480. *The Basic Aluminium Sulphates.*

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The present investigation has followed more or less conventional phase-rule methods so far as the less basic compounds are concerned. The more basic compounds are so insoluble that their study had to depend much more upon finding satisfactory methods by which they could be prepared. Having found such methods it has been possible to examine their mutual relations and to determine, at least qualitatively, their regions of existence in the phase-rule diagram of the system Al_2O_3–SO_3–H_2O.

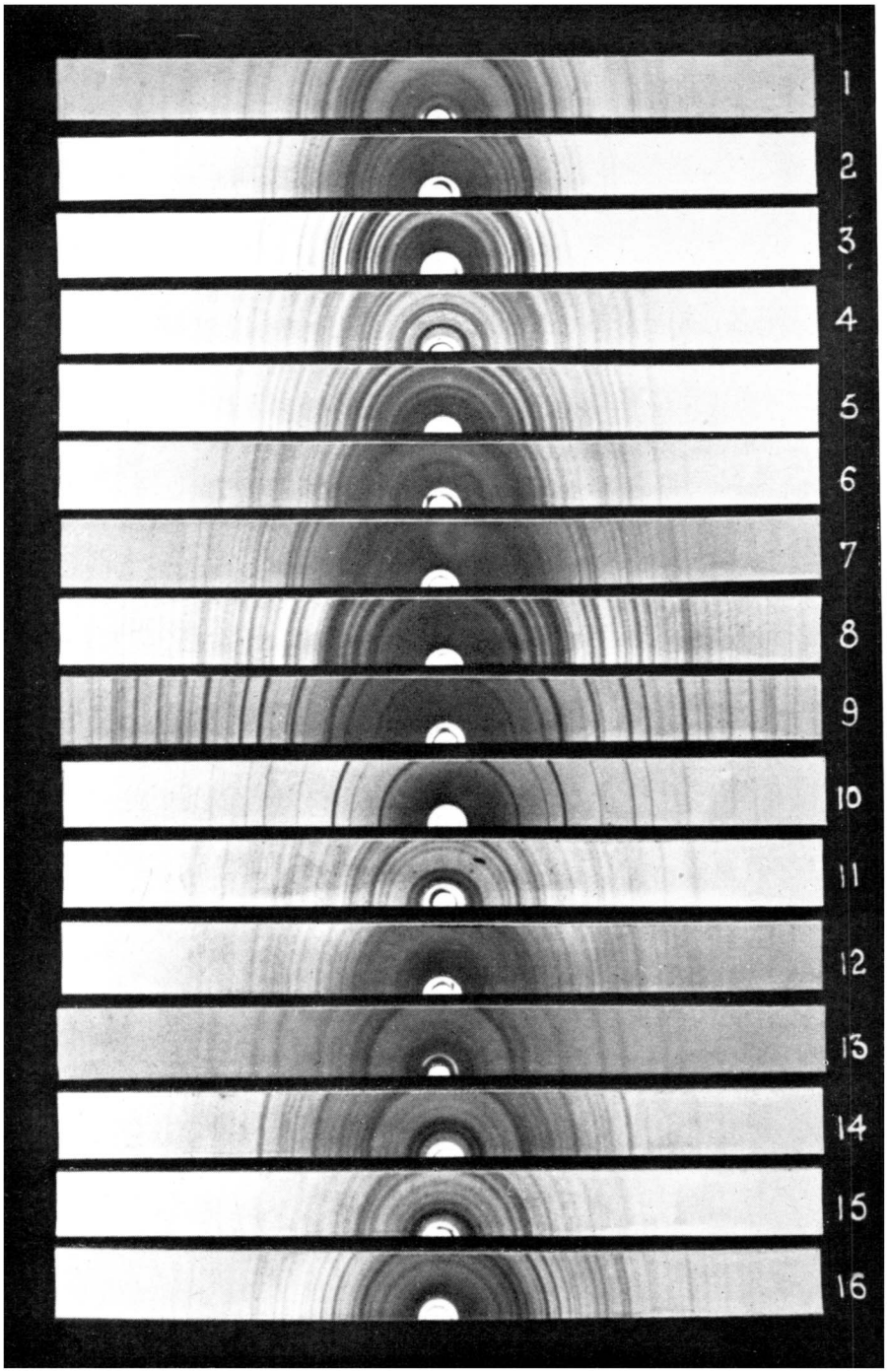
So far as the three-component system is concerned, the stable fields of existence of the more basic compounds are crowded into a very small space in the neighbourhood of the water point. It is clear that complex ionic, molecular, and micellar equilibria exist involving the numerous basic sulphates. The positions of these equilibria can be altered by change of temperature and are then readjusted only slowly, so that solutions can be obtained which have the same composition but yield different compounds. The system contains a great variety of phases. There are, besides $Al_2(SO_4)_3.16H_2O$, at least eight well-defined crystalline basic sulphates, most of which occur in more than one state of hydration.

In addition to these crystalline compounds, there are two quite different sets of two-liquid systems. Both of these form rough ellipses when plotted in an isothermal of the Al_2O_3–SO_3–H_2O system. Two-liquid system I is found in a relatively weakly basic region of the three-component system, and the second liquid phase occurs in the form of glassy discs or spheres.

Two-liquid system II occurs in the very basic region of the three-component system. Its second liquid phase constitutes the so called " hydroxide " precipitates obtained from sulphate solutions with ammonia and the gels thrown down from hydroxide sols with sulphate ions. The recognition of the liquid nature of " hydroxide precipitates " appears to be of some importance.

Two well-defined and well-crystallised basic double salts have been obtained. These are $(NH_4)_2SO_4,[11Al_2O_3,6SO_3,xH_2O]$ and $6(NH_4)_2SO_4,[11Al_2O_3,6SO_3,xH_2O]$. The " alunites," another group of basic double salts, are also important in connection with the system Al_2O_3–SO_3–H_2O. These compounds are usually given the formula $M^I[Al_3(OH)_6](SO_4)_2$, but such varied types of substitution are possible in the crystal lattice that the composition can differ greatly from that required by the conventional formula. Alunites can exist which contain only Al_2O_3, SO_3, and H_2O.

The *X*-ray diagrams of all the compounds obtained during the investigation have been examined, as have those of a number of minerals reputed to be basic aluminium sulphates. The only basic aluminium sulphate minerals (other than the alunites) which are really well-defined compounds are " aluminite " $Al_2O_3,SO_3,9H_2O$, and a new mineral $2Al_2O_3,SO_3,xH_2O$, which occurs in two different stages of hydration (Bannister and Hollingworth, *Nature*, 1948, **162**, 565). The less hydrated form with x about 10 has been called " basaluminite "; the other, with x of the order of 30, has been distinguished by the name " hydrobasaluminite." These three minerals have perfectly distinct and characteristic *X*-ray spectra but, for some reason, all our efforts to prepare them synthetically have failed. Two of the other supposed basic aluminium sulphate minerals examined by us gave " alunite " *X*-ray diagrams. All these minerals appear to need re-examination. The *X*-ray diagrams of aluminium sulphate and of all the basic sulphates dealt with in this paper are shown on the plate. Measurements of the spacings and intensities of their lines are recorded in the appendix.



Key to Plate.

