In submitting the following thesis I wish to record my deep sense of gratitude to Professor R.M. Caven, my Director and Supervisor, for the help and advice he has at all times gladly given.

I also wish to put on record my sincerest thanks to Professor F.J. Wilson for his helpful criticism and advice.

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Contents

Page

The Systems:

Systems of the type:

The System :

Appendices

GENERAL INTRODUCTION.

That the molecules of two different salts were capable of entering into combination to produce a third salt differing considerably in physical properties from either of the constituent salts was known at an early date in the study of chemistry. Just to whom the distinction of drawing attention to this point can be given is somewhat doubtful; but we know that Berzelius (Schweiggers Journal, 1812, 6, 119) used the case of the formation of potassium alum to illustrate his Dualistic Theory of Chemical Compounds, and that Thomas Graham employed many of the salts of the alkali metal - bivalent metal sulphate type in his extensive investigations on the properties of water of crystallisation, (Phil. Mag. 1837, et seq).

While Graham was undoubtedly interested in the formation of double salts, as indicated by notes on their preparation and their peculiarities, it needed the advance of chemical theory by Arrhenius, Van't Hoff, and others of the more modern school, to supply suggestions regarding the properties of solutions of single electrolytes before any ideas regarding the formation of double salts could be evolved.

Despite the tremendous increase in the study of chemistry along the avenues of physical chemistry, our knowledge of solution is still very imperfect, and modern work in all but the case of dilute solution, tends to make the problem very much more complicated than was at first believed.

It has been common practice to talk of two different types of salts formed by the uniting of two single salts, and the two types have been described as double and complex salts respectively.

According to this view Double Salts are those which in the solid state have physical properties differing from either of their component salts, but in solution give chemical reactions for each of the ions of the individual salts present.

Complex salts are those which not only differ in physical properties from their component salts in the solid state, but in solution give chemical tests for only two ions one of which, the complex ion, is completely different from any of the components' ions being composed of an ion of one salt combined with a complete molecule of the other substance present.

We may illustrate this by reference to the following examples:-

In solution

1. $K_2SO_4.FeSO_4 \rightleftharpoons 2K^{\cdot} + Fe^{''} + 2\ SO_4^{''}$ - potassium ferrous sulphate.
2. $K_4[Fe(CN)_6] \rightleftharpoons 4K^{\cdot} + [Fe(CN)_6]^{''''}$ - potassium ferrocyanide
3. $Cu(NH_3)_4.SO_4 \rightleftharpoons [Cu(NH_3)_4] + SO_4^{''}$ cuprammonium sulphate.

1. represents a typical double salt while 2. and 3. are complex salts with a complex anion and a complex cation respectively.

It is suggested here, however, that the distinction between double and complex salts is one of degree rather than of kind; in all probability the two types tend to merge into one another instead of exhibiting a sharp distinction as the two names would suggest.

That complex salts show differences of stability among themselves is well known, and results have been obtained which indicate that the tendency to dissociate into simple ions is present even in the case of potassium ferrocyanide. Thus Morgan (Zeit. physikal. Chem. 1895, 17, 513) has shown that normal potassium ferrocyanide solution contains 0·000533 gm. equivalents of cyanide ion. Potassium ferrocyanide is one of the most stable of complex cyanides and one from which it is possible to obtain hydroferrocyanic acid by treatment with hydrochloric acid. Incidentally all degrees of stability of complex cyanides exist, from potassium ferrocyanide down to potassium nickelocyanide which is decomposed by water and weak acids; and the well known separation of copper from cadmium depends on the relative instability of the cadmium complex which is split up by such a weak acid as hydrogen sulphide.

Just as one finds it possible to arrange the complex cyanides roughly, according to the stability of the complex cyanide ions present, so it is conceivable that the double sulphates of the alkali-heavy metal type might also be arranged in some such order; and from a systematic study of the effect of alteration of alkali and of heavy metal some idea of the forces establishing the union might be obtained.

With the exception of the work of Koppel (Zeit. physikal. Chem. 1905, 52, 385) on systems of sodium sulphates, heavy metal sulphate water; and a recent paper by Benrath on thallium double salts (Zeit. anorgan. Chem. 1926, 151, 21) no such survey has been carried out, although many scattered results exist in the literature.

The present thesis records therefore, some of the results obtained in carrying out suggestions made by Professor Caven who initiated this work.

Investigations on the formation and decomposition of double salts may be of two types - firstly those that deal with saturated solutions, i.e., are susceptible of treatment by the Phase Rule, and demonstrate the possibility of double salt formation from two given components; and secondly those that deal with dilute solutions, and are concerned with the existence, and persistence on dilution, of double salts in solution.

The work to be described in this thesis contains results of both types, but no effort has been made to divide the material rigorously along these lines, since it has been found more convenient to treat the subject matter in the order in which experiments were performed, and under the general type of system examined, rather than in two general divisions as mentioned above.

THEORETICAL.

Abnormal reactions of electrolytes in solution were supposed by Ostwald (Zeit. physikal. Chem. 1889, 3, 596) to be due to the formation of complex ions. Chief among the abnormal reactions now recognised are the cases in which well-known pairs of salts with a common ion do not conform to the requirements of the law of Solubility Product [worked out by Nernst (Zeit. physikal. Chem. 1889, 4, 372), and verified by Noyes (Zeit. physikal. Chem. 1896, 6, 241), and later by Noyes and his co-workers for many systems containing slightly soluble salts], which is of fundamental importance in all work connected with ions.

When a binary electrolyte is dissolved in water the molecule dissociates in solution according to the scheme

$$AB \rightleftharpoons A^{\bullet} + B' \quad . \quad . \quad . \quad . \qquad (1)$$

where AB is the undissociated molecule; $A^{\bullet}$ is the positive ion and B' the negative. If the salt is added until saturation results we have another equilibrium

$$AB \text{ (solid)} \rightleftharpoons AB \text{ (undissociated in solution)}..(2)$$

At a given temperature and pressure, therefore, the concentration of AB molecules in solution is fixed if the solution is in equilibrium with solid salt. Indeed the interpretation Nernst puts on matters is that the constant total solubility of a solid salt at a given temperature in water is due to the constant concentration of non-ionised salt in the solution.

Applying the Mass Law we have

$$[A^{\cdot}][B'] = k[AB]$$

(where the square brackets have the usual significance, viz., "concentration of").
which expresses the condition of equilibrium between ionised and non-ionised salt in solution.

The product $[A^{\cdot}][B']$ is called the Solubility Product.

The Solubility Product Law may be stated thus:-
"A salt is in equilibrium with a solution containing its ions when the product of the concentrations of these ions in the solution has a certain value. This value is called the Solubility Product. It depends upon temperature."

It is evident that $[A^{\cdot}]$ and $[B']$ may vary reciprocally within any limits.

Introduction into the solution of another salt with a common ion, say B', the volume being constant, will disturb the concentration of the common ion, and if complex ion formation does not take place, some of AB will be precipitated, because the concentration of $A^{\cdot}$ must be diminished in the inverse ratio of that in which the concentration of B' has been increased.

Van't Hoff in "Vorlesungen über Bildung und Spaltung von Doppelsalzen", Leipzig 1897, examined the theoretical conditions regulating the formation and decomposition of double salts from the standpoint of the Law of Solubility Product. He admitted that the treatment was not quite adequate since he had left questions of chemical affinity out of account. "Yet", he succinctly says, "such affinity exists, otherwise double salts would not be formed."

"Heat-toning" he claimed was an indication of chemical affinity and whilst the relative solubilities of the single salts might influence the proportions in which they should be present to form double salt, temperature decided whether a double salt could be formed or not since an exothermic double salt could not be formed above the transition point nor an endothermic salt below it. [See Appendix II].

Van't Hoff seems to have neglected the possibility of the existence of double salts in solution altogether, and his argument depends on the assumption of complete dissociation for saturated solutions; while it is not suggested that he did not appreciate the fact that the salts were far from completely dissociated his calculations have little practical value if it can be shown that any other ion intervenes in the course of the complete dissociation of the double salt.

The experimental verification of the law of Solubility Product as carried out by Noyes depended on the employment of sparingly soluble salts and on the assumption of complete dissociation both in the case of the slightly soluble component and in that of the added soluble salt. Further work, however, has indicated, that even in cases where double or complex salt could not be obtained as a stable solid phase exact agreement between theory and practice cannot be obtained even with the most elaborate methods of modern times. The practical difficulties are very great and the theoretical treatment is extremely involved. Despite these facts some of the abnormalities observed in systems of soluble salts are of such magnitude as to support the view of Ostwald (loc. cit.) and it is necessary to assume the formation in solution of aggregates other than those that would result from the normal association of ions to form undissociated molecules.

The assumption of a complex ion (so easily proved by chemical methods in the case of "complex salts") can be extended to double salts whose abnormalities differ only in that they are less marked than those of complex salts.

Let us consider first the formation of a complex salt such as potassium ferrocyanide. As generally prepared, potassium cyanide is added to a neutral solution of a salt of the heavy metal, the first result is the formation of heavy metal cyanide which then redissolves in excess of potassium cyanide to give the complex salt. For the formation of double salt one usually dissolves equi-molecular quantities of each component and evaporates the resulting solution till crystallisation sets in. There is, however, no reason, except that of expediency, why one should not start with a saturated solution of the heavy metal sulphate in contact with excess of the salt and add the alkali sulphate - then the two cases would be strictly analogous.

Using the two cases of potassium ferrocyanide and potassium ferrous sulphate we have

$$1.\quad \left(\begin{array}{l} FeSO_4 + 2\ KCN \rightleftharpoons Fe(CN)_2 + K_2SO_4 \\ \\ Fe(CN)_2 + 4\ KCN \rightleftharpoons K_4[Fe(CN)_6] \end{array} \right.$$

$$2.\quad FeSO_4 + K_2SO_4 \rightleftharpoons FeSO_4.K_2SO_4.$$

But we have a saturated solution of the very slightly soluble ferrous cyanide and a saturated solution of ferrous sulphate. Each solid phase is in equilibrium with the molecules in solution and these in turn are in equilibrium with ions.

$$\begin{tikzcd} Fe(CN)_2\ (solution) \arrow[r, rightleftharpoons] \arrow[d, shift left] & Fe^{\cdot\cdot} + 2CN' \\ Fe(CN)_2\ (solid) \arrow[u, shift left] & \end{tikzcd} \qquad \Bigg\| \qquad \begin{tikzcd} FeSO_4\ (solution) \arrow[r, rightleftharpoons] \arrow[d, shift left] & Fe^{\cdot\cdot} + SO_4^{''} \\ FeSO_4\ (solid) \arrow[u, shift left] & \end{tikzcd}$$

Any influence such as introduction of a common ion that will cause formation of molecules in solution will cause precipitation from solution. Similarly any influence that will prevent molecules from acting as such or will effectively remove them will cause increased solution of the solid phase.

Such an influence would be complex formation.

It has been shown (Caven and Mitchell, J.C.S. 1924, <u>125</u>, 1428) that addition of either potassium sulphate or ammonium sulphate to saturated copper sulphate solutions caused increased solubility of the copper sulphate. This instance is not an isolated example, as other similar results have been recorded by Britton and Allmand (J.C.S. 1921, 119, 1463) for the system potassium sulphate, glucinum sulphate, water; Britton (J.C.S. 1922, 121, 982) for the system aluminium sulphate, ammonium sulphate, water; Lipscombe and Hulett (J. Phys. Chem. 1916, 20, 75) for the systems cadmium chloride, potassium chloride, water; and zinc chloride, potassium chloride, water; Schreinemakers (Z. physikal. Chem. 1910, 71, 110) for ferrous sulphate, ammonium sulphate, water; - to mention only a few cases.

In view of the ideas adopted above, the increased solubility of copper sulphate means the adoption of the formula $K_2(Cu(SO_4)_2)$ for copper potassium sulphate which might therefore be called potassium cupri-sulphate, and the retention of this demands proof of the existence of the complex ion $(Cu(SO_4)_2)''$.

As far as copper is concerned the existence of this complex ion has not been definitely proved although a great deal of electrochemical evidence has been brought to bear on the subject -

Thus E. Klein (Wied. Ann. 1886, 27, 151) from an examination of the electrical conductivities of this and similar double salt solutions demonstrated in the case of concentrated solutions a departure from the mean of the sum of the conductivities of equimolecular solutions on mixing the components, while with dilute solutions the equivalent conductivity became practically the mean of the conductivities of the components. The same observer also showed by means of conductivity experiments that the double salt in solution was dissociated by diluting or by raising the temperature.

MacGregor and Archibald (Trans. Nov. Scot. Inst. Sci. 1897, 307) determined the conductivity of copper potassium sulphate at 18°C. and calculated, according to a method due to MacGregor (Trans. Nov. Scot. Inst. Sci., 1895, 101), the conductivity assuming non-formation of double salt. They concluded that the difference between observed and calculated values of the conductivity was such as would be accounted for by the presence of double salt in solution.

MacGregor and McKay (Trans. Nov. Scot. Inst. Sci. 1897, 348) examined in the same way magnesium potassium sulphate at 18°C. and concluded that in strong solutions at least the salts are partly united.

Jones and Caldwell (Am. Chem. Jour. 1901, 25, 349) showed that the double sulphates of ammonium with cadmium, copper, magnesium, ferrous iron, and nickel, and the double sulphate of potassium and nickel remain partly undissociated in concentrated solution and even in dilute solution are not entirely broken down into their constituents.

E. Rieger (Z. Elektrochem. 1901, 7, 863; 871) showed that in the case of copper potassium sulphate the electrolytic transference and the conductivity (less than the sum of the constituents) indicated the presence in solution of complex ions.

W. Pfanhauser (Z. Elektrochem. 1901, 7, 698) studied the conductivity and the electrical transference of nickel ammonium sulphate and showed that the conductivity of the double salt solution was less than the sum of constituents' conductivities in the more concentrated solutions. This was confirmed by the transference experiments which showed that the double salt existed in the saturated solutions at 18°C. mainly in the form of the ions $NH_4^{\bullet}$ and $[Ni(SO_4)_2]''$.

Application of the principles of the Phase Rule and observations of conductivity and electrolytic transference in the cases of solutions of salts that are known to form double salts can at best be regarded in the light of qualitative evidence. The results indicate whether or not double salt can be formed and provide evidence of the possibility of continued existence in solution.

Is it possible to foretell double salt formation ? Can we measure the tendency to form double salts ? The answer to these questions involves a discussion regarding the measurement of chemical affinity which it is not proposed to give here - indeed it is doubtful if any method of measuring affinity by ordinary methods, e.g., E.M.F. determinations, could be taken to apply to the residual affinity which comes into play where two compounds, in whose respective formations energy has already been expended, form molecular compounds. Not until we have very complete information, which is lacking at present, on the total free energies of formation of all the ions in any system, and can then estimate the energy that has actually been expended, shall we be able to deal with residual affinity in a quantitative manner.

Van't Hoff in 1883 came to the conclusion that "the only true measure of chemical affinity between substances which manifests itself by chemical reaction when the substances are brought into contact is given by the maximum external work at constant temperature and at constant, or practically constant, volume which is done by the system in passing from the initial state to the final state."

There are two methods of measuring external work:

(1) vapour pressure determinations:

(2) electro-motive force measurements - the second interests us more.

The study of the e.m.f's. of cells and the establishment of the connection existing between metals and solutions of their ions, or between metals and solutions of ions of another metal, has led to the establishment of a series of the elements in order of their electro-potentials - which can be interpreted as the order of the tendency of the elements to form ions. If hydrogen is taken as reference with zero potential we have:

Li > K > Ba > Na > Sr > Ca > Mg > Al > Zn > Cd > Ni > Pb > Fe(ic) > H > Cu > Ag.

From an examination of this series taken in conjunction with chemical experience it is possible to put forward the hypothesis that the position of each element relative to hydrogen is the determining factor in compound formation.

