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DOUBLE SALTS

by

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PREFACE

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The following work is original except in so far as is noted in the text, where due reference is given to sources from which information has been obtained. The experimental work was carried out in the Chemical Research Laboratory of the Royal Technical College, Glasgow, while the author was Research Assistant to the late Professor Caven. It was to Professor Caven that the work owed its initiation, and he was ever helpful with criticisms, and encouragement, whilst it was in progress.

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INTRODUCTION

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When a solution which contains two salts is evaporated or cooled, the first crystals which separate are, as a rule, those of one salt only. Later, both the dissolved substances may separate side by side, giving a heterogeneous deposit in which the proportions of the substances vary according to the conditions, and are not in any definite molecular ratio. In certain cases, however, a solution of two substances yields homogeneous crystals, which contain definite and simple molecular proportions of both substances, and perhaps a certain number of molecules of solvent. When this occurs the proportions of the two substances in the solution may often be varied very considerably, without changing the composition of the crystals which separate. To take the oldest, and probably best known example, crystals of potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$ are deposited from a saturated solution containing potassium sulphate and aluminium sulphate, and, within certain limits, the proportion in which the salts are present in the solution makes no difference to the composition of the solid phase. Crystalline substances of this kind are termed double salts. An aqueous solution of a double salt shows all the reactions of both component salts, and the physical and chemical properties are usually, qualitatively at least, those to be expected from the properties of solutions of the components. On the other hand the solution may deposit physically homogeneous crystals, the chemical composition of which varies to a greater or less extent. When, for example, a mixed solution of cupric and ferrous sulphates is allowed to evaporate slowly, and the crystals which form are picked out from time to time and analysed, it is found that both sulphates may be present in each crystal, but the proportion need not be constant. Mixtures like this are called solid solutions, presumably because they resemble ordinary solutions in being homogeneous, and being of a composition variable within limits, which are sometimes fixed, sometimes indefinite. The behaviour of a liquid mixture which may deposit a solid solution differs markedly from that of one which deposits only pure crystals of one or more kinds. The formation of solid solutions is of special interest in the study of alloys. Here we are more particularly to deal with the formation of double salts, and hence shall have to consider ternary systems containing two inorganic salts having a common anion in aqueous solution.

Double salts have always been of considerable theoretical interest, and formulators of theories of valency have tried to answer the question of how the single salts are united to form double salt. A distinction was formerly drawn between "atomic compounds" which were formed by the normal exercise of valency, and "molecular compounds" in which "residual affinity" accounted for the union between molecules. As the outcome of his studies of the ammines Werner developed a much more satisfying theory of valency, which was essentially geometrical. Werner's theory met with considerable success not only when applied to ammines, but also with salt hydrates, and double salts. Although Werner's theories have been largely superseded yet results in qualitative agreement with the newer theories were often obtained. According to Werner ordinary alum is $Al(H_4O_2)_6 .(SO_4)_2.K$, the water having to be supposed coordinated in double molecules in order to give the coordination number six. On the contrary let us quote Sidgwick (The Electronic Theory of Valency): "It cannot always be assumed that a 'double salt' - a solid phase whose composition can be expressed as the sum of an integral number of single salt molecules of more than one kind (with or without solvent molecules) - really contains a complex molecule; there is always a possibility that it is only a crystalline aggregate of simple salt molecules. It is an experimental question, which in general can only be decided by determining whether the complex exists in solution, although in some cases the X-ray evidence of crystal structure may be sufficient. Proof that dissociation into the components occurs in solution is not decisive against the existence of the complex, unless the dissociation can be shown to be complete: many true complex salts, like the fluosilicates, are considerably dissociated in this way."

Caven and his co-workers obtained much evidence in support of his idea that complex ions are often formed in solution previous to crystallisation of double salt. His views may be summarised somewhat as follows, (Caven, Journ.Roy.Tech.Coll., 1, 18, 1924). A double or complex salt is formed in solution from two salts with a common ion when there is sufficient difference in basigenic character between the two metals forming the cations to yield,simultaneously,sufficient concentrations of the common ion, and the undissociated salt of the weaker cation to cause their union. In this theory it is supposed that complex ions are formed in solution previous to crystallisation of a double salt, and that there is no rigid distinction between a double and a complex salt; and further, that double salt formation depends to some extent on a certain difference of position in the electropotential series between the two metals concerned.

Double salts have been studied in many different ways. Many investigators were content simply to mix strong solutions of the single salts, and call the solid phase a double salt if its analysis at all corresponded with a simple stochiometric ratio of the single salts. Once the value of Gibb's Phase Rule had come to be appreciated a great deal of work of a much more fundamental nature was carried out. In 1887 Roozeboom made fairly widely known the generalisation, which had been discovered about ten years previously by Willard Gibbs. Gibbs' work was rather mathematical, and had lain practically unknown for that time. Once this powerful tool had come to be used, rapid advances were made in the study, and classification of chemical equilibria. A few years earlier Van't Hoff had propounded his "law of the incompatibility of condensed systems", which is in some respects similar to the phase rule, but is not so widely applicable. The study of equilibria was rapidly advanced by a big army of workers among whom may be noted, Van't Hoff, Schreinemakers, and Roozeboom. As far as work concerning double salts is concerned particular note may be taken of that done in Van't Hoff's laboratory. During the last ten years of his life he spent much time studying the Stassfurt salt deposits. In connection with this work many systems of salts in aqueous solution were examined, and incidentally the existence and properties of many double salts discovered. Accounts of much of this work are given in Van't Hoff's books, "Vorlesungen über Bildung und Spaltung von Doppelsalzen" and "Etudes de Dynamique Chimique". This work was mostly very thorough, and set an excellent example to later investigators. Van't Hoff plotted the isotherms of many ternary, and more complicated systems, and developed very sensitive methods for finding the transition temperatures of salt hydrates, and of double salts.

The methods of X-ray crystal analysis have been applied to the study of double salts with many valuable results. Sometimes this work alone elucidates the method of binding, and tells what rearrangements have to take place in order that the simple salts may unite to form double salt. Potassium alum was naturally one of the first double salts to be studied by the Bragg method. The crystal system is cubic, and hence fairly simple to examine. The main interest of the work lay in the complication introduced by the presence of so much water of crystallisation. As the result the arrangement of the metallic, sulphur, and oxygen atoms in the structure have been arrived at by Vegard and Schjelderup, not directly, but by a process of elimination of all the impossible arrangements having regard to the angles and intensities observed. The net result is that the twenty-four molecules of water of crystallisation in the molecule $K_2Al_2(SO_4)_4.24H_2O$ (which appears to be the correct constitutional formula) are divided into six groups of $(H_2O)_4$, which are cubically disposed with reference to the four tetrahedrally arranged sulphur atoms.

Double salts are also of interest to theorists interested in the theory of strong electrolytes. The theories of Debye and Hückel, and their later modifications, have been applied with varying success to several ternary systems.

In this laboratory much time has been spent by Professor Caven and his co-workers in determining the isotherms of ternary systems of metallic sulphates in aqueous solution at temperatures from 0°C to 30°C, but mostly at 25°C or 30°C. The present work extends the scope to isotherms of systems containing other anions, and at the same time includes two extra series of sulphates. An account will now be given of several matters relating more closely to the present investigation.

The systems examined are ternary ones consisting of two inorganic salts with a common anion in aqueous solution. The first consideration is to find graphic methods of representing the isotherms. The simplest method is, perhaps, to express the concentration of each salt as grams of anhydrous salt per 100 gm. of water, and to plot on rectangular coordinates. If no double salts or solid solutions are formed in the system the isothermal curve consists of two simple solubility curves (one for each single salt, which it is here assumed crystallises as only one hydrate) meeting at the triple point, where the liquid phase is in equilibrium with both solid phases (Figure 4). If the moist solid phases are analysed the results are again expressed as grams. of each anhydrous salt per 100 gm. of water. If double salts are formed the compositions of these can be found indirectly from the analyses of liquid phases, and moist solid phases with which they are in equilibrium (Schreinemakers, Z.physikal.Chem., 1893, 11, 76; Bancroft, J. Physical Chem., 1902, 6, 179).

The points representing corresponding liquid phases and moist solid phases are joined by lines called "tie lines", and these meet (as will be shown later) in a point whose coordinates give the composition of the solid phase (Figure 9). In the case of the rectangular diagram the composition of the solid phase is given in gm. of each anhydrous salt per 100 gm. of water. Whilst this method of representation is very effective for showing the relations existing in the liquid phase it becomes rather clumsy when the tie lines, indicative of the composition of the solid phase, have to be produced great distances before they intersect. The existence of anhydrous double salt is, of course, shown by a set of parallel tie lines (Figure 13). When the two components can form a compound, the isothermal diagram exhibits three curves. As before, two curves representing ternary solutions in equilibrium with each single salt, and an additional one to represent ternary solutions in equilibrium with double salt. Another method of representing the isothermal relations in a ternary system was suggested by Jänecke (Z.anorgan.Chem., 1906, 51, 132), but has not been used herein.

In those cases, however, where the three components behave in much the same manner towards one another, rectangular coordinates are not very suitable, and some form of triangular diagram is usually employed. Several methods of representing systems of three components by means of a triangle have been put forward. Of these, only two have been much used. Gibbs proposed using an equilateral triangle of unit height. The method used here is that due to Roozeboom, and consists in employing an equilateral triangle the length of whose side is made unity. The sum of the fractional amounts of the three components is therefore represented by a side of the triangle. The composition of a ternary mixture is determined by the distances, in a direction parallel to the sides of the triangle, of the point representing it, from the sides of the triangle. The apices of the triangle represent the components. In the simple case where no compound formation takes place two curves meeting at the triple point are again obtained. Where double salts are formed an additional curve is introduced for each, representing ternary solutions in equilibrium with it. It must, of course, be understood that the temperature is on that side of the transition point on which the double salt is stable. For the indirect determination of the composition of the solid phase the same data viz. composition of liquid phase, and of moist solid phase in equilibrium with it, are required. This time the results are expressed as fractional amounts of each component, and plotted in the triangle exactly as for the liquid phase. The most solid phase consists, on the double salt part of the curve, of double salt, together with adhering mother liquor. All possible compositions of the moist solid phase must hence lie between that of the equilibrium solution and that of the double salt, and therefore fall somewhere on the line joining the points representing the compositions of these two media. Thus, one tie line is fixed, and the composition of the solid phase is shown by the point, where two, or more, tie lines intersect. On the Roozeboom triangular diagram the composition of a hydrated double salt is shown by the tie lines intersecting within the triangle, whilst, if there is more than one double salt there is more than one set of intersecting tie lines (Figure 10). On the other hand (Figure 14), when the double salt is anhydrous, the tie lines intersect on the side of the triangle, and show the composition of the double salt in fractional amounts of the two anhydrous single salts.

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EXPERIMENTAL

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Since much of the work to be described consisted in determining the isotherms of mixtures of two inorganic salts, containing a common anion, in aqueous solution it seemed well to give the general experimental procedure here, and to treat the details under each system as it was considered later. In general a saturated solution of one of the salts at the requisite temperature was prepared by agitating the salt with water at that temperature, until equilibrium was attained. The equilibrium solid and liquid phases were then separated, by some method which did not involve changing their composition, and analysed. Duplicate analyses were performed on each sample. To ensure that it was the true equilibrium solution, which was being analysed, the solution was again agitated for at least a day, and the processes of sampling and analysing repeated. In general equilibrium was attained after two days, but in some cases (for example the triple points for the systems of cerous sulphate and alkali sulphates) periods of over a week were necessary. The composition of solid and liquid phase was likewise determined for a whole series of points after adding certain quantities of the second salt, until finally the aqueous solubility of the second single salt was determined. At the triple points the composite nature of the solid phase could often be readily demonstrated by microscopic observation. Thus it remains to describe in this section:-

1. Thermostatic and stirring arrangements.
2. Method of separating and sampling liquid phase.
3. Method of separating and sampling solid phase.

1. Thermostatic and Stirring Arrangements.

At first the apparatus which had been used by previous workers in this laboratory was employed. A big galvanised iron thermostat bath was kept at the predetermined temperature by a gas flame placed underneath, and controlled by a mercury regulator as described in Findlay's "Practical Physical Chemistry". A flat-bottomed glass bottle containing the materials was set on a tray in the thermostat, and kept up to the neck in the bath water by a heavy lead collar. Stirring was effected by a glass rod, which was bent at the end to cause suitable agitation of the crystals in the liquid. The rod protruded vertically from the bottle, and was rotated by an electric motor through reduction gearing. This method suffered from the fact that it was possible to close the mouth of the bottle only loosely, and hence, since there was always a little evaporation from the contents, it was rather difficult to ensure equilibrium. Most of the work was done with much improved apparatus. The thermostat was heated, and controlled, electrically. The heating element was a Robertson's 250 watt lamp immersed in the water. For making and breaking circuit a mercury relay was used. Control was by sensitive mercury regulator, and current to operate the relay was tapped off from the 250 volt. D.C. supply. The materials were contained in 350 cc. ground glass stoppered bottles. The stopper was brushed round the edge with paraffin wax, and totally immersed in the water of the thermostat. There it was clamped in a rectangular brass frame, which could carry three such bottles at a time. The frame was held horizontally between two pins set in vertical brackets mounted on the bottom of the thermostat. The frame, carrying the bottles under water, was rotated at about twenty revolutions per minute by means of a pair of toothed wheels, and a vertical spindle set revolving by an electric motor. This motion served not only to agitate the contents of the bottles, but also to stir the water in the thermostat sufficiently well to maintain a uniform temperature. By this means solutions could be shaken for long periods at constant temperature.

2. Method of Separating and Sampling Liquid Phase.

Where the nature of the solid phase permitted it, the separation of solid and liquid phases was effected simply by settling and decanting. After stirring for the desired time the bottle was unclamped from the frame, and the stopper removed whilst only the neck of the bottle was exposed from the thermostat water. A sample of from 5 to 50 cc. was then rapidly run into a clean dry tube, previously heated to bath temperature. The tube was then stoppered, and immersed up to the neck in the thermostat. Care was taken always to have the tube filled to as near the stopper as possible, in order to avoid the evaporation and condensation which would have ensued had there been a clear space above the liquid. After standing for at least half an hour any solid phase present had separated leaving a clear supernatant liquid, which was decanted in suitable quantities into tared weighing bottles. It was found advantageous to make a constricted neck towards the bottom of the sampling tube. Then the solid phase separated into the bulb at the bottom, and there was no fear of mixing it with the clear liquid being poured from the top side of the constriction.

Whilst this method was excellent for sampling the liquid phase it was not good for the solid phase, and in any case it sometimes could not be applied because the solid phase did not separate well enough. Hence filtration was often adopted.

3. Method of Separating and Sampling Solid Phase.

A small Büchner filter was well dried in the steam oven. The solution to be sampled was shaken up, and filtered using very gentle suction, whilst the Büchner was kept as nearly at thermostat temperature as possible. The filtrate was at once poured into stoppered weighing bottles. It was at first feared that this process might alter the concentrations in the liquid phase a little, but tests gave results in good accord with those found by settling and decanting. If the method of solutions and rests was being employed the moist solid phase was quickly transferred to a weighing bottle, and used for analysis. If, however, a direct analysis of the solid phase was to be undertaken, the crystals were pumped as dry as possible. They were then washed with a little cold water to remove adhering mother liquor, and dried on a porous plate in the air for some time, before being analysed.

The analytical weights used were checked against a set standardised at the National Physical Laboratory. Also, the volumetric instruments used were standardised or calibrated by the usual methods of weighing the water which they contained or delivered.

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PERCHLORATES

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Comparatively few double perchlorates have been reported. Weinland and Ensgraber (Zeitsch. Anorg. Chem. 1913, 84, 340) published observations on the investigation of a ferriperchlorate, and on sodium ferri tetraperchlorate. They stated that aluminium and chromium could form analogous compounds. In the second part of their paper it is shown that aluminium behaves very like iron. It forms the perchlorate of the hexaquo base, $[Al(H_2O)_6](ClO_4)_3$ and sodium tetraperchlorato aluminate

$$[Al(ClO_4)_4]Na \cdot 12H_2O$$

The salts form colourless crystals. The aluminium double salt, in contrast to the ferric one, is hardly hygroscopic at all.

The evidence of Weinland and Ensgraber for the existence of sodium tetraperchlorato aluminate is not good, and a full translation of that part of their paper relating to this subject is given below.

"Sodium tetraperchlorato aluminate $[Al(ClO_4)_4]$ $Na.12H_2O$ - 90 gm. of pasty hydrated alumina, containing 3% Al, were dissolved in 252 gm. of 20% perchloric acid, and mixed with a solution of 12.25 gm. of sodium perchlorate in a little water ($Al : ClO_4H : Na = 1 : 5 : 1$ i.e. equimolecular proportions of the single salts).

The solution was concentrated on the water bath, and left over sulphuric acid to crystallise: colourless, granular crystals which were slightly hygroscopic.

Analysis.

