with the statements in the patent literature (36 and 37), that if a saturated solution of sodium alum (i.e. a solution containing equimolar proportion of sodium, and of aluminium sulphates) is cooled below 10°C, sodium sulphate hydrate crystals are obtained as the solid phase, instead of alum. Thus, as explained heretofore (page 55) if sufficient sodium alum was stirred with water at 0°C, the alum would decompose the solid phase would become sodium sulphate, and the composition of the solution would be represented by some point on P b (Figure 14).

The double salt is formed between the concentration of aluminium sulphate of .82 mols - 1.09 mols/litre, - a range of 0.27 mols of aluminium sulphate.

Qualitative Explanation of Results on the Debye Theory.

Owing to the high concentrations, the equations derived from the Debye theory of solution cannot be applied quantitatively in this case.

The results obtained, however, may be dealt with qualitatively. The increase of the solubility of the sodium sulphate is in accordance with the principles outlined on pages 37 and 38, as is the increase in concentration, where aluminium sulphate hydrate is the solid phase salt, and sodium sulphate is the influencing salt.

In the double salt section of the isotherms, however, a different state prevails; here a decrease in concentration of the sodium sulphate is produced by an addition of aluminium sulphate, to an almost quantitative extent. The probability of oppositely charged ions striking one another must be considered to be so greatly increased that the other ionic effects (page 38) become small in comparison.

The shape of the curves, however, do not rule out the possibility of ionic complexes being formed.

The System K_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C. and 25° C.

Potassium alum is perhaps the best known of the alums, probably on account of its wide application in the dyeing industry as a mordant, and its use in making showerproof fabrics. Its manufacture is of great antiquity. Since the fifteenth century it has been prepared at La Tolfa (32) from a naturally occurring basic potassium alum known as alum stone. It may also be prepared by the addition of potassium sulphate to aluminium sulphate solution.

The solubility of the alum has been determined by numerous investigators (39) (40) (41) (42) and Marino (43) has determined the composition of solutions which are in equilibrium with two solid phases, alum and potassium sulphate, or alum and aluminium sulphate, at various temperatures.

Though the alum itself is well known, only one solubility isotherm has been worked out for the above system. This was done recently by Britton (38), who demonstrated the exceedingly wide limits of formation of the double salt at 25° C. His results were expressed in a peculiar way, and have been recalculated, and expressed in a form suitable for comparison with the results of the series studied herein. Below is given a description of the determination of the isotherm at 0° C.

Experimental.

The equilibrium mixtures were prepared in a manner similar to those for the Na_2SO_4-$Al_2(SO_4)_3$-H_2O system, except that pure potassium sulphate of analytical quality was used instead of sodium sulphate.

The mixtures were stirred for three days in a bottle at the temperature of melting ice. This period was found by experiment to be sufficient for the establishment of equilibrium.

The analyses were carried out as described for system Na_2SO_4 - $Al_2(SO_4)_3$-H_2O, and the potassium was estimated by difference.

Results.

The results obtained are given in Table 3, whilst Table 4 shews the results obtained by Britton (loc. cit.) for the solubility isotherm at 25·0° C, recalculated for comparison with the series. Figure 15 shews a graph of these results.

Discussion of Results.

It will be seen that in both isotherms the addition of aluminium sulphate to a saturated solution of potassium sulphate, produces an increase in the solubility of the solid phase salt up to the triple point, at which the alum appears in the solid phase.

Where potassium alum alone is the solid phase, further increase in the concentration of the aluminium sulphate is associated with a decrease in the concentration of the potassium sulphate, until the concentration of the aluminium sulphate reaches about 0.6 mols. From this value onwards to the point at which the solid phase consists of aluminium sulphate hydrate, and potassium alum, increase in the concentration of the aluminium sulphate is attended by a slight increase in the concentration of potassium sulphate.

TABLE 3.

System K_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C.

Mols of K_2SO_4 per 1000g H_2O	Mols of $Al_2(SO_4)_3$ per 1000g H_2O.	Solid Phase
0·427	0·000	K_2SO_4
0·538	0·018	"
0·589	0·0158	(K_2SO_4 ((K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O
0·491	0·0145	K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O
0·227	0·026	" "
0·171	0·031	" "
0·058	0·058	" "
0·053	0·118	" "
0·047	0·497	" "
0·0728	0·903	" "
0·072	0·963	" "
0·117	1·131	(K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O (($Al_2(SO_4)_3$ 18 H_2O
0·095	0·995	$Al_2(SO_4)_3$ 18 H_2O
0·000	0·915	$Al_2(SO_4)_3$ 18 H_2O

TABLE 4.

System K_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 25°C.

Gm H_2O in which 100g of solute dissolves to give a saturated solution	Composition of Solute		Gm K_2SO_4 per 1000g H_2O	Gm $Al_2(SO_4)_3$ per 1000g H_2O	Mols K_2SO_4 per 1000g H_2O	Mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
	% K_2SO_4	% $Al_2(SO_4)_3$					
830	100·0	0·0	120·5	0·000	0·692	0·000	K_2SO_4
773	93·4	6·6	120·5	8·50	0·692	0·025	K_2SO_4
679	89·6	10·4	131·7	15·0	0·757	0·044	(K_2SO_4 (K. Alum
731	87·9	12·1	120·4	16·6	0·692	0·049	($K_2SO_4Al_2(SO_4)_3$ (24 H_2O
999	79·6	20·4	79·6	20·4	0·457	0·059	"
1190	73·8	26·2	62·0	22·0	0·356	0·064	"
1415	53·7	46·3	38·1	32·9	0·219	0·096	"
1424	45·5	54·5	31·9	38·1	0·178	0·111	"
1384	33·7	66·3	24·3	47·7	0·139	0·139	"
1362	30·2	69·8	22·1	50·9	0·127	0·149	"
1150	23·2	76·7	20·3	66·7	0·116	0·195	"
1028	20·1	79·9	19·5	77·5	0·112	0·227	"
886	16·9	83·1	18·9	93·1	0·109	0·272	"
754	12·8	87·2	17·0	116·0	0·098	0·339	"
685	11·4	88·6	16·6	129·4	0·096	0·379	"
508	8·9	91·1	17·5	179·5	0·100	0·525	"
235	6·5	93·5	27·7	398·3	0·159	1·165	"
211	6·0	94·0	28·4	445·6	0·163	1·303	($K_2SO_4Al_2(SO_4)_3$ (24 H_2O ($Al_2(SO_4)_3$ 18 H_2O
245	3·4	96·6	13·9	394·1	0·080	1·153	($Al_2(SO_4)_3$" 18 H_2O
261	0·000	100·0	0·000	383·0	0·000	1·120	

The first three columns from the left shew the figures obtained by Britton (loc.cit.). The figures in the other columns are calculated from those of Britton.

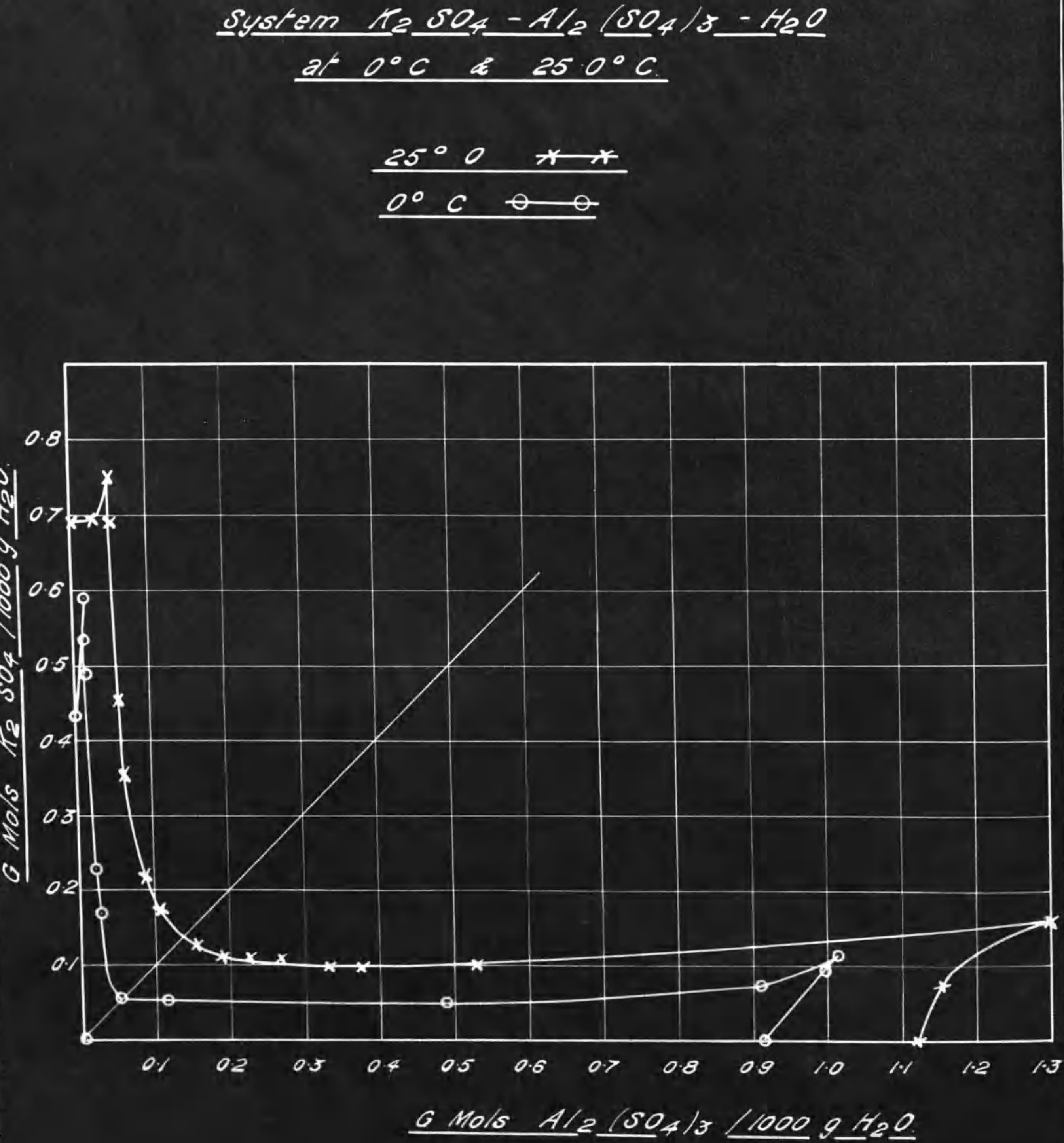
System $K_2SO_4 - Al_2(SO_4)_3 - H_2O$
at 0°C & 25.0°C
25° 0
0° C
G Mols K_2SO_4 /1000 g H_2O
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
1·3
G Mols $Al_2(SO_4)_3$ /1000 g H_2O

Fig. 15.

At those portions of the curves where aluminium sulphate hydrate is the solid phase, it will be observed that a comparatively small increase in the concentration of the potassium sulphate produces a large increase in the solubility of the aluminium sulphate.

Passing along that portion of the curve from the point at which the solid phase consists of aluminium sulphate hydrate, and potassium alum, to that at which the solid phase is alum, and the aluminium sulphate concentration is about 0.6 mols, it will be observed that the addition of potassium sulphate to the solution will actually produce a decrease in concentration of potassium sulphate as well as of aluminium sulphate, through the separation of potassium alum, i.e. potassium sulphate will deposit from solution more than its equivalent weight of alum.

The concentrations of aluminium sulphate in the solution within which potassium alum can remain as solid phase, are from .016 mols to 1.13 mols at 0^{o} C and from .044 mols to 1.30 mols at 25^{o} C, representing an increase in range with rise in temperature; these figures incidentally are of the same order as those obtained by extrapolation of curves drawn from data obtained from Marino's paper (43).[*]

---

[*] The composition of the solution in equilibrium with $Al_2(SO_4)_3$ 18 H_2O and K alum at $0^{o}C$ is given by Marino as 243.73g $Al_2(SO_4)_3$ 18 H_2O/1000g H_2O; 23.45g K_2SO_4/1000g H_2O), a

The forms of the isotherms are similar to those obtained for the system Na_2SO_4 - $Al_2(SO_4)_3$ - H_2O, except that the equimolecular line passes through the curve representing alum in equilibrium with solution, in both isotherms. Thus shewing that potassium alum can exist in equilibrium with a solution containing molecular proportions of each component at 0° C, in this respect being different from sodium alum.

The solubility curves for the isotherms at 0° C and 25° C were calculated on the basis of the Debye Theory.

These portions of the curves, representing solubilities where potassium sulphate is the solid phase, were calculated as described on pages 34 to. 40.

At the double salt portion of the curves, however, from the triple point, where K_2SO_4 and K alum are in equilibrium with solution, to the point where the double salt curve cuts the equimolar line, the equation 16 could not be applied directly, since the slope of the curve is 'outward'. A fictitious value of 'a' was taken at this part such that the curve obtained is almost parallel to the axis representing the solubility of potassium sulphate.

---

value which does not fit in with the other values given by him. This suggests that the above figure is given by mistake.

The composition of the solution at this point as determined by the author agrees with a value obtained by extrapolation from the other data given by Marino.

The values for 'a' at the other portions of the curves were calculated as previously explained.

No attempt was made to calculate changes in solubility where aluminium sulphate was the solid phase, as it has been shewn (44) that the Debye theory gives as a rule impossible results when applied to such ions as aluminium at such concentrations.

The results obtained are given in Tables 5 and 6.

A study of Figures 16 and 17 shews that there is comparatively good agreement between the calculated, and experimental values, within the concentrations calculated. The middle portion of the double salt curve in the isotherm at 25° C could not, as already pointed out on page 41, be calculated by the method used in the other parts of the double salt curve owing to the slope of the curve being outward.

The system $K_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C.

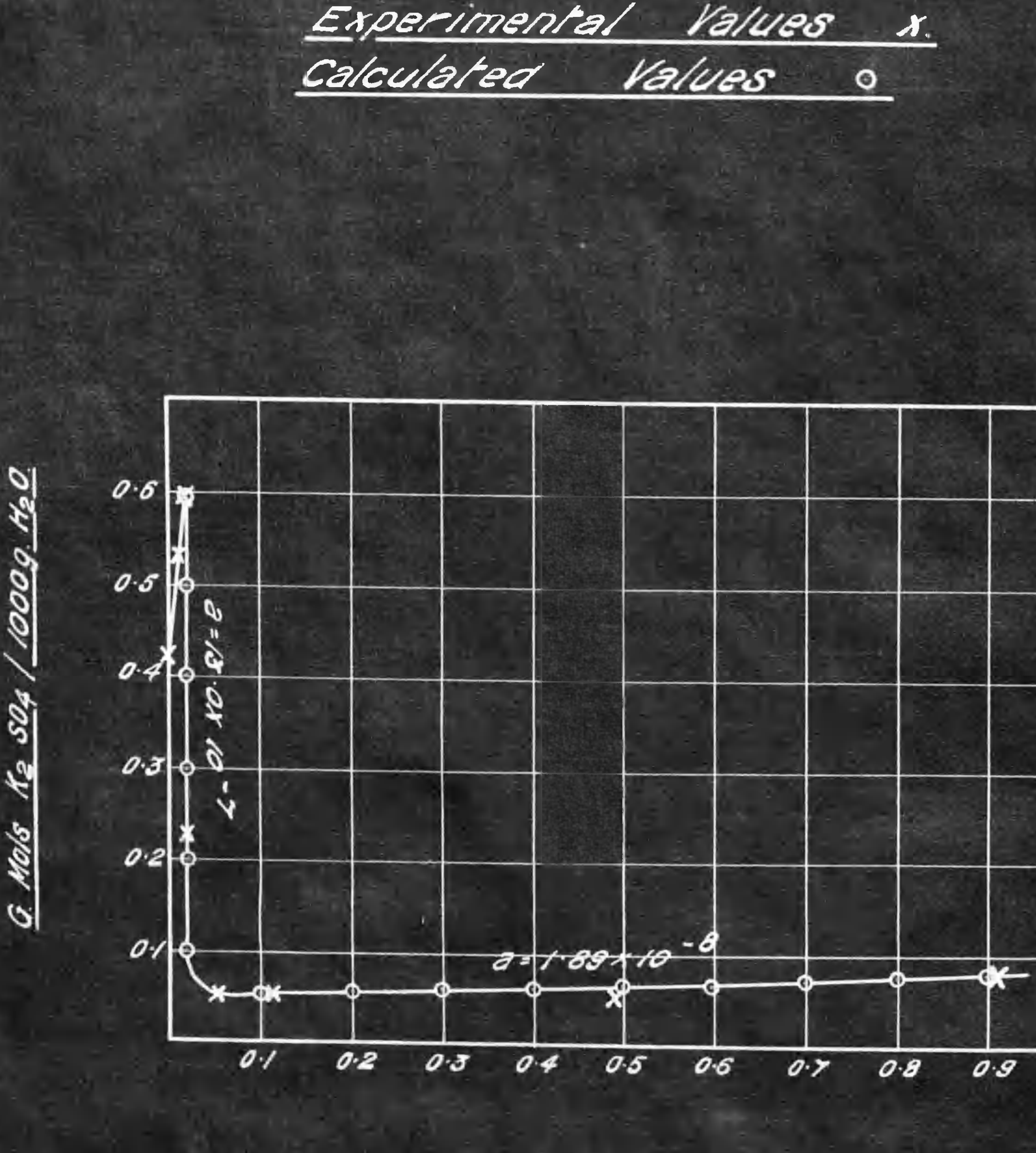

Fig. 16

The System $K_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 25°c.