Kendall and his co-workers (J.A.C.S. 1916, 1917, 1921, etc., etc.) have examined this most thoroughly and have extended the generalisation to include compound formation between elements (the ordinary basic idea of chemistry contained in earlier observations of union between "metals" and "non-metals"); compound formation between molecules of solute and solvent; complex formation (molecular compounds); "ionisation" (dissociation), and order of solubility. Doubtless in such a sweeping generalisation a number of exceptions occur but in the main the contentions of these observers are

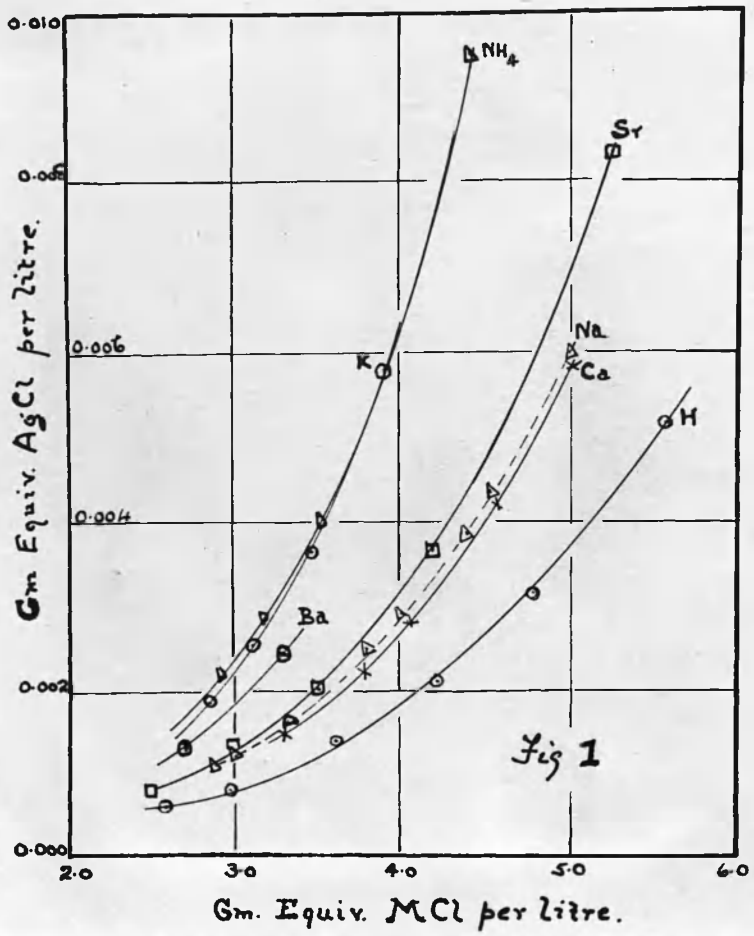

0·010
0·008
0·006
0·004
0·002
0·000
2·0
3·0
4·0
5·0
6·0
Gm Equiv. AgCl per litre.
Gm. Equiv. MCl per litre.
NH4
Sr
K
Na
Ca
H
Ba

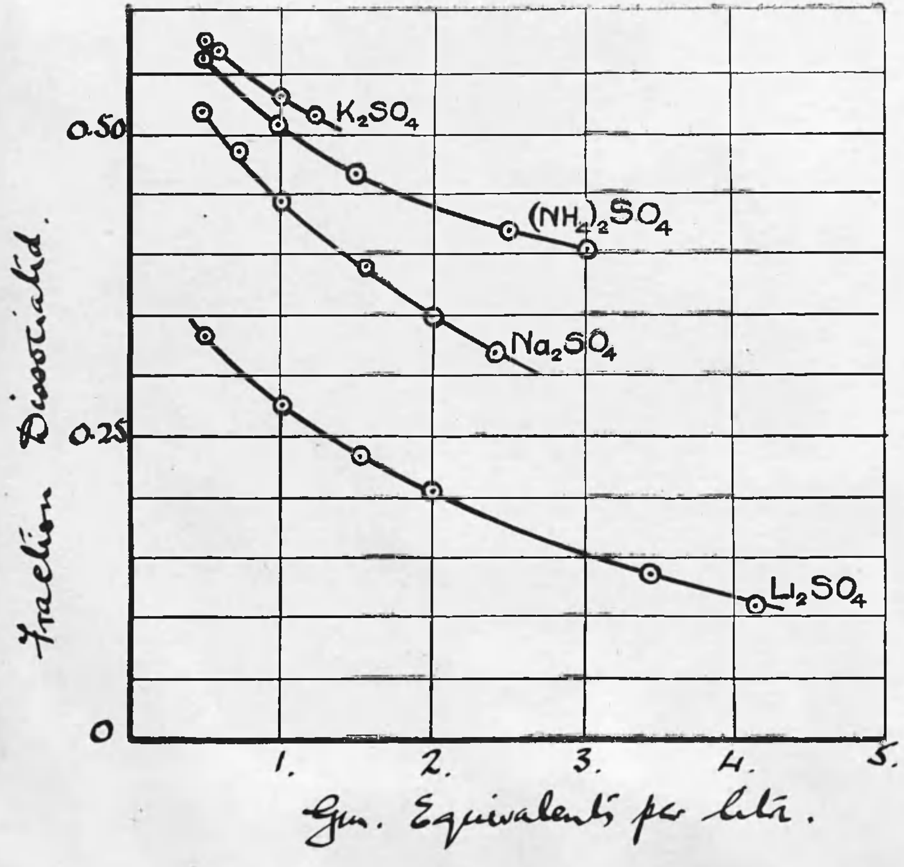
Fig 1

shown to hold.

One extremely interesting figure, (see Fig. I), which is most pertinent to our discussion on complex ion formation is reproduced from a paper by Forbes (J.A.C.S. 1911, 33, 1937). Forbes determined the solubility of silver chloride in water and in aqueous solutions of various chlorides. If the generalisation deduced from the electro-potential series has any validity and complexes can form, we should expect the solubility found to exceed the value given by the Solubility Product Law by an amount dependent upon the stability of these complexes - whose stability is measured qualitatively by the difference in the position of the radicles Ag and M (where M stands for the cation of the added salt) in the electro-potential series. That this is an actual result of experiment can be seen from the figure (Fig. I) - the order of increasing solubility is given by $H < Ca < Na < Sr < Ba <$ K or NH_4.

It is interesting to note that Kendall (J.A.C.S. 1921, 43, 1490) draws a parallelism between dissociation in solution and the electro-potential series. It was suggested by Caven, Mitchell and Ferguson (Jour. Roy. Tech. College, 1924, 1, 16) who were unaware at the time of the existence of Kendall's paper, that a qualitative idea of the tendency of a series of salts to form double salts with any one other

Fig. 2.


K₂SO₄
(NH₄)₂SO₄
Na₂SO₄
Li₂SO₄
0.50
0.25
0
1.
2.
3.
4.
5.
Fraction Dissociated.
Gm. Equivalents per litre.

salt - e.g., the alkali sulphates and copper sulphate - might be obtained from a study of electrolytic dissociation data. Accordingly the following figure (Fig.2) was drawn from material contained in Kohlrausch's book on Electrical Conductivity.

The interpretation put on the figure was that potassium, ammonium, and sodium sulphates by virtue of their power to dissociate to a greater extent provided sufficient sulphate ions to satisfy the equation

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

but that lithium sulphate did not. Sodium sulphate evidently dissociates to a smaller extent than do potassium and ammonium sulphates, and it may be that this is in keeping with the fact that the sodium double salt is slightly different from the other two and only gives a dihydrate instead of a hexahydrate.

From the great mass of material available it is quite easy to produce many examples some of which would seem to support the idea of diversity of position in the electropotential series, or the difference of dissociation in equivalent solution, being a measure of the tendency to form double salt. Just as many examples, perhaps, could be cited in which the relationship does not hold. To take a few cases in point; ferrous sulphate and lithium sulphate behave just like the corresponding pair copper sulphate and lithium sulphate - they do not form a double salt; ammonium sulphate and ferrous sulphate behave like the corresponding copper system - ammonium sulphate forms a double salt and increases the solubility of ferrous sulphate. (Schreinemaker's Z. physikal. Chem. 1909, 66, 692) - in this case the hypothesis would seem to hold.

Lithium cyanide and ferrous cyanide however give a stable lithium ferrocyanide and we are forced to conclude that the anion of the reacting salts must therefore have some influence in complex ion formation.

Forbes (loc. cit.) ascribed to the chlorion in his experiments the powers of complex ion formation which he so ably demonstrated - Kendall is of opinion that the position in the electro-potential series is the determining factor - between these two meantime it is difficult to make a choice since the result of experiment shows that both may be necessary.

There remains one point and that is the part played by the solvent. In all that has been said we have dealt with substances as though they were anhydrous. It has been amply demonstrated that salts in solution are hydrated to a greater or lesser extent and all the double sulphates crystallise with water of crystallisation - it is true that many are capable of existence in the anhydrous or even in the fused state. (Graham demonstrated that copper potassium sulphate, for instance, fuses to a blue liquid whereas potassium sulphate is white and anhydrous copper sulphate is white before starting to decompose at higher temperatures), but we must regard the results of recent X-ray determinations on crystal structure which have demonstrated in the case of alum, at least, that water has a definite place in the lattice (Vegard and Schjelderup, Ann. Physik. 1917, [ii], 54, 146), to say nothing of the evidence on the ease or otherwise with which different groups of water molecules are displaced on heating, as a strong indication that the water of crystallisation is an integral part of the complex molecule.

Foote and his collaborators (J.A.C.S. 1910, 32, 618; 1911, 33, 459; ibid 1032) have examined the effect of replacement of aqueous by non-aqueous solvents for a number of double salts. They have demonstrated the truth of the assertion that water of crystallisation is an essential constituent of the molecule and have shown that replacement of the aqueous solvent by a non-aqueous one is capable of changing the type of double salt formed. Thus cupric potassium chloride and cupric ammonium chloride have the constitutions $2\ KCl.CuCl_2.2\ H_2O$ and $2\ NH_4\ Cl.CuCl_2.\ 2\ H_2O$ respectively, when crystallised from water. On crystallising from alcohol or acetone they are altered to $KCl.CuCl_2$ and $NH_4\ Cl.CuCl_2$.

Double salts with solvent of crystallisation thus become triple complexes - their full study will involve a much more intense examination of the effect of each of these three constituents than was indicated or could even be deduced from the preliminary study of solubility relations outlined by Van't Hoff.

The systems:

Copper sulphate, potassium sulphate, water

and

Copper sulphate, ammonium sulphate, water.

It has been shown (Caven and Ferguson J.C.S. 1922, 121, 1406) by a study of the equilibrium vapour pressures of systems:-

$$CuSO_4.MSO_4.6\,H_2O \rightleftharpoons CuSO_4.MSO_4.2\,H_2O + 4\,H_2O$$

where M stands for alkali metal, ammonium or univalent thallium, that a definite order of resistance to the dissociating power of heat exists in the ascending series thus $K < Rb < Tl < NH_4 < Cs$. The authors have associated this with the increasing electropositiveness of the alkali metal.

The relative positions of potassium and ammonium salts call for special comment.

It was thought that further study of these salts might reveal other characteristics which change with replacement of one alkali metal or group by another.

The crystallographic constants and many other data relating to these salts in the solid state have been most carefully collected by Tutton in a series of researches (see "Crystalline Form and Chemical Constitution", Tutton, Macmillan and Co., 1926, p.109 et seq.); and Locke (Amer. Chem. Jour. 1901, 27, 459) has made a systematic study of their solubilities.

It was decided to investigate the phase systems copper sulphate—potassium sulphate—water and copper sulphate-ammonium sulphate—water in an endeavour to determine the limits of existence of the double salts in equilibrium with their component salts and water and also to discover evidence of the existence of these double salts in aqueous solution.

Related investigations on these salts have been carried out previously.

Regarding cupric potassium sulphate, Rudorff (Pogg. Ann. 1873, 148, 455) stated that cupric sulphate and potassium sulphate mutually replaced each other from saturated solution. This was denied by Trevor (Z. physikal. Chem. 1891, 7, 468), who attempted to ascertain the conditions determining the existence of the double salt, and concluded that no double salt as such existed in solution. Meerburg (Gedenk. aangeboden J.M. van Bemmelen, 1910, 356) examined the system cupric sulphate, potassium sulphate, water at 30°C and at 40°C; Locke (loc. cit.) determined the solubility of the double salt at 25°C.

Regarding cupric ammonium sulphate, Engel (Compt. rend., 1886, 102, 113) studied the system cupric sulphate, ammonium sulphate, water at 0°C and Schreinemakers and Miss de Baat (Z. physikal. Chem. 1909, 66, 693) examined the same system at 30°C; Locke (loc. cit.) stated that the double salt did not exist in solution at 25°C.

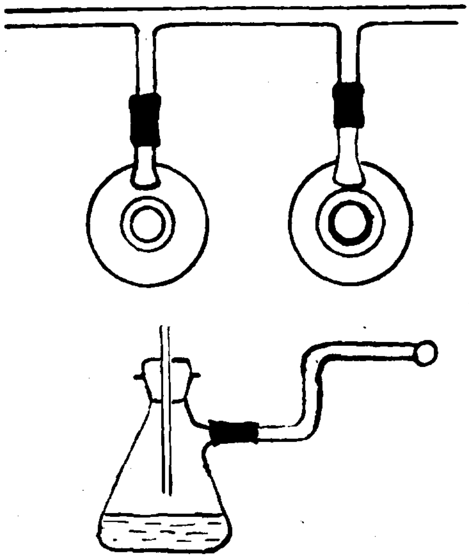


Fig 3

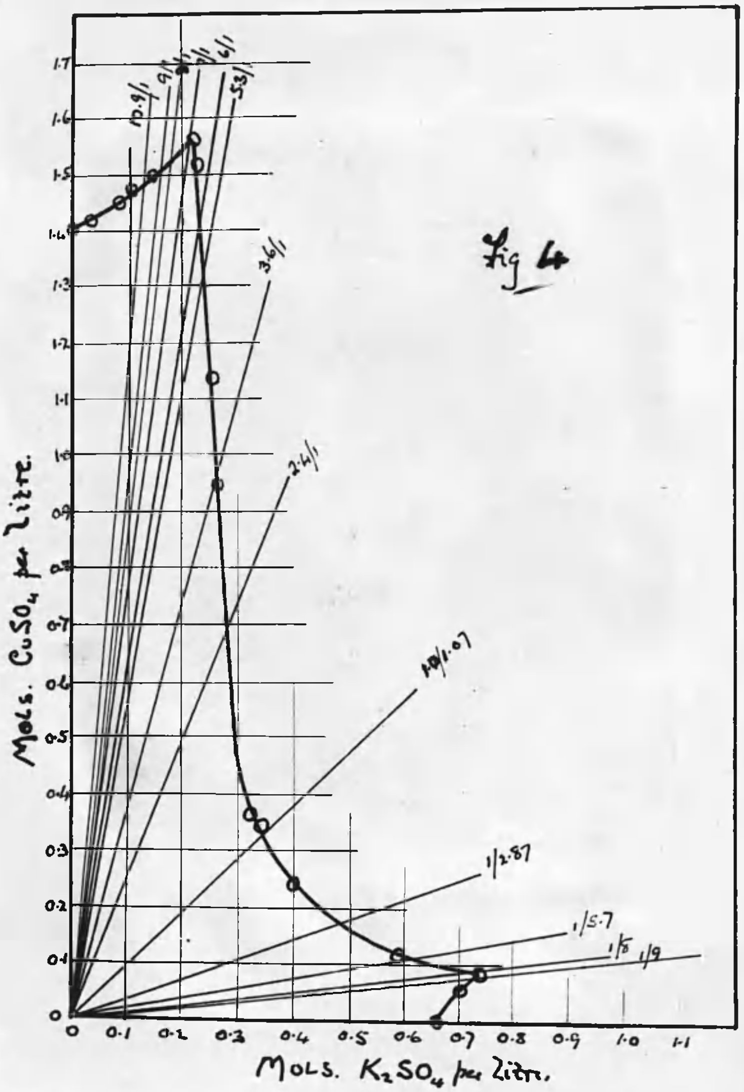
Experimental.

The investigations were of two kinds:- (i) to discover the kind of salt which first crystallised on isothermal evaporation at 25°C from solutions containing known amounts of each single salt, and (ii) to determine the effect of varying amounts of one or other salt on the contents of solutions in equilibrium with cupric sulphate, the double salt $CuSO_4.M_2SO_4.6\ H_2O$, and potassium sulphate or ammonium sulphate respectively.

(i) Isothermal Evaporation at 25°C.

A number of small Büchner flasks, suspended in a thermostat at 25°C, were connected with a common suction tube leading to a suction pump (see fig.3). In the flasks were placed mixtures of varying quantities of solutions of cupric sulphate and alkali sulphate of known concentration. The solutions were allowed to evaporate, with frequent shaking to prevent crystallisation on the sides of the flasks, and evaporation was hastened by the current of air drawn over the surface of the liquid. As soon as a quantity of the salt sufficient for analysis had crystallised, the crystals were separated, drained at the pump, and analysed, the copper content being estimated by titration with sodium thiosulphate after addition of potassium iodide. (See Appendix V "Analysis").

Fig 4


Mols. CuSO₄ per Litre.
Mols. K₂SO₄ per Litre.
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
10.9/1
9/1
6/1
5.3/1
3.6/1
2.4/1
1.0/1.07
1/2.87
1/5.7
1/8
1/9

Results

System Copper Sulphate, potassium sulphate, water.

Molecular Ratio $\frac{CuSO_4}{K_2SO_4}$ in solution	First Crystals to Separate
11:1	$CuSO_4.5H_2O$
9:1	$CuSO_4.5H_2O$
8:1	$CuSO_4.5H_2O$
7:1	Mixture
6:1	$CuSO_4.K_2SO_4.6H_2O$
5:1	"
4:1	"
3:1	"
2:1	"
1:1	"
1:3	"
1:6	"
1:8	Mixture
1:9	K_2SO_4

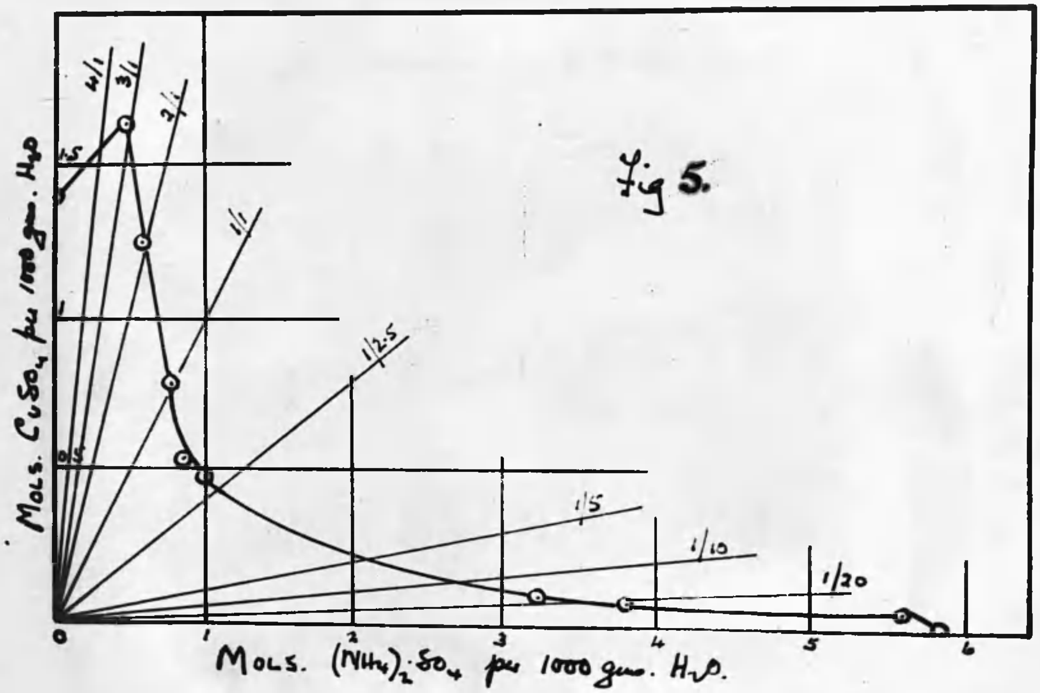


Fig 5.