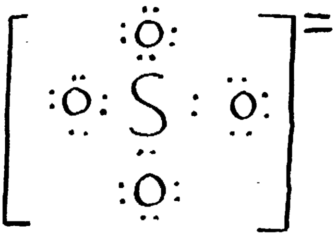
Calc.	4.08%Al;	59.90%ClO_4;	3.46%Na
Found	4.35%	59.88%	3.55% "

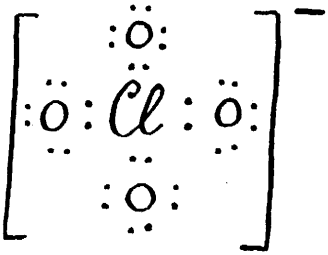
Interest was aroused in these supposed double perchlorates when it was noticed that their empirical formulae might suggest them to be of the alum type. Thus:

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \quad - \quad \left[Al(H_4O_2)_6\right] \cdot (SO_4)_2 \cdot NH_4$$

$$(NH_4)_2(ClO_4)_2 \cdot Al_2(ClO_4)_6 \cdot 24H_2O \quad - \quad \left[Al(H_4O_2)_6\right] (ClO_4)_4 \cdot NH_4$$

Furthermore the structures assigned to the perchlorate ion and the sulphate ion by the Lewis-Langmuir theory of valency were similar.





These formulae, of course, take no account of possible hydration. The most striking difference between the sulphate ion, and the perchlorate ion is that whilst $(SO_4)^=$ is bivalent, $(ClO_4)^-$ is univalent. Thus if ClO_4 were to replace SO_4 in a compound twice as many groups (of approximately the same size) would be required for valency considerations. Thus it was thought to be of interest to study the double perchlorates of Weinland and Ensgaber, and to compare them with the corresponding double sulphates.

Preparation of Aluminium Perchlorate $Al(ClO_4)_3.6H_2O$.

The salt was prepared by the method used by Weinland and Ensgraber (loc.cit.).

12.2 gm. of $Al\ Cl_3.6H_2O$ were dissolved in 93 gm. of 19% perchloric acid, and the solution was heated on the water bath until no more hydrochloric acid fumes were evolved. The solution was evaporated to small bulk and put in a crystallising dish over sulphuric acid. Long white prismatic crystals separated, and were filtered off with suction, and washed with a very little cold water. The crystals were shown to be free from chloride. They were left for a week on a porous plate in vacuo over sulphuric acid.

Analysis.

The aluminium in the sample was determined by precipitation with ammonia using methyl red at the boiling point to indicate when just sufficient alkali had been added. After boiling two minutes the liquid was filtered and the alumina very thoroughly washed with hot 2% ammonium nitrate solution. The precipitate was then ignited in a platinum crucible before the blast lamp, and weighed, after cooling, as Al_2O_3.

According to Hillebrand and Lundell ("Mineral Analysis") it is necessary to heat Al_2O_3 to 1200°C in order completely to dehydrate it. Heating to this high temperature has a further advantage in that it changes the oxide to a more dense crystalline form which is less hygroscopic, and hence is easier to weigh accurately.

Calc.	$Al(ClO_4)_3 \cdot 6H_2O$	6.22% Al.
Found		6.115% Al.

The usual methods (1. Ignition, reduction methods; 2. Colorimetric; 3. Wet reduction - say with titanous sulphate) of estimating perchlorate are rather cumbrous and untrustworthy, and could not well be applied to the aluminium salt.

Britton (J.C.S., 121, 1922 - further references are given in this paper) describes a method of analysing aluminium sulphate by titration at the boiling point with caustic soda, using phenol phthalein as indicator. He states that it is advisable to work with solutions containing less than 0.1 gm. of alumina per 100 cc. With stronger solutions the end point is masked by the precipitated alumina, and low results may be obtained due to some aluminium sulphate being carried down with the aluminium hydroxide. This method was adapted for the analysis of aluminium perchlorate. The caustic soda was standardised under conditions similar to those in which it was used, viz. by titration against standard H_2SO_4 using phenol phthalein as indicator at the boiling point.

Found 67.25% ClO_4

Calc. Ratio $\frac{(ClO_4)_3}{Al}$ = 11.06 Found 11.00.

Hence the prepared salt is $Al(ClO_4)_3.6H_2O$, and is pure.

In the first instance attempts were made to prepare double salts of aluminium perchlorate with sodium potassium and ammonium perchlorates by mixing fairly strong solutions of the appropriate single salts in different proportions. All these attempts met with failure, and it was found (for several temperatures, including room temperature, and for widely varying proportions of the single salts) that addition of aluminium perchlorate solution to solutions of the perchlorates of the alkalis caused the latter salts to crystallise out.

The matter was much more fully examined by determining the isotherms of several ternary perchlorate systems.

Sodium Perchlorate with Aluminium Perchlorate.

Commercial sodium perchlorate was dissolved in alcohol and a small residue of potassium perchlorate filtered off. The solution was then evaporated to dryness and $NaClO_4.H_2O$ crystallised from water. For analysis the salt was dehydrated in the air-oven, and by the method to be described was found to contain 18.91% Na. $NaClO_4$ requires 18.77%Na.

In the equilibrium solutions aluminium perchlorate was found by the method of estimation as Al_2O_3 already described. Since prechlorate is troublesome to determine it was thought better to estimate the sodium directly. Barber and Kolthoff put into practice a method for the direct determination of sodium (J.A.C.S., 50, 1625). This method was first suggested by Streng (Z.wiss.Mikroskop 3, 129, 1886) and was also studied by Miholic (Bull.Acad.Sci.Zagreb. 1920, 16), and Blanchetière (Bull.Soc.Chem. 33, 807, 1923). In this method the sodium was precipitated as sodium zinc uranyl tri-acetate. The method was then improved by Caley and Foulk (J.A.C.S., 1929, 51, 1664) by precipitating as sodium magnesium uranyl tri-acetate. The following solutions were prepared.

A	B
Crystallised A.R.uranyl Acetate, 90 gm. Glacial acetic acid 60gm. to 1000 cc. with distilled water.	Crystallised magnesium Acetate, 500 gm. Glacial acetic acid 60 gm. Distilled water to 1000cc

Each solution was heated to 70°C until the salts were dissolved, and then the solutions were mixed, left at room temperature for a few days, and filtered into a dry bottle. For each analysis the sample of sodium (aluminium) perchlorate solution was evaporated down to 2-5 cc. on the water bath, and at least 100 cc. of the above reagent added at room temperature. Precipitation took place at once, but in order to hasten the

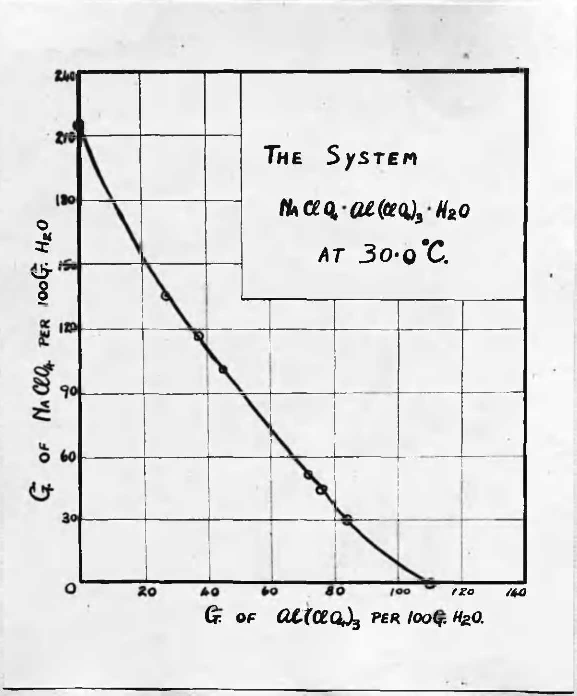

THE SYSTEM
NaClO4·Al(ClO4)3·H2O
AT 30·0°C.
G. OF NaClO4 PER 100G. H2O
G. OF Al(ClO4)3 PER 100G. H2O.
240
210
180
150
120
90
60
30
0
20
40
60
80
100
120
140

Figure 1.

process, and ensure its completion, the solution was stirred by a water turbine for 30 to 40 min. The yellow precipitate was then filtered off in a Gooch crucible, and washed with 95% alcohol until the washings were colourless. The tri-acetate was dried in the air oven at 105-110°C for 30-40 minutes and weighed. The amount of alcohol used in washing was measured, and a very small correction applied for the solubility of the triacetate in this liquid. Not less than 100 cc. of reagent were used in each case, and where the quantity of sodium exceeded 0.01 gm. the number of cubic centimetres of reagent used was at least ten times the number of milligrams of sodium present. According to Caley and Foulk the precipitate as weighed is $Mg(C_2H_3O_2)_2.NaC_2H_3O_2.3UO_2(C_2H_3O_2)_2.6\frac{1}{2}H_2O$ and contains 1.527% Na.

The method was tested with standard solutions of A.R. NaCl, alone, and containing varying proportions of aluminium chloride (which had to be prepared specially, free from sodium, since the best available samples contained sufficient, completely to vitiate the results). The analyses were correct to within one half per cent, and showed this method of sodium estimation to suit the present purpose very well.

The value found for the solubility of sodium per-

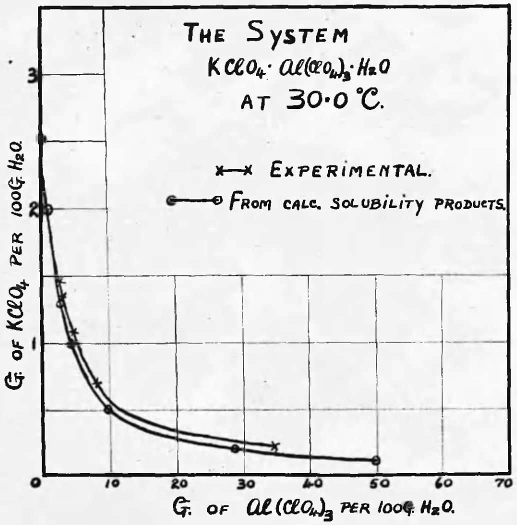

THE SYSTEM
$KClO_4 \cdot Al(ClO_4)_3 \cdot H_2O$
AT 30·0 °C.
x—x EXPERIMENTAL.
o—o FROM CALC. SOLUBILITY PRODUCTS.
G. OF $KClO_4$ PER 100G. H_2O
G. OF $Al(ClO_4)_3$ PER 100G. H_2O
0
1
2
3
10
20
30
40
50
60
70

Figure 2.

chlorate in water at 30°C was 215 gm. $NaClO_4$/100 gm.H_2O. Calculations from the results of Freeth gave 219.7, and Carlson 208.5.

Potassium Perchlorate with Aluminium Perchlorate.

Potassium perchlorate was several times recrystallised from water and used. The method devised for the analysis of mixed solution of potassium and aluminium perchlorates was very simple, and sufficiently accurate. The sample of solution to be analysed was evaporated almost to dryness on the water bath. Sufficient 95% alcohol to dissolve the aluminium perchlorate was added, and the residue of potassium perchlorate ground up and stirred in the liquid. The potassium perchlorate was then filtered off in a tared Gooch crucible, washed with 95% alcohol, and weighed after drying at 120°C in the air oven. A small correction for the solution of a little potassium perchlorate in the volume of alcohol used was necessary. The alcoholic filtrate containing the aluminium was then evaporated to dryness on the water bath. The residue was dissolved in water, and estimation by precipitation as Al_2O_3 carried out as before described. The curve was followed to the point where addition of aluminium perchlorate had so far reduced the concentration of potassium perchlorate as to make estimation of the latter salt difficult.

Ammonium Perchlorate with Aluminium Perchlorate.

In the first instance pure ammonium perchlorate was prepared from the commercial salt. 150 gm. of the salt, which contained a trace of iron, were dissolved in 600 cc. of distilled water. A few cubic centimetres of bench ammonia solution were then added, and the liquid kept hot for an hour. The liquid was filtered through an asbestos pad and (after evaporation and cooling) ammonium perchlorate crystallised out in pure white glistening rhombic crystals. After drying, the crystals analysed 14.45% NH_3; NH_4ClO_4 requires 14.49% NH_3. Furthermore the crystals were free from iron, and a 1 gm. sample left no appreciable residue after very careful (the salt is liable to explode if ignited strongly) ignition in a platinum crucible. When the solubility of this purified ammonium perchlorate in water at 30.0°C was determined (28.0 gm. NH_4ClO_4 per 100 gm. water), it was found to disagree with that obtained by graphing and interpolating the results of Carlson (Klason's Tidsskrift, 247, 1910). Hence the solubility was redetermined after the salt had

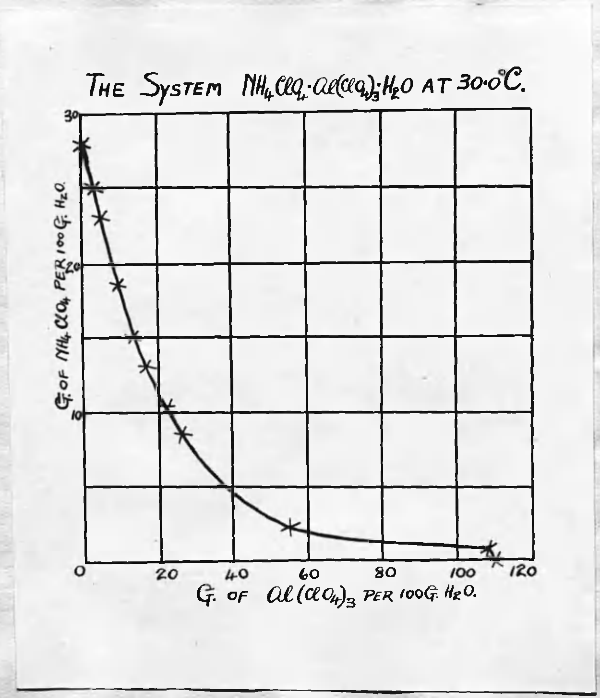

THE SYSTEM NH_4ClO_4-$Al(ClO_4)_3$-H_2O AT 30·0°C.
G. OF NH_4ClO_4 PER 100 G. H_2O.
G. OF $Al(ClO_4)_3$ PER 100 G. H_2O.
30
20
10
0
20
40
60
80
100
120

Figure 3.

been twice further recrystallised from fairly large volumes of distilled water. The same value was obtained.

In addition ammonium perchlorate was prepared by neutralising A.R. perchloric acid with synthetic ammonia. The crystals analysed 14.43% NH_3, and gave the same value as before for the solubility in water at 30.0°C. No data, other than Carlson's, cover the solubility of ammonium perchlorate in water in this temperature region. However, when values for the solubility of ammonium perchlorate in water at 15.0°C are calculated from the results of Hofmann, Höbald and Quoos (Liebig's Ann., 336, 304, 1912) and Carlson (loc.cit.), they are found to be 18.5 gm. NH_4ClO_4, and 20.52 gm. NH_4ClO_4 per 100 gm. of water. Thus again Carlson's result is high.

In the equilibrium solutions ammonium perchlorate was estimated as follows. An aliquot portion of the solution was pipetted into a long-necked flask. A long delivery tube with splash-trap and safety-bulb led up from this flask, and then down through a water-cooled condenser into a conical flask. In the conical flask was a measured volume of standard sulphuric acid, and the end of the delivery tube was led beneath the surface of this. An excess of ammonia-free caustic soda was then run in from a tap funnel fitted to the long-necked flask. The alkaline solution was boiled gently, and steadily, for half an hour, and all the ammonia driven over,and absorbed in the cold standard acid. It was found advisable to add a little zinc dust to the alkaline solution, so that the slow evolution of hydrogen might prevent bumping. The excess of sulphuric acid remaining in the receiving flask was determined by adding a measured volume of standard caustic soda, and back titrating with standard sulphuric acid using methyl orange indicator. Hence the ammonium perchlorate content of the equilibrium solution was calculated.

The aluminium perchlorate was found as already described by precipitation with ammonia,and weighing as Al_2O_3.

Ammonium Perchlorate with Cupric Perchlorate.

G.S. Sérullas (Ann.Chim.Phys. (2), 46, 306, 1831) stated that copper perchlorate forms large blue deliquescent crystals. R.Roth's analyses of the crystals gave $Cu(ClO_4)_2.6H_2O$ (Zur Kenntnis der Perchlorate, München, 1910). That the salt crystallises with six molecules of water of crystallisation was confirmed by C. Smeets (Natuurwetensch. Tijds, 1931, 13, 247, 253).

The preparation of cupric perchlorate was first attempted by G.S. Sérullas's method, viz:- 22 gm. of basic copper carbonate were dissolved in 200 gm. 20% $HClO_4$ by heating on the water bath. The basic copper carbonate mostly dissolved quickly in the 20% $HClO_4$, but a small white residue remained. Qualitative analysis showed this to be silica, and potassium perchlorate. The slightly acid solution was filtered free from this insoluble matter. On evaporation and cooling blue-green deliquescent crystals were obtained. These crystals were pumped as dry as possible on a Büchner filter, crushed on a porous plate, and analysed. 19.92% Cu; theory for $Cu(ClO_4)_2.6H_2O$ = 17.16% Cu.

This first crop of crystals was found (as the above analysis might suggest) to be basic. The mother liquor was acidified with perchloric acid, and concentrated, until on cooling it gave a mass of deep blue crystals. After recrystallisation from one per cent perchloric acid, the crystals were dried as far as possible by crushing between sheets of filter paper, and a sample weighed, and made up to 250 cc. solution.

The following very effective method was devised for the estimation of perchlorate in this solution:-

The copper in an aliquot portion of the solution was completely precipitated by bubbling in an excess of purified hydrogen sulphide. About 1 gm. of A.R. sodium chloride was added to the solution before passing hydrogen sulphide, in order to promote coagulation of the precipitate. The precipitated cuprous sulphide was rapidly filtered off with suction. It was exposed as little as possible to the air, in order to avoid oxidation, and resolution as cupric sulphate. The precipitate was well washed with hydrogen sulphide water, and rejected. The filtrate containing perchloric acid was boiled down to very small bulk in order completely to expel the hydrogen sulphide. After cooling and diluting this solution, an excess of standard caustic soda was added, and the excess estimated by back titration with sulphuric acid using methyl orange indicator. The sulphuric acid was standardised against a standard solution prepared from dried A.R. sodium carbonate. As a check for the method the sulphuric acid was also standardised against a solution of A.R. copper sulphate, the method of titration being similar to that described above for the perchlorate. The factors for the sulphuric acid obtained by the two methods agreed within ½ per cent.