Experimental Values X

Calculated Values ○

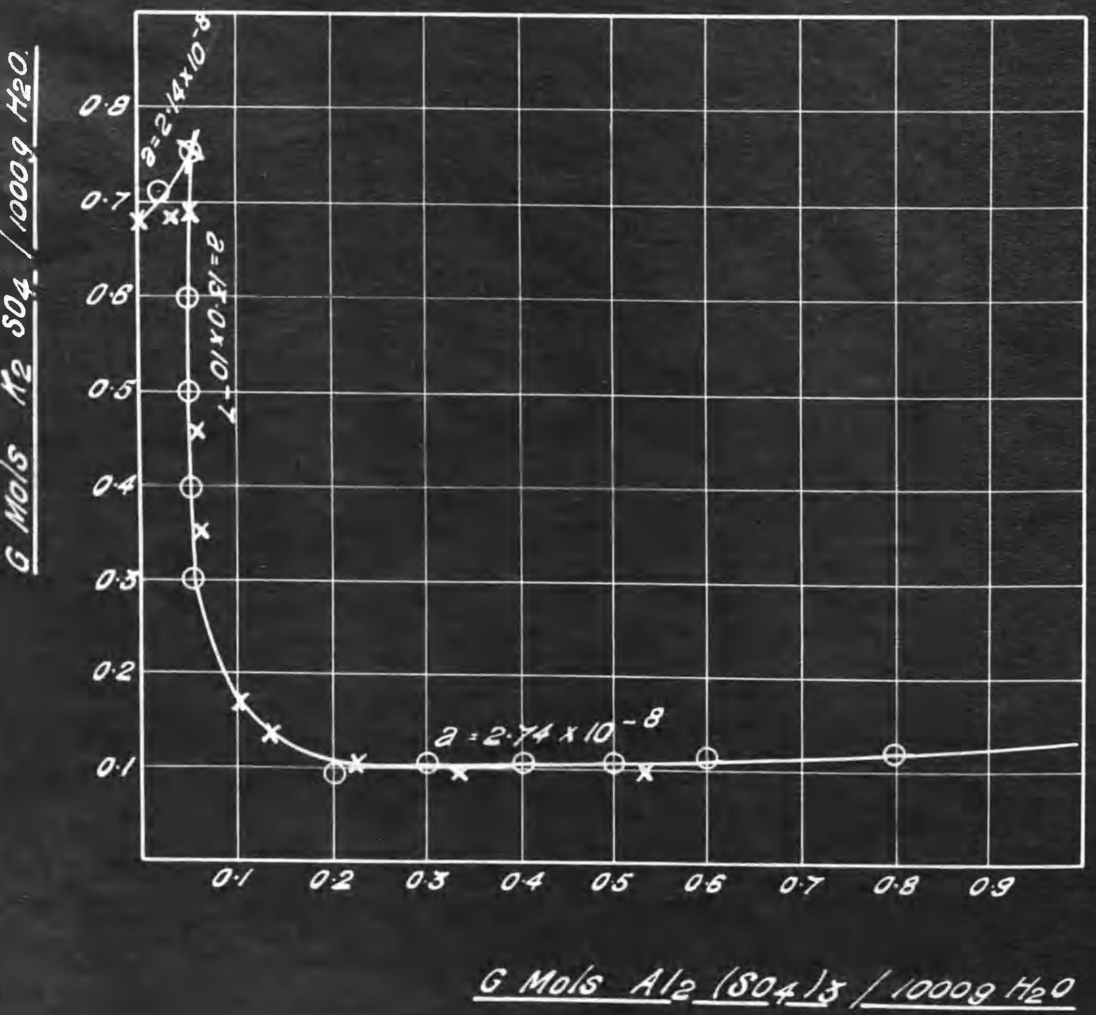

Fig. 17

TABLE 5.

The System K_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C.

K_2SO_4 in the solid phase

$a = 3.34 \times 10^{-8}$

Concentration of K_2SO_4 mols/1000g. H_2O		Concentration of $Al_2(SO_4)_3$ mols/1000g.H_2O
0.427	(experimental)	0.000
0.587		0.010
0.590	calculated	0.016

Solid Phase K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O

$\bar{a} = 13.0 \ 10^{-7}$ (fictitious value)

log f_{Al}	Concentration of K_2SO_4 mols/1000g. H_2O	Concentration of $Al_2(SO_4)_3$ mols/1000g. H_2O
	Taken	Calculated
-0.2391	.589	·020
-0.2386	.500	·01999
-0.2378	-400	·01998
-0.2371	.300	·01996
-0.2364	.200	·01993
-0.2357	.100	·01990

Solid Phase K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O

$a = 1.89 \times 10^{-8}$

	Calculated	Taken
-1.252	0.0800	0.900
-1.198	0.0758	0.800
-1.144	0.0717	0.700
-1.090	0.0677	0.600
-1.036	0.0644	0.500
-0.982	0.0611	0.400
-0.928	0.0579	0.300
-0.874	0.0548	0.200
-0.8202	0.0520	0.100

TABLE 6.

The System K_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 25° C.

Where $K_2 SO_4$ is the solid phase.

$a = 2.14 \times 10^{-8}$

Concentration K_2SO_4 mols/ 1000g.H_2O	Concentration $Al_2(SO_4)_3$ mols/1000g. H_2O	Solid phase
Calculated	Taken	
0.692 (experimental)	0.000	K_2SO_4
0.710	0.020	K_2SO_4
0.757	0.044	K_2SO_4 Alum

Solid Phase K_2SO_4 $Al_2(SO_4)_3$ 24 H_2O at 25° C.

$a = 13.0 \times 10^{-7}$. (fictitious).

log f_{Al}	Concentration of K_2SO_4 mols/1000g H_2O	Concentration of $Al_2(SO_4)_3$ mols/1000g H_2O
	Taken	Calculated
-0.2496	0.757	0.050
-0.2493	0.600	0.0499
-0.2491	0.500	0.4998
-0.2489	0.400	0.4998
0.2487	0.300	0.4997

$a = 2.74 \times 10-8$

log f_K	Calculated.	Taken
-1.000	0.120	0.800
-0.9716	0.1175	0.700
-0.9087	0.109	0.500
-0.8784	0.106	0.400
-0.8479	0.103	0.300
-0.8174	0.0998	0.200

These results, along with the experimental values are shewn in Figs. 16 and 17.

The System $(NH_4)_2SO_4$ - $Al_2(SO_4)_3$ - H_2O at 0°C and 25°C.

Although several investigators (39, 41, 42) have determined the solubility of ammonium alum, no one has apparently worked out isotherms for the system $(NH_4)_2SO_4$ - $Al_2(SO_4)_3$ - H_2O. Rudorff, however, (45) determined the solubility of ammonium alum in presence of ammonium sulphate and in presence of aluminium sulphate in water at 18.5° C.

Experimental.

Saturated solutions containing ammonium and aluminium sulphate in varying proportions were made up a few degrees above the temperature of the isotherm. These solutions were placed in bottles fitted with stirrers, and placed in a thermostat regulated to remain at 25° C, or at 0° C. Agitation was continued for a period of three days, when a portion of the solution about 20 g. - was removed, made up to 250 ccs and analysed.

Method of Analysis.

The most convenient method of analysis in this case was to estimate the ammonium sulphate by the ammonia evolution method; and to determine the total sulphate by precipitation with barium chloride as before. The aluminium sulphate content could then be obtained.

Results.

The results obtained are given in Tables 6 and 7. Table 6 correlates the solubility values for the isotherm at 0° C and Table 7 those for the isotherm at 25° C.

Graphs of the isotherms are shewn on Figures 18 and 19.

Discussion of Results.

The isotherms are of a shape somewhat similar to those obtained for K_2SO_4 - $Al_2(SO_4)_3$ - H_2O, but with certain differences.

First, the additionsof aluminium sulphate produces a decrease in the concentration of the ammonium sulphate up to the point where double salt and ammonium sulphate form the solid phase. Further addition of aluminium sulphate causes a further decrease in the concentration of the ammonium sulphate, and the gradient of the curve is such that the addition of aluminium sulphate to a solution, of constitution as represented by a point on the double salt portion of the curve near to the triple point, in equilibrium with double salt, would cause the deposition of a quantity of ammonium alum, greater

TABLE 7.

The System $(NH_4)_2$ SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C.

g mols (NH_2) SO_4 per 1000g H_2O	g mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
5·34	0·00	$(NH_4)_2$ SO_4
5·22	0·066	($(NH_4)_2$ SO_4 ($(NH_4)_2$ $SO_4Al_2(SL_4)_3$ 24 H_2O
5·06	0·069	($(NH_4)_2$ $SO_4Al_2(SO_4)$ 24 H_2O
4·18	0·050	"
1·10	0·036	"
0·213	0·0203	"
0·0443	0·0443	"
0·0258	0·425	"
0·0165	0·485	"
0·0456	0·7307	"
0·064	1·004	($(NH_4)SO_4Al_2(SO_4)_3$ 24 H_2O ($Al_2(SO_4)_3$ 18 H_2O
0·000	0·915	$Al_2(SO_4)_3$ 18 H_2O

TABLE 8.

The System $(NH_4)_2 SO_4 - Al_2(SO_4)_3 - H_2O$ at 25°O.

g.mols $(NH_4)_2SO_4$ per 1000g H_2O	g.mols $(Al)_2(SO_4)_3$ per 1000g H_2O	Solid Phase
5·802	0·000	$(NH_4)_2 SO_4$
5·70	0·043	"
5·512	0·088	$(NH_4)_2 SO_4$ $(NH_4)_2 SO_4 Al_2 (SO_4)_3 24 H_2O$
5·37	0·089	"
1·460	0·0358	"
0·558	0·0468	"
0·229	0·0892	"
0·190	0·190	"
0·065	0·388	"
0·049	0·796	"
0·0405	0·933	"
0·034	1·068	"
0·0425	1·190	$NH_4\ {}_2SO_4\ Al_2(SO_4)_3 24\ H_2O$ $Al_2(SO_4)_3\ 18\ H_2O$
0·000	1·120	$Al_2(SO_4)_3\ 18\ H_2O$

$(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$

at 0°C.

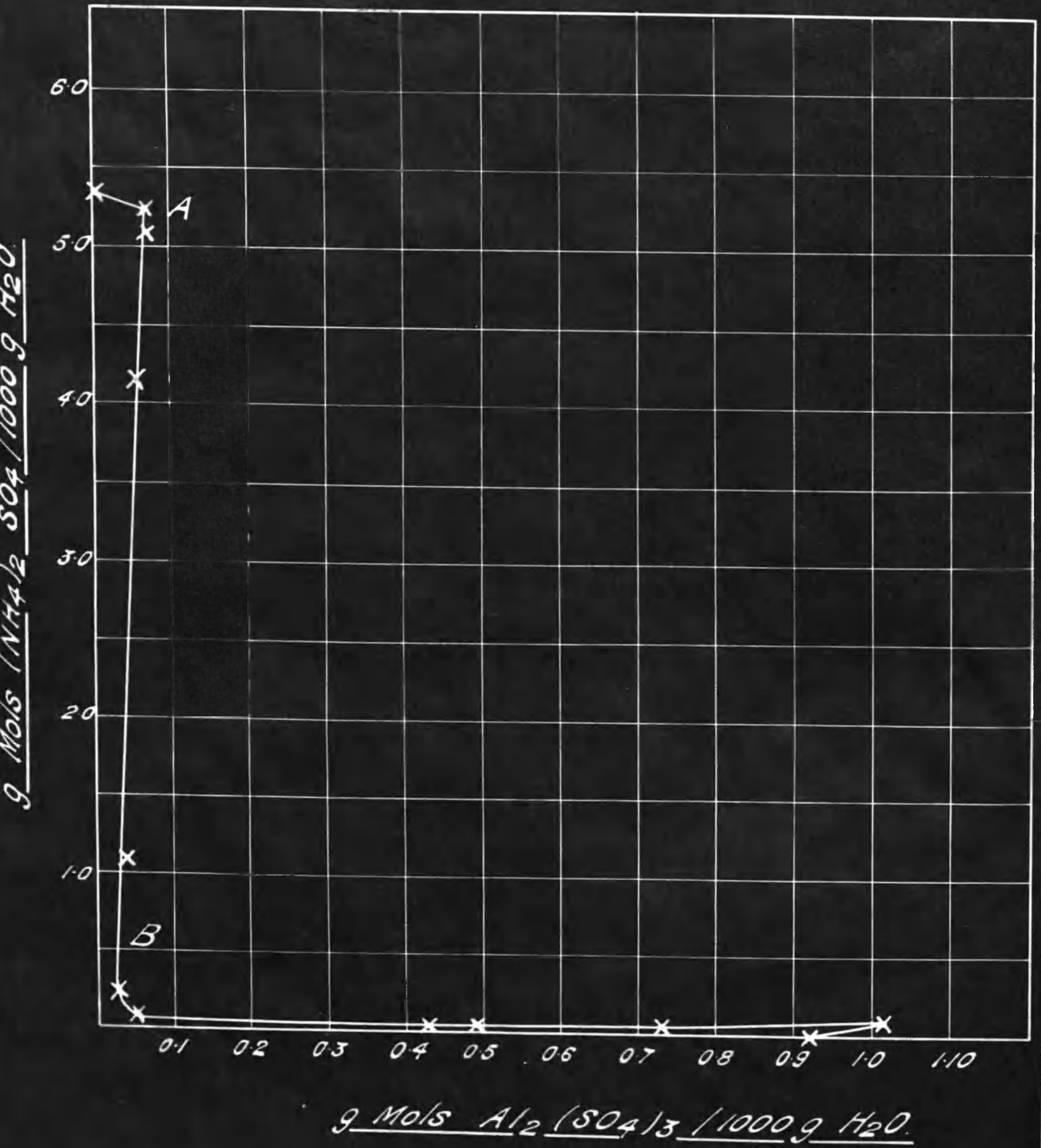

Fig. 18.

$(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$

at 25° C.

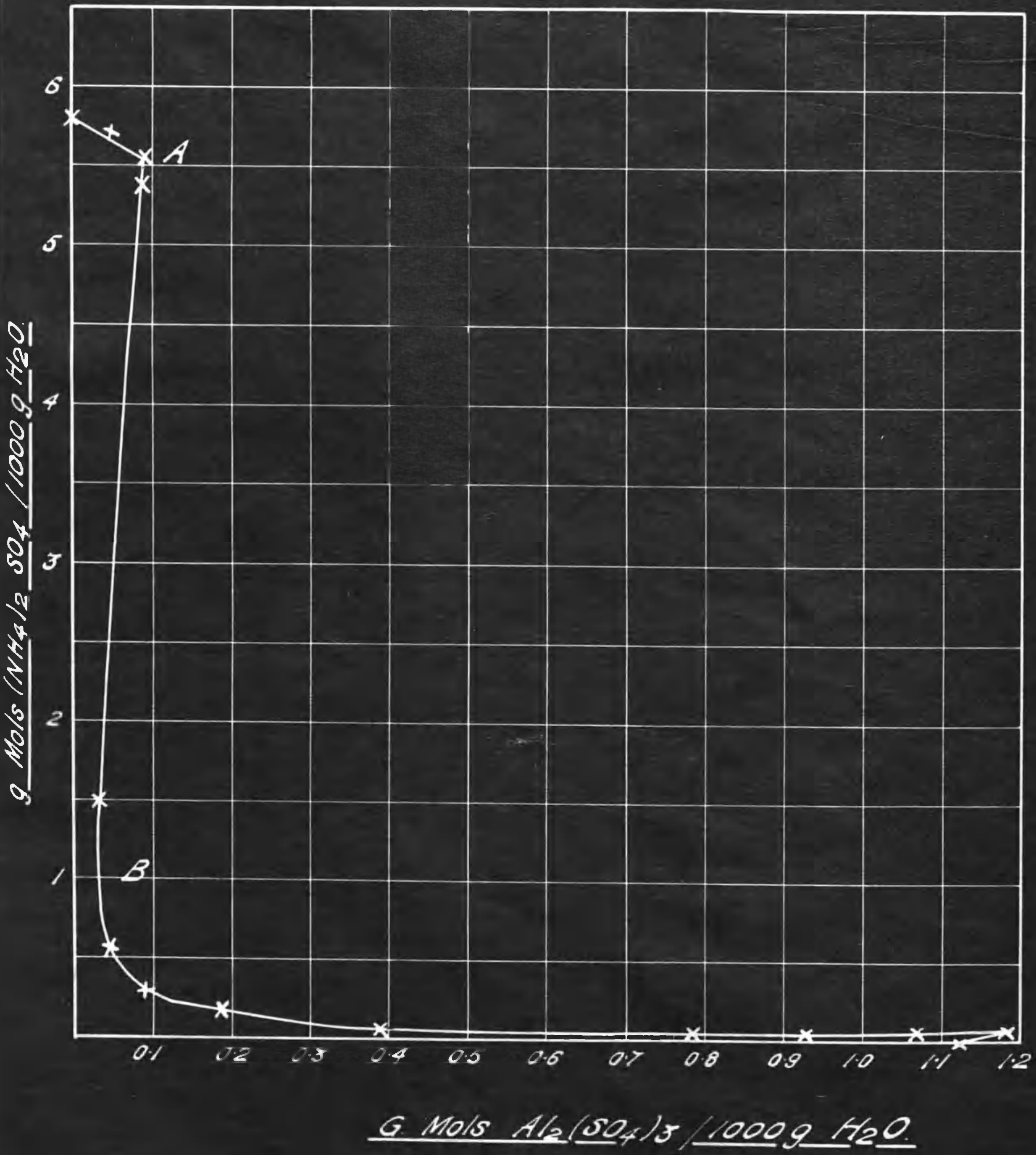

Fig. 19.

than that, equivalent to the weight of aluminium sulphate added. In this particular portion of the curve (A - B Figs. 18 and 19) we have the peculiar phenomenon of the addition of a salt to a saturated solution actually decreasing the concentration of that salt in the solution.

Owing to the high concentrations, the solubility theory of Debye and Hückel was not applied where the solid phase was ammonium sulphate. On the other hand, the change in concentrations in the double salt portions of the curves may be calculated as described on pages 38 to 40. The values obtained are given on Tables 9 and 10.

Figures 20 and 21 shew how closely the calculated and experimental values agree. As in the case of the K_2SO_4 - $Al_2(SO_4)_3$ - H_2O system, the agreement is better in the case of the isotherm at 0° C than at 25° C, possibly owing to lower concentrations. The middle portion of the curve at 25° C was not calculated for the same reason as in the case of the analogous curve of potassium alum at 25° C.