Mols. CuSO4 per 1000 gms. H2O
1.5
1
0.5
4/1
3/1
2/1
1/1
1/2.5
1/5
1/10
1/20
0
1
2
3
4
5
6
Mols. (NH4)2SO4 per 1000 gms. H2O.

Results(cont.).

Copper sulphate, ammonium sulphate, water.

Molecular Ratio $\frac{CuSO_4}{(NH_4)_2\ SO_4}$ in solution	First Crystals to Separate
4:1	$CuSO_4.5H_2O$
3:1	Mixture
2·5:1	$CuSO_4.(NH_4)_2\ SO_4\ 6H_2O$
2:1	" "
1·5:1	" "
1:1	" "
1:1·5	" "
1:2·5	" "
1:5	" "
1:10	" "
1:15	" "
1:20	" "
1:40	" "
1:60	" "

In both cases the range of double salt formation was very wide, this being especially so in the case of cupric ammonium sulphate. By these experiments the range of double salt formation was approximately outlined. The results thus obtained were confirmed and made more definite by the second procedure.

(ii) Effect of alkali sulphate on the solubility of cupric sulphate, and vice versa, in the presence of the appropriate solid phase.

Experiments were carried out to furnish data for successive isothermal curves for cupric sulphate, double salt, and alkali sulphate. The experiments were performed at three temperatures, viz., 25°, 51° and 61°C.

Materials. The materials used in this work were carefully purified by recrystallisation of "pure" products. Copper sulphate was recrystallised from hot aqueous solutions to which a small quantity of sulphuric acid had been added to prevent hydrolysis. The final product gave no test for iron. The potassium and ammonium sulphates were likewise purified by recrystallisation.

The following are the mean results of several analyses:

$CuSO_4\ 5H_2O$	Cu % 25·35	Theory	25·46
	SO_4 % 38·40		38·48
K_2SO_4	SO_4 % 55·06		55·13
$(NH_4)_2\ SO_4$	SO_4 % 72·62		72·73

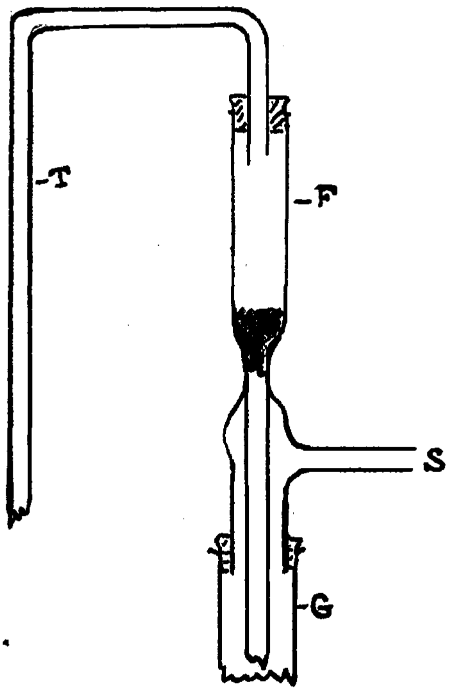


Fig 6.

Method.

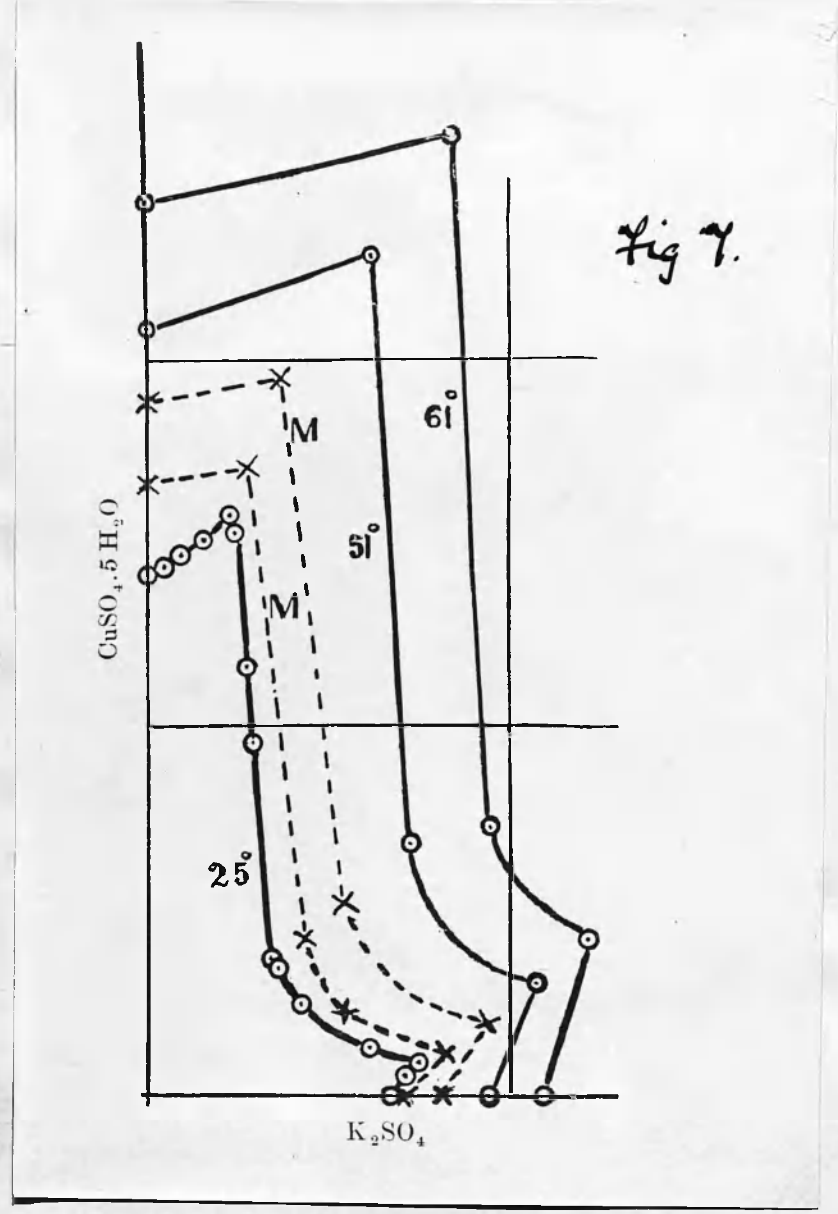
The materials were contained in a number of tightly stoppered bottles, which were immersed in a large thermostat at the required temperature. In each set of experiments there were three sets of solutions: those containing (a) increasing quantities of alkali sulphate in presence of excess of solid cupric sulphate: (b) varying quantities of alkali and cupric sulphates in the presence of solid double salt in excess; and (c) decreasing quantities of cupric sulphate in the presence of excess of solid alkali sulphate. In the case of experiments at 25°C one bottle contained double salt and water only. The bottles remained in the thermostat for several weeks at constant temperature and were shaken frequently. Quantities of solution were withdrawn from time to time, by the use of a suction device containing a filtering chamber (see fig.6) from which the liquid was delivered into a weighed graduated flask. The copper and total sulphate were estimated, and the amounts of cupric and alkali sulphate were calculated from the values obtained. When two consecutive analyses agreed within the limits of experimental error, equilibrium was regarded as established. The results were calculated as mols per 1000 gms of water.

In the experiments at 61° in the case of cupric potassium sulphate slight hydrolysis with deposition of an insoluble basic salt occurred after long standing.

The results obtained are tabulated below and represent the mean of closely agreeing values. Figs 7 and 8 show these results graphed on rectangular co-ordinates for comparison with the curves developed theoretically by Van't Hoff. The results of previous observers are indicated by broken lines.

For a discussion on the accuracy claimed for these and other results in this thesis see Appendix V on Analyses.

Fig 7.



M = Meerburg.

Results.

Copper sulphate, potassium sulphate, water at 25°C.

Mols. $CuSO_4$ per 1000 g. H_2O	Mols K_2SO_4 per 1000 g. H_2O	Solid Phase
1·410	nil	C
1·415	0·014	C
1·430	0·037	C
1·457	0·086	C
1·477	0·110	C
1·504	0·150	C
1·570	0·225	C and D
1·525	0·228	D
1·149	0·261	D
0·955	0·270	D
0·365	0·331	D
0.350	0·350	D
0·237	0·412	D
0.120	0·598	D
0·092	0·737	D and K
0·060	0·708	K
nil	0·661	K

C = $CuSO_4.5\ H_2O$

D = $CuSO_4.K_2SO_4.6\ H_2O$

K = K_2SO_4

Results(contd.)

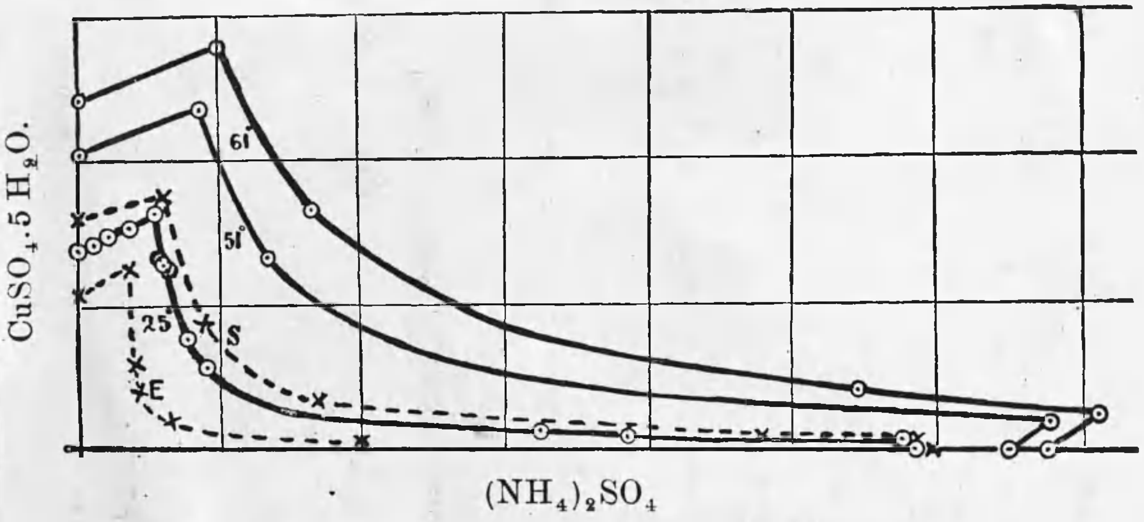
Copper sulphate, potassium sulphate, water at 51°C.

Mols $CuSO_4$ per 1000 g. H_2O	Mols K_2SO_4 per 1000 g. H_2O	Solid Phase
2·073	nil	C
2·266	0·618	C and D
0·677	0·706	D
0·312	1·036	D and K
nil	0·923	K

Copper sulphate, potassium sulphate, water at 61°C.

Mols $CuSO_4$ per 1000 g. H_2O	Mols K_2SO_4 per 1000 g. H_2O	Solid Phase
2·419	nil	C
2·586	0·838	C and D
0·728	0·932	D
0·422	1·187	D and K
nil	1·064	K

Fig 8.



S. Schreinemakers. E. Engel.

Results (contd.)

Copper sulphate, ammonium sulphate, water at 25°C.

Mols $CuSO_4$ per 1000 g. H_2O	Mols $(NH_4)_2 SO_4$ per 1000 g. H_2O	Solid Phase
1·410	nil	C
1·470	0·096	C
1·486	0·121	C
1·494	0·158	C
1·513	0·183	C
1·558	0·293	C
1·646	0·534	C and D
1·413	0·572	D
1·368	0·575	D
1·259	0·601	D
0·779	0·779	D
0·565	0·897	D
0·507	0·989	D
0·112	3·233	D
0·070	3·826	D
0·051	5·715	D
0·042	5·762	D and A
nil	5·801	A

A = $(NH_4)_2 SO_4$.

Results (contd)

Copper sulphate, ammonium sulphate, water at 51°C.

Mols. $CuSO_4$ per 1000 g. H_2O	Mols $(NH_4)_2SO_4$ per 1000 g. H_2O	Solid Phase
2·073	nil	C
2·365	0·861	C and D
1·302	1·351	D
0·180	6·733	D and A
nil	6·462	A

Copper sulphate, ammonium sulphate, water at 61°C.

Mols. $CuSO_4$ per 1000 g. H_2O	Mols $(NH_4)_2SO_4$ per 1000 g. H_2O	Solid Phase
2·419	nil	C
2·753	0·998	C and D
1·631	1·695	D
0·396	5·387	D
0·249	7·079	D and A
nil	6·714	A

Summary and Discussion.

The following facts are revealed by a study of the isothermal diagrams of the systems:-

(1) The double salts of the type $CuSO_4.M_2SO_4.6\ H_2O$ where M is K or (NH_4) are stable over a very large range as regards the molecular proportions of alkali sulphate to cupric sulphate present in solutions from which they crystallise. Thus cupric potassium sulphate crystallises at 25°C. from solutions containing cupric sulphate to potassium sulphate between limits which are approximately Cu:2K 7:1 and 1:8; and cupric ammonium sulphate from solutions in which $Cu:2NH_4$ are 3:1 and 1:137.

(2) The solubility of cupric sulphate is increased by the presence of alkali sulphate, and reciprocally the solubility of alkali sulphate is increased by the presence of cupric sulphate until the triple points are reached at which the solution is in equilibrium with cupric sulphate and the double salt, and double salt and alkali sulphate respectively. The observed increases in solubility disprove the statement of Rudorff (loc. cit.) that mutual displacement of one salt by another takes place.

Transition Point.

An attempt was made to find a transition point corresponding to the change given by the following equation:

$$CuSO_4.K_2SO_4 \rightleftharpoons CuSO_4. + K_2 SO_4.$$

In the dry state changes corresponding to

$$CuSO_4.K_2SO_4.6 H_2O \rightleftharpoons CuSO_4.K_2SO_4 2 H_2O + 4 H_2O$$

and

$$CuSO_4.K_2SO_4 \ 2 H_2O \rightleftharpoons CuSO_4.K_2SO_4 + 2 H_2O$$

would be realised, (Caven and Ferguson, (loc.cit.)). Again, it has been shown that $CuSO_4.K_2SO_4$ can be fused without decomposition.

Because of these facts an attempt was made to find the transition point sought in a dilatometer after having moistened the salt with distilled water so that at higher temperatures a little of the solution of double salt would be present. The finely divided salt was charged into a dilatometer as described in elementary text-books on practical physical chemistry, the salt was moistened with distilled water and the bulb of the instrument was sealed off. The bulb was then filled with toluene, connected with a long capillary attached to a scale and immersed in a thermostat. Readings of temperature and the height of toluene thread were taken at frequent intervals while the temperature was slowly raised. On plotting temperature against height of toluene column no irregularities were noted.

A second attempt to find the transition point was carried out in much the same way as the isothermal evaporations were carried out.

Saturated solutions of the double salts were caused to evaporate rapidly at different temperatures by drawing a current of air across the surface of the solutions contained in Büchner flasks. The first product to separate out was filtered off and analysed.

Above 61°C copper potassium sulphate hydrolysed rapidly and deposited a bright green powder of the composition shown by the formula $K_2SO_4.3\ CuSO_4.CuO.4\ H_2O$, a compound which has already been described in the literature.

At all temperatures up to 100°C. copper ammonium sulphate was the first product to separate from solutions of copper ammonium sulphate, showing that no decomposition of the double salt had taken place.

This observation regarding cupric ammonium sulphate has recently been confirmed by E. Rouyer (Compt. rend. 1926, <u>183</u>, 46) who, by the ebullioscopic method, has shown the existence of double salt molecules in aqueous solution at 100°C.

Hydrolysis in Solutions of Copper Salts.

It was noted in connection with the attempt to find the transition point in solution by isothermal evaporation at temperatures higher than those used for the equilibrium system that copper potassium sulphate hydrolysed while copper ammonium sulphate did not.

It was thought that this interesting phenomenon might be further studied with a view to comparing the behaviour of the salts in solution.

Accordingly equivalent solutions of copper sulphate, copper potassium sulphate, and copper ammonium sulphate were made up in a series of dilutions.

These solutions were placed in conical flasks fitted with reflux condensers and heated on water baths for periods of six hours. At the end of this time the solutions were filtered off and the acidity developed measured by titration with standard alkali to a standard "neutral" tint. The neutral tint employed was that of a freshly prepared solution of copper sulphate coloured with a known quantity of methyl orange indicator. The standard was prepared each time immediately before use since it has been shown by Caven (Jour. Soc. Chem. Ind. 1900, 19, 18) that the acidity of freshly prepared copper sulphate solution changes on standing.

The results were interesting although only of comparative value. They are tabulated below, and graphed in fig. 9.