X-Ray powder diagrams of :

(1) $Al_2(SO_4)_3,16H_2O$, *alunogen from Chile*.
(2) $Al_2O_3,2SO_3,11H_2O$.
(3) $5Al_2O_3,6SO_3,46H_2O$.
(4) $5Al_2O_3,6SO_3,40H_2O$.
(5) $Al_2O_3,SO_3,9H_2O$ (*aluminite*).
(6) $Al_2O_3,SO_3,6{\cdot}78H_2O$.
(7) $Al_2O_3,SO_3,5H_2O$.
(8) $Al_2O_3,SO_3,4H_2O$.
(9) *Australian alunite*.
(10) *Synthetic ammonium alunite* (1 *of Table IIA*).
(11) $2Al_2O_3,SO_3,xH_2O$ (*basaluminite*).
(12) $5Al_2O_3,3SO_3,xH_2O$.
(13) $11Al_2O_3,6SO_3,xH_2O$.
(14) $13Al_2O_3,6SO_3,xH_2O$.
(15) *Basic double salt I*.
(16) *Basic double salt II*.

[*To face p.* 2239.

Compounds discussed in this paper.

Formula.	Compn. of solid, %. Al_2O_3.	SO_3.	Referred to as :	No. of *X*-ray diagram on the plate.
$Al_2O_3,3SO_3,16H_2O$ $[Al_2(SO_4)_3,16H_2O]$	16·19	38·10	Aluminium sulphate	(1)
$Al_2O_3,2SO_3,11H_2O$ [possibly $[Al(OH)(H_2O)_5][SO_4]$]	22·18	34·79	—	(2)
*$5Al_2O_3,6SO_3,46H_2O$	28·05	26·40	—	(3)
*$5Al_2O_3,6SO_3,40H_2O$	29·83	28·07	—	(4)
$Al_2O_3,SO_3,9H_2O$	29·65	23·26	Aluminite	(5)
*$5Al_2O_3,6SO_3,36H_2O$	31·14	29·30	—	(6)
*Al_2O_3,SO_3,xH_2O (x = *ca.* 6·78)	33·56	26·31		
*$Al_2O_3,SO_3,5H_2O$	37·50	29·42	—	(7)
*$Al_2O_3,SO_3,4H_2O$	40·16	31·42	—	(8)
A very wide range of solid solutions (see text)	—	—	The alunites	(9)
derived from the original compound $K[Al_3(OH)_6][SO_4]_2$	—	—	—	(10)
An aqueous and a glassy phase in equilibrium	—	—	Two-liquid system I	—
An aqueous and an amorphous phase in equilibrium	—	—	Two-liquid system II	—
$2Al_2O_3,SO_3,xH_2O$ (x = perhaps 30)	—	—	Hydrobasaluminite	—
$2Al_2O_3,SO_3,yH_2O$ (y = *ca.* 10)	43·96	17·25	Basaluminite	(11)
*$5Al_2O_3,3SO_3,xH_2O$ (x ,, 32)	38·47	18·10	—	(12)
*$7Al_2O_3,3SO_3,xH_2O$ (x ,, 33)	46·13	15·51	—	—
*$11Al_2O_3,6SO_3,xH_2O$ (x ,, 66)	40·22	17·20	—	(13)
*$13Al_2O_3,6SO_3,xH_2O$ (x ,, 83)	40·13	14·54	—	(14)
*$(NH_4)_2SO_4,[11Al_2O_3,6SO_3,xH_2O]$ (x = *ca.* 66)	38·40	19·17	Basic double salt I	(15)
*$6(NH_4)_2SO_4,[11Al_2O_3,6SO_3,xH_2O]$ (x = *ca.* 72)	30·41	26·02	Basic double salt II	(16)
α-$Al_2O_3,3H_2O$	—	—	Bayerite	—
γ-$Al_2O_3,3H_2O$	—	—	Hydrargillite (gibbsite)	—
α-Al_2O_3,H_2O	—	—	Diaspore	—
γ-Al_2O_3,H_2O	—	—	Boehmite	—

* New compounds are denoted by asterisks.

THE introduction in 1936 of a solution of basic aluminium sulphate as a scrubbing agent for the removal of sulphur dioxide from smelter gases (I.C.I. Ltd., B.P. 445,711; Fr. Pat. 796,421) made a phase-rule study of the system Al_2O_3–SO_3–H_2O desirable. This was also needed for a proper understanding of the manufacture of aluminium sulphate and of the setting of cement containing added gypsum.

There are at least five methods by which basic aluminium sulphate solutions may be prepared. They are : (i) Removal of part of the SO_4 radical from aluminium sulphate solutions by means of calcium hydroxide or carbonate. (ii) Dissolution of aluminium hydroxide in solutions of sulphuric acid or aluminium sulphate. (iii) Action of sulphuric acid or aluminium sulphate solutions upon amalgamated aluminium. (iv) Action of sulphuric acid upon clay or shale. (v) Methods involving the intermediate formation of positive sols of aluminium hydroxide.

Method (i) is used technically in the I.C.I. sulphur dioxide recovery process, and methods (ii) and (iv) are used technically for the manufacture of aluminium sulphate; none is suitable for preparing the pure solutions required for an exact phase-rule investigation.

Method (ii) was used by the only previous investigators of the basic region of the system Al_2O_3–SO_3–H_2O (Kremann and Hüttinger, *Jahrb. Geol., Reichsanstalt, Wien*, 1908, **58**, 639; Wirth, *Z. anorg. Chem.*, 1913, **79**, 360). The interaction of the aluminium hydroxide and sulphate is slow and difficult, especially in the more dilute and basic solutions, so although the method enabled Kremann and Hüttinger to prepare the least basic of the basic aluminium sulphates and to determine its solubility curve, it did not give correct indications otherwise (but see p. 2249).

Method (iii) was devised by Mr. A. M. Clark at Billingham, who also carried out a preliminary phase-rule study of the Al_2O_3–SO_3–H_2O system. All his results were available and were of great assistance in starting the fuller survey. This method was employed for preparing practically all the mixtures used in the solubility work to be described. It is easy of application, and mixtures of any desired composition can be prepared over a wide range of composition. It has its limitations, however, and pure crystalline basic aluminium sulphates with an Al_2O_3/SO_3 ratio greater than 1 cannot, as a rule, be prepared by this method (but see p. 2260). The very basic compounds are best prepared by method (v), which has been described by Bassett and Durrant (*J.*, 1942, 277). The ratio Al_2O_3/SO_3 is referred to as R in the following pages.

Preparation of Mixtures for the Phase-rule Work by Method (iii).—It was found better to use sulphuric acid rather than aluminium sulphate since even the " AnalaR " quality of the latter contained traces of ammonium which caused trouble. The requisite amounts of pure aluminium, sulphuric acid of suitable concentration, and water, weighed to the nearest deci- or even centi-gram, together with a small amount of metallic mercury, were placed in a beaker, usually of silica, and counterpoised, so that at the end of the reaction water lost by evaporation could be replaced or, alternatively, more could be driven off. Reaction was started by warming, and when all the aluminium had dissolved the solution was decanted from globules of mercury and filtered on the pump, through asbestos, from a small amount of black, finely dispersed, mercury containing traces of iron. The filtered solutions were either allowed to deposit solid spontaneously or were suitably inoculated with previously obtained solid phase. The mixtures should be prepared of such compositions that solid phase does not start to separate before it has been possible to filter the solutions. This limits the proportion of solid to liquid phase which can be obtained for any one mixture especially in the more basic region. Heating the more basic solutions is liable to cause separation of solid and, when these are being prepared, dissolution of the aluminium should be started by heating and then allowed to proceed to completion without further application of heat.