At the portion of the curve where aluminium sulphate hydrate is the solid phase, it will be observed that the addition of ammonium sulphate produces an increase in the concentration of the aluminium sulphate until the double salt begins to separate from the solution. Further addition of ammonium sulphate produces a decrease in the concentration of

TABLE 9.

The System $(NH_4)_2\ SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C.

Solid Phase $(NH_4)_2\ SO_4\ Al_2(SO_4)_3\ 24\ H_2O$.

$a = 7.01 \times 10^{-8}$.

$\log f_{Al}$.	Concentration of $(NH_4)_2\ SO_4$ g.mols / 1000g H_2O	Concentration of $Al_2(SO_4)_3$ g.mols / 1000g H_2O
	Taken	Calculated
-3·996	4·18	0·0500
-3·832	2·00	0·0424
-3·660	1·100	0·036
-3·418	0·500	0·028
-3·177	0·200	0·022
	$a = 0.442 \times 10^{-8}$	
$\log f_{NH_4}$	Calculated	Taken
-2·576	0·0456	0.730
-2·249	0·0330	0·500
-2·129	0·0290	0·425
-1·616	0·0170	0·200
-1·222	0·0120	0·100

These values are shewn along with the corresponding experimental values, in figure 20.

TABLE 10.

The System $(NH_4)_2SO_4$ $Al_2(SO_4)_3$ - H_2O at 25° C.

Solid Phase $(NH_4)_2SO_4$ - $Al_2(SO_4)_3$ - 24 H_2O.

$a = 6.18 \times 10^{-8}$

log f Al.	Concentration of $(NH_4)_2SO_4$ mol/1000g. H_2O	Concentration of $Al_2(SO_4)_3$ mols/1000g. H_2O
	Taken	Calculated
-4.581	3.00	0.050
-4.458	2.00	0.044
-4.210	1.00	0.0345
-4.052	0.70	0.0295

$a = 3.21 \times 10^{-8}$

log f (NH_4)	Calculated	Taken
-0.8333	.050	0.500
-0.8096	.0488	0.400
-0.7780	.0473	0.300
-0.7298	.0451	0.200

The system $(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C

Portion of Double Salt Curve.

Experimental Values x

Calculated Values ○

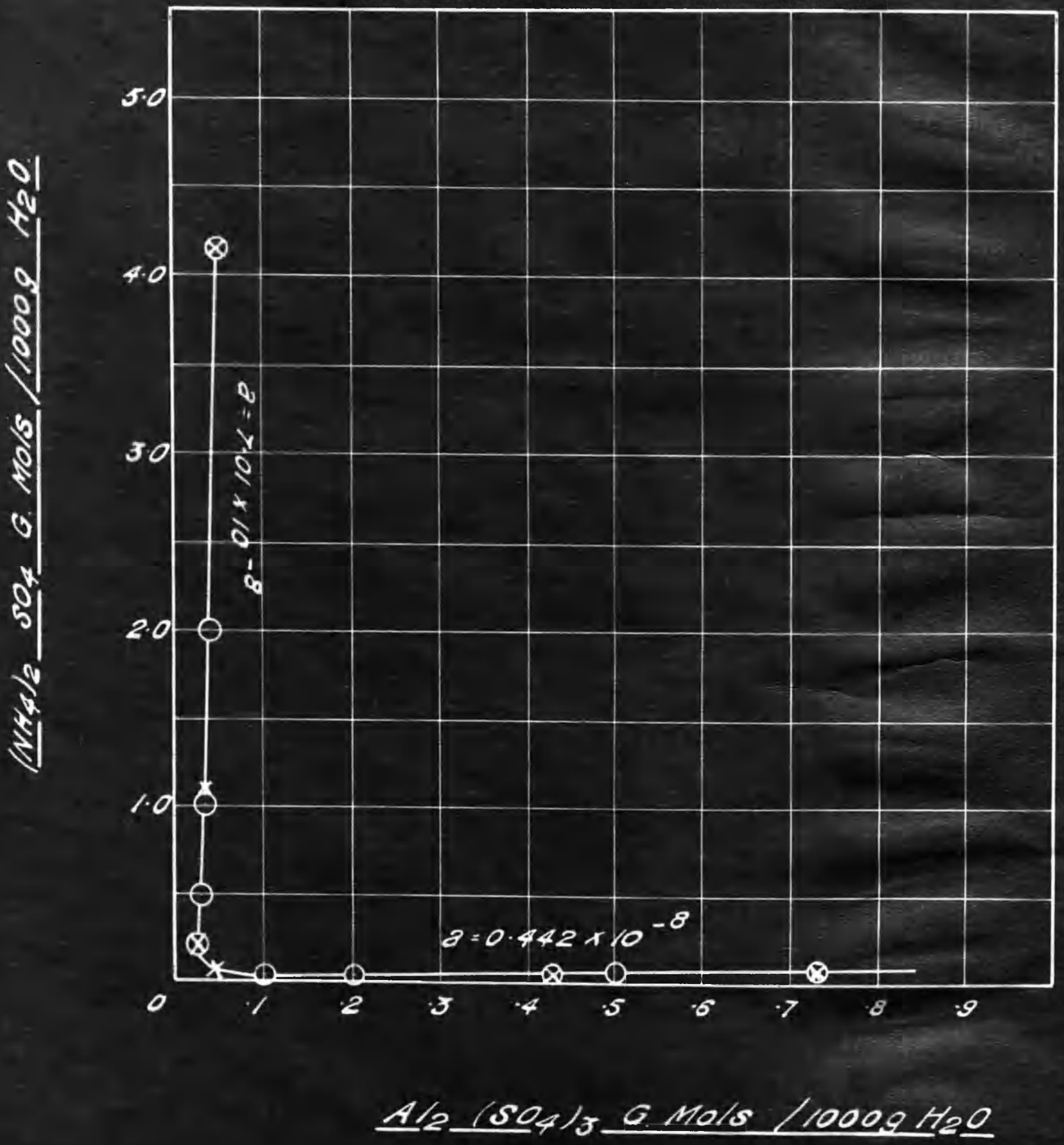

Fig. 20.

The system $(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 25° C.

Portion of Double Salt Curve.

Experimental Values x
Calculated Values ○

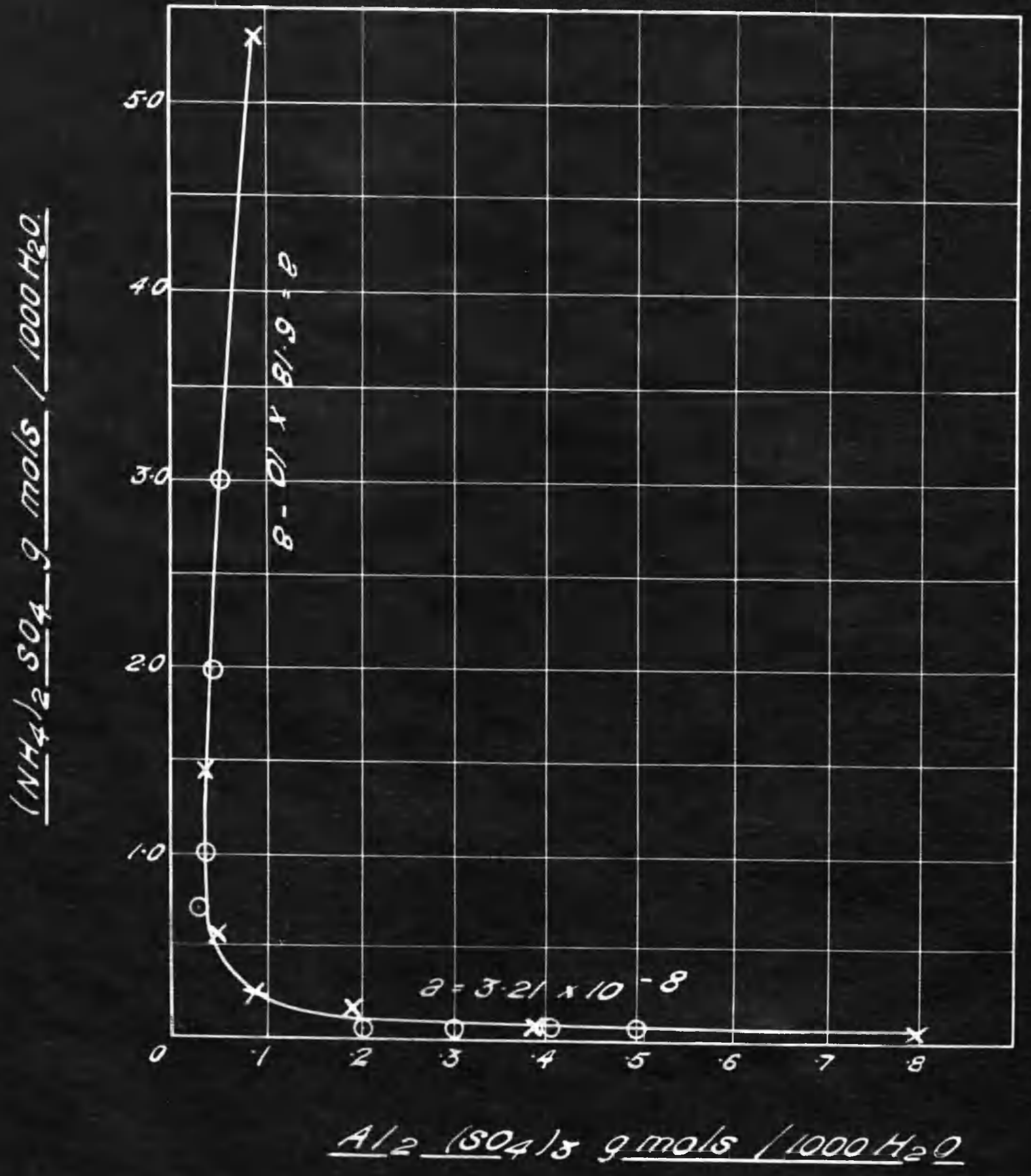

Fig. 21.

the ammonium sulphate, with deposition of double salt.

The range of formation of the ammonium alum is from 0.07 mols to 1.10 mols of aluminium sulphate at 0° C and from 0.09 mols to 1.19 mols at 25° C. Thus there is a slight increase in the limits of formation with rise of temperature.

The cause of the decrease in the solubility of the ammonium sulphate with the addition of aluminium sulphate may be that the decrease in solubility due to the probability of oppositely charged ions colliding and precipitating is greater than the tendency to increase in solubility due to greater total ionic concentration. (Schärer. 25)

In the double salt portion of the curve the inward slope is consistent with practically complete dissociation, and decreased ionic effect with fall of concentration. In this respect the curve for ammonium alum is different from that for sodium alum and differs from a portion of the potassium alum curve.

The System $(Tl)_2 SO_4 - Al_2(SO_4)_3 - H_2O$.
at 0° C and 25° C.

Whilst the solubility of thallium alum has been determined by several workers (41) (42) (46), no one has apparently determined a solubility isotherm of the system $Tl_2SO_4 - Al_2$

$(SO_4)_3$ - H_2O. In view of the close chemical relationship of thallium with the alkali group, a determination of the limits of formation of the thallium alum was of interest, and was accordingly determined at 0° C and 25° C.

Regarding the isotherm at 25° C it must be stated that owing to the short time available (through the author leaving to take up a post with Messrs. The Imperial Chemical Industries), it was impossible to determine the complete isotherm, but in view of the importance of the results in the light of the Debye solubility theory, it was decided to include the work done on this isotherm in this report.

Experimental.

The procedure followed was similar to that used in the determination of the isotherm for the system K_2 SO_4 - Al_2 $(SO_4)_3$ - H_2O. The thallium sulphate used was recrystallised material.

The analytical procedure was the same as in the potassium sulphate - aluminium sulphate - water system; the composition of the solutions being calculated from the analytical determination of the aluminium, and total sulphate contents of the solutions.

A remark is necessary regarding the accuracy of the results. On account of the high molecular weight of Tl_2SO_4

and its low solubility, a very small error in the aluminium estimation causes a comparatively large error in the thallium sulphate figure; the probable accuracy of the thallium sulphate estimation is about 1% - 3%, according to the concentration of the aluminium sulphate.

Results.

The results obtained are given in the following Tables:-

Table 11 shews the figures for the isotherm at 0° C.
Table 12 shews the figures for the isotherm at 25° C.
Figures 22 and 23 shew graphs of the two isotherms.

Discussion of Results.

In both isotherms it is shewn that the addition of aluminium sulphate to a saturated solution of thallium sulphate in presence of thallium sulphate, increases the solubility of the solid phase salt.

At the double salt portions of the curves it will be seen that the form is similar to that obtained in the system $(NH_2)_2SO_4 - Al_2(SO_4)_3 - H_2O$. From the point at which thallium alum and thallium sulphate form the solid phase, a decrease in the concentration of thallium sulphate, as well as aluminium sulphate would be caused by the addition of aluminium sulphate, until the concentration of the aluminium sulphate reaches a

TABLE 11.

The System Tl_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0°C.

g mols Tl_2SO_4 per 1000g H_2O	g mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
0·0535	0·000	Tl_2SO_4
0·0563	0·0275	"
0·0614	0·0500	(Tl_2SO_4 (($Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O
0·0470	0·0260	($Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O
0·0371	0·0371	" "
0·0390	0·181	" "
0·0496	0·277	" "
0·103	0·681	" "
0·154	0·969	" "
0·231	1·22	($Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O (($Al_2(SO_4)_3$ 18 H_2O
0·191	1·052	$Al_2(SO_4)_3$ 18 H_2O
0·000	0·973	" "

TABLE 12.

The System Tl_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 25° C.

g mols Tl_2SO_4 per 1000g H_2O	g mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
0·0998	0·000	Tl_2SO_4
0·136	0·0725	"
0·145	0·0910	Tl_2SO_4 $Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O
0.090	0·090	$Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O
0·0814	0·0885	" "
0·0932	0·405	" "
0·0956	0·433	" "
0·112	0·708	" "
0·231	1·259	$Tl_2SO_4Al_2(SO_4)_3$ 24 H_2O $Al_2(SO_4)_3$18 H_2O
0·000	1·120	$Al_2(SO_4)_3$ 18 H_2O

The system $Tl_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C.

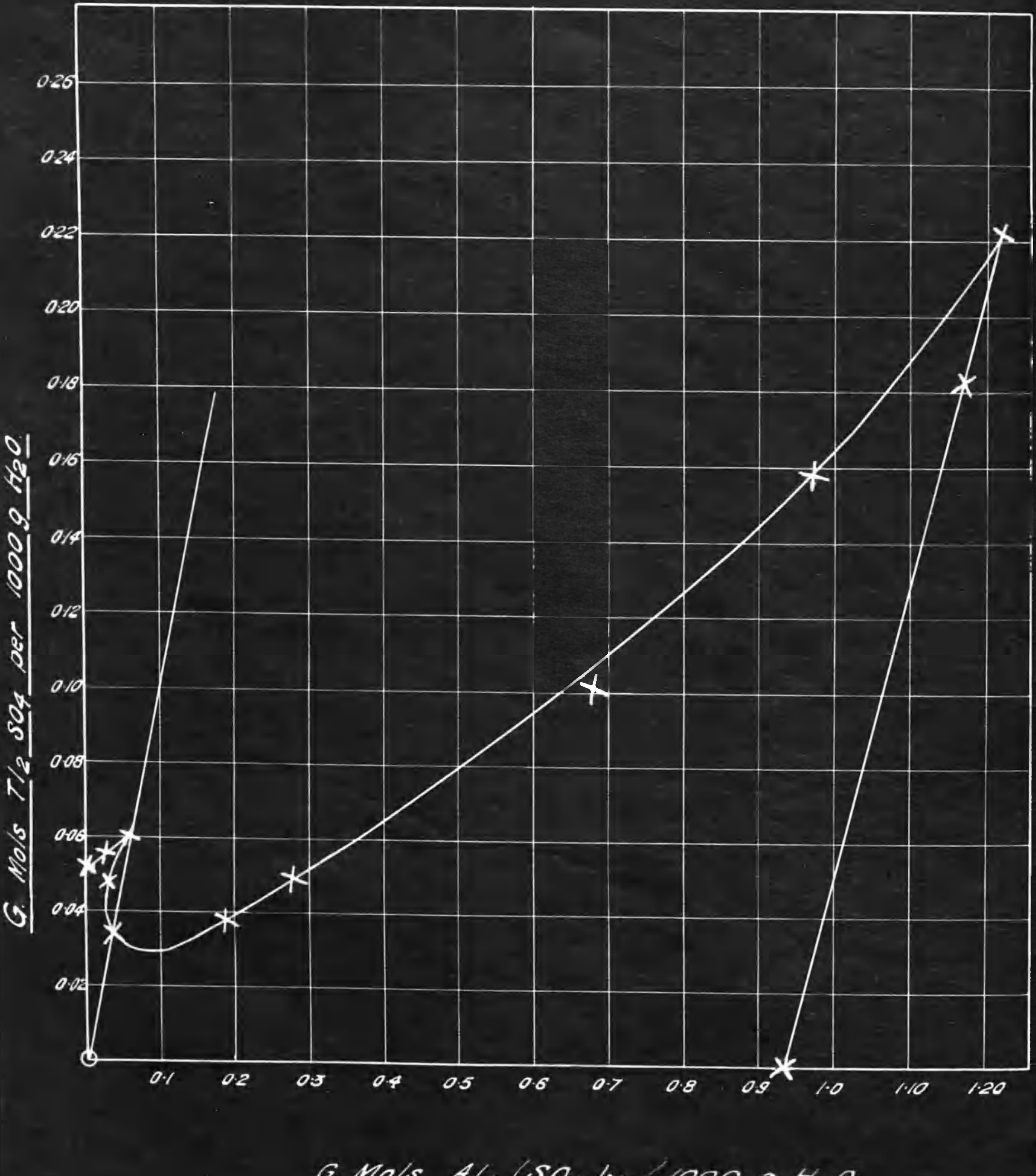

Fig 22.

System $Tl_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 25° C.