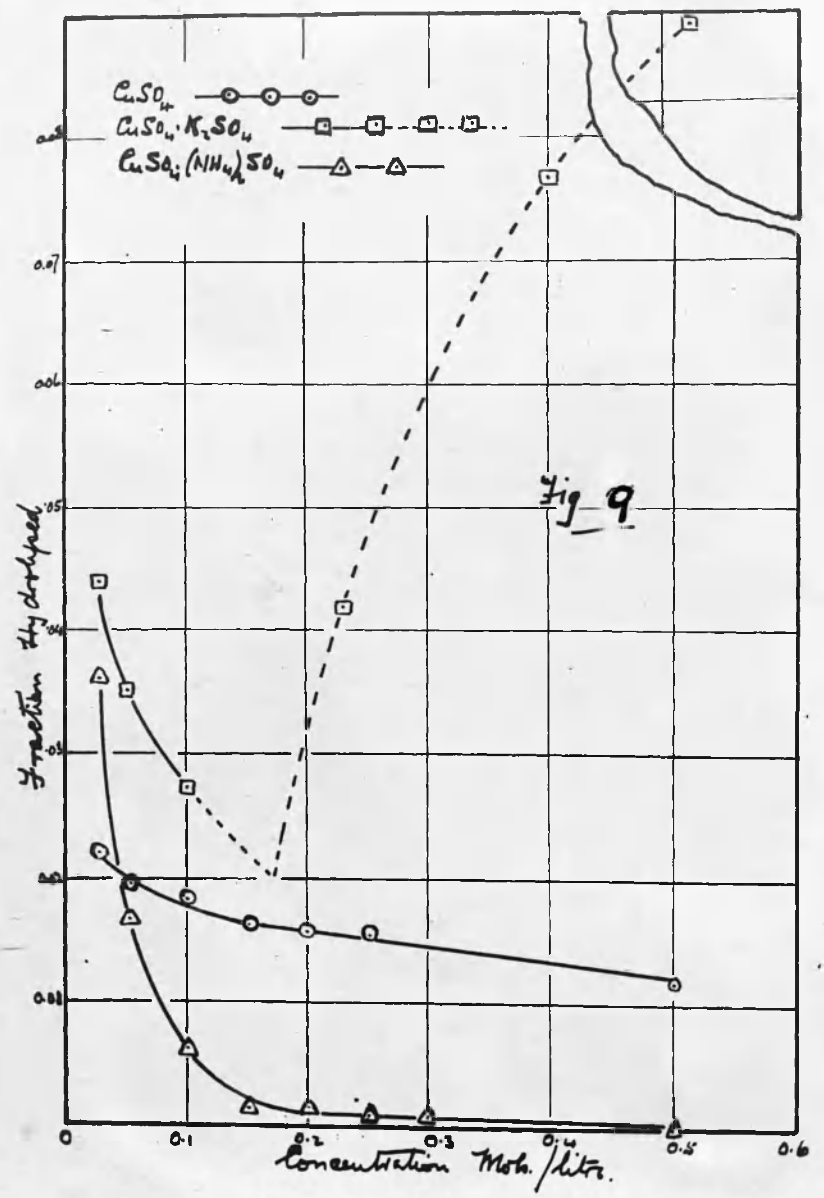

$CuSO_4$
$CuSO_4 \cdot K_2SO_4$
$CuSO_4 \cdot (NH_4)_2SO_4$
0.08
0.07
0.06
·05
·04
·03
0.02
0.01
Fraction Hydrolysed
0
0·1
0·2
0·3
0·4
0·5
0·6
Concentration Mols./litre.

Fig 9

Hydrolysis of Copper Sulphate Solutions.

Conc. of Cu SO_4 mols./litre	Fraction hydrolysed after 6 hours at 100°C
0·025	0·0220
0·05	0·0192
0·1	0.0183
0.15	0·0163
0.20	0·0155
0·25	0·0153
0·5	0·0115

Hydrolysis of copper potassium sulphate solutions.

Conc. of $CuSO_4.K_2SO_4$ 6 H_2O mols./litre	Fraction hydrolysed after 6 hours at 100°C.
0·025	0·044
0·05	0·0354
0·1	0·0271
0·23	0·0423[1]
0·40	0·0765
0·63	0·0968

(1) This and following solutions were in equilibrium with solid salt at room temperature.

Hydrolysis of copper ammonium sulphate solutions.

Conc. of $CuSO_4.(NH_4)_2SO_4.6H_2O$ mols./litre.	Fraction hydrolysed after 6 hours at 100°C.
0·025	0·036
0·50	0·0164
0·1	0·0061
0.15	0·0015
0·20	0·0015
0·25	0·0010
0·30	0·0009
0·5	nil

It will be seen that a little irregularity exists but the comparison these results offer is quite evident. Thus it appears that the presence of ammonium sulphate tends to reduce the susceptibility of copper sulphate to the hydrolysing influence of water, while the presence of potassium sulphate tends to increase it.

Another fact not evident from the results was noted during the experiments. In the more dilute solutions the first product to separate from the copper ammonium salt solutions was a brown powder, followed by a slight quantity of a green substance. What these were was not discovered since only a very small supply was ever obtained. In the case of the potassium salt only one product of decomposition ever settled out and this on analysis proved to be the bright green salt already noted.

Attempts to follow the hydrolysis by the inverting power of the acid formed, using a known sugar sulution failed.

[NOTE. It is doubtful if the results tabulated above express equilibrium conditions since the "constant" calculated according to the following equation shows a steady rise with concentration

$$\frac{x^2}{(1-x)v} = K$$

where x = fraction hydrolysed
v = volume in litres containing 1 mol.

This, after all, is more or less to be expected since the extreme insolubility of the product of hydrolysis will remove it from the reaction which will tend to completion. Indeed cognisance of this fact was taken when the state of acidity of the solution was determined by titration since it was assumed that the rapid alteration of conditions produced by neutralisation of the acid in solution would not immediately be counteracted by a shift of the hydrolysis equilibrium such as would take place, say, in any attempt to study the hydrolysis of potassium cyanide by a like method].

Systems of the type

$Al_2(SO_4)_3 \,..\, M\,SO_4 \,..\, H_2O$.

Studies of Equilibrium in Systems of the type
$Al_2(SO_4)_3$ .. M SO_4 .. H_2O

Introduction.

These investigations were undertaken in the hope that information regarding the interactions in solution of soluble salts (i.e., in contradistinction to "insoluble" salts such as $BaSO_4$, $CaSO_4$, etc.) with a common ion, might be obtained in cases where double salts had not been described. It was hoped that here where, so far as was known, there was no chance of mixed crystals separating (e.g., as in the case of the $FeSO_4$-$CuSO_4$-H_2O system), the ability or non-ability to form double salt might be traceable to differences in the electro-positiveness of the cations of the salts in the system. This point is of importance in view of the ideas already developed in explanation of the union of salt molecules to form double salts.

It was hoped also that the information gained would throw light on the question of the existence of 'pseudo-alums'.

In the appropriate volume of Friend's Inorganic Chemistry under 'pseudo-alums' we find, "very little is known concerning these salts, which require to be re-investigated".

The name 'pseudo-alum' has been given to a class of double sulphates supposed to be related to the alums, thus:

$M_2SO_4, Al_2(SO_4)_3, 24H_2O$	Alum
$M\ SO_4, Al_2(SO_4)_3, 24H_2O$	Pseudo-alum.

The pseudo-alums described in the text-books are those in which the bi-valent metal is manganese, magnesium, ferrous iron, and zinc.

References to this subject are somewhat scanty but the following papers exist:- Klauer (Annalen, 1835, 14, 261), a paper dealing with the preparation of ferrous and magnesium alums in the presence of excess sulphuric acid.

Rammelsberg (Pogg. Ann. 1838, 43, 399) deals with various naturally occurring double salts containing aluminium sulphate.

Kane, (ibid. 1838, 44, 472) mentions the manganous salt with twenty-two molecules of water of crystallisation.

Wirth, (Z. angew. Chem. 1913, 26, 81) discusses the system aluminium sulphate, ferrous sulphate, water.

It is of interest in connection with pseudoaalums that a number of minerals occur which approximate to the "ideal" pseudo-alum of the text-books.

The mineral "pickeringite" was examined by Kane who represented it as $Mg\ SO_4$, $Al_2\ (SO_4)_3$, 24 H_2O, but A. Hayes in 1844, and H. How in 1863 gave 22 instead of 24 molecules of water. Part of the magnesium in the above mineral is replaceable by manganese to give "apjohnite", after Apjohn, who first described it (Proc. Roy. Irish Acad. 1839, 1, 51).

Ferrous pseudo-alum in nature occurs as "halotrichite" and from the investigations of Wirth (loc. cit.) and more recently Occleshaw (J.C.S. 1925, 127, 2598) it would appear to be well established that this salt contains 24 molecules of water.

On the authority of Kane zinc pseudo-alum contains 24 molecules of water also.

The existence of a copper pseudo alum is left doubtful in the literature although two naturally occurring compounds "cyanotrichite" and "woodwardite", both basic cupric-aluminium-sulphates are known, with 8 and 23 molecules of water respectively. From the work of Caven and Mitchell (J.C.S. 1925, 127, 527) confirmed by Occleshaw, (loc. cit.) it appears that no double salt can be obtained from aqueous solution of the constituents at 30°C.

No salt in which M is nickel or cobalt has yet been described.

Experimental.

The systems examined were those containing aluminium sulphate with copper, manganese, and nickel sulphates respectively.

The copper, manganese and nickel sulphates were purified by recrystallisation from solutions to which a little sulphuric acid was added to prevent hydrolysis. In the case of aluminium sulphate the purest salt obtainable was dissolved and the sulution was filtered and evaporated at 25°C. with the aid of a filtered current of air until a very viscous solution was obtained. Despite attempts to "seed" this with small fragments of solid aluminium sulphate it could not be made to crystallise and the solution was used. The hydrolysis was extremely small and the faint precipitate that did collect on standing was never disturbed when quantities of the solution were withdrawn for use. The solution gave no test for ferric iron after addition of a few drops of concentrated nitric acid.

The following are the mean results of several closely agreeing analyses of the salts employed

$CuSO_4\ 5\ H_2O$	Cu %	25·35	Theory 25·46
	SO_4 %	38·40	38·48
$Ni\ SO_4\ 7\ H_2O$	Ni %	20·11	20·18
	SO_4 %	34·11	34·21
$Mn\ SO_4\ 7\ H_2O$	Mn %	19·76	19·82
	SO_4 %	34·59	34·67

For the copper system pure copper sulphate and aluminium sulphate were placed with water in separate flasks in a thermostat kept at 40°C. A large vessel, fitted with a cork carrying a stirrer and a filtering device, was kept in another thermostat at 30° ± 0·1, and in this were placed mixtures in different proportions of the two single salt solutions.

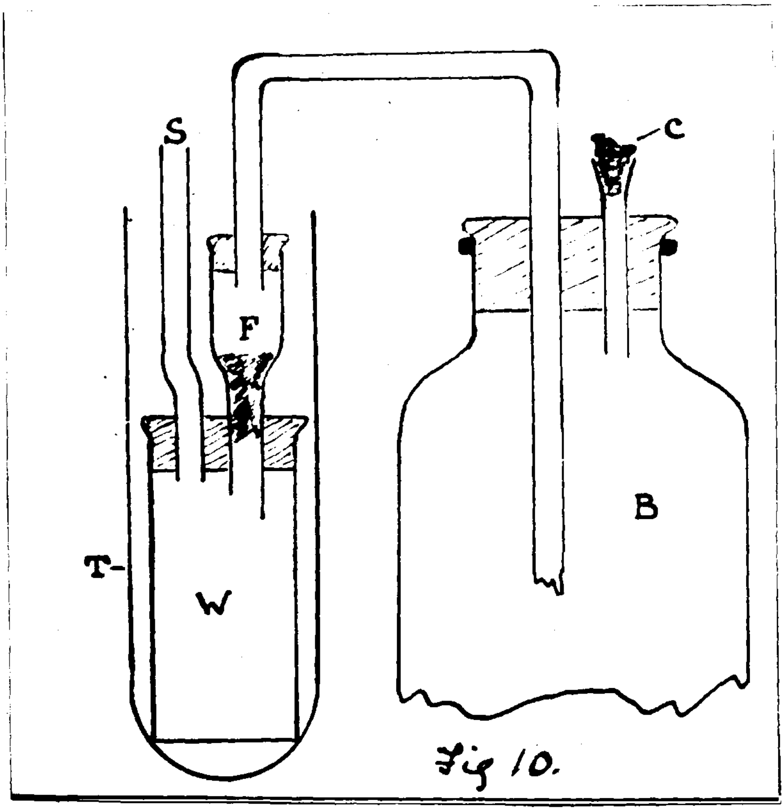


Fig 10.

B. Reaction vessel.

C. Cotton-wool plug.

F. Filter chamber.

W. Weighing bottle.

S. Connection to suction.

T. Guard tube.

The mixtures were stirred for three days, and each resulting solution was then decanted through a filter (Fig.10) into a weighing bottle, both of which were kept at the temperature of the bath. The solid phase was filtered off, drained at the pump and transferred while moist to a weighing bottle. The solution and moist solid phases were then weighed and made into solutions measuring known volumes.

The copper was estimated iodometrically, and the aluminium was calculated after determination of the total sulphate.

The system $MnSO_4$-H_2O shows a transition point at 26°C., whereafter the solubility decreases. It was therefore of no advantage to commence with a solution of manganous sulphate above this temperature. In this case solutions of the single salts, saturated at room temperature, were mixed in the reaction vessel and isothermally evaporated by means of a filtered current of air, with constant stirring. When a solid phase separated the current of air was stopped, and stirring was continued for three days, whereafter the solution and solid phases were removed for analysis.

Manganese was estimated by precipitating it as the hydrated dioxide (using ammonium persulphate in the presence of excess of sulphuric acid as recommended by Knorre (Z. angew. Chem. 1901, 14, 1149), dissolving the precipitate in standard oxalic acid, and titrating the solution with potassium permanganate. Aluminium was again estimated after determination of the total sulphate.

The equilibrium mixtures in the nickel system were prepared in the same way as those of the manganese system.

Nickel was estimated with potassium cyanide, with silver iodide as indicator, and aluminium was obtained as before.

It has been noted by Britton (J.C.S. 1922, 121, 982) that aluminium sulphate hydrolyses above 30°C. In the experiments carried out, the amount of hydrolysis in the single solutions from which equilibrium systems were obtained was very small, and was neglected.

The results given below represent the mean of duplicate determinations which agreed within the limits of experimental error. Results are expressed in gms. per 100 gms of solution (for the solutions) or moist solid (for the rests). For a discussion on the triangular diagram see Appendix IV.

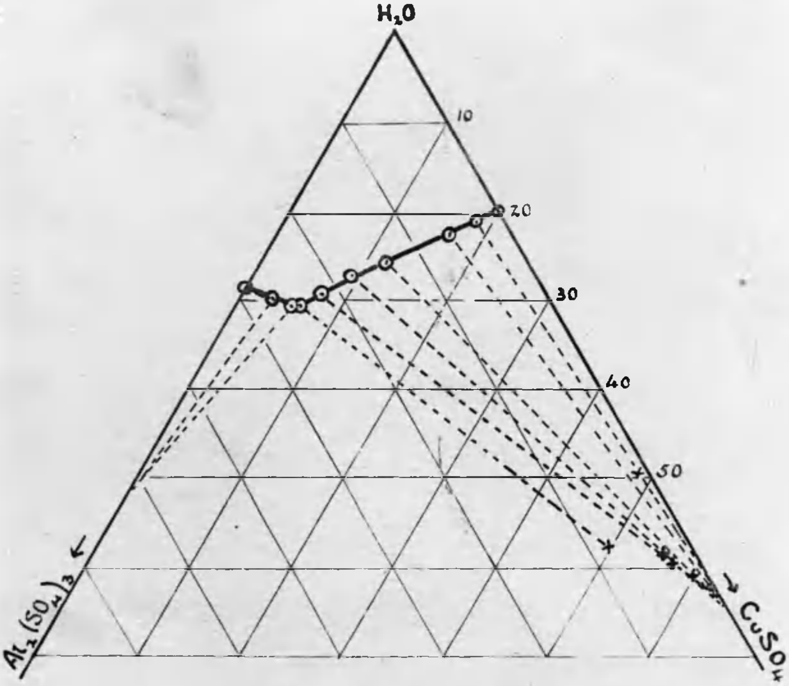


Fig 11

Results.

$Al_2(SO_4)_3$-$CuSO_4$-H_2O at 30°C. (See fig.11).

Solutions			Rests		
$Al_2(SO_4)_3$	$CuSO_4$	H_2O	$Al_2(SO_4)_3$	$CuSO_4$	H_2O
nil	20·33	79·67	...	...	...
2·75	18·65	78·60	0·92	48·61	50·47
5·97	16·76	77·27	0·13	61·72	38·15
13·80	12·13	74·07	1·51	59·38	39·11
17·65	9·79	72·56	3·21	55·25	41·54
22·00	7·67	70·33	2·94	56·69	39·37
24·64	6·30	69·06	8·20	49·78	42·02
25·22	5·74	69·04	50·1	0·30	49·60
26·83	3·39	69·78	49·52	0·25	50·23
28·86	nil	71·14	...	...	...