Time required for Establishment of Equilibrium between Solid Phase and Solution.—Supersaturated solutions of the basic salts may persist for long periods in absence of suitable nuclei. Once the latter have appeared, or been introduced, separation of solid occurs at a rate, roughly proportional to the amount of solid present, which is hastened considerably by shaking. Four months were sometimes needed for the attainment of equilibrium, especially with the more basic mixtures, though a fortnight sufficed with the more acidic ones. Good crystals suitable for single crystal *X*-ray work were obtainable with difficulty and only from solutions allowed to crystallise slowly without stirring. All of the compounds are, however, well crystallised on a microscopic scale.

Methods of Analysis.—The comparatively rapid volumetric method (Craig, *J. Soc. Chem. Ind.*, 1911, **30**, 184), involving titration with standard sodium hydroxide with and without addition of potassium fluoride, which is suitable for purposes of plant control, was found not to be accurate or reliable enough for the present work. Gravimetric methods had to be employed.

It is usually stated in text-books (see, *e.g.*, Vogel, " Quantitative Inorganic Analysis," 1939, 479) that the direct precipitation of sulphate in the presence of aluminium is unsatisfactory and gives low results owing to adsorption of aluminium sulphate by the barium sulphate. On ignition the weight of Al_2O_3 formed from such aluminium sulphate is far less than that of the extra amount of $BaSO_4$ which would have been obtained had no adsorption of aluminium sulphate occurred. Previous separation of the aluminium as hydroxide after double precipitation is advised.

We find, however, that the presence of aluminium does not affect the results if the barium sulphate is precipitated from sufficiently dilute solutions which are not less than 0·2N with respect to free hydrochloric acid. The barium sulphate should, of course, be precipitated slowly with stirring from nearly boiling solutions, and the mixture digested for some hours, and left to cool and stand over-night before filtration. Excellent results are obtained by this procedure, which is not only less troublesome than that involving previous separation of the aluminium, but is also more accurate for, even after a second precipitation, the aluminium hydroxide still retains an appreciable amount of sulphate. The following experiments illustrate the correctness of the above statements.

Five determinations were made of the weight of barium sulphate obtained from 25·06 c.c. of 0·1094N-sulphuric acid. Precipitation as above, using 10 c.c. of approx. N-barium chloride, gave weights of barium sulphate as follows: (i) 10 C.c. approx. 2N-hydrochloric acid, 65 c.c. water: 0·3204 g. (ii) As in (i) but with the addition of 0·35 g. of $AlCl_3.6H_2O$: 0·3201 g. (iii) As in (i) but with 0·036 g. of aluminium dissolved in the hydrochloric acid: 0·3199 g. (iv) As in (i), but 0·19 g. of aluminium dissolved in 20 c.c. of the approx. 2N-acid was added and only 55 c.c. of water: 0·3203 g. (v) Without hydrochloric acid but with 75 c.c. of water: 0·3199 g. The proportion of aluminium to sulphate in (iii) was rather higher than that in $Al_2(SO_4)_3$, while in (iv) it was rather more than that in our most basic compound $7Al_2O_3,3SO_3,xH_2O$.

The average of the five determinations would make the normality of the sulphuric acid 0·1094. By standardisation against $K_2O,5B_2O_3.8H_2O$, the normality was 0·1093. In order to see what variations might be expected in a series of determinations carried out under as nearly as possible identical conditions, four successive lots of 25·06 c.c. of the standard sulphuric acid were withdrawn, and each was diluted to 100 c.c. and precipitated just below the boiling point by means of 10 c.c. of approx. N-barium chloride solution. After precipitation, the mixtures were digested for 3 hours over small flames and then left overnight before filtration. The weights of $BaSO_4$ obtained were 0·3194, 0·3198, 0·3201, 0·3197 g. The average of these weights would make the sulphuric acid 0·10935N.

The variation in the weights of barium sulphate obtained from these sulphuric acid solutions is of the same order as that found in the previous series in which aluminium was also present.

A curious feature of barium sulphate precipitates was noticed to which no previous reference has been found. Small amounts seem to be particularly liable to pass over the tops of filter papers and down the groove of the fold, and this occurs even when the precipitate is quite coarse, as after long-continued digestion of the precipitated mixture. This is not a question of passage *through* the filter paper or of subsequent separation from solution in the filtrate. The only way to avoid it seems to be by taking great care (i) to fit the filter paper very carefully, (ii) to keep the precipitate as near the apex of the filter-paper cone as possible, (iii) not to stir the precipitate on the paper during the washing, and (iv) to wash the rim of the filter paper with great care by letting drops of wash-water fall vertically on to it.

If the filtration and washing are carried out without special precautions, and filtrate and washings are stirred round gently with a glass rod, a small sediment of barium sulphate will be found to collect on the centre of the bottom of the beaker which may amount to 0·0002 g. or, in extreme cases, to 0·001 g.

The following results are instructive and were obtained during a further check of the analytical

methods. The material analysed was the " normal " aluminium sulphate which had been prepared by method (iii) (see p. 2240) and washed with absolute alcohol till quite free from acid and then air-dried. The Al_2O_3 content was 15·96% [Calc. for $Al_2(SO_4)_3,16H_2O$: 16·19%]. A series of determinations of the SO_3 content was made upon approx. 0·3 g. of the solid in each case. Other conditions are stated below. The percentage of SO_3 calculated for $Al_2(SO_4)_3,16H_2O$ is 38·10.

Vol. of 2N-HCl used, c.c.	0	3	6	5	3	10	20	20
Total vol. before addition of $BaCl_2$, c.c.	100	30	30	50	100	100	100	100
Vol. of approx. N-$BaCl_2$ used, c.c.	10	5	5	5	10	5	10	10
SO_3, %, in solid	37·30	37·41	37·21	37·41	37·41	37·53	37·55	37·56

In the last experiment in the above table the mixture after precipitation was digested for 16 hours over a small flame and then left to cool for 2½ hours before filtration. The precipitate could be seen with a pocket lens to be quite coarsely crystalline. In other cases the precipitated mixtures had been left overnight at room temperature, and the precipitates were finer.

In a final experiment using 0·3008 g. of the same aluminium sulphate, the aluminium was precipitated with a small excess of ammonia, the aluminium hydroxide was given several washes, rinsed from the paper, dissolved by digestion with 2 c.c. of concentrated hydrochloric acid, and reprecipitated with ammonia. The second precipitate was washed with 40 c.c. of solution containing 0·8 g. of ammonium chloride. Any sulphate still retained by the alumina was recovered by dissolving the hydroxide with 2 c.c. of concentrated hydrochloric acid, evaporating nearly to dryness, diluting to 50 c.c. and adding 2·5 c.c. of N-barium chloride. 20 C.c. of 2N-hydrochloric acid were added to the aluminium-free filtrates and the mixture precipitated hot with 10 c.c. of N-barium chloride and digested overnight over a small flame. The filtrate from the coarsely crystalline barium sulphate was evaporated to dryness, and the ammonium chloride volatilised; water was added to the residue and an appreciable amount of barium sulphate was recovered which had been kept in solution by the hydrochloric acid and ammonium salts.