By this method of analysis the second crop of cupric perchlorate crystals was found to contain 16.54% Cu and 51.92% ClO_4.

Ratio $\frac{ClO_4}{Cu} = 3.139$; Theory for $Cu(ClO_4)_2 = 3.128$.

Although it was thus possible to prepare pure cupric perchlorate from the carbonate, yet it was found better to use electrolytic copper foil as a starting product, and avoid the loss of perchlorate which was involved in the purification by fractional crystallisation when basic copper carbonate was used as the source of copper.

Cupric Perchlorate in quantity was prepared by the following method: 38.2 gm. of electrolytic copper were covered with water, and dissolved in 100 cc. conc. HNO_3. 200 gm. of 60% A.R. perchloric acid were then added, and the solution evaporated down in a porcelain basin. The process of adding more perchloric acid (in all 270 gm. of 60% perchloric acid were used) and evaporating down, was repeated until the meal of crystals was free from nitrate. The crystals which separated could not be freed from the large excess of perchloric acid without considerable loss. Hence an excess of copper carbonate was stirred into the acid solution. (The copper carbonate was precipitated by adding ammonium carbonate to a solution of electrolytic copper in nitric acid. Before

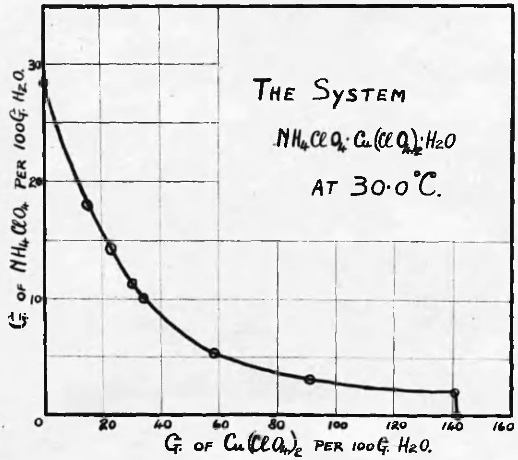

THE SYSTEM
$NH_4ClO_4 : Cu(ClO_4)_2 : H_2O$
AT 30·0°C.
G. OF NH_4ClO_4 PER 100G. H_2O.
30
20
10
0
20
40
60
80
100
120
140
160
G. OF $Cu(ClO_4)_2$ PER 100G. H_2O.

Figure 4.

use it was thoroughly washed with hot water). The slight excess of copper carbonate was then filtered off, and enough perchloric acid added to make the solution one to two per cent acid. On evaporating and cooling the solution a good yield of beautiful sky-blue crystals was obtained. The crystals deliquesced in the air, and so, for analysis, a sample was crushed as dry as possible between sheets of filter paper, and weighed.

Found: 16.66% Cu ; 52.24% ClO_4

$$\text{Ratio } \frac{ClO_4}{Cu} = 3.135.$$

Theory for $Cu(ClO_4)_2 \cdot 6H_2O$ 17.16% Cu ; 53.67% ClO_4

$$\text{Ratio } \frac{ClO_4}{Cu} = 3.128$$

It was noted that the salt melted in its water of crystallisation at just over 80°C. Perchloric acid was lost when a sample was heated at 100°C.

In the equilibrium solutions ammonium perchlorate was determined by boiling the sample with excess caustic soda, and absorbing the liberated ammonia in an excess of cooled standard sulphuric acid. For the titration excess standard caustic soda was added, and the excess found by titration with standard sulphuric acid using methyl orange indicator. Cupric perchlorate was estimated iodometrically. About six times the theoretical equivalent of potassium iodide and strong hydrochloric acid was added to the solution to be titrated. The liberated iodine was then titrated with standard sodium thiosulphate in the presence of the flesh-coloured precipitate of cuprous iodide. Just before the end of the titration a little freshly prepared starch solution was added to give a sharper end-point. The sodium thiosulphate solution was standardised by iodide and standard dichromate, and also against A.R. cupric sulphate solution.

Ammonium Perchlorate with Thorium Perchlorate.

P.T. Cleve obtained an amorphous mass - presumably of thorium perchlorate - by treating a thorium salt of a more volatile acid with perchloric acid. (Bull.Soc. Chim. (2), 21, 156, 1874, and (2) 29, 1878. J.C.S., 234, 1875). He described thorium chlorate and perchlorate as soapy hygroscopic bodies. The only pure thorium salt available was the sulphate $Th(SO_4)_2 \cdot 8H_2O$, and it was decided to prepare the perchlorate from this. With this end in view 14.2 gm. of $Th(SO_4)_2 \cdot 8H_2O$ were dissolved in strong nitric acid, and the solution diluted to about a litre. A slight excess of ammonia was then added to the warm solution, and the precipitated thoria filtered off, and washed thoroughly. The thoria was dissolved in 31 gm. of 19% perchloric acid. (This was less than had been calculated as necessary according to the quantity of thorium sulphate used.) On evaporation and cooling a syrupy mass containing long feathery needle-like crystals was obtained. A small sample of the crystals was filtered off, washed with a minimum of cold water, crushed between sheets of filter paper, and weighed for analysis. It was found that the crystals contained too high a percentage of thorium. Since this might have been due to the presence of basic salt, further small samples were prepared and analysed, adding to the thoria in one case the full equivalent of perchloric acid calculated on the thorium sulphate taken, and in the other twenty per cent excess of this amount. Again too high a proportion of thorium was found in the crystals. This discrepancy was then traced to the presence of sulphate in the crystals. It was found that when thoria is directly precipitated by slowly adding dilute ammonia solution to a solution of thorium sulphate in nitric or hydrochloric acid, the precipitated thoria contains a considerable quantity of sulphate,which cannot be removed by prolonged washing with hot water. Sulphate was still present even when the thoria was precipitated in very dilute solution. Hence the thorium was first separated from the acid solution of its sulphate by the addition of a nitric acid solution of potassium iodate. (Hillebrand and Lundell - "Mineral Analysis"). The thorium iodate was well washed, and converted to thoria. The thoria was dissolved in acid, precipitated in dilute solution with ammonia, and well washed. This gave pure thoria free from sulphate. An equivalent of perchloric acid was used to dissolve the thoria. On evaporation and cooling long crystals of thorium perchlorate were obtained. The salt was deliquescent, and very soluble in water. It was ascertained to be pure, but no attempt was made to isolate definite hydrates. Since the salt was so very soluble its solubility was not determined quantitatively, and no isotherms of thorium perchlorate with other metallic perchlorates in aqueous solution were found.

It was thought to be sufficient to investigate the crystallisation of mixed solutions of thorium perchlorate with ammonium perchlorate in various molecular proportions. Thus strong solutions of thorium perchlorate and ammonium perchlorate were mixed in widely varying proportions, and stirred at room temperature until crystals separated. In each case the crystals were filtered off with suction, washed with a minimum of cold water, and analysed. No evidence for double salt formation was obtained, because for all the mixture examined the solid phase was found to be ammonium perchlorate.

Discussion of the Perchlorates.

Figure 1. shows the curve obtained for the ternary system $NaClO_4.Al(ClO_4)_3.H_2O$ at 30.0°C. There is no double salt curve in evidence. At the triple point the saturated solution contains 76.26 gm. $Al(ClO_4)_3$ per 100 gm. H_2O, and 43.84 gm. $NaClO_4$ per 100 gm. H_2O. Addition of aluminium perchlorate to saturated sodium perchlorate solution causes the latter salt to crystallise out, until the triple point is reached. Likewise aluminium perchlorate crystallises, when sodium perchlorate is added to its saturated solution. The solid phases were not analysed quantitatively, qualitative analysis being sufficient to characterise the crystals.

Whilst sodium perchlorate is very soluble, and crystallises from aqueous solution with one molecule of water, potassium perchlorate is but sparingly soluble in water, and crystallises anhydrous. Figure 2. shows that aluminium perchlorate, even in rather small quantities reduces considerably the solubility of potassium perchlorate. In fact it is shown that the result of adding aluminium perchlorate to saturated potassium perchlorate solution is approximately that calculated from the mass action effect of the added perchlorate ions. The solubility of potassium perchlorate in water at 30°C was found to be (2.528/138.56) gm.mol. per 100 gm. of water. Thus the solubility product of potassium perchlorate at 30.0°C is $\left(\frac{2.528}{138.56}\right)^2$ that is 3.329×10^{-4}. Since potassium perchlorate is a sparingly soluble binary electrolyte it was assumed that it was completely dissociated even in saturated solution, and that the concentration of the undissociated part was negligible as compared to that of the ions. Further it seemed reasonable to assume (for small concentrations of aluminium perchlorate), that the aluminium perchlorate added was completely dissociated into aluminium and perchlorate ions. Thus the increase in perchlorate ions following on each addition of aluminium perchlorate was calculated, and hence also the concentration of potassium perchlorate.

Thus:

Let enough aluminium perchlorate be added to reduce the concentration of potassium perchlorate in the liquid phase to 1.00 gm. per 100 gm. of water.

Then $[K^+] = \frac{1}{138.56} = 7.216 \times 10^{-3}$ gm.ion per 100gm.H_2O

$$\text{But} \quad [K^+][ClO_4^-] = 3.329 \times 10^{-4}$$

$$\text{Therefore} \quad [ClO_4^-] = \frac{3.329 \times 10^{-4}}{7.216 \times 10^{-3}} = 4.613 \text{ gm.ion/100gm } H_2O$$

$$\therefore \quad [ClO_4^-] \text{ from } Al(ClO_4)_3 = (4.613 \times 10^{-2}) - (7.216 \times 10^{-3})$$

$$= 3.891 \times 10^{-2} \text{ gm.ion/100gm } H_2O$$

$$\therefore \quad [Al(ClO_4)_3] = 1.297 \times 10^{-2} \text{ gm.mol./100 gm. } H_2O$$

$$= 4.220 \text{ gm./100gm. } H_2O.$$

Thus when the liquid phase in equilibrium with $KClO_4$ contains 4.220 gm. $Al(ClO_4)_3$ per 100 gm. H_2O, the concentration of potassium perchlorate in it is 1.00 gm. per 100 gm. H_2O.

Similarly a whole series of other values was calculated, and the results plotted on a rectangular diagram alongside those obtained experimentally. The curves were remarkably similar, and almost coincided at the lower concentrations of aluminium perchlorate, where the suppositions made for the purpose of calculation were most likely to be true. Whilst the above method of calculating the effect of adding an electrolyte with a common ion to a solution of another is now largely superseded by the newer theories, yet it was thought to be of interest to show just how closely the calculated results agreed with the experimental. This agreement adds weight to the finding that there is no double salt curve in the isotherm of the system $KClO_4.Al(ClO_4)_3.H_2O$ at 30°C.

The solubility of ammonium perchlorate is intermediate, between that of potassium, and that of sodium perchlorate. The crystallisation of ammonium perchlorate ensues as more and more aluminium perchlorate is added to a saturated solution of the former salt. (Figure 3.) In fact so efficacious is aluminium perchlorate in causing the separation of ammonium perchlorate from solution that at the triple point the equilibrium solution at 30.0°C. contains 107.7 gm. $Al(ClO_4)_3$, and only 0.91 gm. NH_4ClO_4. Quantitative analysis of the solid phases was unnecessary, because microscopic examination showed that the crystals were rhombic and like ammonium perchlorate, and furthermore qualitative analysis showed them to be contaminated from the liquid phase with only a trace of aluminium perchlorate, which could be removed by washing them with a very little cold water or alcohol. Again the system showed no double salt curve, nor did anything but ammonium perchlorate crystallise, when strong solutions of the two salts in widely varying proportions were stirred at different temperatures.

The isotherm obtained for the system $NH_4ClO_4.Cu(ClO_4)_2.H_2O$ at 30.0°C (Figure 4) was of a type very similar to the above. The ammonium perchlorate section of the curve was long, and at the triple point the liquid phase contained 2.08 gm. NH_4ClO_4,and 141.0 gm. $Cu(ClO_4)_2$.

On the longer section of the curve the solid phase was shown to be NH_4ClO_4 by the use of the microscope,and by qualitative analysis. Ammonium perchlorate was but slightly soluble in saturated cupric perchlorate solution, and caused hardly any change in the solubility of the latter salt. No evidence for double salt formation was obtained from this isotherm. Over a wide temperature range it was always ammonium perchlorate which crystallised from solutions containing ammonium perchlorate and cupric perchlorate in various concentrations.

It was also shown that when different quantities of strong thorium perchlorate solution were stirred with a strong solution of ammonium perchlorate the crystals which separated were those of ammonium perchlorate.

In representing the results obtained with the above ternary systems it was found most convenient to express them in grams of anhydrous salt per hundred grams of water, and to plot on a system of rectangular coordinates.

The double perchlorates reported by Weinland and Ensgraber could not be prepared. Furthermore no evidence for the existence of double salts of alkali perchlorates with the perchlorates of bi-, ter-, or quadri-valent metals has been obtained. Thus perchlorates do not resemble sulphates in their power of forming double salts. Here it may be noted that the perchlorates are not isomorphous with the corresponding sulphates. It seems probable that the difference in valency of sulphate and perchlorate may be an important factor governing double salt formation. Although $(ClO_4)^-$ and $(SO_4)^=$ have points in common, yet the difficulty of fitting twice as many $(ClO_4)^-$ groups into the lattice (even with thorium) may preclude double salt formation.

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THE SYSTEM $NaClO_4 \cdot Al(ClO_4)_3 \cdot H_2O$ at 30.0°C.

LIQUID PHASE		SOLID PHASE
G. $NaClO_4$/100G. H_2O	G. $Al(ClO_4)_3$/100 G. H_2O	
215.0	—	$Na(ClO_4).H_2O$
135.4	27.76	"
116.6	37.30	"
100.7	45.59	"
50.64	72.46	"
43.84	76.26	$NaClO_4 \cdot H_2O$ & $Al(ClO_4)_3$aq.
30.02	83.87	$Al(ClO_4)_3$ aq.
—	110.1	"

THE SYSTEM $KClO_4 . Al(ClO_4)_3 . H_2O$ at 30.0°C.

LIQUID PHASE		SOLID PHASE
$G. KClO_4/100 G. H_2O$	$G. Al(ClO_4)_3/100 G. H_2O$	
2.528	—	$KClO_4$
1.462	2.652	
1.357	3.043	
1.028	4.956	
0.7041	8.158	
0.2115	34.56	

CALCULATED FROM SOLUBILITY PRODUCTS.

LIQUID PHASE

$G. KClO_4/100 G. H_2O$	$G. Al(ClO_4)_3/100 G. H_2O$
2.528	—
2.000	0.936
1.300	2.830
1.000	4.220
0.500	9.610
0.200	24.86
0.100	49.94

THE SYSTEM $NH_4ClO_4 \cdot Al(ClO_4)_3 \cdot H_2O$ at 30.0°C.

LIQUID PHASE		SOLID PHASE
G. NH_4ClO_4/100 G. H_2O	G. $Al(ClO_4)_3$/100 g. H_2O	
28.00	—	NH_4ClO_4
25.03	3.13	"
23.10	5.25	"
18.66	9.77	"
15.12	14.09	"
13.15	17.47	"
10.47	22.90	"
8.59	26.19	"
2.36	55.69	"
0.91	107.7	NH_4ClO_4 & $Al(ClO_4)_3$aq.
---	110.1	$Al(ClO_4)_3$aq.

THE SYSTEM. NH_4ClO_4. $Cu(ClO_4)_2 \cdot H_2O$ at 30.0°C

LIQUID PHASE		SOLID PHASE
G. NH_4ClO_4/100 G. H_2O	G. $Cu(ClO_4)_2$/100 G. H_2O	
28.00	—	NH_4ClO_4
17.99	14.89	"
14.28	22.51	"
11.42	30.00	"
10.13	34.04	"
5.322	58.12	"
3.059	90.93	"
2.075	141.0	NH_4ClO_4 & $Cu(ClO_4)_2 \cdot 6H_2O$
—	141.6	$Cu(ClO_4)_2 \cdot 6H_2O$

CHROMATES

-oOo-

In many respects the chromates are similar to the sulphates, and corresponding salts are isomorphous. There are many references in the literature to double chromates, but in comparatively few cases has the investigation been at all exhaustive. Gröger (Zeitsch. Anorg. Chem., 54, 185, 1907) and Barre (Compt. rend., 158, 495, 1914) have each prepared a considerable number of supposed double chromates. Many double sulphates have already been very fully investigated in this laboratory, and hence, for comparative purposes, some attention was given to a few of the above double chromates.

Preparation of Calcium Chromate.

Among the methods that have been suggested for the preparation of calcium chromate are:-

(1) Fusing calcium chloride with sodium chromate.

(2) Adding strong sodium chromate solution to a concentrated solution of a calcium salt.

(3) By the action of chromic acid on calcium carbonate or milk of lime.