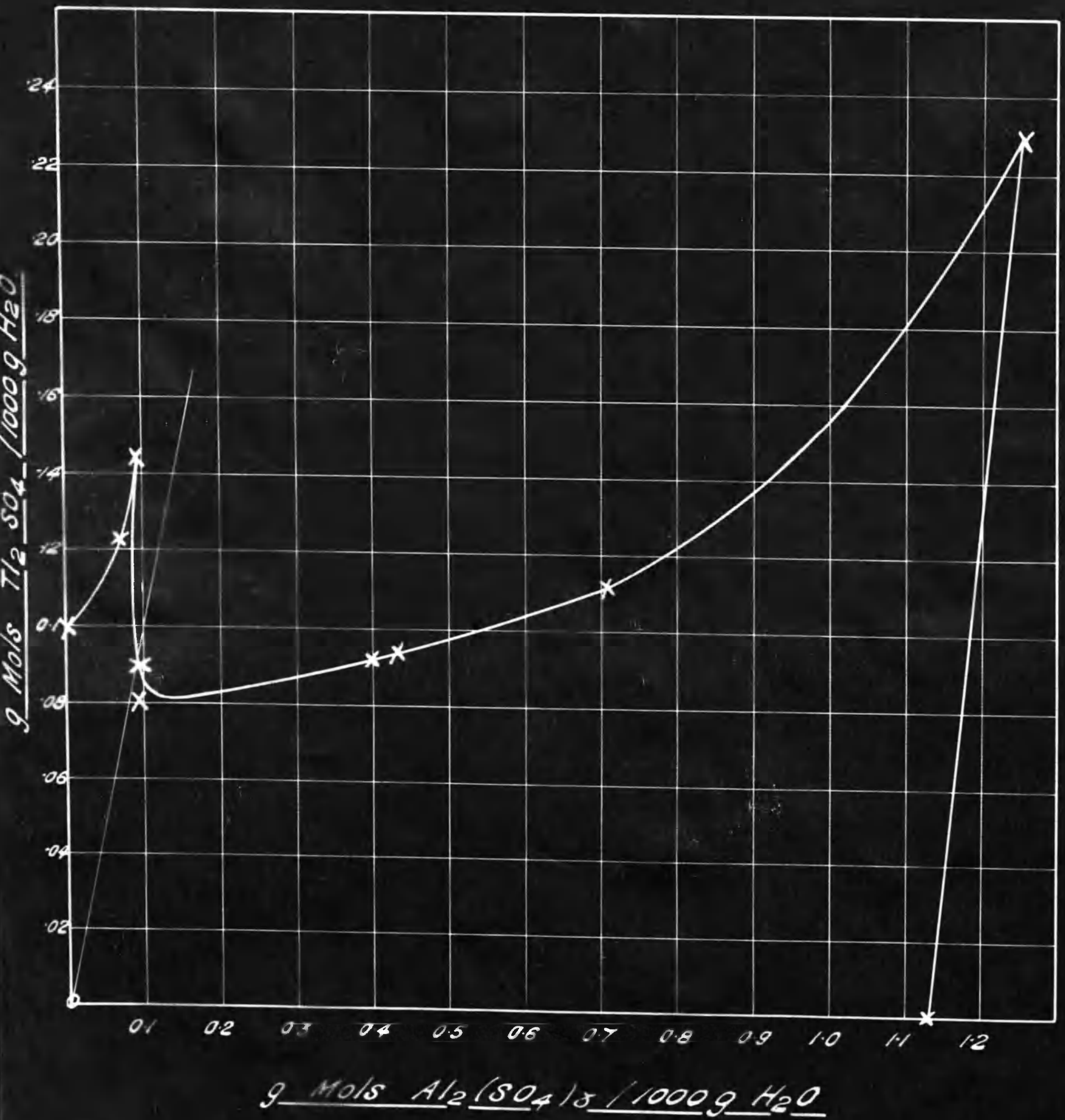

Fig. 23.

concentration of about 0.1 mol. Beyond this concentration further quantities of aluminium sulphate would be dissolved, causing also solution of the solid phase, until that point is reached where thallium alum and aluminium sulphate hydrate constitute the solid phase.

At those parts of the curves where the solid phase is $Al_2(SO_4)_3$ 18 H_2O addition of thallium sulphate causes an increase of solubility of the solid phase salt, up to the triple point at which the alum and aluminium sulphate hydrate are in equilibrium with the solution.

As in the other cases, the alum is formed over very wide limits from 0.05 to 1.22 mols of aluminium sulphate, $Al_2(SO_4)_3$ at 0° C, and from 0.09 to 1.26 mols at 25° C, shewing that the limits of formation of the alum are practically the same for the two temperatures. In this respect thallium alum differs from the other alums of the series, which shew a marked increase in range of formation with rise in temperature from 0° C to 25° C.

As in the case of potassium and ammonium alums, the alum can exist in equilibrium with its solution at 0° and 25° C.

Calculation of Part of the Solubility Curves, on the Basis of the Debye Theory of Solution.

The low concentrations at the thallium sulphate end of the curve allow the Debye theory to be applied over a large part of the curves.

The calculations were made as in the system K_2SO_4 - $Al_2(SO_4)_3$ - H_2O. The results obtained are given in Tables 13 and 14.

An examination of Figures 24 and 25 shews that there is a comparatively close agreement between the calculated and experimental values within the concentrations taken. It will be observed (as in the case where K_2SO_4 is solid phase) that where Tl_2SO_4 is the solid phase the calculated values give a curve which is convex upwards, whilst the experimental curve is concave upwards. The possible significance of this is dealt with in the general discussion of results.

The System Li_2SO_4 - $Al_2(SO_4)_3$ - H_2O.

The solubility isotherm for the above system at 30° C was determined by Schreinemakers and De Waal (47.) This appears to be the only published work on this system. It was shewn that lithium alum was not formed at the above temperature.

TABLE 13.

The System Tl_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C.

Where Tl_2SO_4 is in the solid phase

$a = 2.48 \times 10^{-8}$

Concentration of Tl_2SO_4 mols/1000g H_2O Calculated	Concentration of $Al_2(SO_4)_3$ mols/1000g H_2O Taken	Solid Phase
0·535 (experimental)	0·000	Tl_2SO_4
0·586	0·020	"
0·614	0·050	(Tl_2SO_4 (Thallium alum

Where solid Phase is Double Salt

$Tl_2SO_4 \ Al_2(SO_4)_3 \ 24 \ H_2O$

$a = 9.92 \times 10^{-8}$

log $f_{Al.}$	Concentration of Tl_2SO_4 mols/1000g H_2O	Concentration of $Al_2(SO_4)_3$ mols/1000g H_2O
	Taken	Calculated
-7·612	·0614	·050
-7·518	·550	·045
-7·480	·0500	·044
-7·364	·0400	·039
-7·328	·035	·037

$a = \cdot 386 \times 10^{-8}$

log $f_{Tl.}$	Calculated	Taken
-2·430	·080	0·500
-2·239	·066	0·400
-1·991	·051	0·300
-1·690	·038	0·200
-1·273	·025	0·100

TABLE 14.

The System $Tl_2(SO_4)\ Al_2(SO_4)_3 - H_2O$ at 25° C.

Where Tl_2SO_4 is in the solid phase

$a = 4{\cdot}07 \times 10^{-8}$

Concentration of Tl_2SO_4 mols/1000g H_2O Calculated	Concentration of $Al_2(SO_4)_3$ mols/1000g H_2O Taken	Solid Phase
0·0998 (experimental)	0·000	Tl_2SO_4
0·145	·070	Tl_2SO_4
0·147	·091	Tl_2SO_4 & Thallium Alum

Where solid phase is double salt

$Tl_2SO_4\ Al_2(SO_4)_3\ 24\ H_2O$

$a = 13{\cdot}9 \times 10^{-7}$

log f Al.	Concentration of Tl_2SO_4mols/1000g H_2O	Concentration of $Al_2(SO_4)_3$mols/1000g H_2O
	Taken	Calculated
-1·378	0·145	0·0910
-1·375	0·130	0·0908
-1·371	0·110	0·0904
-1·367	0·090	0·0900

$a = 3{\cdot}26 \times 10^{-8}$

log f_{Tl}	Calculated	Taken
-0·8153	0·100	0·550
-0·8067	·099	0·500
-0·7872	·0973	0·400
-0·7563	·0943	0·300
-0·7129	·0903	0·200
-0·6816	·0875	0·150

Graphs of the calculated and experimental values are shewn in figures 24 and 25.

The System $Tl_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C.

Experimental Values x.

Calculated Values ○

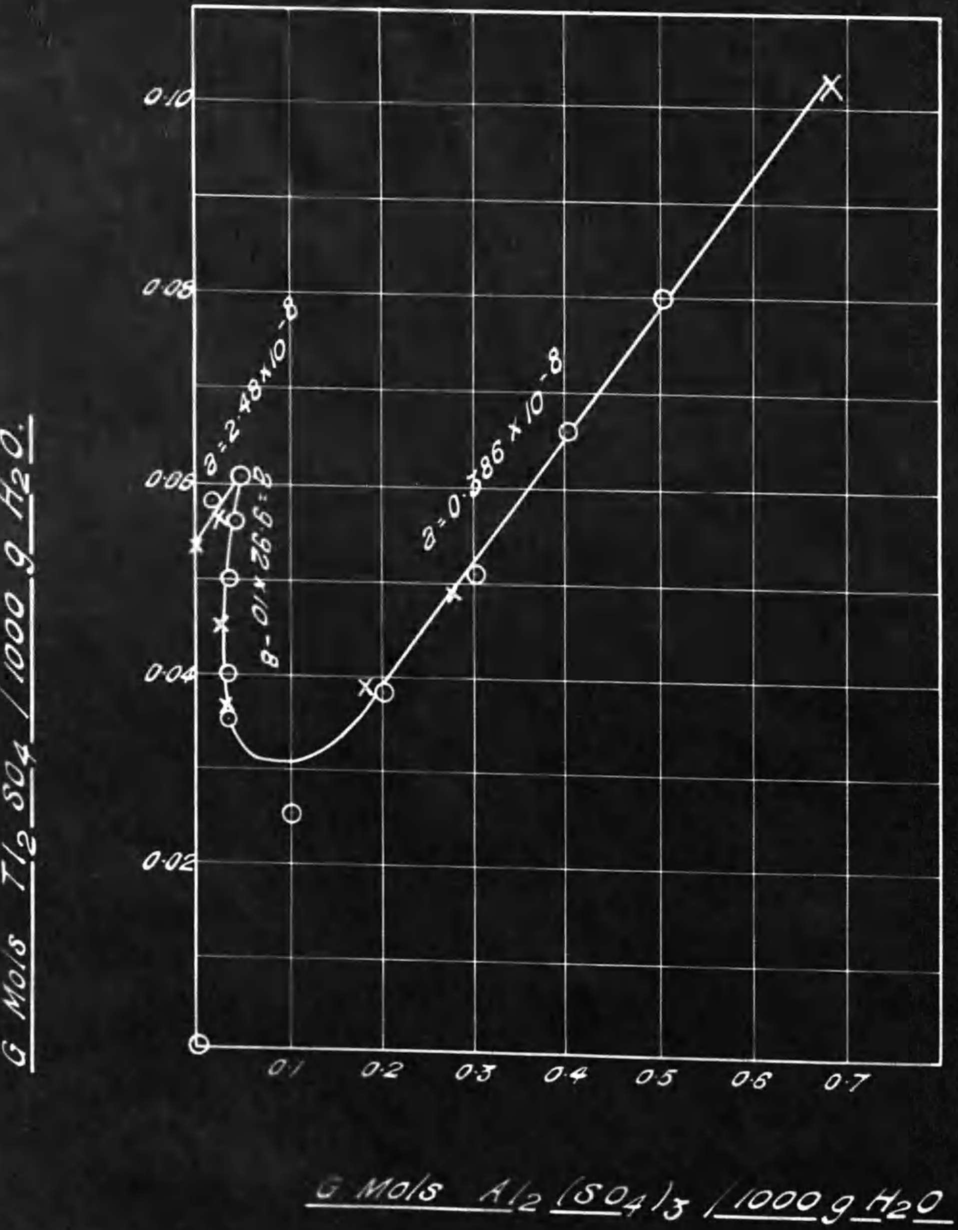

Fig. 24.

The system $Tl_2SO_4 - Al_2(SO_4)_2 - H_2O$ at 25° C.

Experimental Values X

calculated Values O

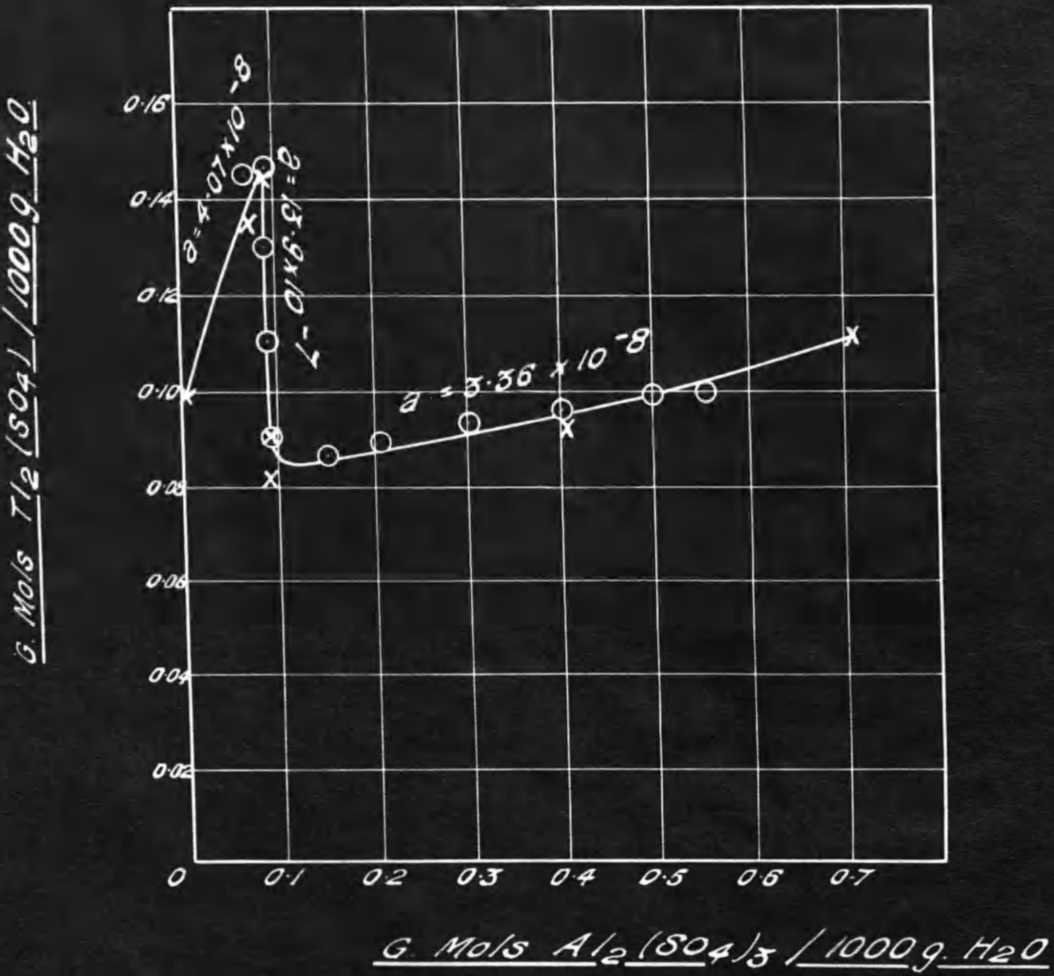

Fig. 25.

Owing to scarcity of time - due to aforesaid reason - it was not found possible to determine the complete isotherm at 0° C - sufficient points, however, were determined, to shew beyond any possible doubt, the form of the isotherm at 0° C, and to prove conclusively that the double salt was not formed at that temperature.

Experimental.

The procedure followed was similar to that for the other systems.

Since the proof of the existence of a solution of definite composition existing in equilibrium with a solid phase consisting of lithium sulphate and aluminium sulphate was of supreme importance, care was taken to determine that the solid phase at this point did not contain alum.

Two separate experiments were carried out to fix this point. In one case, after equilibrium had been attained and a sample of the solution analysed, a quantity of lithium sulphate monohydrate was added to the mixture, and stirring continued for three additional days. A sample of the solution was taken and analysed, and, as it had the same composition as before, shewed that lithium sulphate monohydrate was present in the solid phase.

In the other experiment, some freshly prepared aluminium sulphate hydrate was added, after equilibrium had been obtained, and a sample of the solution analysed, and stirring continued for three to four additional days. The solution was then again analysed, and as it had the same composition as formerly, it may be concluded that the aluminium sulphate hydrate was in the solid phase.

The composition of the solution in the above case was the same, thus it can be concluded that the solid phase consisted of $Al_2(SO_4)_3$ 18 H_2O and Li_2SO_4 H_2O.

Analysis of the solid phases of the curves on each side of this point shewed them to be $Li_2SO_4H_2O$ and $Al_2(SO_4)_3$ 18 H_2O respectively.

Results.

The results obtained for the system at 0^o C are shewn in Table 15, and Table 16 shews the results obtained by Schreinemakers and De Waal (47) expressed in a form suitable for comparison with the other results. Figure 26 shews graphs of these determinations.

Discussion of Results.

The addition of aluminium sulphate to a saturated solution of lithium sulphate at either 0^o C or 30^o C produces a decrease in the solubility of the lithium sulphate, and vice versa.

TABLE 15.

System Li_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° C.

Mols Li_2SO_4 per 1000g H_2O	Mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
3 27	0 00	$Li_2SO_4H_2O$
3 024	0 129	"
2 76	0 277	"
2 356	0 565	"
2 137	0 737	($Li_2SO_4H_2O$ (($Al_2(SO_4)_3$ 18 H_2O
1 59	0 817	$Al_2(SO_4)_3$ 18 H_2O
1 35	0 851	" "
0 00	0 915	" "

TABLE 16.

The System Li_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 30° C.