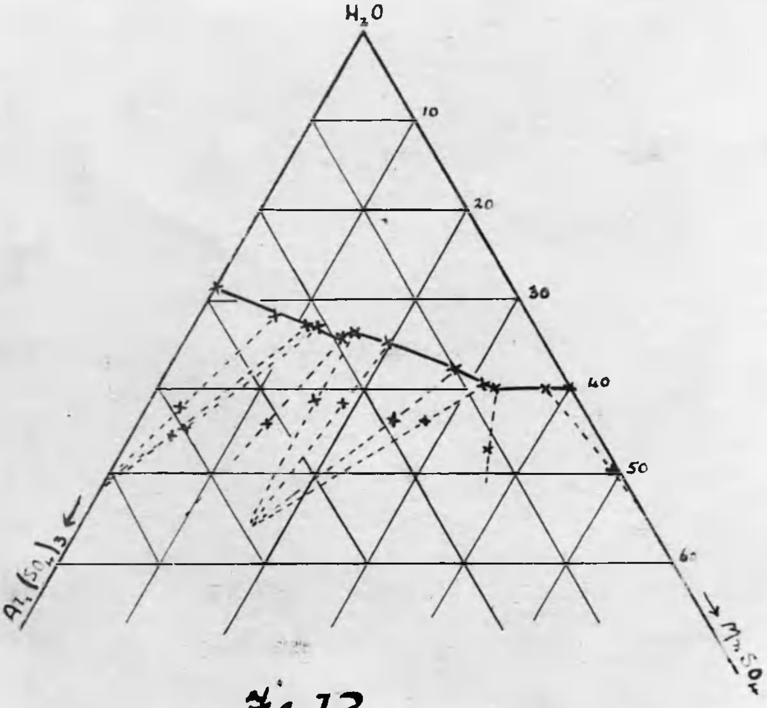


Fig 12.

Results (contd).

$AL_2\ (SO_4)_3$-$MnSO_4$--H_2O at 30° (see fig.12).

Solutions			Rests		
$Al_2\ (SO_4)_3$.	$MnSO_4$	H_2O	$Al_2\ (SO_4)_3$	$MnSO_4$	H_2O
nil	40·03	59·97	---	---	---
2·47	37·94	59·59	1·12	49·03	49·85
7·21	32·97	59·82	11·71	35·23	53·06
8·43	31·43	60·14	16·29	27·76	55·95
10·40	27·39	62·21	18·82	24·62	56·56
15·01	19·91	65·08	22·75	19·11	58·14
18·11	15·96	65·93	25·27	16·15	58·58
19·58	15·23	65·19	31·43	12·21	56·36
21·13	12·14	66·73	39·90	4·95	55·15
21·93	11·09	66·98	41·65	4·72	53·63
24·42	7·41	68·17	38·96	3·12	57·92
28·86	nil	71·14	---	---	---

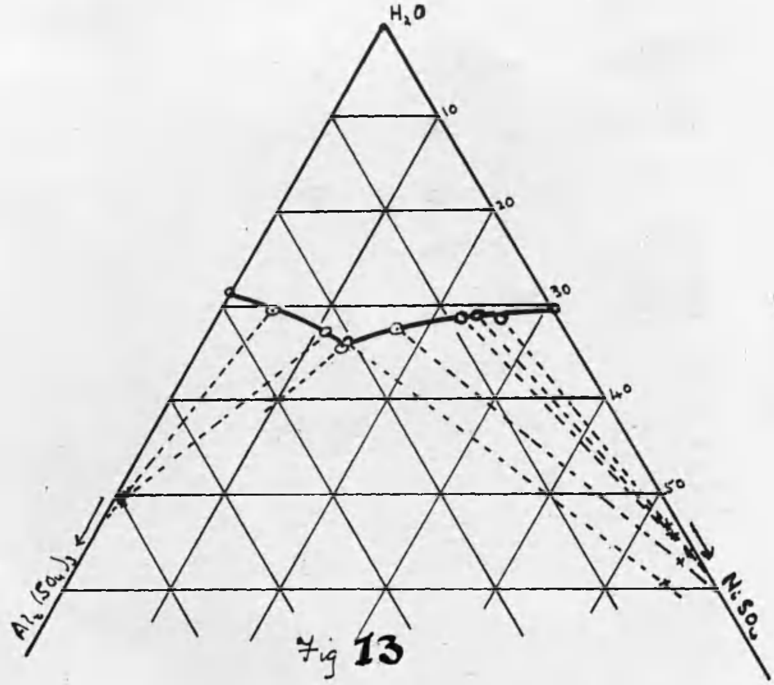


Fig 13

Results (contd).

$Al_2(SO_4)_3$ - $NiSO_4$ - H_2O at 30°C. (see fig.13).

Solutions			Rests		
$Al_2(SO_4)_3$	$NiSO_4$	H_2O	$Al_2(SO_4)_3$	$NiSO_4$	H_2O
nil	30·77	69·23	---	---	---
5·29	26·03	68·68	0·45	57·65	41·90
7·34	23·58	69·08	1·13	52·70	46·17
8·70	22·56	68·74	0·35	55·89	43·76
15·29	17·53	67·18	3·01	52·17	44·82
20·79	13·29	65·92	4·03	55·40	40·57
21·30	12·91	65·79	29·99	9·91	60·10
21·95	10·87	67·18	49·81	0·51	49·68
25·87	4·74	69·39	48·71	0·82	50·47
28·86	nil	71·14	---	---	---

Discussion.

Examination of the triangular diagrams representing the figures given above for the various systems yields the following results.

1. In the case of the system copper sulphate, aluminium sulphate, water the points of intersection of the tie lines joining solution and "rest" points are on the sides of the triangle at those points which represent $CuSO_4.5\ H_2O$ and $Al_2\ (SO_4)_3\ 18\ H_2O$ repsectively. (See Appendix V). This indicates that at 30°C. no combination takes place between these salts, mixtures of which in solution will remain in equilibrium with one or other salt as solid phase depending on the relative concentrations present in the solution phase.

2. In the case of nickel sulphate, aluminium sulphate, water the results are similar to those noted for the copper system, viz., the foci of tie lines are again at those points representing one or other of the single salts. Evidently nickel sulphate and aluminium sulphate do not form a stable double salt at 30°C.

3. For the manganous sulphate, aluminium sulphate system three points of intersection of tie lines are obtained. Two of these foci again represent the single salt points - $MnSO_4.7H_2O$ and $Al_2(SO_4)_3.18H_2O$ respectively. The third point of intersection has the co-ordinates

$MnSO_4$ 16·97% $Al_2(SO_4)_3$ 38·48%. H_2O 44·55% and this corresponds with a solid double salt of composition $Mn\,SO_4.Al_2\,(SO_4)_3.22\,H_2O$. This salt crystallised in masses of fine needles quite unlike the typical alum crystal. On account of these facts it would seem advisable not to apply the name 'pseudo-alum' to the manganous double salt.

A study of the conductivities of bivalent metal sulphate solutions shows them all to have practically the same value at equivalent dilutions - (Lewis and Randall, for instance, class them altogether under $M\,SO_4$ in dealing with their conductivities and "activities") so that it would seem doubtful if the idea of obtaining qualitative evidence of the possibility of complex ion formation from dissociation curves has any true bearing in this case despite the fact that it agrees well in the case of the alkali sulphate, copper sulphate systems.

Plotting the results of the above on rectangular coordinates shows that the solubility curve for $Al_2(SO_4)_3$ with increasing amounts of bivalent metal sulphate is influenced to approximately the same degree by all three sulphates employed - a fact that would follow from the dissociation evidence. The portion of the curve representing double salt formation in the manganous sulphate system is very shallow and indicates that 30°C. is a temperature not far from the transition point.

The system

$Al_2(SO_4)_3 - Ag_2SO_4 - H_2O$

The system aluminium sulphate, silver sulphate, water at 30°C.

Introduction.

The possibility of union between silver sulphate and aluminium sulphate to form double salt possesses considerable interest. Silver belongs to Group I of the periodic table and gives a sulphate which is not so freely soluble as the alkali sulphates. It is, however, not unlike thallous sulphate with regard to solubility and thallous sulphate gives an alum as well as double salts with the bivalent metal sulphates. Examination of conductivity data shows, however, that silver sulphate is dissociated to a large extent in solution.

In view of the suggested parallelism between dissociation in solution (as a measure of electro-positiveness) and complex ion formation it was decided to examine the system.

Previous investigators are not in agreement. Thus S. Kern, (Chem. News. 1875, 31, 209), claims to have made typical crystals of silver alum, $Ag_2\ SO_4.Al_2\ (SO_4)_3\ 24\ H_2O$, by evaporation of a mixed solution of the component salts, and A.H. Church and A.B. Northcote (ib. 1864, 9, 155) describe the preparation of this salt by heating a mixture of silver sulphate, aluminium sulphate, and water under pressure in an oil-bath till all the silver salt had dissolved. J.W. Retgers (Z. physikal. Chem. 1886, 3, 497) has denied the existence of silver alum.

In the laboratory at the Royal Technical College J. Wilkie repeated the method of Church and Northcote without success (Unpublished work).

Experimental.

Two methods were employed in making up the equilibrium mixtures. In the first method recrystallised silver sulphate was placed in contact with solutions of aluminium sulphate and stirred continuously for several days in a reaction vessel fixed in a thermostat maintained at 30°C. The second method consisted in evaporating isothermally with the aid of a filtered current of air, a mixed solution of the constituents. The contents of the vessel were stirred while evaporation was going on and the stirring was continued without evaporation (when a sufficient quantity of solid phase had accumulated) for two days.

The solution and the moist solid phases were separated in the usual way, weighed, made up to known volume and aliquot portions taken for analysis.

Silver could not be estimated by precipitation in the usual way as chloride since it was found that silver chloride dissolved in aluminium chloride solution on heating - indeed if hydrochloric acid was used to precipitate the silver considerable quantities of silver chloride could be dissolved.

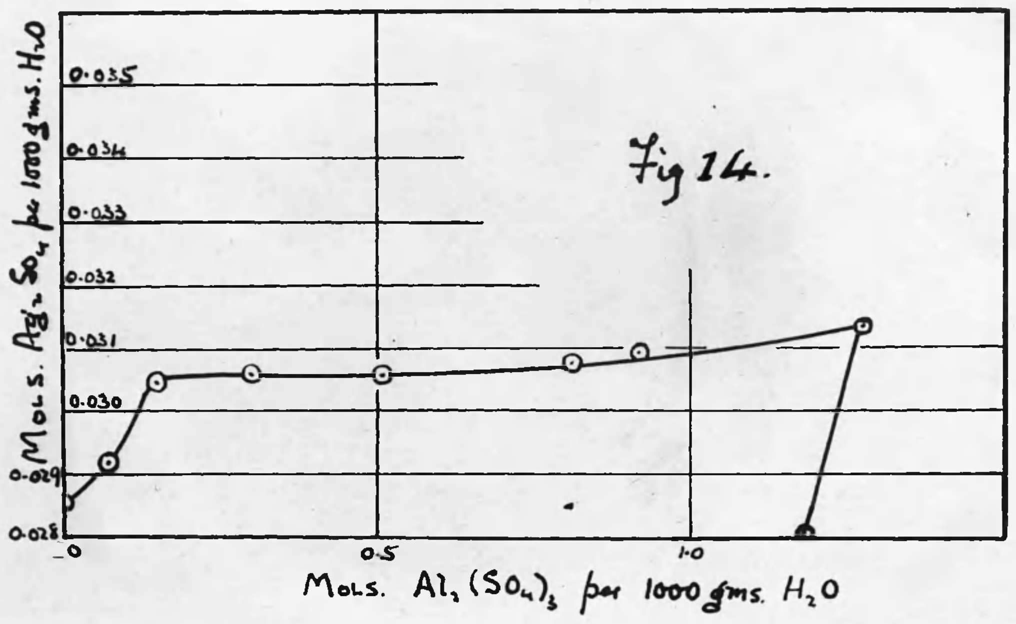


Fig 14.
0.035
0.034
0.033
0.032
0.031
0.030
0.029
0.028
0
0.5
1.0
Mols. Ag_2SO_4 per 1000 gms. H_2O
Mols. $Al_2(SO_4)_3$ per 1000 gms. H_2O

Silver was estimated by electrolysis of the double cyanide solution, as recommended in text-books on electrochemistry. The aluminium was afterwards estimated by precipitation as the hydroxide following the destruction of the cyanide by heating with sulphuric acid.

<u>Results</u> (see fig.14).

Mols. Ag_2SO_4 per 1000 gms. H_2O	Mols $Al_2(SO_4)_3$ per 1000 gms. H_2O	Solid Phase
0·0285	nil	Ag_2SO_4
0·0292	0·0777	Ag_2SO_4
0·0304	0·1449	"
0·0306	0·3026	"
0·0306	0·5114	"
0·0308	0·8153	"
0·0310	0·9210	"
0·0314	1·276	$Ag_2SO_4+Al_2(SO_4)_3$
nil	1·187	$Al_2(SO_4)_3$

The continuous increase in the solubility of silver sulphate was most marked but seems in no way extraordinary in view of the results for systems silver sulphate, ammonium sulphate, water; and silver sulphate, sodium sulphate, water, recorded by Barre (A. Ch. 1911, (8), 24, 149, 202, 210; Comt. rend. 1910, 150, 1323). Ephraim and Wagner, (Ber. 1917, 50, 1103) found as the result of one determination, that silver sulphate was more soluble in aluminium sulphate solution than in water.

Conclusion.

From the results obtained it is evident that silver sulphate and aluminium sulphate do not form an alum from mixtures of their solutions at 30°C.

The Conductivities of Double Salt Solutions.

The conductivities of double salt solutions have been measured on numerous occasions by many investigators with a view to finding the limits of existence of the complex ions in solution.

Theoretical.

Any attempt to estimate the extent of complex ion formation from conductivity measurements necessitates a calculation, for comparison, of the conductivity of a solution on the assumption that no complex ion is present.

Whilst it is theoretically possible to calculate according to the law of solubility product the change in solution caused by the introduction into a given salt solution of a salt with a common ion, such a calculation is invalidated when the salts under consideration are of the extremely soluble type that usually give rise to double salts. Even in the cases that have been examined (e.g., silver halides, Noyes, loc. cit.) it was necessary to assume that the dissociation of the small amount of slightly soluble electrolyte was not materially altered in the presence of the more soluble second salt.

In the absence of any satisfactory method for computing the change of dissociation in a solution of two electrolytes with a common ion it has been customary to compare the sum of the conductivities of the components with the conductivity

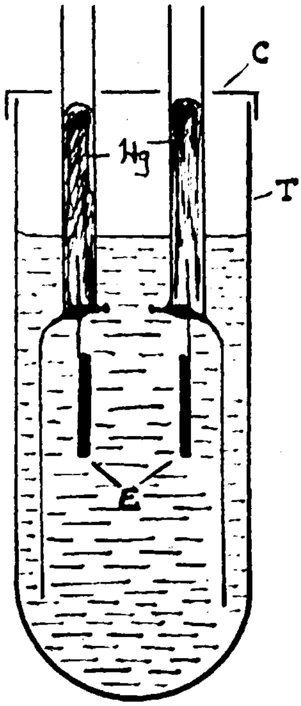


Fig 15.

of the double salt solution. Thus Jones and his co-workers compared the observed conductivity of a double salt solution with the mean of the conductivities of the components at equivalent dilution; and Rây and Dhar used this method to test the existence in solution of a complex ion in the case of potassium mercurinitrite, (J.C.S. 1912, 101, 965).

With the idea of attempting to correlate and compare the extent of complex ion formation in such a series of double salts as the alkali sulphate, bivalent metal sulphates under the same conditions of temperature and dilution the following series of results were obtained.

Experimental.

The salts used in this work were all purified by recrystallisation, and the double salts were prepared by crystallisation from solutions containing equivalent proportions of the components. Average samples were tested for purity by determining the sulphate content.

The determinations of conductivity were made in the ordinary way, according to Kohlrausch, using a telephone and alternating current. The bridge was one meter long with movable tapping contact. The cell, fig.15, consisted of two portions - a hard glass boiling tube and a movable portion in which the electrodes were mounted.

The advantages observed with this type (modified immersion electrodes) were constancy of the cell "constant" - due no doubt to the fact that the electrodes remained rigidly separated by a fixed amount - and efficiency in stirring the contents of the cell.

Specially prepared conductivity water was not used. "Boiled-out" distilled water was stored in a vessel that had been used for the purpose for some considerable time. The supply lasted throughout the series of experiments and at most introduced a small constant error. Trial showed that after standing in the cell for 72 hours the resistance was of the order of 10,000 ohms, a quantity so large as to be negligible in comparison with the resistances measured.

The electrodes were cleansed in acid and alkali and were plated in the normal way by repeatedly reversing a current through a chloroplatinate solution. After thorough cleaning, the cell was standardised by means of N/50 potassium chloride solution, as advised by Kohlrausch. The standardisation was repeated at intervals during the work.

The conductivity cell was immersed in a thermostat at 18·5°C.

Solutions of definite concentrations (checked by analysis) of each of the single and double salts used were made up, and their conductivities obtained. When readings of resistance at point of minimum sound were being taken it was arranged that readings occurred as far from the centre point of bridge as possible, and duplicates first on one side and then on the other side of the centre point were also noted in an effort to cut out small irregularities in the bridge wire.

The actual results obtained will be found in Appendix I. To enable a comparison of results to be made these figures were graphed and the smoothest possible curve was drawn through the points - subsequently results were read off the graph for incorporation in the tables of results that follow.

The applicability of the method of summing conductivities was tested for a case in which it was assumed no double salt formed. For this the conductivities of solutions containing equivalent proportions of copper and zinc sulphates were determined and results obtained were treated in the same way as used for the other salts.