Methods (1) and (2) require sodium chromate. The best commercial sodium chromate contains considerable quantities of sulphate which is not readily separated from it. Hence some pure sodium chromate was prepared as follows - 30 gm. of chromium sesquioxide, prepared from chrome alum, were fused with 46 gm. of sodium peroxide in a nickel basin, and the melt was extracted with water. The solution was neutralised with hydrochloric acid, and filtered. The sodium chromate solution thus prepared was poured into an equivalent of calcium chloride solution made from A.R. calcium carbonate and hydrochloric acid. The calcium chromate was precipitated at the boiling point,when the pH had been adjusted by adding a few drops of caustic soda. This method gave a good yield of calcium chromate, but the product was not sufficiently pure for the present work, and could not readily be purified.

According to J.F. Bahr, $CaCrO_4.2H_2O$ can be obtained by treating calcium carbonate with a solution of chromic acid. However, it was found that chromic acid would dissolve (under varied conditions of concentration and temperature) only half its calculated equivalent of calcium carbonate. The salt which was thus obtained consisted of very dark red needles, and was very probably an acid chromate of calcium.

It was found that the best method of preparing calcium chromate was that given by Mylius and Von Wrochem (Ber., 33, 3689, 1900). These authors state that solutions containing more than twenty-five per cent of calcium chromate can be prepared by saturating chromic acid with milk of lime at 0°C. The solution is not stable for long, and can be regarded as supersaturated. On standing it gives yellow crystals of calcium chromate, and by warming a thick meal of crystals is quickly obtained. The solution is brought to 100°C to dehydrate the salt, and $CaCrO_4$ is then obtained in a form which is but slightly soluble.

50 gm. A.R. CrO_3 were dissolved in 150 cc. of water, and 28 gm. of CaO were slaked and made into a thin slurry with 150 cc. of water. The chromic acid solution was poured, slowly and with stirring, into the lime which was in slight excess. The solution was not allowed to heat above 0°C, and remained supersaturated with calcium chromate. The excess lime was filtered off, and the filtrate heated up to give a good yield of fine yellow powdery calcium chromate. This preparation was entirely satisfactory except for a small quantity of chocolate-coloured colloidal matter, which contaminated the product. A considerable time was given to discovering the nature and origin of this impurity. It was finally found to be chromic chromate, derived from a little chromic salt present as impurity in the A.R. chromic acid. A.R.

chromic acid as supplied by Merck and by B.D.H. was tested, and, in each case, found to contain a trace of silica and chromic salt. When an aqueous solution of the acid was neutralised with pure sodium carbonate, a brownish opalescence gradually appeared. The brown material was of a colloidal nature, and it was difficult to separate by filtration. A little of it was collected, well washed, and shown by analysis to be chromic chromate. Hence in the preparation of calcium chromate the product had to be purified from this impurity. This was effected as completely as possible by filtering the supersaturated solution through a thick pad of asbestos, before heating to precipitate calcium chromate. The sparingly soluble calcium chromate was heated with a little very dilute acetic acid, and finally boiled up with distilled water and filtered. The salt was dehydrated in the air oven at 250-300°C. At temperatures below 200°C the hemihydrate is obtained as shown by the following analyses on two different specimens. (1) 70.42% CrO_4: (2) 69.58% CrO_4, whilst $CaCrO_4.\frac{1}{2}H_2O$ requires 70.26% CrO_4.

Analysis of prepared Calcium Chromate (not dehydrated).

% Ca = 18.30 % CrO_4 = 52.28

Ratio $\frac{CrO_4}{Ca}$ = 2.857 - Theory - 2.895

Calcium Chromate with ~~Potassium~~ Potassium Chromate.

Gröger (Zeitsch. Anorg. Chem. 54, 185, 1907) prepared $K_2Ca(CrO_4)_2.2H_2O$ by mixing strong potassium chromate solution with calcium chromate solution. The salt was also prepared by Barre (Compt. rend., 158, 495, 1914). It is the existence of this double salt which prevented the preparation of calcium chromate from calcium chloride and potassium chromate. It was thought that if equivalent quantities of calcium chloride and potassium chromate were mixed in boiling solution calcium chromate might be obtained. However, it was shown that the product always contained double salt. The ratio $\frac{CrO_4}{Ca}$ in the product was (1) 3.64, (2) 3.72 for two different preparations. $CaCrO_4$ requires $\frac{CrO_4}{Ca} = 2.895$, and $K_2Ca(CrO_4)_2.2H_2O$ requires $\frac{CrO_4}{Ca} = 5.786$. Thus pure calcium chromate was not to be obtained by this method, since there was always some double salt as well.

The isotherm at 30.0°C for the system $K_2CrO_4.H_2O$ was obtained. The potassium chromate was of A.R. grade, and by iodometric analysis was shown to be 99.8% pure. In the equilibrium solutions calcium chromate was determined volumetrically by the oxalate method. An excess of standard ammonium oxalate solution was added to the solution for analysis, after making slightly acid with acetic

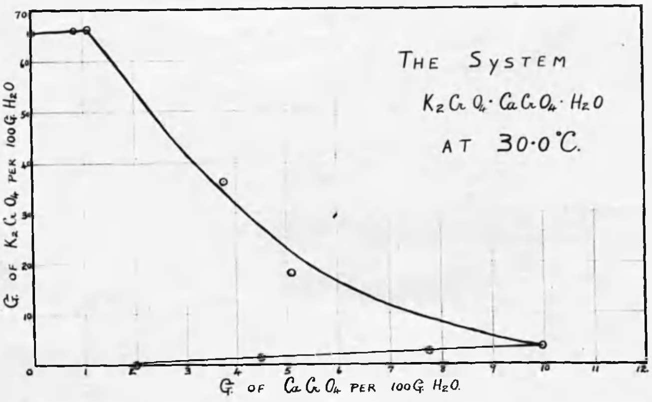
THE SYSTEM
K₂CrO₄·CaCrO₄·H₂O
AT 30·0°C.
G. OF K₂CrO₄ PER 100G. H₂O
G. OF CaCrO₄ PER 100G. H₂O.
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12.

Figure 5.

acid. When precipitation was complete, the calcium oxalate was filtered off with suction, and well washed. The excess of ammonium oxalate in the filtrate was determined by titration with standard permanganate at 60°C., in sulphuric acid solution. The calcium was also directly determined in the precipitate by dissolving in dilute nitric acid, and titrating with standard permanganate. The total chromate in the equilibrium solutions was found by adding an excess of potassium iodide and hydrochloric acid, and titrating the liberated iodine with standard sodium thiosulphate solution, adding starch solution towards the end to give a sharp end-point. The thiosulphate was standardised against A.R. potassium dichromate by the same method. From the results obtained for total chromate, and for calcium, the potassium chromate content of the solution was calculated. The addition of potassium chromate to saturated calcium chromate solution causes a marked increase in the solubility of the latter salt. At the triple point the solution contains 9.96 gm. $CaCrO_4$, and 3.43 gm. K_2CrO_4. On the other hand very little change in concentration of potassium chromate in the liquid phase results when calcium chromate is added to saturated potassium chromate solution. At the triple point the respective concentrations in the liquid phase are 1.12 gm. $CaCrO_4$, and 65.9 gm. K_2CrO_4. The double salt curve is cut by the line representing solutions containing calcium chromate and potassium chromate in equimolecular proportions, and hence $CaCrO_4 \cdot K_2CrO_4 \cdot 2H_2O$ is not decomposed by water. The limits of existence of the double salt at 30.0°C are defined by the triple points given above. The isotherm for the system $CaCrO_4 . K_2CrO_4 . H_2O$ at 30.0°C bears a striking similarity to that for the system $CaSO_4 . K_2SO_4 . H_2O$ at 0°C obtained by Caven and Rooney (J.Roy.Tech.Coll., 32, 1926).

Strontium Chromate with Potassium Chromate.

PREPARATION OF STRONTIUM CHROMATE.

$$\underset{533.3}{2SrCl_2 \cdot 6H_2O} + \underset{294.3}{K_2Cr_2O_7} \longrightarrow \underset{407.3}{2\ SrCrO_4}$$

53 gm. $SrCl_2 \cdot 6H_2O$ were dissolved in 200 cc. of water, and 30 gm. of A.R. $K_2Cr_2O_7$ were dissolved in 100 cc. of water. The solutions were boiled, and mixed. Dilute ammonia was slowly added until the colour changed from orange to more yellow. A golden yellow precipitate was obtained. 100 cc. of alcohol were added, and the mass of fine crystals filtered off. The product was then washed free of chloride with hot water. The $SrCrO_4$ was

pumped as dry as possible at the filter pump, and finally dried on a porous plate in the air oven at 140°C.

Analysis.

Found: 55.90% CrO_4 ; 42.34% Sr

Ratio $\frac{CrO_4}{Sr}$ = 1.320

Theory for $SrCrO_4$: 56.96% CrO_4 ; 43.01% Sr

Ratio $\frac{CrO_4}{Sr}$ = 1.324

For the analysis the sample was dissolved up in fairly strong hydrochloric acid, and the solution at once diluted to 250 cc. Then 25 cc. of this solution were diluted to 100 cc., and dilute ammonia added to change the colour to yellow. The liquid became slightly turbid. It was boiled, and treated with 5 cc. boiling 6N sulphuric acid. After adding 100 cc. of alcohol the solution was left overnight. The strontium sulphate was then filtered off, washed first of all with fifty per cent alcohol containing a small percentage of sulphuric acid, and finally with alcohol alone, until the wash was free from sulphate. The precipitate was then dried, ignited in a platinum crucible, and weighed as $SrSO_4$. To be quite sure that chromate did not appreciably interfere the estimation was repeated, after first boiling the solution with alcohol and hydrochloric acid in order to reduce to chromic salt. The result confirmed the foregoing one. As before, chromate was found iodometrically. The solubility of strontium chromate in water at 30.0°C was found to be 0.100 gm. $SrCrO_4$ per 100 gm. of water. Previous figures given for the solubility of strontium chromate were:

0.12 gm. $SrCrO_4$ per 100 gm. water at 15°C (Fresenius)

0.119gm. $SrCrO_4$ per 100 gm. water at 16°C (Meschtschersky)

When a little strontium chromate was stirred for several days at 30.0°C with saturated potassium chromate solution, no change in the concentration of potassium chromate in the liquid phase took place, and strontium could not be detected in that medium. On the other hand when potassium chromate was added to saturated strontium chromate solution, and stirred at 30.0°C for several days, the liquid phase was found to contain all the potassium chromate, and no strontium chromate. The yellow powder which separated was shown by the microscope, and by analysis, to be strontium chromate. Thus under these conditions (and in aqueous solution at room temperature) potassium chromate and strontium chromate do not yield a double salt. Gröger (Zeitsch. Anorg. Chem., 54, 185, 1907) prepared what he considered to be double salts of strontium and barium chromates with potassium chromate. The above observations show that these findings are in error. Gröger prepared the supposed double salts by mixing very strong solutions of the single salts at room temperature. The crystals which separated were said to be double salt, but must have been a mixture. Since calcium and potassium chromates yield a double salt it would be reasonable to expect that strontium and barium chromates might both do so also, but the sparing solubility of the latter salts must be remembered.

Magnesium and Potassium Chromates.

PREPARATION OF MAGNESIUM CHROMATE:

$$\underset{40.3}{MgO} + \underset{100.0}{CrO_3} \qquad \underset{140.3}{MgCrO_4}$$

45 gm. of A.R. magnesium oxide were gradually stirred into a solution of 100 gm. A.R. CrO_3 in 200 cc. of water. The solution was filtered through a thick pad of asbestos in order to remove the excess of magnesia, and the chocolate-coloured colloidal matter. (Here again the chromic acid was slightly reduced, and when it was neutralised with magnesia the opalescence due to chromic chromate resulted, as was found when preparing calcium chromate.) The solution when concentrated and allowed

to crystallise at room temperature gave yellow prisms, isomorphous with $MgSO_4.7H_2O$. Magnesium chromate has been fairly fully investigated by Kopp and by Mylius and Funk. The heptahydrate yields yellow transparent prisms, rhombic, and isomorphous with the sulphate $MgSO_4.7H_2O$, with which it forms mixed crystals. Its solubility is 72.3 gm. $MgCrO_4$ per 100 gm. of water at 18°C. The crystals lose water when exposed to the air and give $MgCrO_4.5H_2O$, which is also the salt that crystallises from solution above 30°C. On heating to 120°C it loses more water, and yields the dihydrate $MgCrO_4.2H_2O$, from which the remaining water is only expelled on decomposition.

A solution containing 50 gm. of magnesium chromate in about 100 cc. of water was mixed with one containing 50 gm. of potassium chromate in the same volume at 16°C. The solution was stirred for a time at 16°C., and the yellow crystals which separated were filtered off, and washed with a very little cold water. They were then left on a porous plate exposed to the atmosphere for some time. Further crops of crystals were obtained by allowing the mother liquor to evaporate slowly at room temperature.

-

Analysis.

Found: 59.1% CrO_4 ; 6.96% Mg

Theory for $K_2CrO_4.MgCrO_4.2H_2O$: 62.6% CrO_4 ; 6.56% Mg.

Later fractions of the crystals were also double salt.

Discussion of the Chromates.

Magnesium chromate and potassium chromate form the double salt $K_2CrO_4.MgCrO_4.2H_2O$. Calcium chromate forms the double salt $K_2CrO_4.CaCrO_4.2H_2O$ with potassium chromate. The isotherm for the latter system has been obtained, and is similar to that for the corresponding sulphates. That strontium and barium chromates do not form double salts with potassium chromate is perhaps to be explained by the very low solubility of these salts. It has already been pointed out that the chromates resemble the sulphates in many respects, especially in the isomorphism of their salts, and here it is found that this analogy extends to the double salts. The relations between anhydrous calcium chromate, and its hydrates have been carefully studied by Mylius and von Wrochem (Ber., 33, 3689, 1900), and again similarity to the sulphate is shown. The following modifications were studied - anhydrous salt, hemihydrate, monohydrate, monoclinic dihydrate, and rhombic dihydrate.

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THE SYSTEM $CaCrO_4$ - K_2CrO_4 - H_2O at 30.0°C

LIQUID PHASE		SOLID PHASE
G. $CaCrO_4$/100gm. H_2O	G. K_2CrO_4/100gm. H_2O	
2.027	—	$CaCrO_4$
4.483	1.551	"
(1) 7.691 (2) 7.734	(1) 2.634 (2) 2.777	" "
9.770	3.348	
9.956	3.426	$CaCrO_4$ and $CaCrO_4 \cdot K_2CrO_4 \cdot 2H_2O$
5.066	17.04	$CaCrO_4 \cdot K_2CrO_4 \cdot 2H_2O$
3.823	36.39	"
(1) 1.120 (2) 1.118	(1) 65.83 (2) 66.03	$CaCrO_4 \cdot K_2CrO_4 \cdot 2H_2O$ and K_2CrO_4
—	(1) 65.12) (2) 65.40) 65.5 (3) 65.89) (4) 65.46)	K_2CrO_4

THE DOUBLE SALTS OF CEROUS SULPHATE WITH THE SULPHATES OF THE ALKALI METALS.

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Analysis of Cerous Sulphate.

Two samples of cerous sulphate $Ce_2(SO_4)_3.8H_2O$ were supplied as pure. Each of these was very carefully analysed. About 4 gm. of the well-crystallised salt was dissolved in a little dilute hydrochloric acid, and the solution diluted to 250 cc. Sulphate was estimated by diluting 25 cc. of this solution to about 150 cc. boiling, and dropping in a slight excess of 3% barium chloride solution. The liquid was kept hot several hours and the precipitate filtered off, well washed, dried, ignited and weighed as $BaSO_4$. In another 25 cc. of solution cerium was estimated by the method preferred by Hillebrand and Lundell in their book on mineral analysis. To 25 cc. of the solution hydrochloric acid was added, sufficient to give about 75 cc. of liquid 0.5N with respect to HCl. The solution was boiled, and a hot concentrated solution of oxalic acid added in considerable excess. Cerous oxalate rapidly crystallised in beautiful glistening needles. The solution was left overnight, before filtering off the precipitate, and washing it with dilute oxalic acid solution. After drying, the cerous oxalate was ignited in platinum before a blast lamp to CeO_2 (which was yellow and powdery), and weighed. Many analyses were performed in order not only to test the purity of the salt, but also to check the analytical method. The results of some of these are given, and show the cerous sulphate to be satisfactory. (Garver and Brinton, J.A.C.S., 49, 943, 1927).

Found: % Ce (1) 39.36 ; (2) 39.15 ; (3) 39.30

% SO_4 (1) 39.82 ; (2) 39.68 ; (3) 39.79.

$$\text{Ratio } \frac{SO_4}{Ce} = 1.016$$

Theory for $Ce_2(SO_4)_3.8H_2O$: 39.32% Ce ; 40.43% SO_4

$$\text{Ratio } \frac{SO_4}{Ce} = 1.028$$

However, in analysing some of the double salts the ratio of the two single salts was found to be not just exactly stochiometric, and hence it was desirable to test the purity of the simple salts, and to check the analytical methods very carefully.

It was just possible that although the ratio of sulphate to cerium in the cerous sulphate had been found to be fairly near theoretical, yet the salt was impure and contained, say, rare earth sulphates in such proportions as to give the correct ratio of sulphate to cerium by the above methods of analysis. That this was not the case was very neatly shown by determining the cerium by a volumetric method which is specific for cerium, and showing that the result thus obtained was in excellent agreement with that by the oxalate method.

Volumetric Determination of Cerium.