Schreinemakers and De Waal. (47)

Composition of Solution		Mols Li_2SO_4 per 1000g H_2O	Mols $Al_2(SO_4)_3$ per 1000g H_2O	Solid Phase
% Li_2SO_4	% $Al_2(SO_4)_3$			
25·1	0	3·046	0·00	Li_2SO_4 H_2O
21·93	5·34	2·738	0·215	"
16·10	14·89	2·12	0·631	"
13·63	20·76	1·88	0·925	(Li_2SO_4 H_2O (($Al_2(SO_4)_3$ 18 H_2O
13·24	21·71	1·84	0·952	Li_2SO_4 4 H_2O
11·73	22·08	1·606	0·976	$Al_2(SO_4)_3$ 18 H_2O
6·75	24·34	0·89	1·031	"
3·44	26·12	0·444	1·083	"
0·00	28·0	0·00	1·137	"

The system $Li_2SO_4 - Al_2(SO_4)_3 - H_2O$ at 0° C. & 30° C.

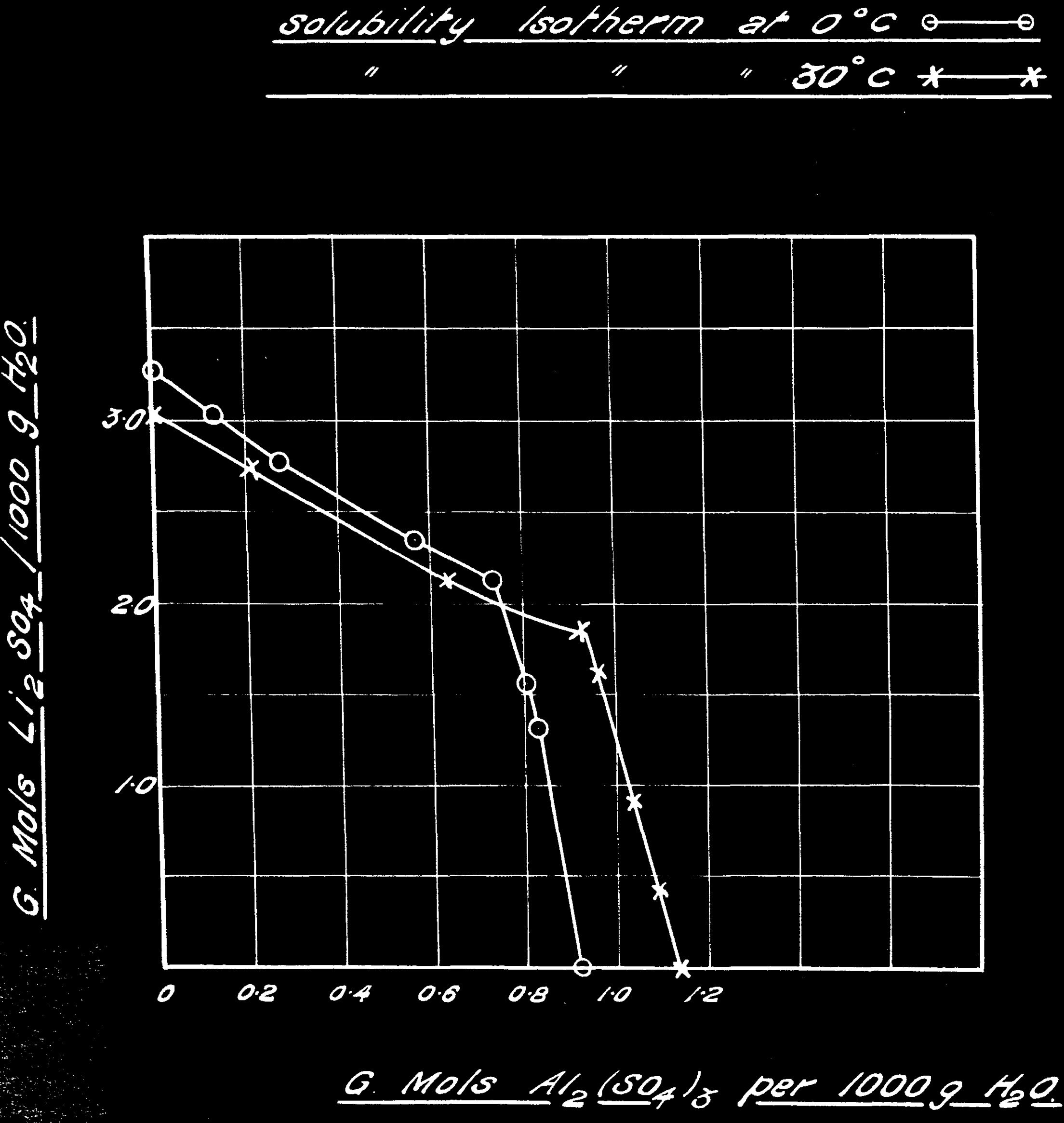

Fig. 26.

The curves obtained (Figure 26) are of the type described on page 18 and shewn in Figure 2, and consist of two branches only. One branch shews the composition of solution containing varying proportions of aluminium sulphate, and lithium sulphate in equilibrium with lithium sulphate monohydrate, at the temperature of the isotherm; the other shews the compositions of a solution containing varying proportions of the two salts in equilibrium with $Al_2(SO_4)_3$ 18 H_2O.

Lithium alum is not formed at either temperature.

A point of interest in this system is the decrease in the initial solubility of the lithium sulphate, with increase in temperature. In this respect lithium sulphate is opposite to the other sulphates of the series, which all shew an increase in solubility with rise in temperature.

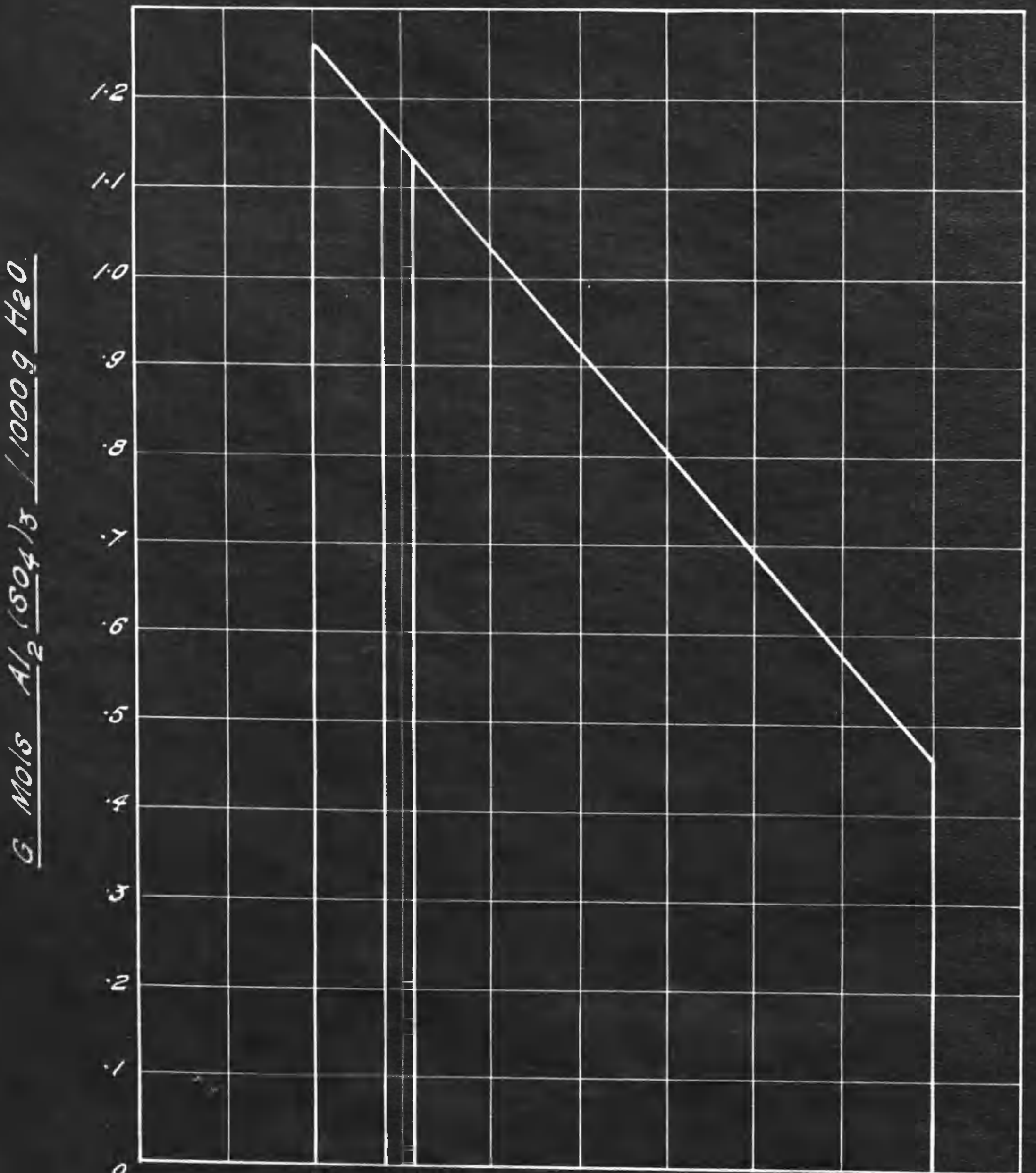

Diagram showing Range of Aluminium Sulphate over which the Alums can be formed at 25° C.

Fig. 27

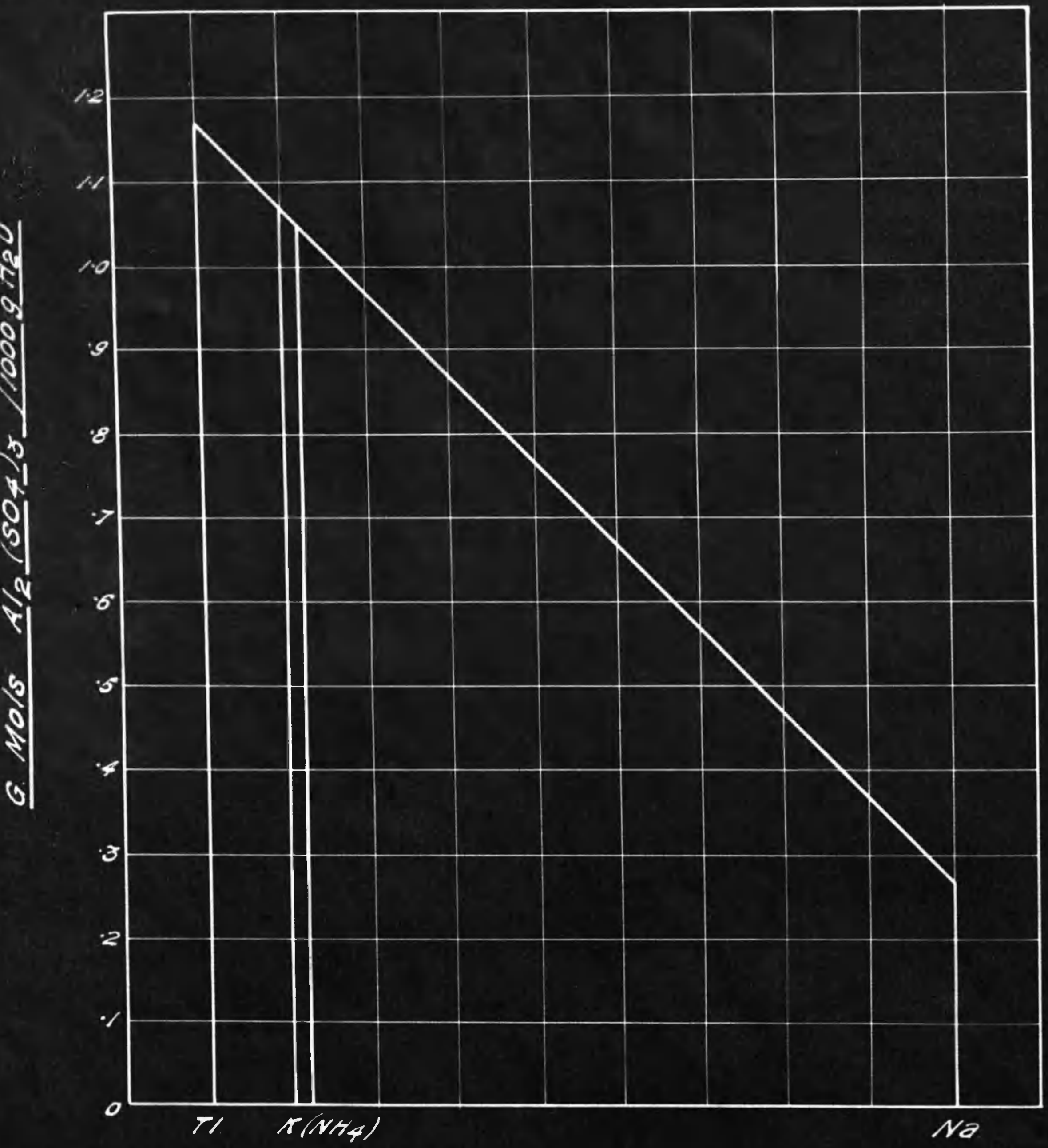

Diagram showing 'Range' of Aluminium Sulphate over which the Alums can be formed at 0° C.

Fig. 28

GENERAL DISCUSSION OF RESULTS.

Range of Formation of the Alums.

Figures 27 and 28 shew diagrammatically the ranges of formation of the alums at 0° C and 25° C.

It will be observed that the order of decreasing range at 25° C is K, Tl, (NH_4) and Na, whilst at 0° C the order is Tl, K, NH_4 and Na.

The order of the limits of formation at 25° C does not agree with the order of the degrees of dissociation shewn in Figure 1; that, however, at 0° C is the same. This change in order may be associated with the change in the dielectric constant of the medium.

Lithium does not form an alum at either 0° C or 30° C.

Form of the Solubility Isotherms.

Branch of the Isotherm where R_2SO_4 is Solid Phase.

R = Li, Na, NH_4, K, or Tl.

This part of the curve existed in two forms, shewn in Figure 29.

The curve PUQ (a) Figure 29 is the type shewn by sodium,

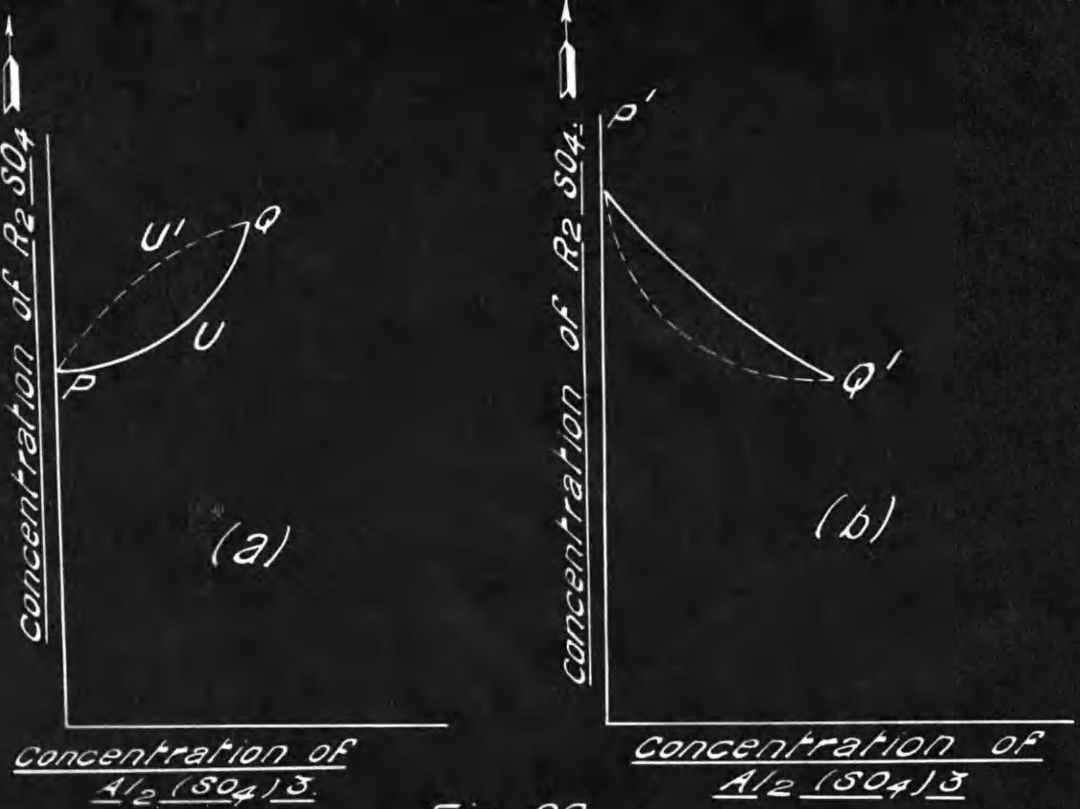
Concentration of R_2SO_4
U'
Q
U
P
(a)
Concentration of $Al_2(SO_4)_3$
Concentration of R_2SO_4
P'
Q'
(b)
Concentration of $Al_2(SO_4)_3$

Fig. 29

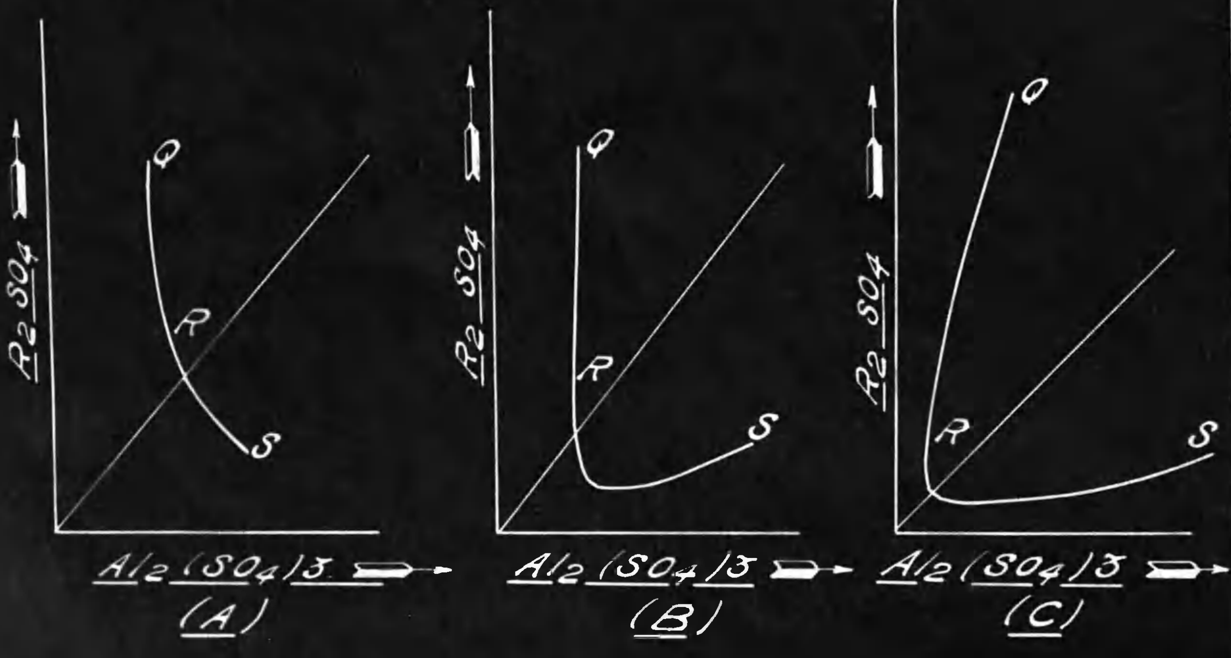
R_2SO_4
Q
R
S
$Al_2(SO_4)_3$
(A)
R_2SO_4
Q
R
S
$Al_2(SO_4)_3$
(B)
R_2SO_4
Q
R
S
$Al_2(SO_4)_3$
(C)

Fig. 30

potassium, and thallium sulphates, whilst the sulphates of ammonium and lithium gave curves of the type P' Q', (b) Figure 29.