The details are :

First wt. of $BaSO_4$ from aluminium-free filtrates (this would correspond to only 37·25% SO_3 in the aluminium sulphate)	0·3268 g.
$BaSO_4$ from sulphate still retained by the aluminium hydroxide	0·0011 g.
$BaSO_4$ obtained after evaporation of filtrate from main lot of $BaSO_4$ and volatilisation of NH_4Cl	0·0022 g.
Deduct for ash of filter papers	0·0003 g.
Total wt. of $BaSO_4$	0·3298 g.

This corresponds to 37·60% of SO_3 in the aluminium sulphate.

The above experiments show that perfectly satisfactory sulphate determinations can be made in presence of large amounts of aluminium salts if a weight of barium sulphate of the order of 0·3 g. is precipitated from a volume of solution of about 100 c.c. containing 10 c.c. of 2N-hydrochloric acid as free acid, using not less than 5 c.c. of N-barium chloride as precipitant (cf. Shu-Chuan Liang and Tze-Wen Ann, *J. Chinese Chem. Soc.*, 1946, **14**, 17; *Brit. Abs. C*, 1948, 4). The figures Al_2O_3, 15·96%; SO_3, 37·60% give $R = 0·333$, which is correct for $Al_2(SO_4)_3$. Aluminium was always determined on a separate portion if possible. It was precipitated in presence of methyl-red with a very small excess of ammonia and the mixture boiled till neutral to the indicator. Thorough washing of the precipitate was not necessary when aluminium was the only non-volatile constituent present, and this saved much time. When thorough washing was needed, as in analyses of alunogen or other minerals, it was essential to do the later part of the washing with a 2% solution of ammonium chloride or nitrate, otherwise serious errors could occur owing to aluminium hydroxide becoming peptised and passing through the filter-paper. The aluminium hydroxide and filter-paper were ignited first over the Bunsen burner until all carbon had been removed and then for an hour in an electric muffle at about 1200°. This ignition at a high temperature is needed for two reasons : (i) to convert the γ-Al_2O_3 into the non-hygroscopic α-Al_2O_3 or corundum form, and (ii) to decompose the last traces of sulphate.

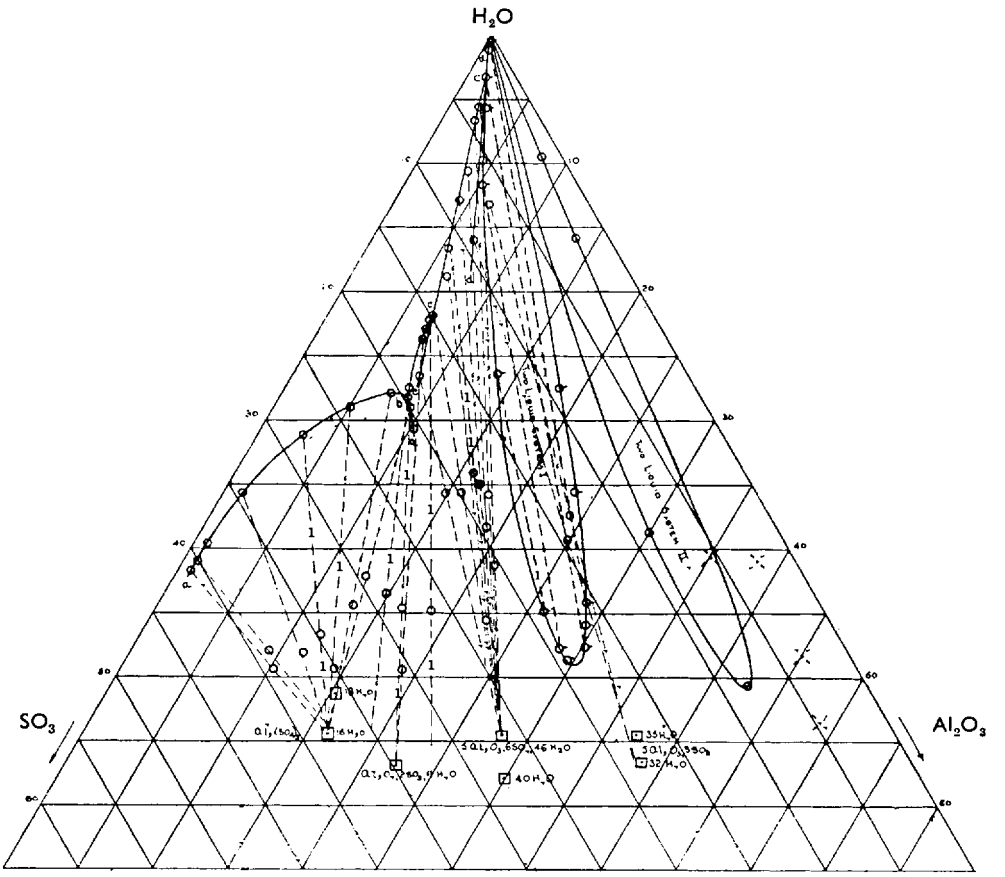
If the alumina remains in the γ-condition it increases in weight so quickly that, even with very rapid weighing, it is difficult to be sure of the correct weight. Quite important errors can be caused by the presence of undecomposed sulphate if the temperature of ignition has not been greater than 800° or 900°. In certain cases owing to shortage of material the sulphate and alumina estimations had to be made on the same sample. It was then essential to precipitate the sulphate first, as above, remove excess of barium as sulphate, and finally precipitate the alumina. If the analysis is done the other way round low results for sulphate are obtained, even after double precipitation of the alumina, as can be seen from the analysis quoted above.

Treatment of Mixtures before Analysis.—The mixtures were placed in either silica or glass tubes closed by waxed corks, the upper part of the tube and the cork being well covered by wax. After the tubes had been shaken at 25° for a sufficient time, solid and solution were separated for analysis through asbestos and a disc of hardened filter paper in a jacketed filter-tube. Solution and " moist solid " were analysed, and in many cases " dry solid " also. The last was obtained from " moist solid " by washing either with water or with alcohol of increasing concentration, and drying at room temperature. Water alone is the best initial wash-liquor for all the basic salts, except the least basic one ($Al_2O_3,2SO_3,11H_2O$) or for $Al_2(SO_4)_3.16H_2O$ which dissolve in cold water, but the minimum amount should be used. In some cases addition of water to the mother-liquor causes a precipitate to form, and in such cases, after removal of the mother-liquor as completely as possible, the wash-water must be added in very small amounts, with the pump full on, so as to ensure that dilution is gradual and that the diluted liquor is

removed before it can deposit any precipitate. When alcohol washing is used the alcohol must be diluted with sufficient water to prevent formation of a precipitate on addition to small amounts of the mother-liquor. The washing is continued with progressively more concentrated alcohol.

All solid phases were examined with the polarising microscope, and *X*-ray powder photographs were taken of all dry solids. The compositions of equilibrium solutions and of the corresponding moist and/or dry solid phases are given in Tables I—VII and shown graphically in Fig. 1. In Tables I and II the compositions of solutions and moist solids are given both as weight and as molecular percentages Molecular percentages are, of course, most suitable if comparisons are to be made with other systems.

FIG. 1.



Key to Fig. 1.

System Al_2O_3–SO_3–H_2O *at* 25°.