Knorre's classical persulphate method has been re-investigated by Lindeman and Hafstad (Z.Anal.Chem., 70, 433, 1927). They found that when there was more than 4.9 gm. of sulphuric acid per 100 cc. of solution hydrogen peroxide was formed, and the results were high. On the other hand sulphuric acid concentrations below 2.7 gm. per 100 cc. caused the separation of basic ceric sulphate, and consequent low results. For the estimation they recommend that the cerous sulphate solution, containing 4 gm. of sulphuric acid and 5 gm. of magnesium sulphate per 100 cc. be boiled with 5 gm. of ammonium persulphate until effervescence ceases. After cooling an excess of standard ferrous sulphate solution is added, and the excess titrated with standard permanganate. The other rare earths and thorium do not interfere.

Willard and Young (J.A.C.S., 50, 1322, 1928) used a slightly different method of oxidising to the ceric state. 100-300 cc. of solution, containing 0.1 to 0.3 gm of cerium, 2.5-10 cc. of concentrated sulphuric acid, and ten drops of decinormal silver nitrate, were boiled for ten minutes with 1-5 gm. of solid ammonium persulphate.

Each of these methods was found to give good results in satisfactory agreement with those obtained by the cerous oxslate gravimetric method. Thus the cerous sulphate was pure. The permanganate was standardised against Mohr's salt, and against freshly dried A.R. sodium oxalate.

Found: 39.12% Ce.

The estimation of sulphate in solutions containing cerium was also investigated. It was found that the barium chloride solution had to be added very slowly from a burette to the boiling test solution in order to minimise contamination of the precipitated barium sulphate. In addition the barium sulphate was kept in the hot liquid for at least six hours to ensure complete precipitation, before it was filtered off. When these precautions were carefully observed the method gave fairly good results, which sometimes fluctuated to the extent of one per cent, but which were normally in better agreement. Previous separations of cerium as oxalate did not alter the results.

Sodium Sulphate with Cerous Sulphate.

A.R. sodium sulphate was used. When the solubility of cerous sulphate had been determined about a gram of sodium sulphate was added, and the solution stirred until equilibrium was attained. Microscopic observation showed the solid phase to contain crystals of cerous sulphate, and of double salt. At this triple point the liquid phase contained 8.48 gm. of $Ce_2(SO_4)_3$ per 100 gm. of H_2O, and so little sodium sulphate that it could not be estimated. Addition of a little more sodium sulphate caused the solid phase to be changed entirely to double salt, and the concentration of cerous sulphate to be greatly lowered in the liquid phase, for the presence of even very small quantities of sodium sulphate in that medium. The double salt curve extended right to the triple point, where the liquid phase contained no cerous sulphate, and 27.88 gm. of sodium sulphate per 100 gm. of water. There was just one double salt - $Ce_2(SO_4)_3.Na_2SO_4.2H_2O$ - formed by these salts at 25.0°C. At first after analysis of the liquid phase had shown that equilibrium had been established, the solid phase was rapidly separated by vacuum filtration, washed with a minimum of cold water, dried on a porous ~~plate~~, and analysed. Whilst the analytical results were sufficient to show that throughout the curve the one double salt $Ce_2(SO_4)_3.Na_2SO_4.2H_2O$ was crystallising, yet the figures were not as accurate as might be desired. This is readily explained when the difficulty of separating the solid phase from the mother liquor, without changing the composition of the former, is considered. Although the double salt is not decomposed by water (when brought to equilibrium in aqueous solution) yet washing with water may preferentially dissolve one of the single salts, especially when there is a big disparity in solubility, as in the case of cerous and sodium sulphates. Again, when the moist double salt is left on a porous plate in the air to dry it may not lose all its adventitious water, or the hydrate which initially crystallised from solution may not be stable under these conditions.

These difficulties were overcome by using the method of solutions and "rests" proposed by Schreinemakers (Z.physikal.Chem., 11, 76, 1893). The theory of this method was discussed in the introduction. When repeated analysis had shown that equilibrium had been established between double salt and solution the crystals were separated from most of the mother liquor as rapidly as

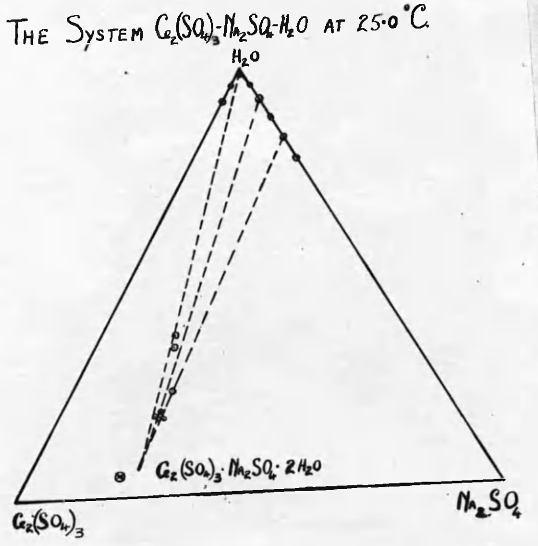
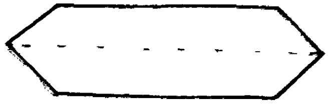

THE SYSTEM Ce$_2$(SO$_4$)$_3$-Na$_2$SO$_4$-H$_2$O AT 25·0°C.
H$_2$O
Ce$_2$(SO$_4$)$_3$·Na$_2$SO$_4$·2H$_2$O
Ce$_2$(SO$_4$)$_3$
Na$_2$SO$_4$

Figure 6.

possible. Two samples of the moist solid phase were at once transferred to stoppered weighing bottles, allowed to cool, and weighed. In some cases the solution was stirred for another day or two, and moist samples of the solid phase again analysed. These analyses of solutions and "rests" were performed for several points on the double salt curve. In plotting the results the point representing a certain composition of the liquid phase was always joined by a "tie line" to that representing the composition of the moist solid phase with which it was in equilibrium. When the results were plotted on a rectangular diagram (composition of liquid phase, and of moist solid phase being expressed in grams of each anhydrous salt per 100 gm. of water) the tie lines intersected at a point whose coordinates gave the composition of the double salt in grams of each anhydrous single salt per 100 gm. of water. The composition of the double salt was rather more neatly arrived at by plotting the results by the equilateral triangle method suggested by Roozeboom (Figure 6). Here the analytical results were in each case calculated as percentages of the whole. The method of plotting in the triangle was given in the introduction. The point of intersection of the tie lines was within the triangle, and lay close enough to the calculated values, to show that the double salt was $Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$.

In the equilibrium solutions and in the moist solid phases cerium was estimated by precipitating as cerous oxalate, igniting in platinum before the blast lamp, and weighing as CeO_2 as already fully described. The total sulphate was then found by the barium sulphate method, exercising the precautions previously noted as being necessary. The sodium sulphate was then calculated from the values found for cerium, and for total sulphate.

When the double salt was examined under the low power of the microscope the crystals presented, in plan, hexagons of the shape shown.



The double salt crystallised well, and most of the crystals were very well formed, and regular. On the other hand when cerous sulphate crystals were examined in their mother liquor they presented the appearance of long worn needles. Thus it was an easy matter to distinguish the two types of crystal. The solubility of the double salt in water was low, and was reduced beyond the detecting power of the methods of analysis by the presence of more than one gram of sodium sulphate per hundred grams of water in the liquid phase. The solubility of cerous sulphate octohydrate in water at 25.0°C was found to be 8.222 gm. of $Ce_2(SO_4)_3$ per 100 gm. of water - a value which agreed very well with the value 8.224 gm. $Ce_2(SO_4)_3$ per 100 gm. of water given by Wirth. For sodium sulphate decahydrate the value 27.61 gm. Na_2SO_4 per 100 gm. of water was found, whilst Berkeley recorded 27.67 gm. Na_2SO_4 per 100 gm. of water as the solubility of this salt in water at 24.90°C.

Potassium Sulphate with Cerous Sulphate.

A.R. potassium sulphate was twice recrystallised from distilled water. On analysis, after drying in the air oven, the salt gave 55.04% SO_4, theory for K_2SO_4 requiring 55.12% SO_4. The solubility of potassium sulphate in water at 25.0°C was found to be 12.04 gm. K_2SO_4 per 100 gm. of water. Berkeley gave 12.04 gm. K_2SO_4 per 100 gm. of water as the solubility at 25.0°C.

Potassium sulphate did not lower the concentration of cerous sulphate in the liquid phase quite as efficiently as did sodium sulphate, and the liquid phase contained 2 gm. of K_2SO_4 per 100 gm. of water, before

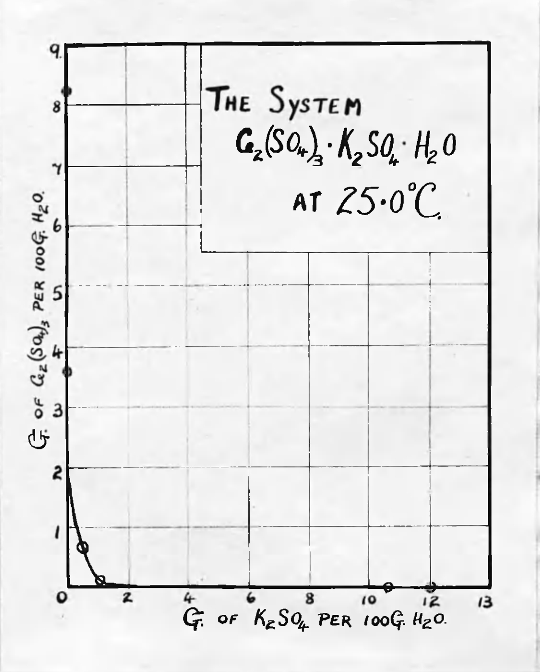

THE SYSTEM
$G_2(SO_4)_3 \cdot K_2SO_4 \cdot H_2O$
AT 25·0°C.
G. OF $G_2(SO_4)_3$ PER 100G. H_2O.
G. OF K_2SO_4 PER 100G. H_2O.
0
1
2
3
4
5
6
7
8
9
2
4
6
8
10
12
13

Figure 4.

the cerium escaped detection. In this case three double salts were found. These were:-

(1) $Ce_2(SO_4)_3.K_2SO_4.2H_2O$, which crystallised between the points where the liquid phase contained practically no potassium sulphate, and about 0.05 gm. K_2SO_4 per 100 gm of water.

(2) $Ce_2(SO_4)_3.3K_2SO_4.8H_2O$, which was the solid phase present when the liquid phase contained between 0.05 gm K_2SO_4 per 100 gm. of water, and about 0.5 gm. K_2SO_4 per 100 gm. of water.

(3) $Ce_2(SO_4)_3.5K_2SO_4$, which was the solid phase present when the concentration of potassium sulphate in the liquid phase exceeded 1 gm. of K_2SO_4 per 100 gm. of water.

The isotherm for this system at 25.0°C (Figure 7) does not show three double salt curves. This was because, even with the first double salt, the solubility was so low that the changes could not be seen. Nevertheless the system was investigated right up to the saturation point of potassium sulphate. The method of solutions and rests was not employed, because each double salt existed for only a limited range of concentrations in the liquid phase, which made it impossible to get tie lines at an angle sufficiently big to make the point of

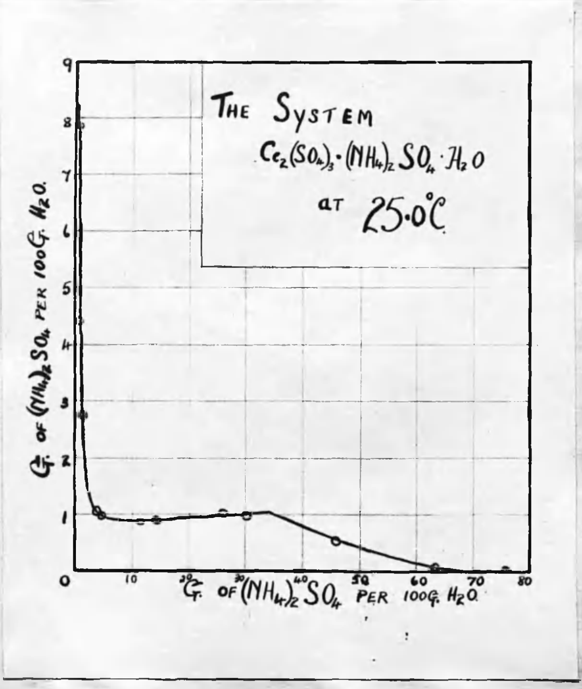

THE SYSTEM
$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot H_2O$
AT 25.0°C
G. OF $(NH_4)_2SO_4$ PER 100 G. H_2O.
G. OF $(NH_4)_2SO_4$ PER 100 G. H_2O.
0
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80

Figure 8.

intersection at all accurate. When the liquid phase had attained equilibrium with the solid phase recourse was therefore had to direct analysis of the solid phase. The crystals were filtered off from the liquid, washed with a very little cold water, dried in the air on a porous plate for about a month (shown by tests to be ample time), and analysed. By this method the existence of the above three double salts was shown, together with the approximate concentration ranges in the liquid phase for which they existed. The exact point of transfer from each double salt to its neighbour was not accurately found. When potassium sulphate was stirred with saturated cerous sulphate solution at 25.0°C, in quantity insufficient to change all the solid phase to double salt, no potassium sulphate was detected in the equilibrium liquid phase, and the concentration of cerous sulphate therein had gone up but a minute amount.

Ammonium Sulphate with Cerous Sulphate.

A.R. Ammonium sulphate was twice recrystallised from distilled water, dried on a porous plate in the air oven, and found to contain 72.72% SO_4. Theory for $(NH_4)_2SO_4$ requires 72.73% SO_4.

Ammonium sulphate was much less efficient at removing cerous sulphate from solution than either of the

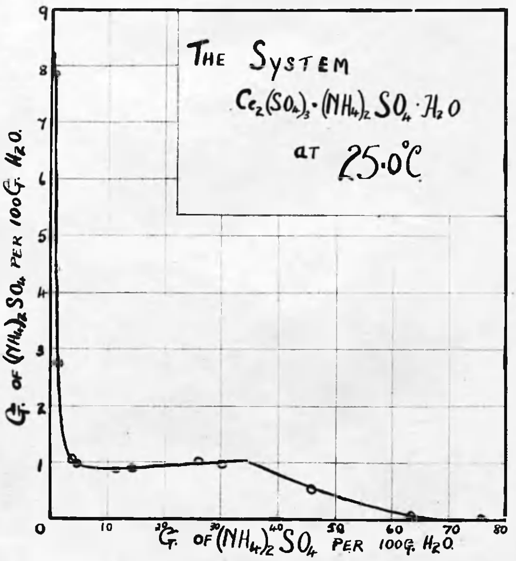

THE SYSTEM
$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot H_2O$
AT 25.0°C
G. OF $(NH_4)_2SO_4$ PER 100G. H_2O.
G. OF $(NH_4)_2SO_4$ PER 100G. H_2O.
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9

Figure 8.

other alkali sulphates had been. At the triple point, where the solid phase was composed of $Ce_2(SO_4)_3 \cdot 8H_2O$ and $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$, the liquid phase contained 7.884 gm. $Ce_2(SO_4)_3$ and 0.718 gm. $(NH_4)_2SO_4$ per 100 gm. of water.

When the concentration of ammonium sulphate had risen to 63 gm. per 100 gm. of water the liquid phase still contained 0.087 gm. of $Ce_2(SO_4)_3$ per 100 gm. of water. There were two double salts in this system:-

(1) $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$ - stable in solutions containing from 0.72 gm. to about 35 gm. of $(NH_4)_2SO_4$ per 100 gm. of water.

(2) $Ce_2(SO_4)_3 \cdot 5(NH_4)_2SO_4$ - formed in solutions containing more than 35 gm. of $(NH_4)_2SO_4$ per 100 gm. of water.

Here the double salts were rather more soluble in the alkali sulphate solution than in the previous cases examined, and the isotherm shows clearly (Figure 8) where the change from the one to the other occurs. However, at the triple point, where the solid phase is composed of $(NH_4)_2SO_4$ and $Ce_2(SO_4)_3 \cdot 5(NH_4)_2SO_4$, no cerium could be detected in the liquid phase, and the concentration of ammonium sulphate was the same as in its saturated aqueous solution.

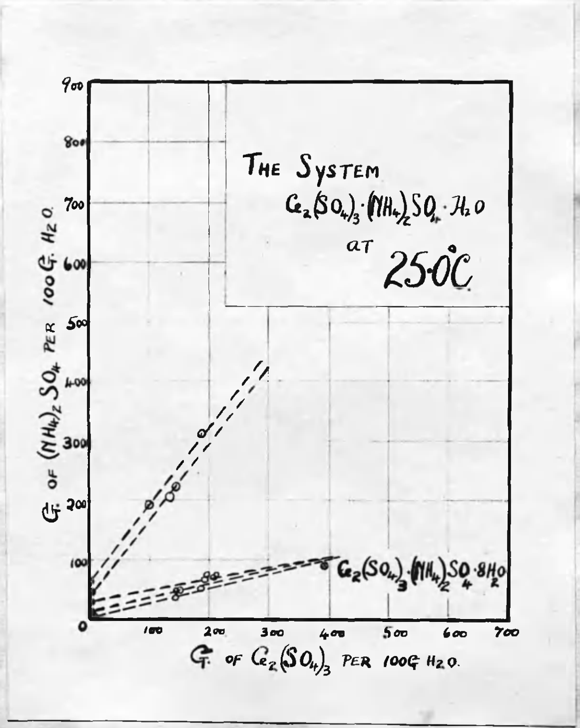

THE SYSTEM
$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot H_2O$
AT 25·0°C
$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$
G. OF $(NH_4)_2SO_4$ PER 100 G. H_2O
G. OF $Ce_2(SO_4)_3$ PER 100 G H_2O.
0
100
200
300
400
500
600
700
800
900

Figure 9.