Results

Analytical

Salt	Sulphate per cent	
	Found	Theory
$CuSO_4.5\ H_2O$	38·40	38·48
$ZnSO_4.7\ H_2O$	A.R. Sample	
$CoSO_4.7\ H_2O$	34·21	34·17
$Ni\ SO_4.7\ H_2O$	34·11	34·20
K_2SO_4	55·06	55·13
$(NH_4)_2\ SO_4$	72·62	72·73
$CuSO_4\ K_2SO_4.6\ H_2O$	Not done. They had been used previously.	
$CuSO_4.(NH_4)_2SO_4.6\ H_2O$		
$NiSO_4.K_2SO_4.6\ H_2O$	43·88	43·95
$NiSO_4.(NH_4)_2SO_4.\ 6\ H_2O$	48·68	48·64
$CoSO_4.K_2SO_4.\ 6\ H_2O$	43·85	43·92
$Co\ SO_4.(NH_4)_2\ SO_4.6\ H_2O$	48·55	48·61
$ZnSO_4.K_2SO_4.\ 6\ H_2O$	43·10	43·17
$Zn\ SO_4.(NH_4)_2.SO_4\ 6\ H_2O$	47·62	47·72

Results (contd).

Conductivities of Single Salts at 18·5°C (from smooth curves)

Dilution V in litres	Equivalent Conductivity					
	K	Am.	Ni	Co	Zu	Cu
1	79·5	77·0	26·7	26·5	27·3	27·0
1·5	85·0	83·1	31·2	30·7	31·6	31·0
2	88·9	87·5	34·3	33·8	35·0	34·4
2·5	91·7	90·7	36·8	36·1	37·4	37·0
3	94·4	93·4	38·9	38·3	39·7	39·4
3·5	96·6	95·5	40·8	40·2	41·8	41·2
4	98·5	97·3	42·3	41·9	43·5	43·0
5	101·3	100·3	44·8	44·4	46·3	45·7
6	103·5	102·6	46·8	46·4	48·2	47·8
7	105·1	104·2	48·3	48·1	49·6	49·2
8	106·4	105·4	49·7	49·5	51·1	50·6
9	107·2	106·3	50·9	50·7	52·2	51·7
10	108·0	107·1	52·0	51·8	53·5	52·8

Where K = K_2SO_4 Ni = $NiSO_4$ 7 H_2O Zn = $ZnSO_4$ 7 H_2O
Am = $(NH_4)_2SO_4$ Co = $CoSO_4$ 7 H_2O Cu = $CuSO_4$ 5 H_2O

Results (contd).

Conductivities of Double Salts at 18·5°C. (From smooth curve)

Dilution V in litres per Equiv.	$NiSO_4.K_2SO_4.6H_2O$				$NiSO_4.(NH_4)_2SO_4.6\,H_2O$			
	Equiv. Cond.		Diff.	Diff.	Equiv. Cond.		Diff.	Diff.
	Obs.	Calc.	A	P.	Obs.	Calc.	A	P
1	---	---	---	---	50·0	51·9	+1·9	+3·7
1·5	56·0	58·1	+2·1	+3·6	55·5	57·2	+1·7	+3·0
2	59·2	61·6	+2·4	+3·9	59·2	60·9	+1·7	+2·8
2·5	62·5	64·3	+1·8	+2·8	62·0	63·8	+1·8	+2·8
3	65·0	66·7	+1·7	+2·6	64·3	66·2	+1·9	+2·9
3·5	67·0	68·7	+1·7	+2·5	66·3	68·2	+1·9	+2·8
4	69·0	70·4	+1·4	+2·0	68·0	69·8	+1·8	+2·6
5	72·0	73·1	+1·1	+1·5	71·0	72·6	+1·6	+2·2
6	74·5	75·2	+0·7	+0·9	73·3	74·7	+1·4	+1·9
7	76·5	76·7	+0·2	+0·3	75·1	76·3	+1·2	+1·6
8	77·9	78·1	+0·2	+0·3	76·8	77·6	+0·8	+1·0
9	79·0	79·1	+0·1	+0·1	78·2	78·6	+0·4	+0·5
10	80·0	80·0	nil	nil	79·5	79·6	+0·1	+0·1

In this and following tables the equivalent weight of a double salt is taken as $\frac{\text{Mol. Wt}}{4}$

Diff. A is calculated value - observed value.

Diff. P is $\frac{\text{Diff.A} \times 100}{\text{Calculated value}}$

Results (contd).

Conductivities of Double Salts at 18·5°C (from smooth curve).

Dilution V in litres per Equiv.	$CoSO_4.K_2SO_4.6\ H_2O$				$CoSO_4.(NH_4)_2\ SO_4\ 6\ H_2O$			
	Equiv. Cond.		Diff.	Diff.	Equiv. Cond.		Diff.	Diff.
	Obs.	Calc.	A	P	Obs.	Calc.	A	P
1.	49·0	53·0	+4·0	+7·6	50·0	51·8	+1·8	+3·5
1·5	55·0	57·9	+2·9	+5·0	55·0	56·9	+1·9	+ 3·3
2	59·0	61·4	+2·4	+3·9	59·0	60·7	+1·7	+2·8
2·5	62·0	63·9	+1·9	+3·0	62·0	63·4	+1·4	+2·2
3	64·7	66·4	+1·7	+2·6	64·5	65·9	+1·4	+2·1
3·5	67·0	68·4	+1·4	+2·0	66·6	67·9	+1·3	+1·9
4	68·7	70·2	+1·5	+2·1	68·5	69·6	+1·1	+1·6
5	71·5	72·9	+1·4	+1·9	71·5	72·4	+0·9	+1·2
6	73·7	75·0	+1·3	+1·8	73·6	74·5	+0·9	+1·2
7	75·5	76·6	+1·1	+1·4	75·5	76·2	+0·7	+0·9
8	77·1	78·0	+0·9	+1·2	77·2	77·5	+0·3	+0·4
9	78·6	79·0	+0·4	+0·5	78·7	78·5	-0·2	-0·3
10	79·9	79·9	nil	nil	80·0	80·0	-0·5	-0·6

Results (contd).

Conductivities of Double Salts at 18·5°C (from smooth curve)

Dilution V in litres per Equiv.	$ZnSO_4.K_2SO_4$ 6 H_2O				$Zn\ SO_4\ (NH_4)_2SO_4$ 6 H_2O			
	Equiv. Cond.		Diff.	Diff.	Equiv. Cond.		Diff.	Diff.
	Obs.	Calc.	A	P	Obs.	Calc.	A	P
1	50·5	53·4	+2·9	+5·4	50·5	52·2	+1·7	+3·3
1·5	56·6	58·3	+1·7	+2·9	56·0	57·4	+1·4	+2·4
2	60·5	62·0	+1·5	+2·4	59·5	61·3	+1·8	+2·9
2·5	63·8	64·6	+0·8	+1·2	62·5	64·1	+1·6	+2·5
3	66·5	67·1	+0·6	+0·9	65·0	66·6	+1·6	+2·4
3·5	68·5	69·2	+0·7	+1·0	67·0	68·7	+1·7	+2·5
4	70·5	71·0	+0·5	+0·7	68·5	70·4	+1·9	+2·7
5	73·4	73·8	+0·4	+0·5	71·5	73·3	+1·8	+2·5
6	75·7	75·9	+0·2	+0·3	73·5	75·4	+1·9	+2·5
7	77·5	77·4	-0·1	-0·1	75·0	76·9	+1·9	+2·5
8	78·8	78·8	nil	nil	76·5	78·3	+1·8	+2·3
9	80·0	79·7	-0·3	-0·4	78·0	79·3	+1·3	+1·6
10	81·0	80·8	-0·2	-0·2	79·5	80·3	+0·8	+1·0

Results (contd)

Conductivities of Double Salts at 18·5°C. (from smooth curve)

Dilution V in litres per Equiv.	$CuSO_4.K_2SO_4.\ 6\ H_2O$ Equiv. Cond. Obs.	Calc.	Diff. A	Diff P	$CuSO_4(NH_4)_2SO_4.6\ H_2O$ Equiv. Cond. Obs.	Calc.	Diff. A	Diff. P
1	48·5	53·3	+4·8	+9·0	50·0	52·0	+2·0	+3·8
1·5	54·0	58·0	+4·0	+6·9	55·0	57·1	+2·1	+3·7
2	57·5	61·7	+4·2	+6·8	58·5	61·0	+2·5	+4·1
2·5	60·5	64·4	+3·9	+6·1	61·2	63·9	+2·7	+4·2
3	62·5	66·9	+4·4	+6·6	63·7	66·4	+2·7	+4·1
3·5	64·3	68·9	+4·6	+6·7	66·0	68·4	+2·4	+3·5
4	66·0	70·8	+4·8	+6·8	67·5	70·2	+2·7	+3·8
5	68·0	73·5	+5·5	+7·5	70·0	73·0	+3·0	+4·1
6	69·5	75·7	+6·2	+8·2	72·0	75·2	+3·2	+4·3
7	71·0	77·2	+6·2	+8·0	73·5	76·7	+3·2	+4·2
8	72·0	78·5	+6·5	+8·3	74·7	78·0	+3·3	+4·2
9	73·0	79·5	+6·5	+8·2	76·0	79·0	+3·0	+3·8
10	74·0	80·4	+6·4	+8·0	77·2	80·0	+2·8	+3·5

Results (contd).

Conductivities of Mixtures of Copper Sulphate and Zinc Sulphate at 18·5°C. (From smooth curve).

Dilution V in litres containing ½ equiv. each of $ZnSO_4$ and $CuSO_4$	Mixture $ZnSO_4$ and $CuSO_4$			
	Conductivity		Diff. A	Diff. P
	Obs.	Calc.		
1	27·0	27·2	+ 0·2	+ 0·7
1·5	31·0	31·3	+ 0·3	+ 1·0
2	34·5	34·7	+ 0·2	+ 0·6
2·5	37·0	37·2	+ 0·2	+ 0·5
3	39·5	39·6	+ 0·1	+ 0·3
3·5	41·5	41·5	nil	nil
4	43·5	43·3	- 0·2	- 0·5
5	46·0	46·0	nil	nil
6	47·9	48·0	+ 0·1	+ 0·2
7	49·6	49·4	- 0·2	- 0·4
8	50·9	50·9	nil	nil
9	51·9	52·0	+ 0·1	+ 0·2
10	53·0	53·2	+ 0·2	+ 0·4

Conclusions.

From the results obtained it is possible to draw one or two interesting conclusions:-

(1) In the case of a mixture of two salts with a common ion and incapable of double salt formation it is possible to calculate the conductivity of an equimolecular mixture with a fair degree of accuracy using, for want of any better method, the mean of the conductivities of the components.

(2) In the case of the double salt solutions:

(a) From the results obtained, and in view of (1) above, it appears that all the salts examined do exist in solution, over a small range of dilution, as complexes.

(b) Of all the differences observed those in the cases of the copper salts are notably outstanding, and seem to offer one more example of the exceptional behaviour of copper in this interesting series.

It has been suggested that these conclusions do not necessarily follow from the results obtained. It must be granted that the choice of two salts of the same ionic type - copper sulphate and zinc sulphate - does not furnish a strict test of the method of summing conductivities, especially as the satisfactory agreement noted is assumed to be possible of attainment in a mixture of different ionic types where double salt does not form. This difficulty is a very real one which it is impossible to discuss satisfactorily.

If the conclusions reached in numerous phase rule studies of systems containing mixtures of univalent and bivalent metal sulphates are taken into account it would seem to be difficult to choose a test mixture in which double salt (complex ion) formation is impossible - and yet on a study of the conductivity of such a mixture the value of the above results depends.

Lewis and Randall (thermodynamics 1923, p. 319) discuss the question of the conductivity of strong electrolytes (at concentrations beyond those in which the salts may be assumed to be completely dissociated), and indicate the difficulties that lie in the way of any theoretical interpretation based on conductivity data alone. Recent work seems to show that the original assumption of Kohlrausch, viz., that the mobility of an ion is independent of its concentration - can no longer be taken as valid. This fact taken in conjunction with Lewis' demonstration (loc. cit.) of the differences between ionic concentrations calculated from conductivity data and those calculated from electromotive force measurements tends to make any calculation (based on the behaviour of single salt solutions) of the theoretical conductivity of a mixture of salts purely of academic interest - especially as the values required would have to run up into concentrations that for the time being are well beyond those for which even empirical dilution laws can be made to hold.

In the face of the difficulties both practical and theoretical it might be better to refrain from drawing conclusions from the results obtained and to leave them as a record of work done.

APPENDIX I

Conductivity figures (as measured)

Conductivities of Single Salts at 18·5°C.

K_2SO_4

Dilution V in litres.	Equiv. Cond.
0·980	78·5
1·43	84·8
1·95	88·3
2·83	93·4
3·86	98·2
5·60	102·8
7·69	105·9
11·18	108·8

$(NH_4)_2SO_4$

Dilution V in litres.	Equiv. Cond.
0·960	75·5
1·43	83·0
1·92	86·7
2·85	92·3
3·82	96·6
5·65	102·0
7·55	104·8
11·20	107·8

$NiSO_4$

Dilution V in litres	Equiv. Cond.
1·000	26·7
1·49	31·0
1·99	34·3
2·95	38·7
3·93	42·2
5·90	46·7
7·80	49·3
11·75	53·6

$CoSO_4$

Dilution V in litres	Equiv. Cond.
0·990	26·5
1·48	30·5
1·98	34·0
2·94	38·1
3·95	42·1
5·93	46·3
7·85	49·1
11·80	53·5

Conductivities of Single Salts at 18·5°C. (contd).

Zn SO_4

Dilution V in litres.	Equiv. Cond.
1·00	27·3
1·49	31·4
1·99	35·0
2·96	39·9
3·95	41·8
5·92	48·0
7·90	51·0
11·79	55·3

Cu SO_4

Dilution V in litres.	Equiv. Cond.
0·985	27·0
1·48	31·0
1·97	34·2
2·95	39·0
3·96	43·0
5·91	47·3
7·93	50·4
11·82	54·4

Conductivities of Double Salts at 18·5°C.

$NiSO_4.K_2SO_4$

Dilution V in litres.	Equiv. Cond.
1·49	56·0
1·99	58·9
2·13	59·7
2·90	64·3
3·95	68·6
4·20	69·4
5·83	74·4
7·81	77·4
8·15	78·3
11·60	80·9

$NiSO_4.(NH_4)_2\ SO_4$

Dilution V in litres	Equiv. Cond.
1·00	50·0
1·50	55·3
1·99	59·4
2·20	60·2
2·95	64·3
4·32	68·7
5·90	73·3
8·50	77·7
11·75	81·4

$CoSO_4.K_2SO_4$

Dilution V in litres.	Equiv. Cond.
1·00	49·0
1·50	55·0
2·10	59·2
2·98	64·5
4·13	68·9
5·93	73·4
8·10	77·0
11·80	81·9

$CoSO_4.(NH_4)_2\ SO_4$

Dilution V. in litres.	Equiv. Cond.
1·00	50·0
1·49	54·8
2·05	59·2
2·95	64·2
4·00	68·5
5·86	73·1
7·95	77·0
11·70	82·0

Conductivities of Double Salts at 18·5°C. (contd).

$Zn\ SO_4.K_2SO_4$

Dilution V in litres	Equiv. Cond.
1·00	50·5
1·49	56·5
1·99	60·4
2·95	66·5
3·99	70·7
5·87	75·3
7·90	78·8
11·72	82·5

$Zu\ SO_4.(NH_4)_2SO_4$

Dilution V in litres	Equiv. Cond.
1·00	50·5
1·50	56·0
1·98	59·3
2·97	64·8
3·92	68·5
5·90	73·1
7·81	76·5
11·82	81·7

$Cu\ SO_4.K_2SO_4$

Dilution V in litres.	Equiv. Cond.
1·00	48·5
1·49	53·7
2·02	57·7
2·95	62·5
3·90	65·4
5·86	69·2
7·87	72·1
11·64	75·1

$Cu\ SO_4.(NH_4)_2\ SO_4$

Dilution V in litres.	Equiv. Cond.
0·952	49·4
1·42	54·4
1·90	57·5
2·80	63·1
3·80	66·9
5·71	71·3
7·58	74·4
11·35	78·7

Results (contd).

Conductivities of Mixtures of Copper Sulphate and Zinc Sulphate at 18·5°C. (as measured).

Dilution V in litres containing ½ equiv. each of $ZnSO_4$ and $CuSO_4$.	Conductivity
1·00	27·0
1·49	31·0
1·99	34·6
2·95	39·1
3·97	43·7
5·86	47·5
7·91	50·9
11·60	54·3

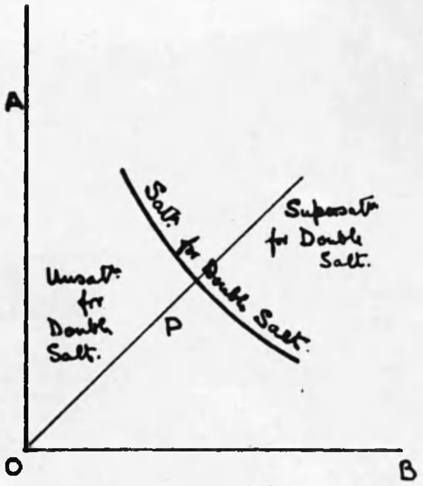

A
Satd. for Double Salt.
Supersatn for Double Salt.
Unsatd. for Double Salt.
P
O
B

Fig 16.

APPENDIX II

Van't Hoff's treatment from "Vorlesungen über Bildung und Spaltung von Doppelsalzen".