Solubility curves of :

$Al_2(SO_4)_3,16H_2O$	*a b a*
$Al_2O_3,2SO_3,11H_2O$	*b c*
$5Al_2O_3,6SO_3,46H_2O$	*c c c*
$5Al_2O_3,3SO_3,xH_2O$	*d c d*

Two-liquid system I

Two-liquid system II

Points given by hydroxide sol curds

They do, however, suffer from the disadvantage that, owing to the small molecular weight of " H_2O," the results for a system such as the present one are unduly crowded up towards the H_2O apex when plotted in a triangular diagram. Weight percentages have been used, for this reason, in plotting Fig. 1.

In the case of solid phases containing combined water it is important to know that the separated dry solid contains the same amount of water as it did when in equilibrium with the saturated solution. In a number of cases the separated solid phases were equilibrated as follows. A light glass bucket containing a weighed amount (0·1—0·2 g.) of air-dried solid phase was suspended above some of the equilibrium solution, contained in a wide glass tube of about 25 c.c. capacity. The bucket was hung on a platinum hook fixed into the waxed cork closing the tube. The upper part of the tube and the cork were thoroughly waxed over and the tube was then placed in a suitable rack and immersed in the thermostat at 25°. The tube was periodically opened after known time intervals and the bucket

transferred to a weighing bottle and weighed. By plotting the various weighings it could easily be seen how the approach to the final equilibrium weight was proceeding. This procedure was found to be very satisfactory and simpler and better than several others which were tried. The pressure of aqueous vapour given off by a hydrated salt is equal to or less than that of its equilibrium solution at a given temperature. If the partially dehydrated salt is exposed over some of the equilibrium solution at this temperature water vapour will be absorbed by the salt until the hydrate has been fully re-formed, the salt then ceasing to increase in weight. Further absorption of moisture will not normally occur in a three-component system, for, even if a slight irregularity of temperature causes momentary condensation on the solid, this cannot dissolve in the condensed moisture to give a solution of the same composition as the equilibrium solution unless the solid is congruent to the particular solution. In all other cases in three-component systems any moisture condensed in this way on the crystals tends to evaporate as soon as the temperature disturbance is over. The method will lead to somewhat high results for the water content of the equilibrated solid if this is finely divided and if there is any marked adsorption of water vapour by the surface of the fully hydrated material. This appears to happen with $Al_2(SO_4)_3,16H_2O$ (see p. 2245).

It would have been very difficult, if not impossible to unravel the complicated relationships existing among the various compounds dealt with in this paper without the assistance given by *X*-ray examination of all solid phases. The *X*-ray diagrams of all the new compounds and a few others are shown in the plate, and tables of the spacings and intensities of the lines in these diagrams are given in the appendix. Similar measurements are also recorded for the alunites of which analytical details are given in Table IIa.

TABLE I.

$Al_2(SO_4)_3,16H_2O$ *and* $Al_2O_3,2SO_3,11H_2O$ *at* 25°.

(*w* = weight %; *m* = molecular %.)

Solution.				Moist solid.				Dry solid.			
Al_2O_3.		SO_3.		Al_2O_3.		SO_3.		Al_2O_3.	SO_3.	Nature of	
w.	*m.*	*w.*	*m.*	*w.*	*m.*	*w.*	*m.*	*w.*	*w.*	solid phase.	Notes.
0·92	0·24	40·98	13·41	10·18	2·93	39·23	14·42	—	—	$Al_2(SO_4)_3,16H_2O$	
0·97	0·25	40·03	13·21	9·13	2·59	38·90	14·04	15·96	37·64	,,	(1), (2)
0·97	0·25	38·90	12·67	—	—	—	—	15·96	37·54	,,	(2)
1·39	0·34	34·39	10·72	11·53	3·28	36·61	13·26	—	—	,,	
3·09	0·72	28·07	8·34	11·96	3·34	34·79	12·39	—	—	,,	
5·20	1·19	23·93	6·98	14·20	4·11	35·22	12·99	—	—	,,	
7·36	1·66	20·55	5·93	13·05	3·55	31·45	10·91	—	—	,,	
7·74	1·75	20·20	5·83	13·49	3·71	32·06	11·27	—	—	,,	
7·71	1·74	20·14	5·80	12·47	3·32	30·14	10·22	16·07	37·82	,,	(1), (2)
8·56	1·94	19·71	5·71	14·80	3·98	28·74	9·86	—	—	$Al_2(SO_4)_3,16H_2O$ and $Al_2O_3,2SO_3,11H_2O$	
9·08	2·08	19·98	5·83	12·86	3·40	29·37	9·92	—	—	$Al_2(SO_4)_3,16H_2O$	(2)
10·15	2·36	20·50	6·09	13·51	3·46	25·82	8·44	—	—	$Al_2(SO_4)_3,16H_2O$ and $Al_2O_3,2SO_3,11H_2O$	(3)
8·62	1·95	19·55	5·66	15·61	4·17	27·30	9·31	22·22	34·95	$Al_2O_3,2SO_3,11H_2O$	(4)
8·48	1·92	19·44	5·61	16·45	4·49	28·15	9·80	—	—	,,	(5)
7·39	1·61	16·40	4·54	—	—	—	—	22·15	34·85	,,	(6)
7·34	1·60	16·35	4·53	—	—	—	—	22·15	34·80	,,	
7·25	1·57	15·90	4·38	18·86	5·47	30·54	11·30	—	—	,,	
7·16	1·53	15·11	4·12	18·52	5·08	26·40	9·24	—	—	$Al_2O_3,2SO_3,11H_2O$ and $5Al_2O_3,6SO_3,46H_2O$	

Notes to Table I.—(1) These two solid phases were shown to be identical by their *X*-ray powder photographs.

(2) Mixtures prepared by the amalgamated aluminium process; the other mixtures where the solid phase was only $Al_2(SO_4)_3,16H_2O$ had been prepared from " AnalaR " aluminium sulphate.

(3) This experiment gives a point on the metastable portion of the $Al_2(SO_4)_3,16H_2O$ curve. Microscopic examination showed that some crystals of $Al_2O_3,2SO_3,11H_2O$ were present in the solid phase which was, however, mostly $Al_2(SO_4)_3,16H_2O$. As more $Al_2O_3,2SO_3,11H_2O$ separated the composition of the solution would gradually approach the value 8·56% Al_2O_3; 19·71% SO_3.

(4) The solubility experiment with potassium alum (see p. 2246) was done with the solution from this experiment.

(5) Prepared as a residue from " AnalaR " $Al_2(SO_4)_3,16H_2O$ (see p. 2245).

(6) Particularly well-crystallised solid used for *X*-ray single-crystal work.