Composition of the solid-phases was determined both by direct analysis after filtering off a sample from the equilibrium solution, and by the method of solutions and rests. For the direct analyses the double salt crystals were freed from mother liquor by washing with a little cold water, dried on a porous plate for about a month, and analysed. The results for the indirect determination of the solid phase were plotted on a rectangular diagram (Figure 9). The point of intersection of the lower tie lines shows that the double salt is here $Ce_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$. That the double salt formed at higher concentrations of ammonium sulphate is anhydrous, was shown by the parallelism of the other tie lines. On the Roozeboom triangular diagram (Figure 10) the composition of the two double salts is clearly shown by the intersection of the corresponding tie lines. That of the hydrated double salt within the triangle, whilst the anhydrous double salt is represented by a point on one side.

Discussion of Double Salts of Cerous Sulphate with Sulphates of Alkali Metals.

Barre (Compt.Rend., 151, 871, 1910) examined the lowering of the solubility of cerous sulphate in water by alkali sulphates. His results for sodium sulphate

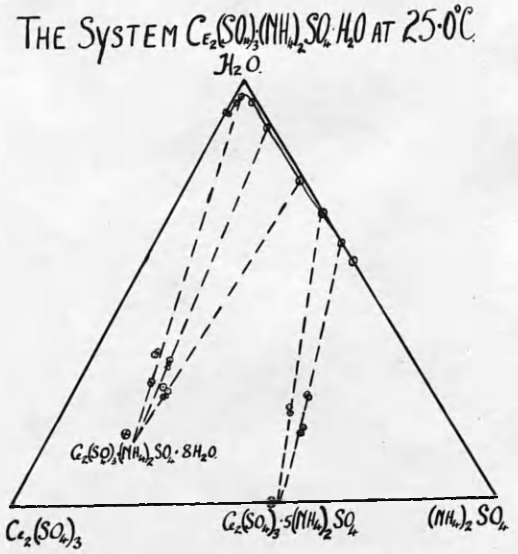

THE SYSTEM $Ce_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot H_2O$ AT 25·0°C.
H_2O.
$Ce_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot 8H_2O$.
$Ce_2(SO_4)_3$
$Ce_2(SO_4)_3\cdot 5(NH_4)_2SO_4$
$(NH_4)_2SO_4$

Figure 10.

apply to 19°C whilst those for potassium and ammonium sulphates are for 16°C. He left the subject in an empirical stage, without examining the phenomena in the light of the phase rule. His results, so far as they go, are in qualitative agreement with those recorded here. He gave a list of the double salts which had been found in these systems up to that time, but he himself gave no analytical figures confirming their existence. He did not state on which parts of the curves he obtained, the different double salts crystallised. He also found that the sodium and potassium double salts were very sparingly soluble in alkali sulphate solution, whilst the solubility of the ammonium ones in ammonium sulphate solution was greater. The same applied to the double lanthanum alkali sulphates. Up to the time of Barre's work only the following double salts were definitely known to be formed by cerous sulphate with sodium, potassium, and ammonium sulphates:

$Ce_2(SO_4)_3.Na_2SO_4.2H_2O$ (Jolin, Bull.Soc.Chim, 2, 21, 533, 1874)

$Ce_2(SO_4)_3.K_2SO_4.2H_2O$ (Czudnowicz, Jour.prakt.Chem., 1, 80, 31, 1860)

$Ce_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$ (Wyrouboff, Bull.Soc.Min., 14, 83, 1891; and Ann,Chim.Phys, 8, 9, 290, 1906).

Barre stated that he verified the existence of these, and added others to make the list exactly that which has been found in this work. Nevertheless it seemed desirable to reinvestigate the matter by phase rule methods, and to establish not only what double salts could be formed by these combinations, but under what conditions each was formed. The result of the present investigation has been to substantiate, and greatly extend, Barre's earlier work. Not only have all his double salts been shown to be capable of existence, but their conditions of formation at 25.0°C have been discovered by a full investigation of the isotherms, and analysis has proved beyond doubt the composition of each double salt.

Before this investigation was undertaken it was thought that existence of the simpler double salts, previously listed, had been fairly well established, but Barre's additional ones (especially the anhydrous ones containing five molecules of potassium or ammonium sulphate to one of cerous sulphate) seemed to require further, and fuller examination. Detailed investigation has confirmed the existence, not only of the simpler and better-known double salts, but also of Barre's more complicated ones, where the stochiometric ratios of the single salts in the double salt is less simple.

In qualitative analysis cerium is usually precipitated as hydroxide in Group IIIA. After several separations have been performed, a solution is obtained which may contain thorium and several rare earths. It is then customary to separate these further, by adding potassium sulphate. The double salts of lanthanum, cerium, zirconium, and thorium crystallise out, and leave the yttrium earths in solution. The present results show that, as far as cerium is concerned, either sodium or potassium sulphate may be used to give a sparingly soluble double salt, and that separation is virtually complete, even when the concentration of alkali sulphate in the liquid is but one or two grams per 100 gm. of water. If ammonium sulphate were used, however, the liquid would require to be almost saturated with the salt to ensure complete separation of cerium. There is little to choose between sodium and potassium sulphates for effecting the separation of cerium. Here it is shown that sodium sulphate is slightly the more effective, whereas Barre's results showed potassium sulphate to be just the more efficient. Sodium double salts are usually more soluble than the corresponding potassium ones, and they, than the ammonium ones. Here the results are reversed, and the fact that the sodium salt is slightly the less soluble accords with the gradation of solubility of these double salts.

Dihydrated sodium cerous sulphate is the only double salt formed at 25.0°C by sodium sulphate, and cerous sulphate. A similar double salt of potassium sulphate exists, together with $2Ce_2(SO_4)_3.3K_2SO_4.8H_2O$ and $Ce_2(SO_4)_3.5K_2SO_4$. All these double salts are very sparingly soluble. Ammonium sulphate, on the other hand, does not form a dihydrated double salt with cerous sulphate. It is interesting to note that in this case the double salt is more highly hydrated, $Ce_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$, and is considerably more soluble than the foregoing. The only other double salt formed by ammonium sulphate and cerous sulphate is $Ce_2(SO_4)_3.5(NH_4)_2SO_4$, which resembles the corresponding potassium one in being anhydrous, and having a low solubility.

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THE SYSTEM. $Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot H_2O$ at 25.0°C

	LIQUID PHASE		SOLID PHASE (moist).	
	G. $Ce_2(SO_4)_3$/100 G H_2O	G. Na_2SO_4/100 H_2O	G. $Ce_2(SO_4)_3$/100 H_2O	G. Na_2SO_4/100 H_2O
I.	8.222	-	$Ce_2(SO_4)_3 \cdot 8H_2O$	
II.	(1) 8.519 (2) 8.441 8.480	-	$Ce_2(SO_4)_3 \cdot 8H_2O$ and	$Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$
III.	(1) 4.256 (2) 4.307 4.286	-	Analysed after drying.	
IV.	0.1084	0.1820	(1) 136.1 (2) 122.8	(1) 46.29 (2) 40.66
V.	(1) 0.05075 (2) 0.04774 0.04925	(1) 0.5593 (2) 0.5446 0.5520	Analysed after drying.	
VI.	-	7.437	Analysed after drying.	
VII.	- -	(1) 7.771 (2) 7.848 7.820	(1) 300.69 (2) 305.6 (1) 323.0 (2) 331.5	(1) 101.4 (2) 106.3 (1) 105.7 (2) 113.4
VIII.	-	19.71	(1) 216.6 (2) 220.0	(1) 83.47 (2) 84.24
IX.	-	27.88	$Na_2SO_4 \cdot 10H_2O$ and $Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$	
X.	-	(1) 27.64 (2) 27.57 27.61	$Na_2SO_4 \cdot 10H_2O$	

THE SYSTEM. $Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot H_2O$

Analyses of Phases after drying at Room Temperature for about a month.

LIQUID PHASE		SOLID PHASE	
G. $Ce_2(SO_4)_3$/100 H_2O	G. Na_2SO_4/100 H_2O	% Ce	% SO_4
I. (1) 4.265) (2) 4.307) 4.286	—	Washed three times with little cold water (1) 36.88 (2) 36.67	(1) 50.66 (2) 50.47
II. (1) 0.05075) (2) 0.04774) 0.04925	(1) 0.5593) (2) 0.5446) 0.5520	One wash with cold water. (1) 36.32	(1) 49.36
III. —	7.437	One wash with cold water. (1) 36.33 (2) 36.67	(1) 52.99 (2) 53.95

Theory $Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$

$$\% \text{ Ce} = \frac{28026}{746.55} = 37.55$$

$$\% \text{ SO}_4 = \frac{38426}{746.55} = 51.47$$

Ce – Na RESULTS FOR TRIANGULATION

	100 gm. LIQUID PHASE			100 gm. MOIST SOLID PHASE		
	G. $Ce_2(SO_4)_3$	G. Na_2SO_4	G. H_2O	G. $Ce_2(SO_4)_3$	G. Na_2SO_4	G. H_2O
I.	7.598	—	92.40	$Ce_2(SO_4)_3 \cdot 8H_2O$		
II.	(1) 7.850 (2) 7.775	— —	(1) 92.15 (2) 92.22	$Ce_2(SO_4)_3 \cdot 8H_2O$ & $Ce_2(SO_4)_3 \cdot NaSO_4 \cdot 2H_2O$		
III.	(1) 0.1081	(1) 0.1814	(1) 99.71	(1) 48.20 (2) 46.59	(1) 16.39 (2) 15.44	(1) 35.41 (2) 37.97
IV.	— —	(1) 7.228 (2) 7.278	(1) 92.77 (2) 92.72	(1) 59.88 (2) 59.70 (1) 61.10 (2) 60.84	(1) 20.20 (2) 20.76 (1) 19.99 (2) 20.81	(1) 19.92 (2) 19.54 (1) 18.91 (2) 18.35
V.	—	16.47	83.53	(1) 54.14 (2) 54.42	(1) 20.86 (2) 20.84	(1) 25.00 (2) 24.74
VI.	—	21.80	78.20	$Ce_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$ & $Na_2SO_4 \cdot 10H_2O$		
VII.	—	21.63	78.37	$Na_2SO_4 \cdot 10H_2O$		

THE SYSTEM. $Ce_2(SO_4)_3 \cdot K_2SO_4 \cdot H_2O$ at 25°C

Analysis of Solid Phases after drying at Room Temperature
for about a month.

LIQUID PHASE		SOLID PHASE	
G. $Ce_2(SO_4)_3$/100g. H_2O	G. K_2SO_4/100g. H_2O	% Ce	% SO_4
I. 8.222	—	$Ce_2(SO_4)_3 \cdot 8H_2O$	
II. (1) 8.245 (2) 8.332 (3) 8.305	(1) — (2) — (3) —	$Ce_2(SO_4)_3 \cdot 8H_2O$ & $Ce_2(SO_4)_3 \cdot K_2SO_4 \cdot 2H_2O$	
III. (1) 3.594 (2) 3.599	(1) — (2) 0.021	One wash with cold water. (1) 35.82 (2) 35.72	(1) 47.73) $Ce_2(SO_4)_3$ 72.6 (2) 47.78) K_2SO_4 20.7
IV. 0.5702	0.4652	One wash (1) 31.17 (2) 31.14	with little cold water (1) 45.55) $Ce_2(SO_4)_3$ 63.2 (2) 46.99) K_2SO_4 27.9
V. 0.1171	1.134	No (1) 23.34 (2) 23.32	washing. (1) 53.40) $Ce_2(SO_4)_3$ 47.3 (2) 53.07) K_2SO_4 53.6
VI. —	10.66	One wash (1) 20.26 (2) 20.28	with little cold water (1) 48.66) Ce (SO) 41.1 (2) 49.96) K SO 53.3
VII. —	11.92		and K_2SO_4
VIII. —	12.04	K_2SO_4	

Theory for $Ce_2(SO_4)_3 \cdot K_2SO_4 \cdot 2H_2O$: $\%Ce = \frac{28026}{778.75} = 35.99$; $\%SO_4 = \frac{38426}{778.75} = 49.34$;

$\%Ce_2(SO_4)_3 = \frac{56860}{778.8} = 73.02$; $\%K_2SO_4 = \frac{1742}{778.8} = 22.37$

Theory $2Ce_2(SO_4)_3 \cdot 3K_2SO \cdot 8H_2O$:

$\%Ce = \frac{56120}{1803.8} = 31.12$

$\%SO_4 = \frac{86400}{1803.8} = 47.92.$

$\%Ce_2(SO_4)_3 = \frac{1137.2}{1803.8} = 63.84$

$\%K_2SO_4 = \frac{52260}{1803.8} = 28.97$

Theory $Ce_2(SO_4)_3 \cdot 5K_2SO_4$:

$\%Ce = \frac{28060}{1440.1} = 19.47$

$\%SO_4 = \frac{76848}{1440.1} = 53.37$

$\%Ce_2(SO_4)_3 = \frac{56860}{1439.6} = 39.47$

$\%K_2SO_4 = \frac{87100}{1439.6} = 60.50$

THE SYSTEM. $Ce_2(SO_4)_3 \cdot (NH_4)_2 \cdot SO_4 \cdot H_2O$ at 25.0°C.

	LIQUID PHASE		SOLID PHASE	
	G. $Ce_2(SO_4)_3$/100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O	G. $Ce_2(SO_4)_3$/100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O
I.	8.222	—	$Ce_2(SO_4)_3 \cdot 8H_2O$	
II.	7.884	0.7183	$Ce_2(SO_4)_3 \cdot 8H_2O$ & $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$	
III.	4.411	0.8616	Analysed after drying	
IV	(1) 2.755 (2) 2.701	(1) 1.275 (2) 1.302	(1) 142.4 (2) 141.4 (3) 186.2 (4) 187.8	(1) 35.85 (2) 36.49 (3) 51.06 (4) 51.01
V.	1.055	3.892	Analysed after drying.	
VI.	0.9872	4.626	Analysed after drying.	
VII.	(1) 0.8740 (2) 0.8810	(1) 11.58 (2) 11.62	(1) 144.0 (2) 147.7 (3) 151.0	(1) 49.06 (2) 49.87 (3) 49.94
VIII.	0.9001	14.20	Analysed after drying.	
IX.	1.021	26.02	Analysed after drying.	
X.	(1) 0.9576 (2) 1.017 (3) 1.076	(1) 30.07 (2) 30.48 (3) 30.17	(1) 193.8 (2) 197.8 (3) 213.6 (4) 209.0	(1) 66.00 (2) 71.81 (3) 75.06 (4) 76.79
XI.	0.5488	45.98	(1) 137.0 (2) 146.4	(1) 207.1 (2) 221.3

(continued on next page)

LIQUID PHASE		SOLID PHASE	
G. $Ce_2(SO_4)_3$100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O	G. $Ce_2(SO_4)_3$/100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O
XII. (1) 0.08758 (2) 0.08732	(1) 63.51 (2) 63.16	(1) 99.22 (2) 99.61 (3) 188.2 (4) 174.4	(1) 191.0 (2) 194.4 (3) 315.9 (4) 298.2
XIII. —	76.03	$(NH_4)_2SO_4$ and $Ce_2(SO_4)_3 \cdot 5(NH_4)_2SO_4$	
XIV. —	75.98	$(NH_4)_2SO_4$	

THE SYSTEM. $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot H_2O$ at 25.0°C

Analysis of solid phases after drying at room temperature for about a month.

	LIQUID PHASE		SOLID PHASE	
	G. $Ce_2(SO_4)_3$/100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O	% Ce	% SO_4
I.	8.222	—	$Ce_2(SO_4)_3 \cdot 8H_2O$	
II.	7.884	0.7183	$Ce_2(SO_4)_3 \cdot 8H_2O$ & $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$	
III.	4.411	0.8616	Washed three times with cold water (1) 33.18 (2) 33.11 % $Ce_2(SO_4)_3$ = 67.08 ;	(1) 44.67 (2) 44.53 % $(NH_4)_2SO_4$ = 15.26
IV.	1.055	3.892	Washed once with little cold water (1) 33.08 (2) 33.07 % $Ce_2(SO_4)_3$ = 66.94 ;	(1) 44.89 (2) 44.85 % $(NH_4)_2SO_4$ = 15.68
V.	0.9872	4.626	Unwashed. (1) 32.94 (2) 33.00 % $Ce_2(SO_4)_3$ = 66.73 ;	(1) 46.92 (2) 47.42 % $(NH_4)_2SO_4$ = 18.63
VI.	0.9001	14.20	One wash with cold water (1) 33.80 (2) 33.62 % $Ce_2(SO_4)_3$ = 68.21 ;	(1) 47.66 (2) 48.83 % $(NH_4)_2SO_4$ = 18.65
VII.	1.021	26.02	One wash with cold water (1) 33.05 (2) 33.08 % $Ce_2(SO_4)_3$ = 66.92 ;	(1) 46.81 (2) 48.48 % $(NH_4)_2SO_4$ = 18.35

LIQUID PHASE		SOLID PHASE	
G. $Ce_2(SO_4)_3$/100 H_2O	G. $(NH_4)_2SO_4$/100 H_2O	% Ce	% SO
VIII. —	76.03	$(NH_4)_2SO_4$ & $Ce_2(SO_4)_3 \cdot 5(NH_4)_2SO_4$	
IX. —	75.98	$(NH_4)_2SO_4$	

Theory $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$:

$$\% \ Ce = \frac{28026}{844.73} = 33.18$$

$$\% \ SO_3 = \frac{38426}{844.73} = 45.48$$

$$\% \ Ce_2(SO_4)_3 = \frac{56846}{844.73} = 67.30$$

$$\% \ (NH_4)_2SO_4 = \frac{13214}{844.73} = 15.64$$

$Ce - NH_4$ RESULTS FOR TRIANGULATION.