It was observed that curves for K_2SO_4 and Tl_2SO_4 calculated on the basis of the Debye theory were of the form P U' Q (a) Figure 27, i.e. convex upwards, whilst the experimental curves were concave upwards. There are several possible explanations for this discrepancy, the most probable being

(1) change in value of '$\bar{a}$', due to increased concentration.

(2) hydration of ions with increase in concentration

(3) formation of ionic complexes.

In calculating the curves, a mean value for $\bar{a}$, - the limiting distance between the ions, - was taken, based on experimental values. Now, as the concentrations increase there will be increased interionic effect and consequent change in the value of '$\bar{a}$'. This change is value is not allowed for in the calculations, and it is possible that the discrepancy may be due to this factor.

The hydrations of the ions with increase in concentration will have an influence on the shape of the curve, but since the change in concentrations is not very great in these particular curves this factor will not be very great. It is worth noting here that there will probably be solvation of the ions to some extent. The work of Kendall (2) shews that interaction between the solute and solvent is very probable. Water is such a very powerful dipole that it is difficult to conceive the solute ions entirely free.

In his papers (26) (27) whilst postulating complete dissociation, Debye admits the probability of the formation of ions of the type of $'Na\,SO_4$, $'K\,SO_4$, etc., and it is possible that these ions are formed as the concentration of the aluminium sulphate increases relative to the concentration of the alkali sulphate. Such a formation would certainly cause the form of the solubility isotherm to be concave upwards.

In considering the formation of complex ions, the formation of double salt ions in solution must also be considered. With increase in concentration of the aluminium sulphate, the probability of the orientation of the like and the unlike ions, at any instant, being that peculiar to the double salt, will become great, and probably greater than the effect of hydration, and the probability of ionic complexes of the type $'Na\,SO_4$, etc., being formed, will become small in comparison. Such an assumption would explain the very steep gradient of the curves near the triple point.

The shape of the curves, therefore, admits of the possibility of ionic complexes, including double salt ions, being formed in solution.

With reference to curves of the type P' Q (b) Figure 29, e.g. as obtained with ammonium and lithium sulphates, the theoretical curves are of the form shewn by the dotted line in (b) Figure 29 (Schärer, 25). The theoretical curves were not calculated in the above cases, for reasons previously given. The fact that the experimental curves have a different slope, however, may be due to the same factors that produce the discrepancy between the experimental and theoretical curves of the type shewn in Figure 29 (a).

Lithium sulphate gives a curve concave downwards of the form indicated by the theoretical equations, suggesting little complex ion formation.

Branch of the Isotherms where $Al_2(SO_4)_3\ 18\ H_2O$ is the solid Phase.

In all cases except lithium sulphate the addition of the alkali sulphate produced an increase in the concentration of the aluminium sulphate. Consequently, the arguments applied to curves of the type (a) Figure 29, may be applied in this case.

Branch of the Isotherms where the Solid Phase is

$R_2SO_4Al_2(SO_4)_3\ 24\ H_2O$: R = Na, K, NH_4, or Tl.

The central branches of the solubility isotherms in the above cases where double salt was the solid phase consisted of three types, shewn in Figure 30.

To the type(A) belongs sodium alum. From Q, at which alkali sulphate exists in the solid phase to S where aluminium sulphate is in the solid phase, there is a decrease in concentration of the alkali sulphate with increase of aluminium sulphate.

Potassium alum belongs to the type (B). The portion from Q, to R where the double salt curve cuts the equimolar line, shews a decrease in concentration of the alkali sulphate with increase in concentration of aluminium sulphate. The portion of the curve RS, however, for the most part shews an increase in the concentration of the alkali sulphate with increase in concentration of aluminium sulphate.

Ammonium and thallium alums give curves of the type (C), where, from Q to near R, there is a decrease in concentration of the alkali sulphate along with a decrease in concentration of the aluminium sulphate, as allowed by the activity theory. The portion R S of the curve is similar to the analogous part of the curve in (B).

The indentation of the experimental curves of the type

(C) round about the point 'R', is probably due to the increased ionic effects of the ions of the one salt on the other, as the concentration of the salts approach equality. Near the point 'Q' the influence of the aluminium ions on the alkali sulphate ions will be negligible compared with the influence of the alkali sulphate ions on the aluminium ions, since the concentration of the alkali salt ions (e.g. in the case of ammonium and potassium alums) is very much greater. The influence of the aluminium sulphate ions will become appreciable as R is approached.

The form of curve (C) Figure 30, is that required according to equation 16, based on the assumption of complete dissociation. We have then to find the cause of the formation of the curves of the types (A) and (B).

An explanation of the discrepancy has already been suggested on pages 38, 69, but in addition to this factor, since the possibility of complex ion and double salt formation in solution is admitted, where the solid phase is one of the component salts, such formation must be considered here, along with the possibilities of hydration and change of value of $\bar{a}$, due to change in interionic effects with variation of the total concentrations.

Change in the value of $\bar{a}$, with concentration, would admit of the curves of the type A.

Different degrees of solvation of the ions with different concentrations must also influence the shape of the curves.

The formation of complex and double salt ions in solution would account for the slope of the part Q R of the curves in Figure 30 A and B being outwards, instead of inwards, and from our previous reasoning, we would look for Q R to have a greater outward slope in these isotherms where the gradient of the branch P Q where the alkali sulphate is solid phase, became very great near Q. Thus in the isotherms at 25° C for sodium and potassium, sulphates, where the gradients of the curves approach infinity near the triple point Q, one would look for the slope of Q R to be outwards, as is the case. Similarly, if the branch of the isotherms where aluminium sulphate is the solid phase, shewed an infinitely great gradient near S, one would expect that the portion S R would shew an increase in concentration of alkali sulphate, with decrease in concentration of aluminium sulphate. This is borne out to some extent in the case of the system $Na_2(SO_4)$ - $Al_2(SO_4)_3$ - H_2O at 25° C.

From the foregoing it would appear probable that the alums of sodium and potassium are not completely dissociated in solution.

In the case of the isotherms of the alums of ammonium and thallium which correspond to the types (6) Figure 27, the same arguments used above can be applied. Thus since in the case of ammonium alum the isotherm is of the form required on the assumption of complete dissociation, and the experimental and theoretical values agree closely, it is probable that ammonium alum in solution is practically completely dissociated. On the other hand, whilst the form of the thallium alum curve is that required by the theoretical equation, the experimental and theoretical values can be made agree only within certain limits, particularly on the part R S of the curves. These limitations may well be due to the fact that the equation does not take into account the change in value of $\bar{a}$ with change in concentration. Also, the variation of the degree of hydration of the ions with concentration may be an important factor. The combined effects due to the change in concentration would account for the divergence of the experimental values from the theoretical. It is unlikely that ionic complexes are formed to any great extent in this case, though, of course, the possibility of their formation is not eliminated.

The Bearing of the Results on the Theories of Double Salt Formation.

The theory developed by Caven and his co-workers accounts, in a general way, for the results. Modification is, however, necessary to explain the shape of the isotherms.

The contention that the tendency for double salt formation between single salts is a function of the difference in the degree of basicity between the cations is borne out by the order of ranges of formation of the alums at 0° C but not at 25° C.

It is shewn that increase in the solubility of one compound with the addition of the other, may not be due to complex ion formation. The change in gradient of the solubility isotherm is the main indication of such combination, and the results obtained, whilst they by no means prove that complex ion formation does take place, admit of the possibility.

Hydration of the ions in solution must also be considered to influence the shape of the curves.

It is suggested that the separation of double salt from solution is a function of the probability of the ions being in a certain configuration at any instant. Consider, for example, a saturated solution of a salt AB at a certain temperature, in equilibrium with solid AB. There will be a certain magnitude of the probability of the ions A and B at any instant being that of AB. Now if A'B is added to the solution other probabilities must also be considered, e.g. those of the configuration of the ions being AB A'B and A'B. As the concentration of A'B is increased the probability of the configuration of the ions at any instant being ABA'B and

A'B must also increase, and whichever probability is greater will determine which salt or salts constitute the solid phase. Thus double salt will separate from solution when the probability of the configuration of the ions being that of AB A'B is the greatest.

When the salts or double salt are hydrated the same argument will, of course, apply; it being assumed that in this case the water molecules or ions take up definite positions relative to the other ions just previous to the precipitation of the salt, or double salt.

The factors most likely to influence the probability of the ions assuming certain configurations are the size and valency of the ions, and the dielectric constant and temperature of the solvent; and since it is the magnitude of this probability which determines the solubility of the salts, it may be said that double salt formation is a function of the solubility of the double salt and of its component salts.

It has been pointed out in the case of the alums that direct analytical tests do not indicate the presence of complex ions in solution. This is evidence in support of the above conception of complex ion formation in which the ions of the component salts would still shew their individuality in analytical tests.

APPENDIX.

Methods of Analysis.

Determination of Total Sulphate.

Total sulphate was determined by precipitation as barium sulphate.

The procedure adopted was to dilute an aliquot portion of the solution to be analysed, to a volume of about 500 ccs, and to add to this solution about 5 ccs of 36 % hydrochloric acid. The acid mixture was then heated to boiling, and the sulphate precipitated by adding very slowly an approximately N/5 solution of barium chloride in very slight excess. The beaker containing the mixture was then placed on a hot plate, until the precipitate settled. The supernatant liquor was then poured through a Swiss filter paper, and the precipitate washed from the beaker into the filter paper by means of a wash bottle, using hot water.

The precipitate, after washing thoroughly with hot water, was ignited in a tared silica crucible over a bunsen flame, and weighed.

There was no reduction of sulphate by the above method of ignition, as after-treatment with sulphuric acid failed to produce a difference.

The weight of solution taken for analysis was such as would give a precipitate of barium sulphate of weight 0.5g to 1.0g.

Duplicate analysis were carried out in all cases. The maximum difference between the weights of barium sulphate obtained in duplicate experiments was of the order of 0.2 %.

Determination of Aluminium.

Except in the case of the system $(NH_4)_2 - SO_4\ Al_2(SO_4)_3 - H_2O$, determination of aluminium was carried out by titration with sodium hydroxide solution using phenol phthalein as indicator, as described by Britton (38).

The procedure adopted was as follows:-

An aliquot portion of the solution to be analysed containing from .05g to 0.12g of aluminium sulphate was diluted to 100 ccs, and titrated while boiling with N/10 sodium hydroxide solution, using phenolphthalein as indicator.

Duplicate results obtained with this method agreed within a maximum percentage error of 0.2%.

The presence of sodium sulphate, potassium sulphate, thallium sulphate, and lithium sulphate did not effect the accuracy of the determination.

The above determination can be carried out in presence of excess barium chloride (50), but as found by Tingle (51) satisfactory results were obtained either with or without barium chloride.

If the solutions contained more than 0.12 g aluminium sulphate, the end point became masked by the aluminium hydroxide precipitated.

Determination of Ammonium Sulphate.

In solutions of the system $(NH_4)_2SO_4 - Al_2(SO_4)_3 - H_2O$ the ammonium sulphate content was determined by the well known distillation method.

An aliquot portion of the solution to be analysed was treated with excess of sodium hydroxide solution, and the liberated ammonia, absorbed in an excess of standard sulphuric acid solution. The excess of sulphuric acid was then determined by titration with standard sodium hydroxide solution using methyl red as indicator, and the ammonia liberated calculated.

Derivation of equation for Activity Coefficient.

The equation for the activity coefficient of the i^{th} sort of ion in a solution has been developed on the Debye theory of the solubility of electrolytes by Schärer (25) somewhat as follows:

It is generally established that the properties of a solution may be predicted if the free energy - expressed in suitable variables - of that solution is known.

However, instead of the free energy, it is convenient to use the thermodynamical potential ϕ of Helmholtz where

$$\phi = U - TS + pV.$$

in which U = the energy, T the absolute temperature, S the entropy, p the pressure, and V the volume. The physical significance of this is similar to that of the free energy, as will be seen from the following deliberation.

From the first law of thermodynamics

$$dU = \delta Q + \delta A.$$

where δQ is the heat added, and δA is the work done during a reversible change. If δA is split into two parts, $\delta A' = -pdV$ against the external pressure and the remainder termed $\delta A''$; then for a change which takes place at constant temperature and pressure

$$d\phi = d\,(U - TS + pV) = \delta(A-A') = \delta A''.$$

The change $d\Phi$, which the considered system undergoes is accordingly similar to the total work less that done against external pressure. If the solution is incompressible, it follows that the thermodynamical potential and the free energy have the same significance.

Consider the solution to consist of N_0 molecules of solvent and $N_1, N_2 \ldots\ldots N_i \ldots N_s,$ ions of the sort
$1, \; 2, \; \; i, \; s,$ then
from classical thermodynamics the potential

$$\Phi = \Phi^* = \sum_{i=0}^{s} N_i \left(\varphi_i + kT \lg c_i \right) \qquad (I).$$

where φ_i represents for a single particle or ion that part of the potential dependent only on p and T but not on the concentration. The universal Boltzman constant $k = 1,371 \times 10^{-16}$ is used in place of the gas constant is independent of the concentration and c_i is the concentration of the ith sort of particle defined

$$c_i = \frac{N_i}{N_0 + N_i + \cdots N_j \cdots + \cdots N_s} = \frac{N_i}{\sum_0^s N_i}$$

or, since only dilute solutions are considered, with approximation

$$c_i = \frac{N_i}{N_0}$$

Solutions, whose properties can be expressed through equation (1) are ideal solutions, i.e. solutions in which the particles are 'uncharged' and in which random distribution of the particles exist as in the gaseous state. Experience has shewn, however, that solutions of strong electrolytes are not ideal - so that an additional term representing the potential due to the interionic effects must be added to equation (1). Let us represent this additional term by $W = \sum n_i w_i$, (cf. Debye, 26), and we thus obtain an expression applicable to all solutions

$$\emptyset^* = \sum_{i=o}^{s} N_i \left(\varphi_i + k\,T\,\lg \sigma_i + w_i\right) \qquad (2).$$

Now when actual or non ideal solutions are infinitely diluted the charged particles are separated to such an extent that practically random distribution prevails, so that they approximate to ideal solutions, and in such state the value of w_i tends to zero. This extension is analogous to the transition of real gases to ideal, as shewn by van der Waal, where the real gases are differentiated from the ideal by the forces of attraction and repulsion which the molecules exert on each other in real gases.

Let us provisionally make

$$w_i = k\,T\,\lg h_i \qquad (3)$$

and equation (2) becomes

$$\emptyset = \sum_{i=0}^{s} N_i\,(\varphi_i + kT \log h_i\, c_i) \qquad (4)$$

so that h_i is the activity potential of the i^{th} sort of ion. The activity coefficient, in the sense that Lewis uses the term, may be obtained from the above by differentiation in the following manner. Let us consider a change in condition of our system at constant pressure and temperature, which only consists in the number of particles per unit space, as is always the case in solubility examples, where diluting decreases the particles per unit space, and concentrating increases the number of particles. Differentiating (4) and since

$\sum N_i \delta(\varphi_i + kT \log c_i) = 0$ when p and T constant[*]

we obtain

$$\delta\emptyset = \sum_{i=0}^{s} \delta N_i \left[\varphi_i + kT\log c_i + kT\log h_i + kT\sum_{j=0}^{s}\frac{N_j\,\delta\log h_j}{\delta N_i}\right] \qquad (5)$$

where h_j is dependent on the particle N_i.

If expression (5) is written in the form

$$\delta\emptyset = \sum \delta N_i\,\mu_i$$

where μ_i refers to the chemical potential of the i^{th} sort of ion ; the ideal chemical potential can be written

$$\overset{+}{\mu}_i = \varphi_i + kT\log c_i$$

---

[*] For proof of this cf. Debye and Hückel (loc. cit.)

and the actual chemical potential

$$\mu_i = \varphi_i + kT \log (f_i c_i)$$

where

$$\log f_i = \log h_i + \sum_{j=1}^{s} N_j \frac{\delta \log h_j}{\delta N_i} \qquad (6)$$

f_i is thus defined as the activity coefficient of the ith sort of particle. The laws of ideal solutions can therefore be made applicable to actual solutions if the analytical concentration can be replaced by a fictive concentration fc, which is a multiple of the analytical concentration and the activity coefficient.