Consideration of the Compounds (i) $Al_2(SO_4)_3,16H_2O$ *and* (ii) $Al_2O_3,2SO_3,11H_2O$—(i) $Al_2(SO_4)_3,16H_2O$ (Plate I, Nos. 1 and 2). There still appears to be much uncertainty about the correct formula of ordinary aluminium sulphate. Most modern text-books and the " AnalaR " reagent labels call it $Al_2(SO_4)_3,18H_2O$ [some of the latest labels call it $Al_2(SO_4)_3$, aq.], although careful work by de la Charlonny (*Compt. rend.*, 1883, **96**, 844; 1890, **111**, 229;

Ann. Chim. Phys., 1884, **1**, 425) had shown that the hydration corresponded to 16 and not $18H_2O$. The reason for this uncertainty is to be sought in the characteristics of the compound. It is very soluble but extremely difficult to obtain in any but small, thin, fragile crystals. It is not easy to be sure that such crystals when analysed contain neither too much nor too little water. The present work has enabled the question to be settled by the method of residues in favour of the hydrate with only $16H_2O$. This method must be used with discretion, however. Motida published a paper on the system $Al_2(SO_4)_3$–H_2SO_4–H_2O (*Sci. Rep. Tôhoku*, 1938, **26**, 611) in which he stated that at 25° $Al_2(SO_4)_3,16H_2O$ was the stable hydrate in equilibrium with solutions containing from 41·5 to 21·6% of SO_3, but $Al_2(SO_4)_3,18H_2O$ was the solid phase over the range 21·4—19·7% SO_3. When his evidence is examined it is found to give no support to this statement. The analytical results are closely similar to those given in the present paper. The solution points all lie on one smooth curve with no sign of any break at the point suggested. At the strongly acid end of the curve the tie-lines run very near to the point for $Al_2(SO_4)_3,16H_2O$, but at the weakly acid end they run almost as well to the point for $Al_2(SO_4)_3,18H_2O$ as to that for $Al_2(SO_4)_3,16H_2O$, and so cannot make a clear distinction between them. This is because over the weakly acid range the tie-lines are inclined at only a very small angle to the line joining the $Al_2(SO_4)_3,16H_2O$ and the water point. The diagram in Motida's paper shows the one set of tie-lines running exactly to the point for $Al_2(SO_4)_3,16H_2O$ and the other set to that for $Al_2(SO_4)_3,18H_2O$, but this is found to be an unjustified simplification when his results are plotted on a large enough scale. There is no evidence in Motida's paper that he even looked at the solid phases under the microscope or that the supposed two different hydrates appeared in any way different. All the solid phases over the whole range of the $Al_2(SO_4)_3$ region in our experiments had the appearance of the crystals described by de la Charlonny (*loc. cit.*) and all the tie-lines run very closely to the point for $Al_2(SO_4)_3,16H_2O$. To make the identity still more certain, *X*-ray powder photographs were taken of one solid from the very acid end of the range and of one from the weakly acid end. They were indistinguishable. Lastly, it may be added that the dry crystals of $Al_2(SO_4)_3,16H_2O$ separated from the strongly acid solution (at 40·03% SO_3) had not changed in weight after exposure for 2 years at room temperature over some of the weaker solution (20·14% SO_3) which according to Motida should be in equilibrium with $Al_2(SO_4)_3,18H_2O$.

The latest claim (Smith, *J. Amer. Chem. Soc.*, 1942, **64**, 41), *viz.*, that $Al_2(SO_4)_3,17H_2O$ is the stable solid in equilibrium with saturated solution at 25°, can probably also be explained on the above lines.

It is of some interest, however, that the numerous preparations of pure aluminium sulphate obtained by filtration from acid mother-liquor followed by thorough alcohol-washing and air-drying invariably contained more water than corresponded to $Al_2(SO_4)_3,16H_2O$. The composition was generally very close to that required by $Al_2(SO_4)_3,16{\cdot}5H_2O$ (Al_2O_3, 15·96%; SO_3, 37·56%). This applies also to the very pure specimen of alunogen from Chile (see p. 2246). The phase-rule isothermal seems to make it certain that the compound is really $Al_2(SO_4)_3,16H_2O$ and it is probable that the extra half molecule of water in the air-dried solid is held by adsorption on the very large surface of the thin platy or fibrous crystals.

The results in Table I show that $Al_2(SO_4)_3,16H_2O$ is only just able to form a stable congruent solution at 25°. The solution at the point where it becomes metastable towards $Al_2O_3,2SO_3,11H_2O$ has an *R* value of only 0·3398 as compared with 0·333 for the congruent solution. " AnalaR " preparations of aluminium sulphate are often slightly basic and this is due to the presence of a small proportion of crystalline $Al_2O_3,2SO_3,11H_2O$.

51·9 G. of " AnalaR " sulphate were shaken at 25° with 48·1 c.c. of water which should just give 100 g. of saturated solution. After a very short time all but a very small amount of the solid had dissolved. This was allowed to settle and a little withdrawn for microscopic examination. It consisted of characteristic prisms of $Al_2O_3,2SO_3,11H_2O$. After further shaking for a fortnight the mixture was allowed to settle, and the bulk of the clear solution decanted. The rest was filtered for analysis and the figures recorded in Table I were obtained.

The weight of moist solid was 1·02 g., equivalent to 0·58 g. of dry $Al_2O_3,2SO_3,11H_2O$ from the position of the moist-solid point on the tie-line. This corresponds to 1·12% of $Al_2O_3,2SO_3,11H_2O$ in the " AnalaR " $Al_2(SO_4)_3,16H_2O$ or to slightly more if allowance is made for the small amount which had dissolved.

After 4 days at room temperature a number of small, bright, well-formed isotropic octahedral crystals had crystallised from the solution which had been decanted from the $Al_2O_3,2SO_3,11H_2O$. There was also present a little of the latter compound carried over during the original decantation. The actual amount of the octahedral crystals was very small, but most of it was obtained in a clean dry state by decantation, filtration, and washing with a little cold water followed by alcohol of increasing concentration. The weight of dry crystals finally obtained was only 0·0048 g., though little appeared to be lost in the separation. The crystals were identified as ammonium alum by the refractive index,

found to be 1·460 as compared with 1·4594 given in the International Critical Tables. This alum originates from the trace of ammonia (up to 0·02% according to the label) contained in " AnalaR " aluminium sulphate. The possibility of separating it in the manner described depends upon its enormously decreased solubility in the saturated aluminium sulphate solution as compared with pure water. This decreased solubility was studied with potassium alum at a time when it was thought that the octahedral crystals observed in several experiments might consist of potassium alum. The effect on the solubility of ammonium alum would be similar. 0·0181 G. of potassium chloride was shaken at 25° with 14·8 g. of the solution containing 8·62% Al_2O_3 and 19·55% SO_3 (see Table I) and after several days the potassium sulphate which had formed was dissolved by gentle heat. After 24 hours' further shaking the octahedral crystals of alum were filtered off and weighed on a sintered-glass Gooch crucible after being washed with alcohol of increasing concentration and air-drying. The weight was 0·0762 g. as compared with 0·115 g. theoretically obtainable. Since 100 g. of water at 25° can dissolve 14·14 g. of $KAl(SO_4)_2,12H_2O$ (Seidel, " Solubilities of Inorganic and Organic Substances," 1912, p. 13), the water present in the 14·8 g. of solution used in the experiment could have dissolved 1·502 g. of alum had it been pure water instead of the 0·0388 g. which it did dissolve.

The above experiments explained the very puzzling appearance in small amounts of isotropic octahedral crystals (or other cubic forms) from solutions in the immediate neighbourhood of the intersection of the solubility curves of $Al_2(SO_4)_3,16H_2O$ and $Al_2O_3,2SO_3,11H_2O$. For a long time it was thought that these must consist of some other basic aluminium sulphate or even of aluminium sulphate itself. They are not obtained when the solutions are prepared from aluminium and sulphuric acid. A similar separation of alum crystals probably explains a remarkable statement by Rammelsberg (" Handbuch der Krystallographischen Chemie," Berlin, 1855, p. 88) that $Al_2(SO_4)_3,18H_2O$ crystallised at the ordinary temperature in " regular(?) octahedra." He added : " It is, however, still doubtful whether the observed octahedra consist of the pure alkali free-salt."