100 gm. LIQUID PHASE			100 gm. SOLID PHASE		
G. $Ce_2(SO_4)_3$	G. $(NH_4)_2SO_4$	G. H_2O	G. $Ce_2(SO_4)_3$	G. $(NH_4)_2SO_4$	G. H_2O
1. 7.598	—	92.40	$Ce_2(SO_4)_3 8H_2O$		
II. 7.262	0.6615	92.08	$Ce_2(SO_4)_3 \cdot 8H_2O$ & $Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8H_2O$		
III. 4.190	0.8183	94.99	—	—	—
IV. (1) 2.648 (2) 2.596	(1) 1.225 (2) 1.252	(1) 96.13 (2) 96.15	(1) 51.19 (2) 50.88 (3) 55.21 (4) 55.42	(1) 12.88 (2) 13.13 (3) 15.14 (4) 15.06	(1) 35.93 (2) 35.99 (3) 29.65 (4) 29.52
V 1.006	3.709	95.29	—	—	—
VI 0.9348	4.380	94.69	—	—	—
VII. (1) 0.7771 (2) 0.7830	(1) 10.30 (2) 10.33	(1) 88.92 (2) 88.89	(1) 49.14 (2) 49.63 (3) 50.18	(1) 16.74 (2) 16.76 (3) 16.59	(1) 34,12 (2) 33.61 (3) 33.23
VIII. 0.7820	12.34	86.88	—	—	—
IX. 0.8032	20.49	78.71	—	—	—
X. (1) 0.7308 (2) 0.7738 (3) 0.8206	(1) 22.96 (2) 23.18 (3) 22.99	(1) 76.31 (2) 76.05 (3) 76.19	(1) 53.87 (2) 53.51 (3) 54.96 (4) 54.18	(1) 18.34 (2) 19.43 (3) 19.31 (4) 19.90	(1) 27.79 (2) 27.06 (3) 25.73 (4) 25.92

100 gm. LIQUID PHASE			100 gm. SOLID PHASE		
G. $Ce_2(SO_4)_3$	G. $(NH_4)_2SO_4$	G. H_2O	G. $Ce_2(SO_4)_3$	G. $(NH_4)_2SO_4$	G. H_2O
XI. 0.3745	31.39	.. 68.24	(1) 30.80 (2) 31.31	(1) 46.56 (2) 47.31	(1) 22.64 (2) 21.38
XII.(1) 0.05353 (2) 0.053	(1) 38.82 (2) 38.72	(1) 61.13 (2) 61.33	(1) 25.43 (2) 25.28 (3) 31.16 (4) 30.45	(1) 48.94 (2) 49.34 (3) 52.29 (4) 52.08	(1) 25.63 (2) 25.38 (3) 16.55 (4) 17.47
—	43.19	56.81	$(NH_4)_2SO_4$ and $Ce_2(SO_4)_3 \cdot 5(NH_4)_2SO_4$		
—	43.17	56.83		$(NH_4)_2SO_4$	

THE DOUBLE SALTS OF HYDRAZINE MONOSULPHATE WITH THE SULPHATES OF BI, TER, AND QUADRI-VALENT METALS.

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Preparation of Hydrazine Monosulphate.

Ordinary hydrazine sulphate is the disulphate $N_2H_4.H_2SO_4$. It is not very soluble in water - 3.302 gm of $N_2H_6SO_4$ per 100 gm. of saturated aqueous solution at 25°C. The monosulphate is very soluble in water, and crystallises with one molecule of water of crystallisation $2N_2H_4.H_2SO_4.H_2O$, or $(N_2H_5)_2SO_4.H_2O$. The transition point between the anhydrous salt, and the monohydrate is 47.3°C. Sommer and Weise (Zeit.Anorg.Chem., 94, 51, 1916, and Zeit. Anorg.Chem., 86, 85, 1914) called the monosulphate dihydrazonium sulphate, and they prepared it by stirring a hot solution of the ordinary sulphate with barium carbonate, the reaction being -

$$2N_2H_6SO_4 + BaCO_3 \rightarrow (N_2H_5)_2SO_4 + BaSO_4 + H_2O + CO_2$$

The solution became alkaline, and was made faintly acid with sulphuric acid, and filtered. The filtrate was evaporated, and cooled in ice. A crystalline powder of the monohydrate separated. On recrystallisation from water the salt formed large, transparent, doubly-refracting, tabular crystals. A quantity of the monosulphate was prepared by this method, but it was found better to prepare the main bulk of hydrazine monosulphate for use in this investigation from hydrazine monohydrate solution. 250 gm. of 50% hydrazine hydrate solution were neutralised with 125 gm. 98% sulphuric acid, the acid finally being added very slowly until the solution was just acid to litmus.

$$2(N_2H_4.H_2O) + H_2SO_4 \rightarrow (N_2H_5)SO_4.H_2O + H_2O$$

100,13 98.08 180.19

2 parts 50% : 1 part 98%

The solution was evaporated down on the water bath to a fairly thick syrup. The liquid was cooled in ice, and gave a good yield of well-crystallised hydrazine monosulphate. The crystals were filtered off with suction, and left on a porous plate in the air to dry for a week, before samples were analysed. In spite of the rather high solubility of the salt the crystals showed no sign of deliquescing when exposed to the air, and the analyses showed that the monohydrate was quite stable in the air.

Determination of Hydrazine.

According to Peterson (Zeit.Anorg.Chem. 5, 1, 1894) when hydrazine is oxidised by permanganate in the presence of a 6-12% solution of sulphuric acid the reaction which occurs may be represented by the equation:

$$17N_2H_4 + 13O = 13H_2O + 14NH_3 + 10N_2$$

He stated that for the direct titration the solution containing the hydrazine must be at a temperature of 60-70°C.,and the end of the reaction must be taken at that point at which the pink colour, which is some time in completely fading, becomes darker on the addition of more permanganate. This method was thoroughly tested, and found to be rather unsatisfactory. The end point was difficult to judge, and the method gave results, which were sometimes as much as 4-5% out. It was discovered that cupric sulphate was an excellent catalyst for the oxidation of hydrazine by permanganate in sulphuric acid solution. When 0.1 gm. of cupric sulphate was added to the solution to be titrated the reaction went in the cold, and the results were much more consistent.

However, a much superior method of analysis was found to be that given in "Volumetric Iodate Methods" by G.S. Jamieson. The method, which was first proposed by Andrews (J.Amer.Chem.Soc., 25, 756, 1903) for the titration of a number of reducing substances such as free iodine, iodides, arsenites, and antimonites, in a very satisfactory manner, depends upon the formation of iodine monochloride, and the disappearance of the iodine colour imparted to an immiscible solvent such as chloroform or carbon tetrachloride. The titration gives very sharp, consistent, and accurate results. Since all of the iodine which remains during the latter part of the titration is collected in the small volume of immiscible solvent, the accuracy of the end reaction is extraordinary. When a titration has actually been completed there is no return of iodine colour even after standing for a day. It is necessary to have at least twelve per cent of hydrochloric acid present in the titrated solution, otherwise hydrolysis of the iodine monochloride with the formation of iodine is likely to occur. Iodate titrations can be made in the presence of filter paper, alcohol, formaldehyde, acetic and other saturated organic acids, as well as many other kinds of organic matter. The method has the further advantage that the potassium iodate is exceedingly stable, and Jamieson states that he kept a solution for ten years, and could not detect any change in concentration thereafter. To test the method for estimating hydrazine a standard solution of A.R. hydrazine disulphate was prepared. 25 cc. portions of this solution were placed in 250-300 cc. bottles with ground glass stoppers. To each bottle was added 30 cc. of concentrated hydrochloric acid, and 6 cc. of chloroform. Then the standard potassium iodate was gradually run in from a burette, with shaking. The chloroform became cherry red, and then after a certain quantity of iodate had been added the colour began to diminish again, for each addition of iodate. Meanwhile gas was evolved when the hydrazine reacted with the potassium iodate. A very sharp end point was obtained, when the addition of the smallest drop of standard iodate caused the chloroform to change from pink to water white. The method gave very consistent and accurate results.

$$N_2H_4.H_2SO_4 + KIO_3 + 2HCl = N_2 + ICl + KCl + H_2SO_4 + 3H_2O$$

The potassium iodate used was the A.R. salt, specially prepared for use as a volumetric standard. The salt was dried in the air oven at 120°C for two and a half hours, and cooled in a desiccator. Then 7.4381 gm. were dissolved in water, and the solution diluted to two litres. 1 cc of this solution was equivalent to 0.1409 gm. of $(N_2H_5)_2SO_4$.

The following additional references are of interest,

A Volumetric Method for the Determination of Hydrazine,
(Jamieson, Am.Journ.Sci., 33, 352, 1912)

The Volumetric Analysis of Hydrazine by the Iodic Acid, Bromine, and Hypochlorous Acid Methods,
(Bray and Cuy, J.Amer.Chem.Soc., 46, 858, 1924).

The Volumetric Analyses of Hydrazine by the Iodine, Bromate, Iodate, and Permanganate Methods.
(Kolthoff, J.Amer.Chem.Soc., 46, 2009, 1924).

The various preparations of hydrazine monosulphate were analysed, after the crystals had been on a porous plate in the air for periods up to twelve days. The hydrazine was determined by Jamieson's volumetric method, whilst sulphate was readily determined as barium sulphate. The crystals prepared from A.R. hydrazine disulphate and barium carbonate contained 50.66% SO_4 and 34.34% N_2H_4, Ratio $\frac{SO_4}{N_2H_4} = 1.475$. The specimen prepared from 50% hydrazine monohydrate analysed 52.15% SO_4 and 34.94% N_2H_4, Ratio $\frac{SO_4}{N_2H_4} = 1.493$. Theory for $(N_2H_5)_2SO_4.H_2O$ requires 53.31% SO_4 and 35.56% N_2H_4, Ratio $\frac{SO_4}{N_2H_4} = 1.499$.

Copper Hydrazine Double Sulphate.

The solubility of cupric sulphate pentahydrate in water at 25.0°C was estimated as 22.72 gm. $CuSO_4$ per 100 gm. of water. The copper was determined iodometrically as before described. When quantities as small as 0.05gm of hydrazine monosulphate were added to a small quantity of saturated cupric sulphate solution at 25.0°C a bluish-green powder of double salt separated almost at once. After stirring for some time the presence of hydrazine in the liquid phase could just be detected. The double salt was also sparingly soluble in strong hydrazine monosulphate solution. In general it was found that the double sulphates of hydrazine monosulphate with the sulphates of bivalent metals had a low solubility, and hence the isotherms for these systems were not determined. Instead the double salts were prepared, and analysed, and their solubility in water at 25.0°C found.

The copper double salt was prepared by stirring together at room temperature fairly dilute solutions containing equimolecular quantities of the single salt. The meal of bluish-green crystals was filtered off, washed with a little cold water, and dried on a porour plate in the air for several weeks. For analysis 3.334 gm. were boiled with 20 cc. of concentrated hydrochloric acid, and the solution diluted to 250 cc. In one portion sulphate was estimated as barium sulphate, and in another copper was found by the method of Rivot. An excess of sulphur dioxide was bubbled into the solution, and then ammonium thiocyanate solution was added drop by drop with stirring. The first greenish precipitate of cupric and cuprous thiocyanates became almost white when a slight excess of thiocyanate had been added. After standing overnight the precipitate was filtered off, washed with cold water, then 20% alcohol, dried at 110-120°C, and weighed as $Cu_2(CNS)_2$. Hydrazine was not determined because the iodate method was not very accurate in the presence of copper, and the copper and sulphate estimations were sufficient to characterise the double salt.

Found: 19.65%Cu ; 57.27% SO_4

Theory for $Cu(N_2H_5)_2(SO_4)_2$ requires 19.75% Cu, and 59.69% SO_4. The double salt was so slightly soluble in water at 25.0°C that the copper in the saturated solution was determined colorimetrically as ferrocyanide. The solubility in water at 25.0°C was found to be 0.114 gm. of $Cu(N_2H_5)_2(SO_4)_2$ per 100 gm. of saturated solution.

Zinc Hydrazine Double Sulphate.

A solution of 7 gm. A.R. $ZnSO_4.7H_2O$ in 25 cc. of water was mixed with 4 gm. of $(N_2H_5)_2SO_4.H_2O$ dissolved in 20 cc. of water. The solutions gave an immediate precipitate. After some time the crystals were filtered off, throughly washed with cold water, and dried for several weeks on a porous plate in the air. The hydrazine in the product was readily found by the iodate method, and two different specimens gave 19.91% and 19.85% N_2H_4, whilst theory for $Zn(N_2H_5)_2(SO_4)_2$ requires 19.81% N_2H_4. The solubility in water at 25.0°C was estimated by iodate titration to be 0.675 gm. $Zn(N_2H_5)_2(SO_4)_2$ per 100 gm. of saturated solution.

Manganese Hydrazine Double Sulphate.

A solution of 18 gm. A.R. manganous sulphate in

90 cc. of water was stirred at room temperature with 30 cc. of a solution containing 10.5 gm. of $(N_2H_5)_2SO_4.H_2O$. Crystals appeared after about an hour. After filtration and washing with cold water they were left for several weeks on a porous plate in the air.

Analysis by the iodate method showed the crystals to contain 20.39% N_2H_4, the theoretical for $Mn(N_2H_5)_2(SO_4)_2$ being 20.46% N_2H_4. The saturated aqueous solution at 25.0°C contained per 100 gm., 1.77 gm. of $Mn(N_2H_5)_2(SO_4)_2$.

Cobalt Hydrazine Double Sulphate.

A solution of 12 gm. $(N_2H_5)_2SO_4.H_2O$ in 60 cc. of water was gradually stirred, at room temperature, into one containing 21 gm. A.R. $CoSO_4.7H_2O$ in 120 cc. of water. The pink-coloured double salt crystallised almost at once. The solubility in water at 25.0°C was found to be 0.441 gm. of $Co(N_2H_5)_2(SO_4)_2$ per 100 gm. of saturated solution.

Nickel Hydrazine Double Sulphate.

9 gm, of A.R. $NiSO_4.7H_2O$ were dissolved in 90 cc. of water at room temperature, and a solution containing 12 gm. of $(N_2H_5)_2SO_4.H_2O$ in 30 cc. of water was added. Crystals began to separate after a few hours. The salt was well washed with cold water, and dried in the air

on a porous plate. It was found that 0.391 gm. of $Ni(N_2H_5)_2(SO_4)_2$ were present in 100 gm. of saturated aqueous solution at 25.0°C.

In addition to the above it was found that a solution of hydrazine monosulphate gave crystalline precipitates, presumably of double salts, with ferrous, cadmium, and magnesium sulphates.

Hydrazine Monosulphate with Aluminium Sulphate.

The A.R. Aluminium sulphate crystals supplied were analysed, the aluminium being precipitated with ammonia as before described, and the sulphate being determined as barium sulphate.

Found: 9.147% Al; 45.91% SO_4. Ratio $\frac{SO_4}{Al} = 5.020$.

Theory for $Al_2(SO_4)_3.18H_2O$: 8.093% Al, 43.24% SO_4

Ratio $\frac{SO_4}{Al} = 5.343$. The salt was obviously impure, and this was traced to the presence of basic salt, and alkali metal alum. The crystals were purified as follows: 300 gm. were stirred with distilled water, insufficient to dissolve all, for several hours, and the solution filtered. Crystallisation of the solution yielded a product which was still not quite pure enough. The salt was dissolved up again, and recrystallised from water containing alcohol, and a little sulphuric acid. The crystals were filtered off, and freed from alcohol. After being recrystallised from water the aluminium sulphate was sufficiently pure. Some of the crystals were pressed on filter paper, and analysed.

Found: 39.36% SO_4; 7.394% Al. Ratio $\frac{SO_4}{Al} = 5.323$

Theory for $Al_2(SO_4)_2.18H_2O$: 43.24% SO_4; 8.093% Al.

Ratio $\frac{SO_4}{Al} = 5.343$.

The solubility of aluminium sulphate in water at 25.0°C was found to be 38.45 gm. $Al_2(SO_4)_3$ per 100 gm. of water. The results of Kremann and Huttinger (See Seidell - "Solubility") were plotted, and the value 38.3 gm. $Al_2(SO_4)_3$ per 100 gm. of water read off. When a solution containing a mixture of $Al_2(SO_4)_3.18H_2O$ and hydrazine double salt as solid phase was stirred at 25.0°C until it reached equilibrium, the liquid phase was found to contain 38.77 gm. $Al_2(SO_4)_3$, and 4.71 gm. $(N_2H_5)_2SO_4$ per 100 gm. of water. Double salt formed the solid phase between this point, and the triple point where the concentrations of $Al_2(SO_4)_3$ and $(N_2H_5)_2SO_4$ per 100 gm. of water were 12.30 gm. and 189.2 gm. respectively. Hydrazine monosulphate was found to have a solubility of 186.3 gm. $(N_2H_5)_2SO_4$ per 100 gm. of water in water at 25.0°C., the solid phase being $(N_2H_5)_2SO_4.H_2O$. The solid phase present on the double salt part of the curve was

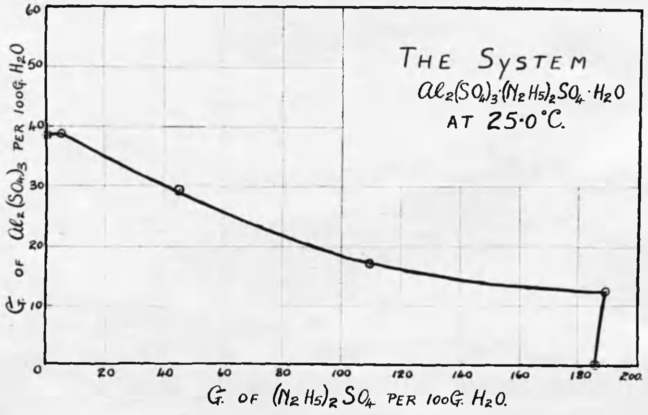

THE SYSTEM
$Al_2(SO_4)_3 \cdot (N_2H_5)_2SO_4 \cdot H_2O$
AT 25·0°C.
G. OF $Al_2(SO_4)_3$ PER 100G. H_2O
G. OF $(N_2H_5)_2SO_4$ PER 100G. H_2O.
0
10
20
30
40
50
60
20
40
60
80
100
120
140
160
180
200.