Hence we obtain

$$\delta \emptyset = \sum \delta N_i (\varphi_i + kT \log f_i c_i)$$

Suppose now that the number of each of the sort of particles in the solution changes in the ratio

$$\delta N_1 : \delta N_2 : \text{-----} \; \delta N_i : \text{-----} \; \delta N_s$$
$$= v_1 : v_2 : \text{-----} \; v_i : \text{-----} \; v_s$$

where v_1 etc., are whole numbers, the laws of classical thermodynamics can now be applied and the following equilibrium expression obtained.

$$\lg (f_i c_i)^{v_i} = \lg K \qquad (7).$$

This, of course, is the expression of the Law of Mass action, only in this case the fictive concentration $(f_i c_i)$ is used in place of the analytical concentration. This expression ($f_i c_i$) might be termed the "active mass" of the i^{th} sort of particle.

The problem, now, is to express the additional term w_i, and with it, h_i and f_i, in explicit values.

Let the s sort of ions all carry charges

$z_1\varepsilon_1$ $z_2\varepsilon$ ------- $z_s\varepsilon$ where ε is the elementary quantum of electricity, and z_i can be either a positive or negative integer. Now, according to the Boltzman principle, (borrowed from the Kinetic theory) the ionic distribution is a function of the ratio of the electrical potential energy of each ion to its thermal energy, i.e. at the centre of a definite ion, the other ions round about will produce (Debye, 27) a potential

$$\psi = - \frac{z_i\, \varepsilon\, X}{D} \; \frac{I}{I + X\bar{a}_i}$$

where $\frac{I}{X}$ (having dimentions of a length) is a measure of the "thickness" of the ionic atmosphere and represents that distance from the ion in which the potential has decreased to an e^{th} part of its original value and is defined by

$$X^2 = \frac{4\pi\varepsilon^2}{D\,k\,T} \sum_{i=I}^{s} n_i\, z_i^{\;2} \qquad (8)$$

where D is the dielectric constant of the solvent, k is the Boltzmann constant, T the absolute temperature and n_i the number of ions of the i^{th} sort per cubic cm. $n_i = \frac{N_i}{V}$ where V is the volume of solution. The term '$\bar{a}_i$' is the closest distance of approach of two ions of the sort i measured from centre to centre.

To calculate the additional term w it is first of all necessary to determine the work done in the dilution which arises out of the interionic forces. This is done by calculating the work done in introducing, infinitely slowly, the electrical charges to the uncharged particles. Let us suppose that at a certain stage in this process of charging the particles, a charge of λ has been introduced ($\lambda < I$). Then the work necessary to increase this charge by $d\lambda$ on an ion of the sort j is

$$- \frac{z_j^2 \varepsilon^2 X}{D} \frac{\lambda^2 d\lambda}{1 + \bar{a}_j X}$$

Correspondingly for all the ions

$$W = \sum N_j w_j = - \sum N_j \frac{z_j^2 \varepsilon^2 X}{D} \int_0^1 \frac{\lambda^2 d\lambda}{1 + \lambda \bar{a}_j X}$$

and from (3) the activity potential for an ion of the sort j is obtained from

$$\lg h_j = \frac{- z_j^2 \varepsilon^2 X}{D k T} \int_0^1 \frac{\lambda^2 d\lambda}{1 + \lambda \bar{a}_j X} \qquad (9)$$

This integral may be left unevaluated since the activity potential is required only as a step to the activity coefficient. Equation (6) is the general expression from which this coefficient will be determined.

If we consider the actual volume of the ions to be negligible compared with the volume of the solution we may differentiate equation (8) as follows:

$$2 X \frac{\delta X}{\delta N_i} = \frac{4 \pi z_i^2 \varepsilon^2}{D k T} \frac{I}{V}$$

From this expression and inserting the expression for log h in equation (6) we obtain

$$\log f_i = \frac{-z_i^2 \varepsilon^2 X}{D k T}\left\{\int_0^1 \frac{\lambda^2 d\lambda}{1+\lambda X \bar{a}} + \frac{4\pi\varepsilon^2}{DkT}\sum n_j z_j^2 \frac{1}{2X}\frac{d}{dX}\left[X\int_0^1 \frac{\lambda^2 d\lambda}{1+\lambda X \bar{a}_j}\right]\right\}$$

Now if we take a mean value of '$\bar{a}$', instead of taking a different value for each sort of ion, we can proceed as follows. With reference to (8) we obtain

$$\log f_i = \frac{-z_i^2 \varepsilon^2 X}{D k T}\left\{\int_0^1 \frac{\lambda^2 d\lambda}{1+\lambda X \bar{a}} + \frac{1}{2}\frac{d}{dX}\left[X\int_0^1 \frac{\lambda^2 d\lambda}{1+\lambda X \bar{a}}\right]\right\}$$

and by evaluating the integrals we finally obtain

$$\log f_i = \frac{-z_i^2 \varepsilon^2}{2DkT} \frac{X}{1+X\bar{a}} \tag{10}$$

By substituting the value of X from (8) in (10)

$$\log f_i = -\sqrt{\pi}\left(\frac{\varepsilon^2}{DkT}\right)^{3/2} z_i^2 \sqrt{\sum_1^s n_i z_i^2}\; \frac{1}{1 + \bar{a}\sqrt{\frac{4\pi\varepsilon^2}{DkT}}\sqrt{\sum_1^s n_i z_i^2}} \tag{11}$$

we obtain a value of the activity coefficient for the ith ion.

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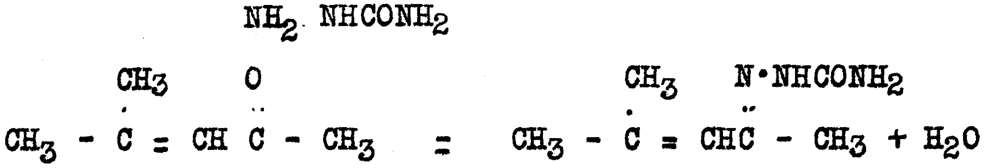
SOME REACTIONS OF
PROPENYL-PHENYL KETONE
WITH SEMICARBAZIDES AND THIOSEMICARBAZIDES.

THEORETICAL.

It has been shewn by Rupe and his collaborators (1) that unsaturated aliphatic ketones can react with semicarbazide in two ways. For example, one molecule of semicarbazide reacts to form mesityloxide semicarbazone, thus:

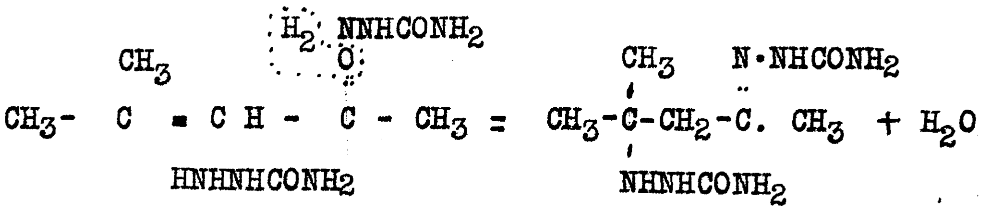
I.



$$CH_3-\overset{CH_3}{C}=CH\,\overset{\overset{NH_2\cdot NHCONH_2}{O}}{C}-CH_3 = CH_3-\overset{CH_3}{C}=CH\overset{N\cdot NHCONH_2}{C}-CH_3+H_2O$$

With two molecules of semicarbazide one molecule of mesityl oxide reacts to form the semicarbazide semicarbazone of mesityloxide

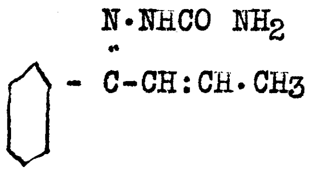
II.



$$CH_3-\overset{CH_3}{C}\underset{HNHNHCONH_2}{=CH}-\overset{\overset{H_2\ NNHCONH_2}{O}}{C}-CH_3 = CH_3-\underset{NHNHCONH_2}{\overset{CH_3}{C}}-CH_2-\overset{N\cdot NHCONH_2}{C}.\,CH_3+H_2O$$

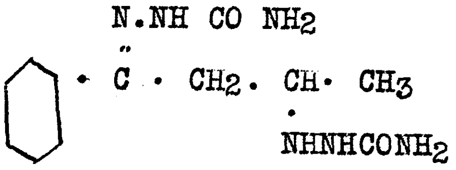
Regarding unsaturated ketones of the aromatic type Rupe with Hinterlach (1), expressed the opinion that these could react with semicarbazide in one way only, the semicarbazone of the ketone being formed. This opinion, however, was shewn by Auwers (2) to be subject to modification. Rupe had based his opinion on experiments (1) carried out with ketones of the type Ar CH:CH·CO·R (where Ar = aromatic nucleus, and R = alkyl group) with the ethylenic linkage next the aromatic nucleus. Auwers (2) shewed, however, that the isomeric ketones of the type ArCO·CH:CH R, where the carbonyl group was attached to the aromatic nucleus, and the ethylenic linkage was adjacent to the carbonyl group, could react with semicarbazide in a manner similar to mesityl oxide.

Propenyl phenyl ketone, for example, reacts with semicarbazide to form the semicarbazone (II) and the semicarbazide semicarbazone (III).



$C_6H_5-C(=N\cdot NHCO\,NH_2)-CH{:}CH\cdot CH_3$

II.



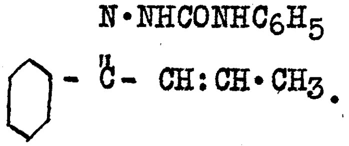
$C_6H_5\cdot C(=N.NH\,CO\,NH_2)\cdot CH_2\cdot CH(NHNHCONH_2)\cdot CH_3$

III.

The structure of the semicarbazide semicarbazone of propenylphenyl ketone III was assumed by Auwers (2) from analogy to that of mesityloxide which had been established by Rupe and Kessler (1).

In the present work the reactions of propenyl phenyl ketone was studied with 4phenyl semicarbazide , 4 phenyl thiosemicarbazide and thiosemicarbazide.

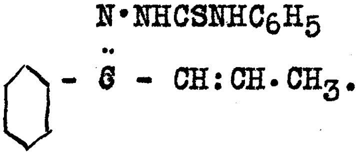
It was found that phenyl semicarbazide reacted only to form the phenyl semicarbazone of the ketone (IV).



IV.

Probably the presence of the phenyl group by increasing the size of the molecule, decreases the activity of the semicarbazide molecule, and thus prevents the formation of the addition compound.

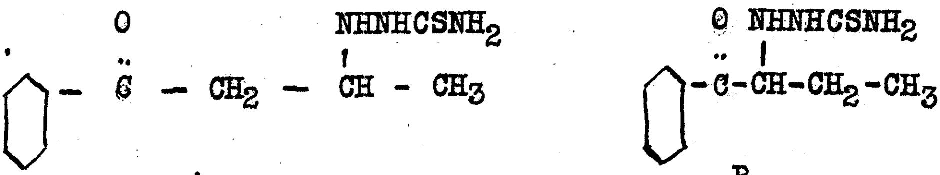
Phenyl thiosemicarbazide reacted in a manner similar to 4 phenyl semicarbazide forming the phenyl thiosemicarbazone only of the ketone (V)



V.

The reaction of thiosemicarbazide was peculiar and of a different nature to semicarbazide - an additive compound being formed by the addition of the thiosemicarbazide at the ethylenic linkage (VI) A or B

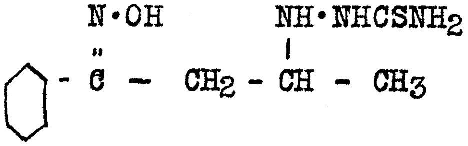
VI.



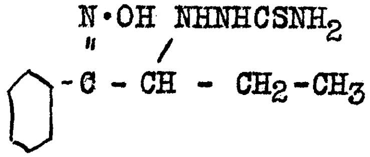
A. B.

This compound which may be termed thiosemicarbazido — propyl-phenyl ketone, did not form a semicarbazone. The ketonic activity was not completely masked by the introduction of the thiosemicarbazide molecule, however, as it readily formed an oxime with hydroxylamine (VII) (A or B).

VII.



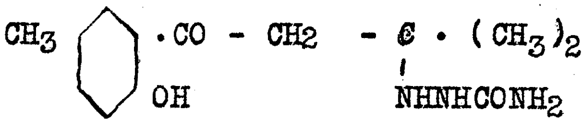
A.



B.

A similar reaction was reported by Anwers (2) who found that p. hydroxy o. tolyl, iso-butenyl ketone reacted with semicarbazide to form the additive compound VIII, which

VIII.

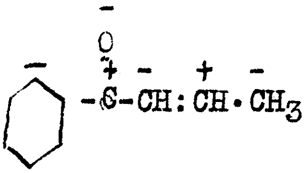


also readily reacted with hydroxylamine to give oxime formation, Anwers (2) suggested formula VIII for the additive compound with semicarbazide but did not prove the constitution.

It thus cannot be argued from analogy to VIII that thiosemicarbazido-propyl-phenyl ketone has the constitution represented by VI.A. The formula VI.B is quite possible, and a similar doubt must exist whether formula VII A or B represents the constitution of the oxime.

It may also be mentioned here that there should be stereoisomerides of the above series of compounds, and whilst no direct efforts were made to isolate such compounds no evidence of them was obtained in the experimental work.

Let us examine the foregoing reactions of propenyl-phenyl ketone from the aspect of Fry's polarity theory (7). By this theory the ketone may be represented



Now the oxygen in semicarbazide reacts very differently from the oxygen in the ketone, though both are linked to carbon, so that it seems reasonable to represent semicarbazide with oxygen as $\overset{+}{O}$, thus:- $\overset{+}{H_2}\underset{1}{\overset{-}{N}} - \underset{2.}{\overset{+}{N}}H - \underset{3.}{\overset{-}{C}}(\overset{+}{O})\underset{4.}{\overset{+-}{N}}H_2$. Such a configuration would explain the reactivity of the hydrogens attached to the 1. nitrogen, with ketones and aldehydes, and this would also account for the acid molecule in semicarbazide hydrochloride being attached to the 1 nitrogen, and not to the 4. nitrogen.

Now thiosemicarbazide differs markedly from semicarbazide in its ability to form a sodium salt. Thiosemicarbazide forms a sodium salt very easily whilst semicarbazide does not form one at all. The linkage of the metal takes place through the sulphur atom of the thiosemicarbazide, and for this reason we may represent the sulphur as $\overline{S}$, and thiosemicarbazide as $\underset{1}{\overset{+-}{N}}H_2 \cdot \underset{2}{\overset{-}{N}}: \underset{3}{\overset{+}{C}}(\overset{-}{S}H)\underset{4}{\overset{-}{N}}H_2$. As thiosemicarbazide reacts with certain aldehydes and ketones in a manner similar to semicarbazide, i.e. through the hydrogens of the 1 nitrogen, we may also represent it as $\overset{-+}{N}H_2 \cdot \overset{+}{N}H\overset{-}{C}(\overset{+}{S})\overset{+-}{N}H_2$.; and it is possible that the two forms exist in equilibrium as

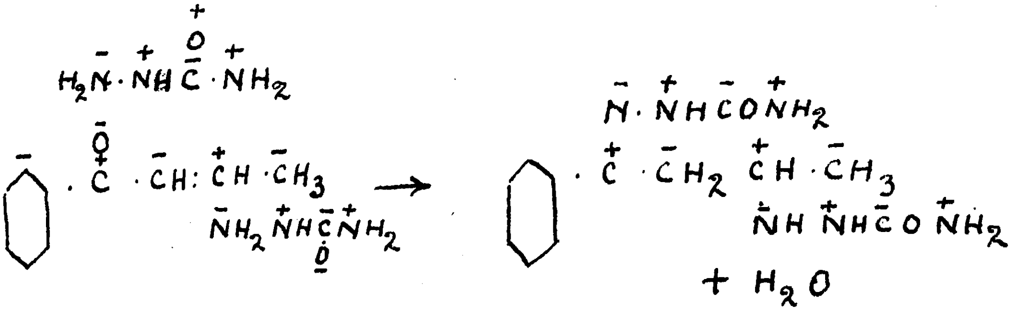
$$H_2\overset{-}{N}\,\overset{+}{N}H\,\overset{-}{C}\,(\overset{+}{S})\cdot\overset{+}{N}H_2 \rightleftharpoons H_2\overset{+}{N}:\overset{-}{N}\cdot\overset{+}{C}\,(\overset{-}{S}\overset{+}{H})\,\overset{-}{N}H_2$$

On account of the strongly negative nature of the sulphur atom it is probable that the form on the right hand side will predominate. Such a form of tautomerism is suggested by Fry (7) in the cases of several other compounds.

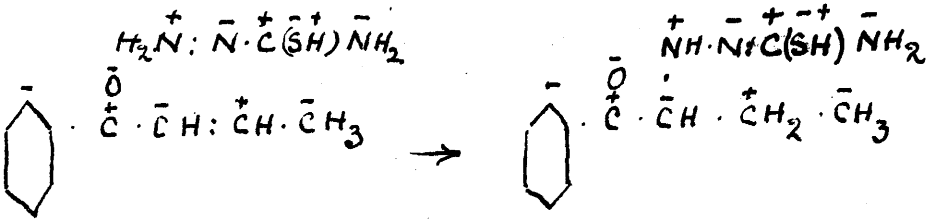
In connexion with the representation of oxygen and sulphur as $\overset{+}{O}$ and $\overset{+}{S}$, it may be noted that Fry represents the oxygen molecule as $\overset{--}{O}\,\overset{++}{O}$, and also represents the oxygen atom in several cases to react as ${}^{+}O^{-}$. No case is quoted by Fry of a sulphur atom being represented as $\overset{++}{S}$, but from analogy to the oxygen atom there seems no reason why this should not be done.

Thus from the foregoing it is probable that semicarbazide will react as $\overset{-}{N}H_2 \cdot \overset{+}{N}H\overset{-}{C}(\overset{+}{O})\overset{+}{N}H$, and thiosemicarbazide mostly as $\overset{+}{N}H_2 \cdot \overset{-}{N} : \overset{+}{C}\,(\overset{-}{S}\,\overset{+}{H})\,\overset{-}{N}H_2$.