$Al_2(SO_4)_3,16H_2O$ occurs naturally as the mineral " alunogen." We have shown that the *X*-ray spectrum of this mineral is identical with that of our $Al_2(SO_4)_3,16H_2O$. It is clear, therefore, that " alunogen " contains only 16 molecules of water and not the 18 assigned to it in most treatises on mineralogy. Under very dry conditions some of this water may be lost (Gordon, *Notulæ Naturæ, Acad. Nat. Sci. Philadelphia*, 1942, No. 101) as is, of course, liable to happen with most hydrated salts. Gordon gives it the correct formula.

We have taken the *X*-ray spectra of two specimens of alunogen : (1) the British Museum specimen B.M. No. 19911 from Rudnó, Nová Baňa, Pohronská Zupa, Slovakia, and (2) a specimen supplied by the Compagnie Minera Herminda, Santiago, Chile (the exact locality from which it came is not known to us). In all cases where we have been able to examine British Museum specimens it has been through the kindness of Dr. Max Hey of the British Museum (Natural History) Dept. of Mineralogy. He also supplied much helpful information about the minerals concerned and the individual museum specimens. The South American specimen is in the form of large white or slightly pink masses with a rather fibrous crystalline structure, and is remarkably pure. It contained only 0·2% of insoluble matter, chiefly angular quartz fragments and a little ferruginous material, and the water-soluble portion contained : Al_2O_3, 15·88; CuO, 0·04; MgO, 0·02; SO_3, 37·40%. No iron was present in the water-soluble material. After deduction of SO_3 equivalent to the CuO and MgO, *R* for the aluminium sulphate is 0·334.

The traces of magnesium and copper sulphates would account for 0·10% of the water present in the mineral if they are present as $MgSO_4,Al_2(SO_4)_3,22H_2O$ and $CuSO_4,Al_2(SO_4)_3,22H_2O$, which is most probable. This would leave, by difference, $46·56H_2O$ for the aluminium sulphate. This would give a composition Al_2O_3, 15·92; SO_3, 37·40; H_2O, 46·68% for the pure compound. This is very close to the composition required by $Al_2(SO_4)_3,16·5H_2O$, which is Al_2O_3, 15·96; SO_3, 37·56; H_2O, 46·49%.

(ii) $Al_2O_3,2SO_3,11H_2O$. The compound $Al_2O_3,2SO_3,11H_2O$ forms well-developed, though small, monoclinic prisms which are very stable in the air and do not pick up any water when exposed over their saturated solutions at 25°. The extinction angle is at about 16° to the length of the prism. The compound dissolves fairly quickly in cold water to give a clear solution, which soon becomes milky, but it cannot form a congruent solution. It is quite clear from our results that only 11 molecules of water are present and not 12.

Unexpected difficulties have been encountered in the interpretation of the crystal structure of $Al_2O_3,2SO_3,11H_2O$, but the *X*-ray data make it very probable that the ion $[Al(OH)(H_2O)_5]^{\cdot\cdot}$ is present and that the compound is to be regarded as the salt $[Al(OH)(H_2O)_5]SO_4$. We have also prepared the compound as follows during experiments to devise a satisfactory method for preparing the corresponding selenate. 2·25 G. of aluminium were dissolved in 112 c.c. of 2·053N-hydrochloric acid, helped by gentle heating, 30 hours being required for complete solution. 35·83 G. of silver sulphate (the calculated amount) were added to the clear boiling solution, and the mixture heated in a gently boiling water-bath

for several hours. The hard lumps of silver chloride were crushed, and the mixture left overnight, but as unaltered silver sulphate was then still present in the solid phase; the mixture was diluted to 200 c.c. and heated over a small flame for another 24 hours, by which time no unreacted silver sulphate remained. The clear filtrate from the silver chloride and washings was evaporated in a silica beaker until the weight was 48·3 g. This concentrated solution after inoculation with a few crystals of $Al_2O_3,2SO_3,11H_2O$ was shaken at 25° for 3 weeks; the solid phase was then filtered off, washed with alcohol of increasing concentration, and air-dried; yield 3·3 g. (Found: Al_2O_3, 22·03; SO_3, 34·60. Calc. for $Al_2O_3,2SO_3,11H_2O$: Al_2O_3, 22·18; SO_3, 34·79%).

The amounts employed in the above preparation were such as should give a solution containing 7·6% Al_2O_3; 17% SO_3, which lies on the 25° solubility curve of $Al_2O_3,2SO_3,11H_2O$, together with several g. of the solid.

Marguerite (de la Charlonny) (*Compt. rend.*, 1880, **90**, 1354) obtained this compound by controlled decomposition of ammonium alum to give a residue almost entirely soluble in water from which it crystallised in rhombohedra. He assigned to it the formula $Al_2O_3,2SO_3,12H_2O$. According to Mans (*Pogg. Ann.*, 1827, **11**, 80) it can be got by evaporation to dryness of a hot filtered solution of aluminium hydroxide in aluminium sulphate, and Spence [B.PP. 25683 (1902); 6458 (1903); Fr. Pat. 331836 (1903); German Pat. 167419 (1903); U.S. Pat. 754824 (1904)] made it by mixing a solution of aluminium sulphate with enough calcium hydroxide or carbonate to give the necessary basicity. The filtered solution was evaporated *in vacuo*, and the crystals obtained were separated by centrifuging. If evaporation is carried to dryness, a pure product would not be obtained by either method, since the compound does not form a congruent solution.

Kremann and Hüttinger (*loc. cit.*) determined the solubility curve of this compound at several temperatures. They accepted the formula $Al_2O_3,2SO_3,12H_2O$ and supposed that it corresponded to the mineral "alumian." This mineral has been under suspicion for some time. It was first described and named by Breithaupt (*Berg. u. Huttenmännische Z.*, 1858, **17**, 53) and was based upon a very incomplete and unsatisfactory analysis by Utendörffer who gave it the formula $Al_2O_3,2SO_3$. It is stated in Breithaupt's paper that the mineral contained 37 to 38% Al_2O_3 and "only hygroscopic water."

Hlawatsch (Festschr. V. Goldschmidt, Heidelberg, 1928, p. 162) suggested on incomplete evidence that "alumian" might be identical with "alunite," and Gordon (*Notulæ Naturæ, Acad. Nat. Sci. Philadelphia*, 1940, No. 57) considered that it was to be identified with "natro-alunite."

We have been able to determine the *X*-ray spectra of two specimens of "alumian" in the British Museum collection. The numbers of these specimens in the British Museum Catalogue are: (i) B.M. 35864 which, according to A. Krantz, Berlin, from whom it was purchased, came from Barranco Farosso, Sierra Almagrera, Granada, Spain; (ii) B.M. 92951, which came from Abelardo Mine, Barranco del Francis, Sierra Almagrera, Almeria, Spain. This was in the Allan Greg collection purchased by the Museum in 1860, came from the original locality and bears a label in Breithaupt's handwriting. It must, therefore, be regarded as "type material." The *X*-ray spectra of these two specimens proved to be almost identical with those of three specimens of "alunite" from our own collection. These were: (i) a very well-crystallised specimen from Muszaj, Komitat Beregh, Hungary; (ii) a massive, coarsely crystalline specimen from near Marysvale, Utah, United States; (iii) a similar specimen, from Bulladelah, near Newcastle, New South Wales, Australia. It seems certain, therefore, that the mineral called "alumian" by Breithaupt and given the formula $Al_2O_3,2SO_3$ was in fact "alunite." Its insolubility in water is in agreement with this. The existence of the anhydrous $Al_2O_3,2SO_3$ as a mineral is improbable in any case.