Adopting some of his figures and method of presentation we have:

In fig.16

OP bisects the right angle AOB. Curve shows the influence on the solubility of a double salt at a given temperature of varying amounts of two single salts. If the double salt alone is dissolved, or the single salts in equivalent proportions, phenomena are represented along the line OP. Point P represents the solubility of double salt in water at temperature t. The equation for the double salt with ions is represented by the chemical equation

$$2\ Z' + M_1' + M_2' \rightleftharpoons Z_2 M_1 M_2$$

$$\text{e.g. } 2\ SO_4' + K_2^{\cdot\cdot} + Cu^{\cdot\cdot} \rightleftharpoons (SO_4)_2.K_2.Cu.$$

Let C_D represent the molecular concentration of double salt when the solution is saturated, then for the constituent parts

$$M_1 = M_2 = C_D \quad \text{but } Z = 2\ C_D$$

So the ionic product $Z^2 M_1 M_2 = 4\ C_D^4$

$$\text{but } Z = M_1 + M_2 \qquad \text{so } 4C_D^4 = Z^2 M_1 M_2 = (M_1 + M_2)^2 M_1 M_2$$

$$\text{or } M_1 M_2 = \left({}^{2CD}/_{M_1 + M_2}\right)^2$$

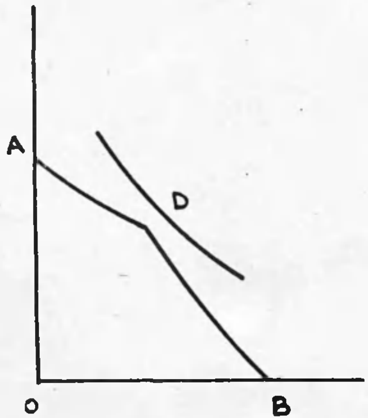


Fig 17.

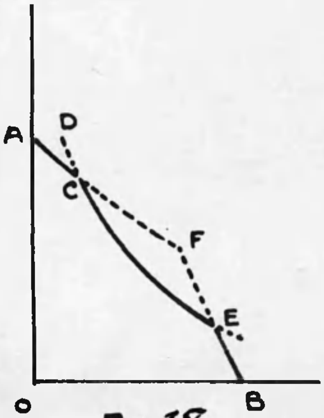


Fig 18

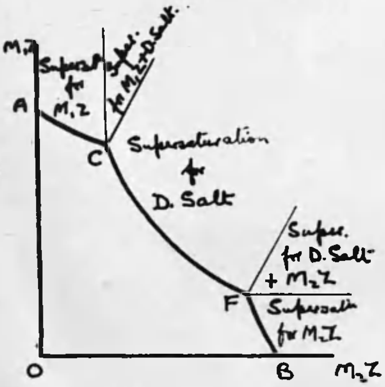


Fig 19.

For the complete curve showing the effect of two single salts in solution capable of giving rise to double salt, we have two cases.

Case I, fig.17.

Solubility curve for double salt lies outside AFB (i.e., the curve showing the mutual effect of two salts with a common ion calculated according to the method of the law of solubility product) and is in the reigon of supersaturation of the single salts. Therefore double salt will split up into single salts yielding crystals of either salt according to previous content of the solution.

Case II, fig.18.

The solubility curve of the double salt passes through the curves for the single salts. Thus the broken curve represents the separation of one salt, double salt and then the other salt on evaporation at constant temperature.

The complete diagram for a system capable of producing double salt at a suitable temperature is shown in fig.19.

A	Saturation	for	M_1Z alone.
AC	"	"	M_1Z with increasing amounts of M_2Z.
C	"	"	M_1Z and double salt so that both salts are present.
CF	"	for	double salt with increasing amounts of M_2Z.

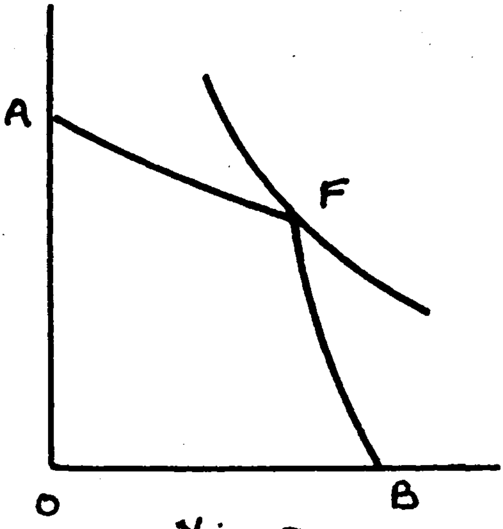


Fig 20.

F Saturation for double salt and M_2Z, both solids present.

FB " " M_2Z with diminishing amounts of M_1Z.

B " " M_2Z alone.

Within OACDB there is general unsaturation.

Transition Temperature.

Figs 17 and 18 illustrate the following conditions. Fig.17 shows a temperature condition in which the double salt cannot exist, but in contact with water splits up into the simple salts.

Fig.18 which may relate to the same double salt at a different temperature shows that this salt can exist in contact with the solution within certain limits of composition of the latter. Between these there is a third case represented by fig.20 which relates to the temperature at which the solubility curve of the double salt in relation to varying amounts of the single salts in solution touches the point of intersection F of the solubility curves of the two simple salts. It must be remembered that all three curves change their positions with changing temperature, therefore for this condition to be realized it is necessary for the position relative to each other of the single salt and the double salt curves to change. Consider what this intersection at F means. At this point the two single salts and the double salt are in equilibrium with the solution. There is thus an

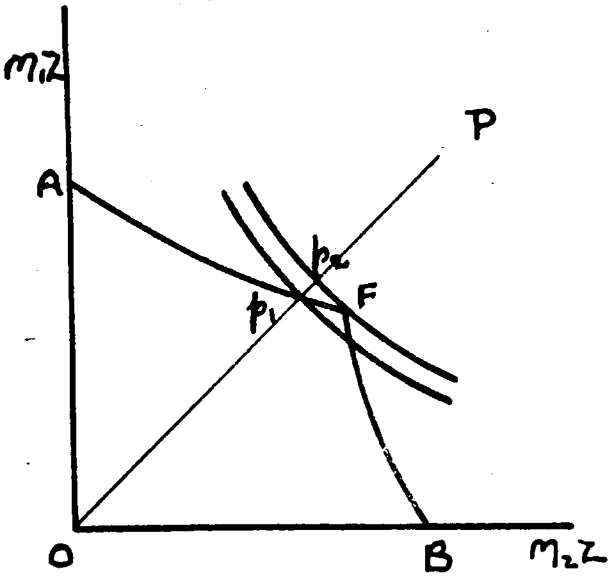


fig 21.

extra phase and the system instead of being univariant becomes invariant. Moreover if the temperature is changed either the double salt or one of the single salts ceases to exist. Thus in traversing this temperature in one direction or the other transformation from single to double or vice versa takes place.

Therefore the temperature at which these curves intersect is called the Transition Temperature.

The conditions for this transition temperature may be expressed by realizing the three conditions which must be fulfilled at F.

Saturation for M_1Z: $C^2_{M_1Z} = M_1 (M_1 + M_2)$

" " M_2Z: $C^2_{M_2Z} = M_2 (M_1 + M_2)$

" " D Salt: $4\ C^4_D = (M_1 + M_2)^2 M_1M_2$

$= C^2_{M_1Z} \cdot C^2_{M_2Z}$

Whence $2\ C^2_D = C_{M_1}\ C_{M_2}.$

Transition Interval.

Let line OP (Fig.21) represent equimolecular proportions of two salts in solution.

Consider points p_1 and p_2. At p_2 corresponding with a certain temperature, the solution is supersaturated with regard to M_1Z which will therefore separate out in the solid state until the proportion between the two salts represented by F is reached. M_2Z then being in solution in excess of M_1Z.

At p_1 the solution is saturated with regard to M_1Z and the double salt but not with regard to M_2Z but since it is not supersaturated with regard to either single salt there is no decomposition of the double salt in contact with the solution. Nevertheless as the temperature rises to that corresponding with the point F the solution will dissolve more of M_2Z until at F it is again in equilibrium with all three salts.

The temperature interval between p_1 and F during which M_2Z is being dissolved is called the Transition Interval. This is the temperature interval between two-solid-phase and three-solid-phase equilibrium, between the points at which the solution is in equilibrium with double salt and one single salt and double salt and two single salts, respectively.

At p_1

Saturation for M_1Z requires $C^2_{M_1Z} = M_1 (M_1 + M_2)$

" " D salt " $4\ C^4_D = M_1M_2 (M_1 + M_2)$

But at p_1 $M_1 = M_2$

$$\therefore\ C^2_{M_1Z} = 2\ M_1^2 \text{ and } 4\ C^4_D = 4\ M_1^4.$$

So $2\ C^2_D = 2\ M_1^2 = C^2_{M_1Z}$

At p_1 $$2\,C_D^2 = C_{M_1Z}^2;$$ At F $$2\,C_D^2 = C_{M_1Z} \cdot C_{M_2Z}$$

So the magnitude of the transition interval depends on the difference between $C_{M_1Z}^2$ and $C_{M_1Z} \cdot C_{M_2Z}$, i.e., upon the difference between C_{M_1Z} and C_{M_2Z} or in other words the difference in solubility of the two salts. This appears directly from consideration of fig.18, for if OA and OB are widely different, the point F will be widely removed from the middle line OP and vice versa.

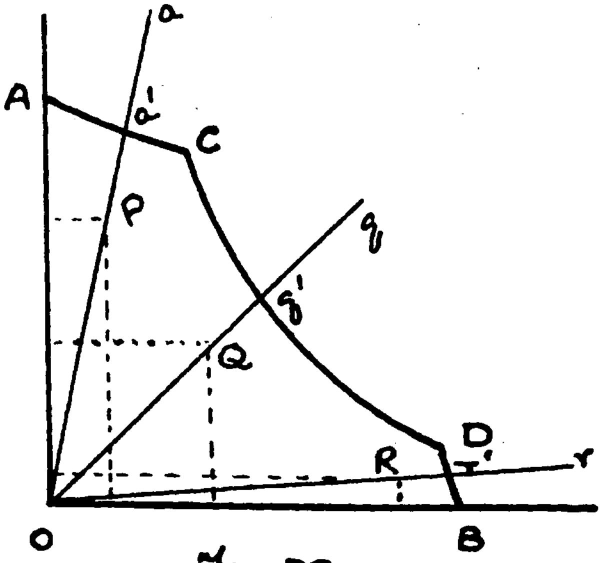


Fig 22.

APPENDIX III

Isothermal Evaporation

As a method for finding roughly the limits of double salt formation and for otherwise gaining an insight into the relations existing in a salt solution the method of isothermal evaporation is decidedly helpful.

From the remarks that have been made on the transition interval it is evident that in a solution of two salts with a common ion continued isothermal evaporation will lead to the separation by crystallisation, depending on the temperature chosen, of either, first one salt and then both salts together, or, separation of one salt followed by the double salt.

If, however, the temperature of evaporation is on that side of the transition point where double salt can form, evaporation of solutions of different initial concentrations, will tell by the nature of the salt separating, the limits of concentrations between which double salt formation is possible.

The discussion will be rendered clearer by reference to the diagram, fig.22, which, however, only deals with the case when double salt can exist, that is, the theoretical second case.

Let there be an unsaturated solution with molecular proportions represented by point P. Evaporation is represented along the line Pa.

At a' the solution becomes saturated and solid begins to separate. If evaporation were now stopped and the product examined definite evidence as to the possibility of double salt formation from the appropriate concentrations denoted by P would be obtained. It was in this way, for instance, that isothermal evaporation was used in the first case, in connection with the copper systems, and again, in the attempt to find a transition point for copper double salts.

If on the other hand evaporation is not stopped at the point where sufficient salt for analysis separates, but is allowed to go on a change takes place. (Note).

The salt concentration in solution alters and with it, eventually, the nature of salt separating is bound to alter, so that with constant deposition of solid the change in solution is represented by movement along the curve in the direction a'C. At C double salt makes its appearance in the solid phase. It can be seen that continued evaporation of any of the solutions P, Q, and R will eventually lead to double salt separation. Theoretically, it is interesting to note what will happen at C and D. Single salt and double salt will continue to deposit by evaporation, i.e., along OC, to dryness, but it is easy to consider another case. Thus in

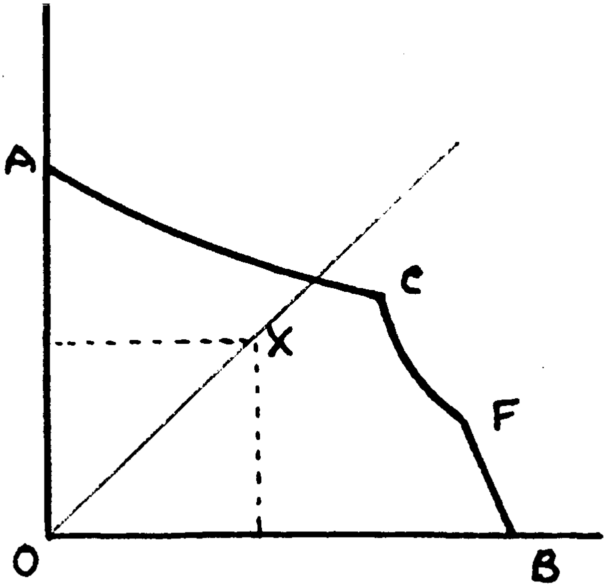


Fig 23

fig.23 we have the case of a double salt which only exists in equilibrium with a solution which contains less than the equivalent proportions of one of the component salts.

Evaporation of solution X (temperature is within the transition interval - case two) will lead to deposition of component A, and the solution will then alter in the direction DC. At C double salt will appear in the solid phase, and the composition of the solution will remain unchanged as long as two solid phases persist. But the solution contains less of component A than is required for the double salt, assuming a salt that contains equimolecular amounts of the two components. Deposition of double salt will lead to a relative decrease of A in the solution, and to counterbalance this, the salt which first separated must redissolve.

The case of evaporation when no double salt can form is simple. Evaporation of a solution must lead to separation of one salt until the point given by the intersection of the solubility curves is reached, when separation of both salts will occur.

(Note. The separation of even a small amount of salt must theoretically result in a slight shift along the solubility curve but if sufficient quantities of solution are used and only qualitative mapping of the field is required no great error is introduced).

APPENDIX IV

The Triangular Diagram

Consideration of the phase rule makes it evident that a system of three components possesses five degrees of freedom and five phases. In dealing with systems of three components, however, it is usual to omit considerations of the vapour phase either as regards composition or pressure. This is done because the equilibria between solids and liquids that have been studied are so little affected by pressure that one can neglect the error resulting from pressure changes.

On the practical side one point requires to be considered, and that is the graphical representation of such systems since the number of variables that can be plotted in a three-dimensional figure is limited.

It was customary to represent isothermal conditions on rectangular axes with ordinates representing molecules of A and abscissae giving molecules of B per 1000 molecules of water respectively. Such a method fails because it is im9 possible to show pure A and B the points for which are then theoretically an infinite distance from the origin.

The triangular diagram was proposed by Gibbs (Trans. Connl Acad. 1876. 3. 176). He made use of the fact that from any point in an equilateral triangle the lines drawn parallel to the respective sides, from any point within the triangle,

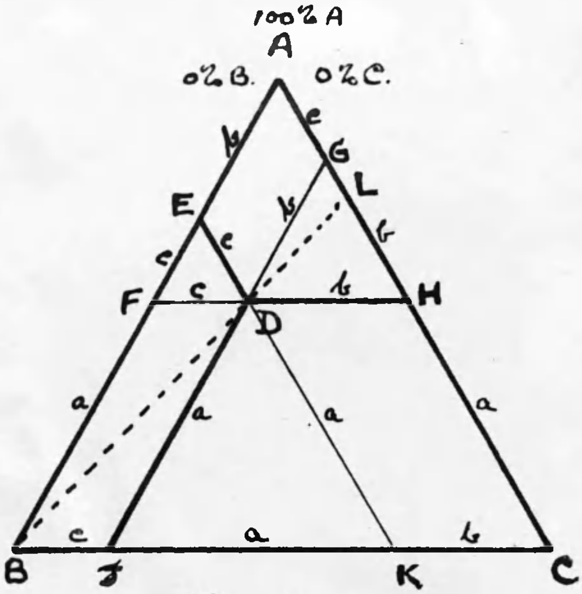


Fig 24.

added together, equal in length each side of the triangle. If then each side is taken as unit length, the composition of any complex may be represented by a point chosen so that the parallels are the same fractions of the unit length as they are of the total quantity of the complex. For convenience the sides are chosen to contain 100 units and the proportions are then plotted as percentages by weight or by molecule.

Fig.24 shows how this is applied.

ABC is an equilateral triangle of side equal to 100 units. If those parallels which pass from any point D within it to the side opposite the angle A, namely, DJ or DK, be taken as the percentage a of component A; those to the sides opposite B and C as the corresponding values, b and c, of components B and C respectively; then it is readily seen at a glance at the various equilateral triangles and parallelograms in the figure that a+b+c equals each of the sides AB, BC ahd CA, or 100 units. Further if D lie on one side instead of inside the triangle, one of the parallels vanishes and a binary mixture is represented. If D coincides with A, B, or C, the corners of the triangle, two parallels vanish, whence it follows that since the corners represent pure substances A, B or C, one or other of the pure substances is,present.