Therefore with semicarbazide and propenyl phenyl ketone we have the following reaction



and with thiosemicarbazide:



This theory then favours formula VI.B. as the constitution of the thiosemicarbazido propyl phenyl ketone.

We have now to explain in terms of this theory why the introduction of a phenyl group into the thiosemicarbazide should prevent the formation of an additive compound. The probable reason is that the negative phenyl group causes the thiosemicarbazide to exist mainly in a form represented by

$$\overset{+}{H_2}\overset{-}{N} \cdot \overset{+}{N}H\,\overset{-}{C}\,(\overset{+}{S})\,\overset{+}{N}H\,\overset{-}{C_6}H_5$$

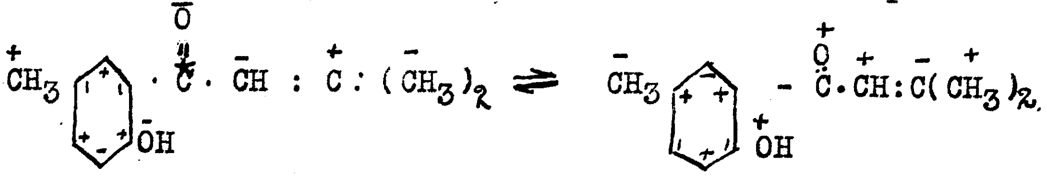
We would thus expect reaction with the ketonic group to form the phenyl thiosemicarbazone, which does take place.

The non-formation of the phenyl-thiosemicarbazide - thiosemicarbazone may be explained as due to steric influences of the phenyl group.

The steric influences of the phenyl group is the probable reason for phenylsemicarbazide forming only the phenyl semicarbazone with propenyl phenyl ketone.

An explanation of the reaction of o-tolyl- isobutenyl ketone with semicarbazide may lie with the conflicting polar influences of the methyl and hydroxyl groups in the aromatic nucleus together with steric influences of the two methyl groups attached to the end carbon atom in the side chain.

We might suppose the ketone to exist as represented



From a consideration of polarity effects one would expect the form represented by the left hand side of the above equation to predominate, and consequently normal reaction to take place at the ketonic group. The steric influences, however, may be great, which would account for the ketone forming with semicarbazide an addition compound at the double bond.

EXPERIMENTAL.

The propenyl phenyl ketone was prepared by the method of Kohler (3).

4-Phenyl semicarbazide was made by hydrolysis of acetone phenylsemicarbazone, as described by Borsche(8).

Thiosemicarbazide was prepared by the method described by Freund and Schander (5).

4-Phenyl thiosemicarbazide was prepared from phenyl mustard oil and hydrazine by the method of Pulvermacher (6).

These preparations are described in the appendix.

Reaction of Propenylphenyl ketone and Phenylsemicarbazide.

Formation of Propenylphenyl4phenylsemicarbazone.

$$C_6H_5CO \cdot CH:CHCH_3 + NH_2NHCONHPh = C_6H_5C(:NNHCONHPh)\ CH:CHCH_3 + H_2O.$$

3g of phenylsemicarbazidehydrochloride (2·5 mols) were dissolved in a minimum amount of alcohol, and to this solution was added a solution of 2g potassium acetate (2·5 mols) in alcohol. The potassium chloride formed was filtered off, and

1.25gm of propenylphenyl ketone $C_6H_5COCH:CHCH_3$ (1 mol) was added to the filtrate.

The mixture was allowed to stand for a week at room temperature, when the crystals of propenylphenyl4phenylsemicarbazone $C_6H_5C(:NNHCONHPh)CH:CHCH_3$ which had separated out were removed by filtering. On crystallising from absolute alcohol the propenylphenyl4phenylsemicarbazone was obtained in the form of fine needles M.P. 212°. This substance is very soluble in chloroform, and moderately soluble in petroleum ether, benzene and alcohol.

Analysis.

	(1)	(2)	Found	
Weight of Substance	.1036g	.096g	Nitrogen	
Values of Nitrogen	13.4 ccs	9.6 ccs	(1)	(2)
Temperature	11.0° C	12. 5·C.	15.1%	15.0%
Barometric Pressure	755 mm	756 mm		

Propenylphenyl4phenylsemicarbazone requires 15.1 % Nitrogen.

Note:

The use of a large excess of 4 phenyl semicarbazide in the above reaction did not alter the course of the reaction.

Reaction of Propenylphenylketone and Thiosemicarbazide.

Formation of Thiosemicarbazidopropylphenyl ketone.

$$C_6H_5COCH{:}CHCH_3 + NH_2NHCSNH_2 = C_6H_5CO\cdot CH_2CH(NHNHCSNH_2)CH_3$$

2.5g (1 mol) of thiosemicarbazide $NH_2NHCSNH_2$ were dissolved in as small a quantity of aqueous alcohol as possible and to this solution was added 4g propenylphenyl ketone $C_6H_5COCH{:}CHCH_3$(1 mol).

The mixture was allowed to stand at room temperature for over a week, when the thiosemicarbazidopropylphenyl ketone $C_6H_5COCH_2CH(NHNHCSNH_2)CH_3$ which had formed was filtered off. When the filtrate was concentrated under reduced pressure more thiosemicarbazido-ketone was obtained. The product was soluble in alcohol, chloroform and nitro-benzene, slightly soluble in petroleum ether and almost insoluble in benzene. Thiosemicarbazidopropylphenyl ketone can be crystallised from alcohol, or from a mixture of chloroform and petroleum ether, in the form of small prisms M.P.140°.

Nitrogen Estimation.

Weight of Substance	.1168g.
Volume of Nitrogen	18.1 ccs.
Temperature	16.0° C.
Barometric Pressure	737mm.
% Nitrogen	17.7
$C_{11}H_{15}N_3SO$ requires % Nitrogen	17.7

Sulphur Estimation.

	(1)	(2)
Weight of Substance	.1034g	.0955g.
Weight of $BaSO_4$	.0977g	.0906g.
% Sulphur	13.0	13.1

$C_{11}H_{15}N_3SO$ required % Sulphur 13.5

Molecular Weight Determination.

Freezing Point Method

Weight of Substance	.336g	.206g
Weight of Solvent (nitro-benzene)	24.1g	24.1g
Freezing Point of Solvent	4.678°	4.932°
Freezing Point of Solution	4.315	4.602
Depression of F.P.	.347	.210
Hence Molecular Weight	282	285

Calculated Molecular weight for $C_{11}H_{15}N_3SO$ is 237.

The associating nature of the solvent may account for the slightly high result obtained by this method, but no other suitable solvent was obtainable. Attempts to carry out molecular weight determination by the boiling point method with chloroform as solvent gave inconsistent results through decomposition of the solute.

Reaction of Propenylphenyl ketone and Thiosemicarbazide.

Formation of Thiosemicarbazidopropylphenyl-ketoxime.

$$C_6H_5COCH_2CH(NHNHCSNH_2)CH_3 + NH_2OH = C_6H_5C(NOH)\cdot CH_2CH(NHNHCSNH_2)CH_3 + H_2O$$

1g (1 mol) of thiosemicarbazidopropylphenyl ketone was dissolved in alcohol, and to the hot solution was added 4.5g hydroxylaminehydrochloride (1.5 mols) immediately followed by an excess of anhydrous potassium acetate. On cooling the thiosemicarbazidopropylphenyl-ketoxime separated out as a white solid which was filtered off.

The thiosemicarbazidopropylphenyl ketoxime was soluble in alcohol, and slightly soluble in benzene, ether and petroleum ether. Purification was accomplished by dissolving in absolute alcohol and adding drop by drop to petroleum ether. M.P. 165°. Yield .9g.

Analysis.

Nitrogen Estimation.

Weight of Substance .0812g Volume of Nitrogen 14.2 ccs.

Temperature 14.5°. Barometric Pressure 750 mm.

% Nitrogen = 20.9.

$C_{11}H_{16}N_4SO$ requires % Nitrogen = 20.9

Sulphur Estimation.

Weight of Substance .1210g. Weight of $BaSO_4$ 1090g.

Sulphur = 12.4%

$C_{11}H_{16}N_4SO$ requires Sulphur = 12.7%

Carbon and Hydrogen Estimation.

Weight of Substance	Weight H_2O	Weight CO_2	% Hydrogen	% Carbon
.1266g	.0805g	.2405g	6.9	52.5
$C_{11}H_{16}N_4SO$ requires		-----	6.4	52.4

Propenylphenyl ketone and 4Phenylthiosemicarbazide.

Formation of Propenylphenyl4phenylthiosemicarbazone.

$$C_6H_5COCH{:}CHCH_3 + NH_2NHCSNHPh = C_6H_5C(NNHCSNHPh)CH{:}CHCH_3 + H_2O$$

1.2g (1 mol) of the ketone were dissolved in a minimum quantity of alcohol and added to a solution of 1.7 g phenylthiosemicarbazide (1 mol). The mixture was left at room temperature for five days when yellow crystals of propenylphenyl4phenylthiosemicarbazone $C_6H_5C(NNHCSNHPh)CH{:}CHCH_3$ were filtered off.

The product was soluble in chloroform, alcohol, and benzene; insoluble in petroleum ether. It was purified by dissolving in benzene and adding the solution to petroleum ether, when it was obtained white and melted at 140°. On exposure to light the compound turned yellow, but without a change in melting point.

The yield was very poor.

Sulphur Estimation.

Weight of Substance -- .0625g. Weight of $BaSO_4$ -- .0493g

Sulphur -- 10.8% $C_{17}H_{17}SN_3$ requires -- 10.8%.

Nitrogen Estimation.

Weight of Substance -- .1052g Volume of Nitrogen -- 13.0ccs.

Temperature -- 17.0°. Barometric Pressure 751mm.

Nitrogen --- 14.4%. $C_{17}H_{17}SN_3$ requires 14.2%.

Note:
The use of a large excess of 4 phenyl thiosemicarbazide in the above experiment did not change the course of the reaction.

APPENDIX

Preparation of Propenyl Phenyl Ketone (3).

From crotonyl chloride and benzene by Friedel and Crafts' reaction.

Preparation of Crotonyl Chloride (4).

50g. crotonic acid (3 mol) were heated on a water bath with 53g phosphorus trichloride (2 mols) for a period of two hours. The liquid chloride was then poured off the jelly like phosphoric acid and purified by distillation at ordinary pressure. The portion which distilled over between 120° - 125° C was taken. Yield 48g - 50g.

Formation of the ketone.

A little more than the calculated quantity of finely ground aluminium chloride, viz. 66g, was added to a solution of 50g crotonyl chloride and 50g benzene in 150 ccs carbon disulphide. The aluminium chloride dissolved without much evolution of gas. The vessel containing the solution was then placed in ice water and exposed to direct sunlight. After a time, there was a brisk evolution of hydrochloric acid gas, and the reaction mixture became darker coloured and more viscous. After about an hour (Kohler states about 15 minutes) the product was poured into iced acid, the organic substances extracted with ether, and dried with anhydrous sodium sulphate.

After the solvents had been removed by distillation at ordinary pressure, the mixture was distilled under reduced pressure. The mixture started boiling at 135° C (20 mm) and most of the product came over between 135-140° C. The temperature then rose rapidly and a second colourless distillate was collected between 175° - 185° C.

The first distillate, which proved to be almost pure propenyl phenyl ketone, on redistillation gave 42g pure ketone.

The second distillate was found by Kohler to be a compound formed from addition of benzene to propenyl phenyl ketone, and was identified as β phenylbutyrophenone $C_6H_5 \cdot CH(CH_3)CH_2 \cdot CO\ C_6H_5$.

Preparation of 4-phenylsemicarbazide,

From acetone semicarbazone. (8).

Formation of acetone semicarbazone:

30g of potassium acetate were dissolved in a minimum quantity of alcohol and the solution added to that of 30g semicarbazide hydrochloride dissolved in the minimum quantity of water at room temperature. The potassium chloride formed was filtered off after about two hours, and 20g of acetone were added to the filtrate. The mixture was then allowed to stand for 12 hours, and the acetone semicarbazone which had separated out filtered off.

The crude acetone semicarbazone was then recrystallised from water. The final yield of recrystallised acetone semicarbazone was about 25g.

Formation of acetone 4.-phenylsemicarbazone:

25g of recrystallised acetone semicarbazone were mixed with 16g of freshly distilled aniline in a flask which was placed in an oil bath at 135° C. Evolution of ammonia commenced, and a clear solution was soon formed. The temperature of the bath was then raised to 140° C, and heating at this temperature continued for over an hour till the evolution of ammonia stopped.

The flask was then removed from the bath, and after cooling to about 100° C the contents were mixed with an equal volume of alcohol, and poured quickly into 600 cc of ice cold water. The remaining acetone-4-phenyl-semicarbazone in the flask was removed with 50 to 100 cc of hot alcohol.

The acetone derivative quickly precipitated on mixing with water, and after stirring with a glass rod, and standing for about two hours became completely granular. It was then filtered off, and well washed with water.

Formation of 4-phenylsemicarbazide.

The crude acetone 4-phenylsemicarbazone was then hydrolised by heating for about half an hour with an excess of hydrochloric acid in the form of a 5% solution. The phenylsemicarbazide formed during the hydrolysis passed into solution, leaving a suspension of insoluble diphenylurea, which was filtered off.

The filtrate containing the phenylsemicarbazide hydrochloride was then evaporated under reduced pressure, to give a large crop of plate form crystals, which were filtered off, and washed with dilute hydrochloric acid. The washings were added to the filtrate, and concentration under reduced pressure again repeated until another crop of crystals were obtained.

This method of working up the phenylsemicarbazide solution under reduced pressure is to be preferred to the method of evaporation on a water bath at ordinary pressures as described by the authors, since it practically eliminates the formation of diphenylurea formed by decomposition of the phenylsemicarbazide during concentration of the solution, and in addition is much quicker.

The total yield of phenylsemicarbazide hydrochloride obtained above, was recrystallised from absolute alcohol.

Ether was added to the alcoholic mother liquor, and the last traces of phenylsemicarbazide hydrochloride precipitated from the solution. The impurities such as diphenyl urea and colouring matter were not precipitated from solution by the addition of ether.

Yield = <u>13g to 14g.</u>

= 40% to 45% yield on the original weight of acetone used.

Preparation of Thiosemicarbazide (5).

100g (2 mols) of commercial hydrazine sulphate were placed in a beaker, 400 cc of cold distilled water were added and the mixture warmed. 54g (1 mol) anhydrous potassium carbonate were then added in small quantities at a time with constant stirring. A brisk evolution of carbon dioxide took place and the readily soluble hydrazine normal sulphate was formed.

80g (2 mols) of potassium sulphocyanide were added, and the mixture stirred and then heated to boiling. Double decomposition takes place with formation of hydrazine sulphocyanide and potassium sulphate. After boiling for about five minutes the potassium sulphate was completely precipitated by the addition of 500 cc commercial alcohol, and was removed by filtering under pressure.

The filtrate containing the hydrazine sulphocyanide was distilled to remove as much alcohol as possible, and was then evaporated down over a free flame in a porcelain basin. The liquid was agitated continuously during evaporation, and after a time the evolution of steam ceased and the substance, which appeared as a yellow solid, began to effervesce - ammonia being evolved. When the reaction became too violent it was checked by the addition of cold water in small quantities. Throughout this vigorous reaction the mass was continuously stirred. Heating was discontinued when the reaction mixture solidified on a glass rod which had been dipped and removed from the basin.

On cooling the reaction mixture solidified down to a crystalline mass which was extracted with a little hot water, and the mixture filtered. The residue consisted of thiosemicarbazide and the filtrate on being evaporated down to a syrup as before yielded more thiosemicarbazide. This was repeated two or three times.

The various crops of crystals were then combined and recrystallised from water the mother liquor yielding more thiosemicarbazide on concentration.

Yield 43g.

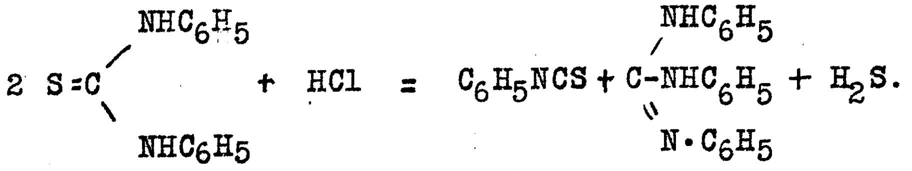
M.P. of product 181 - 183° C.

Preparation of 4.-phenylthiosemicarbazide (6).

From phenyl mustard oil and hydrazine hydrate.

Formation of phenyl mustard oil.

50g thiocarbanilide were added with about 150g of concentrated hydrochloric acid for half an hour in a flask fitted with a reflux condenser. The diphenylthiourea thus obtained was decomposed into triphenyl guanidine, which remained as the hydrochloride in solution, and phenylmustard oil, which separated out as a brown oil.



$$2\ \mathrm{S{=}C}\begin{matrix}\diagup\mathrm{NHC_6H_5}\\ \diagdown\mathrm{NHC_6H_5}\end{matrix} + \mathrm{HCl} = \mathrm{C_6H_5NCS} + \mathrm{C}\begin{matrix}\diagup\mathrm{NHC_6H_5}\\ -\mathrm{NHC_6H_5}\\ \|\ \mathrm{N\cdot C_6H_5}\end{matrix} + \mathrm{H_2S}.$$

The product was distilled with steam and was obtained as an almost colourless oil, being separated from the aqueous layer by means of a tap funnel.

Yield quantitative - 16 g.

Formation of the 4-phenylthiosemicarbazide.

To an alcoholic solution of 7g (1 mol) hydrazine hydrate cooled in ice, was gradually added an alcoholic solution of 16 g (just less than 1 mol) phenyl mustard oil with constant agitation. A solid separated out at once, and after the liquid had almost solidified, the crystals were filtered off and washed with cold alcohol.

Yield of uncrystallised materials:-21 to 22·5g (almost quantitative).

The above product was recrystallised from alcohol, and obtained in a pure state. Yield 18g - 19g. M.P. of product 140° C.

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