Figure 11.

examined under the low power of the microscope. The crystals were at once seen to differ from those of aluminium sulphate, and of hydrazine monosulphate. They were mostly rather worn, probably with the constant agitation to which the solution was subjected, but many seemed octohedral. To settle the point solutions of aluminium sulphate, and hydrazine sulphate were mixed, and set aside to crystallise. This time many fine octohedral crystals were found amongst those which separated. This left little doubt that the double salt was an alum, although this point was not proved conclusively by analysis. In the equilibrium solutions aluminium and hydrazine were both estimated, the former as alumina, and the latter by the iodate method (Figure 11).

Hydrazine Monosulphate with Thorium Sulphate.

Thorium sulphate was supplied as pure. When the thorium was precipitated as iodate, and subsequently decomposed by ammonia, the percentage of thorium was found to be 40.82%. Sulphate analysis showed the salt to contain 33.81% SO_4. Theory for $Th(SO_4)_2.8H_2O$ requires 40.86% Th, and 33.81% SO_4.

In the equilibrium solutions hydrazine was estimated by the iodate method, after test analyses had shown that thorium did not interfere. The best, and most convenient, method of determining the concentration of thorium sulphate was found to be precipitating the thorium as oxalate. Hydrazine monosulphate did not interfere. The solution was diluted to 250 cc. and 2-3 cc. of strong hydrochloric acid added. The solution was boiled, and 30-40 cc. strong boiling oxalic acid solution gradually stirred into it. The dense sandy crystals of thorium oxalate were left in contact with the liquid overnight, before filtering off, and washing with oxalic acid solution. After drying, the precipitate was ignited in platinum before the blast lamp, and weighed as ThO_2.

The solubility of $Th(SO_4)_2.8H_2O$ at 25.0°C was found to be 1.846 gm. $Th(SO_4)_2$ per 100 gm. of water, a value which agreed very well with the 1.85 gm. $Th(SO_4)_2$ per 100 gm. of water given by Roozeboom, but not so well with 1.722 gm. $Th(SO_4)_2$ per 100 gm. of water, given by Barre. The result given by Barre is in error. When small quantities of hydrazine monosulphate were stirred with saturated thorium sulphate solution at 25.0°C the solid phase remained $Th(SO_4)_2.8H_2O$, the hydrazine monosulphate all dissolved, and the concentration of thorium in the equilibrium liquid phase rose steadily with each addition of the hydrazine salt. The maximum was reached at the triple point, where the ~~solid~~ solid phase was a mixture of

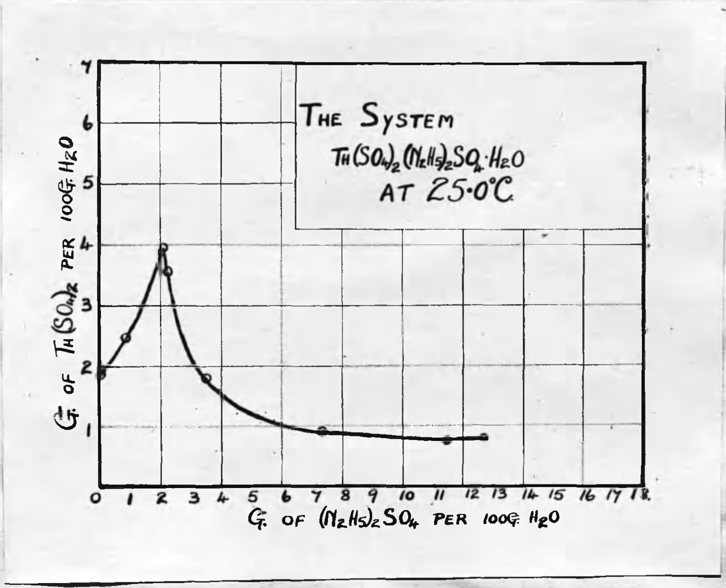
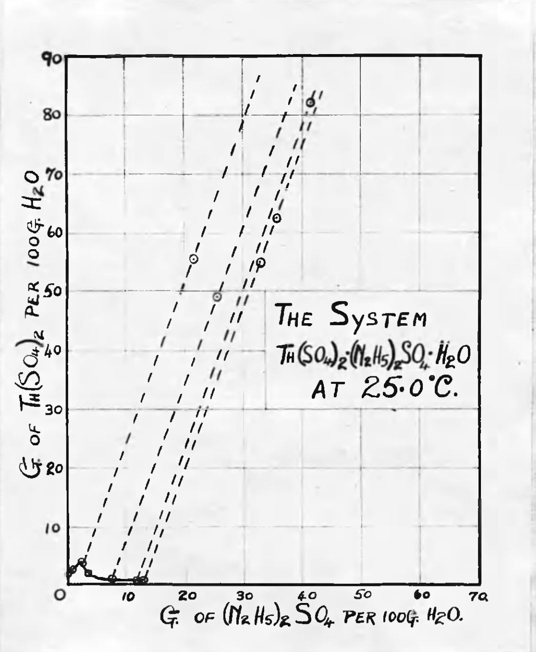

THE SYSTEM
$Th(SO_4)_2 \cdot (N_2H_5)_2SO_4 \cdot H_2O$
AT 25·0°C
G. OF $Th(SO_4)_2$ PER 100G. H_2O
1
2
3
4
5
6
7
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
G. OF $(N_2H_5)_2SO_4$ PER 100G. H_2O

Figure 12.

$Th(SO_4)_2$ with $Th(N_2H_5)_2(SO_4)_3$, and where the liquid phase contained 3.945 gm. $Th(SO_4)_2$ and 2.122 gm. $(N_2H_5)_2SO_4$ per 100 gm. of water. Thereafter came the double salt curve, and as the concentration of hydrazine monosulphate in the liquid phase rose, so did that of thorium sulphate fall. A point was reached at which the concentration of thorium sulphate had fallen to such a low value that the estimation of thorium became difficult. Big quantities of solution had to be taken in order to get weighable precipitates of thorium oxalate, and since the solution contained much hydrazine monosulphate each estimation involved the expenditure of a considerable quantity of that salt. Hence it was found practicable to follow the double salt curve only to the point where the equilibrium liquid phase contained 0.80 gm. of $Th(SO_4)_2$ and 12.66 gm. of $(N_2H_5)_2SO_4$ per 100 gm. of water. The double salt crystals differed very markedly from the "warty" irregular masses of $Th(SO_4)_2.8H_2O$. The double salt crystallised very well in the form of long needles. When stirred up with liquid the crystals had a "silky" appearance, and on being allowed to settle in the mother liquor they formed a "felt-like" mass. The isotherm for 25.0°C., plotted on rectangular coordinates, is shown (Figure 12).

The composition of the solid phases was found in-



90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
G. of Th(SO₄)₂ per 100G. H₂O
G. of (N₂H₅)₂SO₄ per 100G. H₂O.
The System
Th(SO₄)₂·(N₂H₅)₂SO₄·H₂O
at 25.0°C.

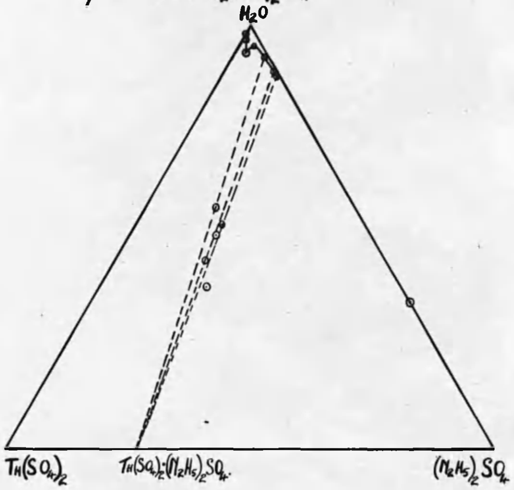
Figure 13.

directly. On the rectangular diagram (Figure 13) the parallel tie lines show that the solid phase, throughout the length of the double salt curve examined, is anhydrous. On the Roozeboom Triangular Diagram (Figure 14) the tie lines meet on one side of the triangle, again showing the double salt to be anhydrous, and the point shows the double salt to be $Th(SO_4)_2.(N_2H_5)_2SO_4$.

Discussion of Double Salts of Hydrazine Monosulphate.

According to Sommer and Weise (Zeit.Anorg.Chem., 94, 51, 1916, and ibid., 86, 85, 1914) hydrazine disulphate $N_2H_6.SO_4$ does not yield double salts with other metallic sulphates under ordinary conditions. They stated, however, that they obtained a definite double salt by adding hydrazine sulphate to a large excess of hot concentrated ammonium sulphate solution. This is the only known double salt, $N_2H_6SO_4.(NH_4)_2SO_4$, of hydrazine disulphate, and its existence has not since been confirmed.

Curtius and Schrader (Journ.Prakt.Chem, (2), 50, 311, 1894), however, succeeded in preparing several double sulphates from the more soluble hydrazine monosulphate $(N_2H_5)_2SO_4$. The double salts were found to be mostly but slightly soluble in water, and to be anhydrous. Sommer and Weise obtained no double salts with sodium,



THE SYSTEM $Th(SO_4)_2 : (N_2H_5)_2SO_4 : H_2O$ AT 25·0°C.

Figure 14.

potassium, and ammonium sulphates, but double salts were easily obtained from lithium, calcium, magnesium, and several sulphates of bivalent metals, with hydrazine monosulphate. Hydrazine monosulphate may be considered as a substituted ammonium sulphate $(NH_3.H)_2SO_4$, $(NH_3.NH_2)_2SO_4$ or $(N_2H_5)_2SO_4$.

The sulphates of the following bivalent metals, Cu, Zn, Mn, Co, Ni, yielded double salts with hydrazine monosulphate. All of the double salts were anhydrous, and sparingly soluble in water. The double salts were analysed, and their solubility in water at 25.0°C was found. The order of increasing solubility is Cu, Ni, Co, Zn, Mn. In addition ferrous, cadmium, and magnesium sulphates gave crystalline precipitates with hydrazine monosulphate, which were in all probability double salts. Thus hydrazine monosulphate resembles ammonium sulphate at least in regard to the case of crystallisation, and number of double salts which it forms with bivalent metals. However, the double salts formed by hydrazine monosulphate contain less water of crystallisation and are less soluble in water, than those formed by ammonium sulphate.

The only tervalent metal which was considered was alluminium. Here the composition of the double salt was not definitely settled, but the isotherm at 25.0°C for the system $Al_2(SO_4)_3.(N_2H_5)_2SO_4.H_2O$ showed, quite definitely, that a double salt was formed, and the appearance of the solid phase under the microscope suggested an alum. This is, of course, what might be expected from analogy with ammonium sulphate.

The literature contains no reference to double salts of hydrazine monosulphate with the sulphates of quadrivalent metals. Hence it was of interest to make a search for this new type of double salt, and if successful, to carry out as complete an investigation as possible. Thorium sulphate is well known to form many double salts, not only with the sulphates of univalent metals, but also with that of manganese, Caven (J.C.S., 354, 2418, 1932). A start was therefore made with thorium sulphate and hydrazine monosulphate. It was soon shown that a double salt was formed. The thorium sulphate part of the isotherm was typical (cf. the manganese thorium system investigated by Caven, loc.cit.) in that the concentration of thorium sulphate in the liquid phase at 25.0°C rose more than two-fold, before separation of double salt commenced. The system was investigated to the point where the concentration of thorium sulphate in the liquid phase was reduced to 0.80 gm. of $Th(SO_4)_2$ per 100 gm. of water, and here the needles of double salt which separated were clearly shown to be $Th(SO_4)_2.(N_2H_5)_2SO_4$ or $Th(N_2H_5)_2.(SO_4)_3$. It is to be noted that we have here again an anhydrous double salt. In this case we cannot talk of the solubility of the double salt, because the isotherm at 25.0°C shows that the double salt is decomposed by water.

Thus hydrazine monosulphate forms definite, well defined, double salts with the sulphates of bi, ter, and quadrivalent metals. The general characteristics of these double salts are that they contain little water of crystallisation, many being anhydrous, and that they are only sparingly soluble in water. The latter statement applies especially to those of the bivalent metals.

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DOUBLE SALTS OF HYDRAZINE MONOSULPHATE.

Formula of Double Salt	Solubility in water at 25.0°C. Expressed as gm. of anhydrous double salt per 100 gm. of saturated solution.
$Cu(N_2H_5)_2(SO_4)_2$	0.114
$Zn(N_2H_5)_2(SO_4)_2$	0.674
$Mn(N_2H_5)_2(SO_4)_2$	1.76
$Co(N_2H_5)_2(SO_4)_2$	0.441
$Ni(N_2H_5)_2(SO_4)_2$	0.391

THE SYSTEM. $Al_2(SO_4)_3 \cdot (N_2H_5)_2SO_4 \cdot H_2O$ at 25.0°C

LIQUID PHASE		SOLID PHASE
G. $Al_2(SO_4)_3$/100g H_2O	G. $(N_2H_5)_2SO_4$/100g H_2O	
38.4	-	$Al_2(SO_4)_3 \cdot 18H_2O$
38.77	4.710	$Al_2(SO_4)_3 \cdot 18H_2O$ and Double Salt
29.47	45.14	Double Salt
16.91	109.4	Double Salt
12.30	189.2	$(N_2H_5)_2SO_4 \cdot H_2O$ and Double Salt
-	186.3	$(N_2H_5)_2SO_4 \cdot H_2O$

THE SYSTEM. $Th\ (SO_4)_2 \cdot (N_2H_5)_2SO_4 \cdot H_2O$ at 25.0°C.

LIQUID PHASE		SOLID PHASE	
G. $Th(SO_4)_2$/100g H_2O	G. $(N_2H_5)_2SO_4$/100g H_2O	G. $Th(SO_4)_2$/100g H_2O	G. $(N_2H_5)_2$/100g H_2O
(1) 1.844) mean (2) 1.847) 1.846	-	$Th(SO_4)_2 \cdot 8H_2O$	
(1) 2.486) mean (2) 2.465) 2.476	(1) 0.8557 }0.8562 (2) 0.8567 }	$Th(SO_4)_2 \cdot 8H_2O$	
(1) 3.895) 3.886 (2) 3.876)	(1) 2.109)2.101 (2) 2.093)	$Th(So_4)_2 \cdot 8H_2O$	
(1) 3.945) 3.945 (2) 3.945)	(1) 2.120) 2.122 (2) 2.124)	$Th(SO_4)_2 \cdot 8H_2O$ + $Th(SO_4)_2 \cdot (N_2H_5)_2SO_4$	
3.561	2.236	55.30	21.46
1.797	3.485	Double Salt	
(1) 0.9908)0.924 (2) 0.8569)	(1) 7.418) 7.38 (2) 7.340)	49.06	25.34
(1) 0.8155)0.789 (2) 0.7625)	(1) 11.52) 11.46 (2) 11.39)	81.94	41.12
(1) 0.8125) (2) 0.8039)0.800 (3) 0.7856)	(1) 12.70) (2) 12.65)12.66 (3) 12.66)	(1) 62.65 (2) 101.8 (3) 55.04	(1) 35.24 (2) 56.89 (3) 32.48
-	(1) 183.4 (2) 183.4 Specially crystallised (3) 186.3	$(N_2H_5)_2SO_4 \cdot H_2O$	

RESULTS FOR TRIANGULAR DIAGRAM.

100gm. Solution			100gm. Solid Phase		
G. Th(SO_4)$_2$	G.(N_2H_5)$_2SO_4$	G.H_2O	G. Th(SO_4)$_2$	G.(N_2H_5)$_2SO_4$	G.H_2O
1.811	-	98.19	-	-	-
(1) 3.720 (2) 3.720	(1) 2.001 (2) 2.004	(1) 94.28 (2) 94.28	-	-	-
3.366	2.113	94.52	31.28	12.14	56.58
(1) 0.9143 (2) 0.792	(1) 6.842 (2) 6.784	(1) 92.24 (2) 92.42	28.13	14.53	57.34
(1) 0.7266 (2) 0.6908	(1) 10.25 (2) 10.15	(1) 89.02 (2) 89.16	36.73	18.44	44.83
(1) 0.7156 (2) 0.7086 (3) 0.6925	(1) 11.19 (2) 11.15 (3) 11.16	(1) 88.09 (2) 88.14 (3) 88.15	(1) 31.66 (2) 39.36 (3) 29.35	(1) 17.81 (2) 21.99 (3) 17.32	(1) 50.53 (2) 38.65 (3) 53.33
-	65.07	34.93	-	-	-