All possible mixtures may thus be shown in this diagram, and the proportions of components may be read off. Thus the

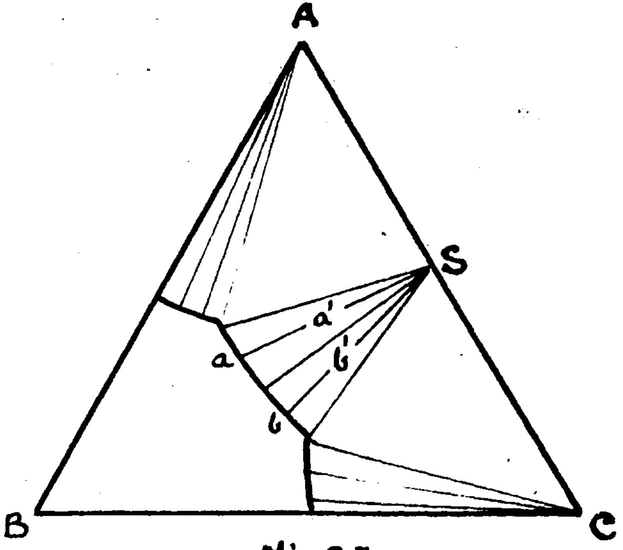


Fig 25

point F is that of a mixture of BF per cent of A and AF of B.

One simple principle of frequent use in dealing with phase systems is that if a mixture X is composed of, or can be resolved into, two other mixtures, or components, Y and Z, the three points representing the three compositions, X, Y and Z, must lie on a straight line, which is termed a conjugation line. Thus a mixture represented by D in figure may be regarded as composed of those given by G and J, respectively, in the proportions DJ/GJ of the former to $DG/_{GJ}$ of the latter. Or, again it may be regarded as composed of pure component B and the mixture L in the proportions LD/LB:DB/LB. Moreover, L in turn is seen to have a composition which may be expressed additively in terms of A and C in the ratio CL/CA:LA/CA.

Use is made of this latter principle to a large extent, as it was used in the systems containing aluminium sulphate, in finding the pure composition of phases separating where it would involve considerable trouble (if it did not altogether vitiate the result) to wash and dry the particular substance.

In Fig.25 a is a solution in equilibrium with a solid phase of unknown composition.

By filtration moist solid, that is solid with solution adhering, is removed at constant temperature. A known weight of moist solid or residue (German - "Rest") is then analysed. Since it is a mixture of the solution a and the pure solid, its composition, represented by a' in figure, must lie somewhere on the straight line connecting those of solution a and pure solid. The more completely the adhering solution has been removed in the filtration, the nearer will a' lie to the pure solid point. The composition of pure solid is somewhere on aa' produced. Similarly it is on bb' produced, and the point of intersection, S, gives at once the composition sought.

If water of crystallisation is part of the solid the point S will be within the triangle.

APPENDIX V

Analytical Methods

Before discussing the methods used in the various analytical processes it is necessary to mention the apparatus used.

All glassware was carefully standardised by weighing with brass weights that had previously been standardised against a standard 20 gm. wt.

Measuring flasks were standardised to contain a definite amount of distilled water while pipettes were always used in one particular manner that had been acquired and used during several years. Burettes were of a well-known German make in which the graduation marks were complete circles to avoid the errors of parallax, and readings were made more accurate by the use of a burette lens.

The gravimetric work consisted mostly of weighing barium sulphate precipitates and of weighing the deposit of silver on a gauze electrode. To facilitate the filtration of the large number of solutions containing precipitates of barium sulphate a platinum Gooch crucible was used in conjunction with a mat of specially prepared asbestos fibre on top of one or two circles of filter paper cut from Whatman No.40 filter circles. The crucible had a cap for fitting on the bottom during ignition.

1. Estimation of Copper.

Throughout the work copper was estimated iodometrically. The method depends on the fact that when potassium iodide is mixed with a copper salt in acetic acid solution cuprous iodide is precipitated and iodine is liberated quantitatively according to the equation

$$2\ Cu\ SO_4 + 4\ KI = Cu_2\ I_2 + 2\ K_2SO_4 + I_2$$

The iodine can then be titrated with standard sodium thiosulphate solution.

The thiosulphate solution was made up as recommended in Treadwell's book on Analysis. It was then standardised against pure electrolytic copper. The method was as follows. The weighed copper foil was dissolved in nitric acid, boiled to expel fumes and neutralised with sodium carbonate solution, sufficient carbonate solution being added to form a faint flocculent precipitate. The precipitate was dissolved in excess acetic acid and a large excess of solid KI freshly dissolved in a small quantity of water was added. The thiosulphate solution was then run in till nearly all the iodine had disappeared when the titration was finished in the usual way in the presence of starch solution. The thiosulphate was checked at frequent intervals throughout the research.

For the solutions examined weighed quantities were made up to known volume in standard flasks and aliquot portions were treated as above. Sodium carbonate was added followed by acetic acid and the procedure was followed through.

For systems containing copper sulphate the accuracy of the iodometric method is very great indeed and most results could be duplicated within one-half to three-quarters of one per cent. Several typical analyses of specially purified copper sulphate are here given.

$Cu\ SO_4 .\ 5\ H_2O$	Cu % Found	25·42
		25·26
		25·36

In the case of the analysis of actual mixtures from equilibrium systems the following are typical results.

Mols $Cu\ SO_4$		Mols. $K_2\ SO_4$	
1·461 1·453	1·457	0·082 0·090	0·086
1·575 1·565	1·570	0·220 0·230	0·225
0·959 0·951	0·955	0·266 0·274	0·270

In all the figures given the accuracy was of the order here noted. It is a pity that closer agreement was not possible between the alkali sulphate results but where these of necessity had to be calculated by difference it was unavoidable that the experimental errors should have more effect on them. The same is true of the copper sulphate, aluminium sulphate system for which a few typical results are given.

The solutions were stirred for 3 days after solid had separated. To show that this was sufficient time in which to estbalish equilibrium portions of a test solution were withdrawn every 24 hours and the copper content was estimated.

<u>Result</u>. At end of 24 hours 9·70 % $Cu\ SO_4$
" " " 48 " 9·75 % "
" " " 72 " 9·79 % "

<u>Solutions</u>

$Al_2(SO_4)_3$		$Cu\ SO_4$	
		20·37 20·29	20·33
2·70 2·80	2·75	18·70 18·60	18·65
13·85 13·74	13·80	12·09 12·17	12·13

2. Estimation of Manganese.

The method that was eventually found most useful for the determinatiom of manganese in all the varying concentrations used depended on the fact that hydrated manganese dioxide is precipitated from aqueous solution containing excess sulphuric acid on addition of ammonium persulphate. The precipitate was filtered off on a Gooch crucible containing a purified asbestos pad, well washed with hot water and crucible and contents were placed in a beaker with standard oxalic acid solution and excess sulphuric acid. On heating, the precipitate dissolved, oxidised some of the oxalic acid and the excess of this substance was then treated with potassium permanganate in the ordinary way. The method was found to be quick and much less troublesome than Volhards.

Estimation of Manganese in $Mn\ SO_4.7\ H_2O$

Mn % Found	19·85
	19·74
	19·65
	19·81

Just as in the case of the copper sulphate system, the manganous sulphate system was tested for the time in which equilibrium was established.

At end of 24 hours	$Mn\ SO_4$	18·73 %
" " " 48 "	"	18·85 %
" " " 72 "	"	18·91 %

Some typical results

$Al_2(SO_4)_3$		$MnSO_4$	
2·44 2·50	2·47	37·99 37·89	37·94
8·39 8·47	8·43	31·49 31·37	31·43
24·36 24·48	24·42	7·44 7.38	7·41

---

3. Estimation of Nickel.

Nickel in the presence of aluminium at first gave considerable trouble but eventually the difficulty was got over and consistent results were obtained.

The method of estimating nickel volumetrically with potassium cyanide is due to Moore (C.N. 1895, 72, 92), and depends on the formation of the complex potassium nickelocyanide in ammoniacal solution. The indicator employed is a suspension of silver iodide which is insoluble in weak ammonia but which is soluble in potassium cyanide solution. The solutions used were:

Standard silver nitrate solution, accurately standardised.

10% potassium iodide solution.

Potassium cyanide solution.

This latter solution is very unstable and required standardising every few days. This standardisation was effected against accurately known silver solution and also against a specimen of a pure nickel salt.

In the case of a solution containing only nickel the following procedure is adopted.

To the nickel solution a little ammonium chloride is added followed by a few drops of ammonia till distinctly alkaline. No precipitate should form. A few drops of iodide solution are added and the whole is diluted to about 150 ccs. A few drops of the silver solution are now added and the solution is stirred to produce a uniform turbidity. The titration with cyanide is then carried out, care being taken to add the cyanide slowly until the turbidity just clears up. The silver solution is then cautiously added until a faint opalescence is produced which can finally be cleared up with less than a whole drop of cyanide solution. The nickel is calculated from the cyanide added less the amount equivalent to that of the silver solution used.

For the solutions under examination it was necessary to keep the aluminium compound in solution during the operations and this can be done effectively with either citric acid or sodium pyrophosphate.

The method finally adopted consisted in adding to the solution sodium pyrophosphate until the precipitate first formed began to redissolve. Excess of concentrated ammonia was then added followed by a small quantity of ammonium chloride, and the solution was nearly neutralised by addition of dilute sulphuric acid, leaving only a faint trace of ammonia. The whole was diluted to 150 ccs and the titration was carried out as above. After adopting this procedure no trouble was experienced by the occurrence of the false end points noted by Sutton (Volumetric Analysis, 1924, p.280).

Estimation of Nickel in "A.R." $NiSO_4$ 7 H_2O

Ni % Found	20·01
	20·23
	20·09

Tests for the period in which equilibrium was established were again carried out.

After	24 hours	12·75	%	Ni SO_4
"	48 "	12·87	%	"
"	72 "	12·91	%	"

Typical Analytical Results.

$Al_2 (SO_4)_3$		$Ni SO_4$	
5·26	5·29	26 08	26·03
5·32		25 98	
15·33	15·29	17·59	17·53
15·25		17·47	

4. Estimation of Silver.

Silver in the presence of aluminium was estimated by electrolysis of the double cyanide. It was found that silver chloride is soluble in aluminium chloride solution on boiling, and this precipitation method could not then be safely used. The addition of potassium cyanide caused slight precipitation of aluminium hydroxide but repeated determinations showed that no inaccuracy was caused by this. After the extraction of the silver by the ordinary rotating cathode the cyanide was destroyed by boiling with sulphuric acid when the aluminium could be determined by precipitation as hydroxide.

Silver in $Ag_2 SO_4$.

Found 69·02 % Ag
68·65. % "
68·79 % "

Test of Equilibrium period

After	24 hours	0·0300 mols.	Ag_2SO_4
"	48 hours	0·0303 "	" "
"	72 hours	0·0304 "	" "

Some typical results

Ag_2SO_4		$Al_2(SO_4)_3$	
0·0290 0·0294	0·0292	0·0781 0·0773	0·0777
0·0304 0·0308	0·0306	0·5127 0·5101	0·5114
0·0313 0·0315	0·0314	1·272 1·280	1·276

APPENDIX VI

Bibliography

The following list contains the titles of most of the original papers mentioned in the text.

General

MORGAN. "Die Bestimmung von Cyanionen auf electrometrischem Wege." (Z. physikal. Chem. 1895, 17. 513).

OSTWALD. "Zur Dissociationstheorie der Electrolyte". (Z. physikal. Chem. 1889, 3, 596).

NERNST. "Uber gegenseitige Beeinflussung der Löslichkeit von Salzen". (Z. physikal. Chem. 1889, 4.372).

NOYES. "Uber die gegenseitige Beeinflussung der Löslichkeit von dissociierten Körpern". (Z. physikal. Chem. 1890. 6. 241).

ABEGG and BÖDLANDER. "Elektroaffinität und Komplexbildung". (Z. anorg. Chem. 1899, 20, 471).

ABEGG "Die Valenz und das periodischen System. Versuch einer Theorie der Molekularverbindungen". (Z. anorg. Chem. 1904, 39. 333).

KENDALL, DAVIDSON and ADLER "Prediction of solution in Polar Solutions". (J.A.C.S. 1921, 43, 1490).

VEGARD and SCHJELDERUP. "Constitution of the Alums". (Ann. Physik. 1917 [ii] 54, 146).

RETGERS. "Das specifisch gewicht isomorpher Mischungen". (Z. physikal. Chem. 1889, 3, 497).

KENDALL CRITTENDEN and MILLER	"Factors influencing compound formation and solubility in fused salt mixtures". (J.A.C.S. 1923, 45, 963).
EPHRAIM and WAGNER	"Uber die Natur der Nebenvalenz". (Ber. 1917, 50, 1103).
BURY	"Langmuir's Theory and the arrangement of electrons in atoms and molecules". (J.A.C.S. 1921, 43, 1602).

Double Salts.

VAN'T HOFF.	"Vorlesungen über Bildung und Spaltung von Doppelsalzen". Leipsig 1897.
BENRATH	"Thallium Double Salts". (Z. anorgan. Chem. 1926, 151, 21).
KOPPEL	"Die Bildung und Löslichkeitsverhältnisse analoger Doppelsalze". (Z. physikal. Chem. 1905, 52, 385).
KLEIN	"Ueber das elektrische Leitungsvermögen von Doppelsalzen". (Weid. Ann. 1886, 27, 151).
JONES and CALDWELL.	"Contributions to the study of Aqueous solutions of Double Salts". (Amer. Chem. Jour. 1901, 25, 349).
LOCKE.	"The solubility of double sulphates of the formula $M^{I}_2.M''(SO_4)_2.6H_2O$. (Amer. Chem. Jour. 1902. 27. 459).
FOOTE and WALDEN.	"The formation of Double Salts". (J.A.C.S. 1911. 33. 1032).
SCHREINEMAKERS and de BAAT.	"Gleichgewicht in quaternären Systemen." (Z. physikal. Chem. 1909. 66. 693).
MACGREGOR	"Calculation of the ionisation in a solution of two salts with a common ion". (T. Nov. Scot. Inst. Sci. 1895, 9. 191).

RIEGER "Determination of the constitution of complex salts by Electrolytic Transference." (Z. Elektrochem. 1901. 7. 863; 871).

FORBES "The solubility of silver chloride in chloride solutions and the existence of complex argentichloride solutions". (J.A.C.S. 1911. 33. 1937).

BRITTON and ALLMAND. "The system potassium sulphate, glucinum sulphate, water at 25°C. (J.C.S. 1921, 119. 1463).

BRITTON "The system potassium sulphate, aluminium sulphate, water at 25°C. (J.C.S. 1922, 121. 982).

LIPSCOMBE and HULETT. "A study of Double Salts in standard cells". (J. physical Chem. 1916. 20. 75).

TUTTON "Crystalline Form and Chemical Constitution" (Macmillan and Co.) 1926, p.109 et seq.

PFANHAUSER "Electrochemical behaviour of nickel ammonium sulphate." (Z. elektorchem. 1901. 7. 698).

RUDORFF "Ueber die Löslichkeit von Salzegemischen". (Pogg. Ann. 1873, 148. 456).

TREVOR "Uber die Lösungen von Doppelsalzen". (Z. physikal. Chem. 1891. 7. 468).

CAVEN and MITCHELL. "The systems copper sulphate, potassium sulphate, water, and copper sulphate ammonium sulphate, water at 25°, 51° and 61°C. (J.C.S. 1924, 125. 1428).

CAVEN and FERGUSON. "The dissociation pressures of hydrated Double Salts. Part I. Hydrated cupric alkali sulphates." (J.C.S. 1922, 121. 1406).

CAVEN, FERGUSON and MITCHELL. "The formation and constitution of certain Double Salts." (J. Roy. Tech. Coll. 1924, 1. 10).

MEERBURG	"The ternary system potassium sulphate, copper sulphate, water below 50°C." (Gedenkboek aangeboden aan J.M.van Bemmelen 1910. 336).
ENGEL	"Sur la solubilité du sulfate du cuivre en présence du sulfate ammonique". (Compt. rend. 1886. <u>102</u>. 113).
ROUYER	"Ebullioscopic Researches". (Compt. rend. 1926, <u>183</u>. 46).
WIRTH	"The crystallisation of pure aluminium salts from solutions containing iron and the artificial preparation of halotrichite". (Z. angew. Chem. 1913. <u>26</u>. 81).
CAVEN and MITCHELL.	"Studies of equilibrium in systems of the type $Al_2(SO_4)_3$ - $M''SO_4$ - H_2O. PART I. Aluminium sulphate, copper sulphate, water, and aluminium sulphate, manganous sulphate water. (J.C.S. 1925. <u>127</u>. 527). PART II. Aluminium sulphate, nickel sulphate, water. (J.C.S. 1925. <u>127</u>. 2549).
OCCLESHAW.	"Equilibrium in the systems aluminium sulphate, copper sulphate, water, and aluminium sulphate, ferrous sulphate, water. (J.C.S. 1925. <u>127</u>. 2598).
KERN.	"On the double sulphate of silver and aluminium". (Chem. News. 1875, <u>31</u>. 209).
CHURCH and NORTHCOTE.	"Silver Alum". (Chem. News. 1864, <u>9</u>. 155).
CAVEN and MITCHELL.	"The system aluminium sulphate, silver sulphate, water at 30°C." (J.C.S. 1925. <u>127</u>, 2550).

BARRE	"Sur les solubilités du sulfate d'argent dans les sulfates alcalins". (Ann. Chim. Phys. 1911. (8).24; 149; 202; 210). (Compt. rend. 1910. 150. 1321).
BAUD	"Sur les combinaisons du chlorure d'aluminium avec les chlorures alcalins". (Compt. rend. 1901. 133. 869). (Ann. Chim. Phys. 1904. (8). 1. 8).
RÂY and DHAR.	"The molecular conductivities of potassium nitrite, mercuric nitrite, and potassium mercurinitrite". (J.C.S. 1912. 101. 965).

Analytical.

MOORE.	"Volumetric estimation of nickel". (Chem. News. 1895, 72. 92).
KNORRE	"A new process for the estimation of manganese". (Z. angew. Chem. 1901. 14. 1149).