The Compound $5Al_2O_3,6SO_3,46H_2O$ (*Plate, No.* 3).—$Al_2O_3,2SO_3,11H_2O$ has a comparatively small range of existence. The next solid phase to appear at 25° on passing into less concentrated and more basic regions of the system is the compound $5Al_2O_3,6SO_3,46H_2O$. This is stable over the range Al_2O_3, 7·17; SO_3, 15·11 to Al_2O_3, 1·24; SO_3, 2·19%. The relevant data are given in Table II (p. 2250). The study of this compound was much more troublesome than that of $Al_2O_3,2SO_3,11H_2O$. In comparison with the latter it is only very sparingly soluble and comes into equilibrium with its solutions far more slowly. At the more dilute end of its range its solubility curve runs very close to the curve of two-liquid system I so that solutions prepared of suitable concentrations to yield reasonable amounts of the compound $5Al_2O_3,6SO_3,46H_2O$ start off by being supersaturated not only to this but also to the glassy solid of the two-liquid system. The latter separates more readily than the former and may become occluded in the crystals of $5Al_2O_3,6SO_3,46H_2O$ when these do eventually separate. All the solution–moist solid tie lines for this part of the diagram run very close indeed to the point for $5Al_2O_3,6SO_3,46H_2O$

(Calc. : Al_2O_3, 28·05; SO_3, 26·40%), so there can be little doubt that the crystals in equilibrium with the solutions have this composition. At one time it was thought that they represented a series of solid solutions, though the fact that the *X*-ray diagrams were identical over the whole range was rather against this view. Many of the solids were separated from their mother-liquors by filtration and washing with either water or a mixture of alcohol and water followed by air-drying. They were then analysed either in the air-dry condition or after equilibration over the mother-liquors. This was to obtain evidence for or against the possibility that the crystals consisted not of a definite compound but of a series of solid solutions. A difficulty in the method lies in the possibility that the composition of the solid phase may be altered during its separation from the liquid. The danger of this in the present case did not seem serious since the crystals are relatively insoluble in water. Two experiments were made to test the point with a preparation to which Note 3 of Table II refers.

(*a*) 1 G. of the preparation was slowly washed on an ordinary filter-paper and funnel with 50 c.c. of distilled water. The washings became slightly milky almost as soon as they had run through, and a small amount of the " glassy solid " phase of the two-liquid system I slowly settled out. The composition of the washed and air-dried solid remaining in the funnel was Al_2O_3, 28·00; SO_3, 26·16%; $R = 0·84$. The *X*-ray diagram of the washed solid was still that of $5Al_2O_3,6SO_3,46H_2O$.

(*b*) 3 G. of the same preparation were washed on a filter-paper and ordinary funnel with 600 c.c. of distilled water for about a week. After air-drying, the solid residue, now 1·79 g., contained Al_2O_3, 32·26; SO_3, 21·09%; $R = 1·20$. The *X*-ray diagram showed that the solid was now mainly amorphous although some of the stronger lines of the original crystalline compound still showed up faintly.

It is clear from the above that decomposition caused by washing with small amounts of water is only slight, and is inadequate to explain such high *R* values as 0·886, as very little wash-liquor was used in separating the solids in dry state. Use of only a small amount of water seems to have had quite a different result. It has led to incomplete removal of the original mother-liquor which on drying has led to separation of some solid $Al_2O_3,2SO_3,11H_2O$ or even of $Al_2(SO_4)_3,16H_2O$ which is the most likely explanation of ratios less than 0·833. On equilibration over the mother-liquor the original amount of mother-liquor should be re-formed so that the equilibrated solids should have compositions corresponding to mixtures of $5Al_2O_3,6SO_3,46H_2O$ with saturated solution of the same composition as that over which equilibration had taken place. Thus if the dry solid of Table II (p. 2250) with $R = 0·824$ had retained 5% of mother-liquor it would have had the composition Al_2O_3, 26·80; SO_3, 25·26% after equilibration. In the case of the dry solid of Table II with $R = 0·815$ an original content of 4% of mother-liquor would give for the equilibrated solid a composition Al_2O_3, 27·04; SO_3, 25·57%. The calculated values for SO_3 tend to be lower than those found, which probably means that equilibration was not fully established. Conditions would actually be more complex than has been assumed in these calculations because of (*a*) slight hydrolysis of the original solid during the washing with even a very small amount of water, (*b*) deposition on the original solid of less soluble basic salt formed by hydrolysis of the mother-liquors being removed by the washing, (*c*) possible precipitation of some of the dissolved salts present in the adhering mother-liquor in cases where alcohol had been used in the washing. For these three reasons the contaminating material present in the washed, air-dry solids would tend to be more basic than would the evaporation residue of some of the original mother-liquor. The equilibrated solids would not represent true equilibrium conditions in the sense originally thought but only an approximation to this. The few cases in which dry solids were obtained with ratios higher than 0·833 are adequately accounted for by the almost certain presence of amorphous material, as the notes to Table II show. Admixture of glassy or amorphous with crystalline material, unless the former is present in very large amount, has such a small effect on the *X*-ray diagrams that it is often hard to draw conclusions from such diagrams as to the presence or absence of amorphous matter.

The compound $5Al_2O_3,6SO_3,xH_2O$ occurs in at least two different stages of hydration, but it seems clear from the tie-line graphical evidence and from the behaviour of air-dry solids on equilibration that only the hydrate in which x has the value 46 is stable in contact with solution at 25°. This hydrate occurs as slender prisms, probably monoclinic, which are thin rhombohedra. These show straight extinction when on edge, and when lying flat extinguish at an angle of 25° to the length of the prism and parallel to an end face. $5Al_2O_3,6SO_3,46H_2O$ tends to lose water on exposure to the air at ordinary temperatures to give $5Al_2O_3,6SO_3,40H_2O$. This formula was confirmed by examination of the preparation of Table II which had $R = 0·836$. It had been kept for 5 years in a lightly corked tube. It was placed in a crucible and left exposed to the air at a temperature of about 22°. Weighings at intervals during 50 hours showed that it was neither losing nor gaining weight. Analysis gave Al_2O_3, 29·76; SO_3, 28·07%; $R = 0·832$ (Calc. for $5Al_2O_3,6SO_3,40H_2O$: Al_2O_3, 29·83; SO_3, 28·07%. Calc. for $5Al_2O_3,6SO_3,39H_2O$: Al_2O_3, 30·14; SO_3, 28·37%). The lower hydrate so formed is crystalline and has a characteristic *X*-ray diagram quite different from that of the higher hydrate. It is, however, readily reconverted into the higher hydrate and both changes can occur at room temperature according to the relative humidity of the air. We have found that a specimen of $5Al_2O_3,6SO_3,xH_2O$, contained in a corked tube, changed backwards and forwards from the higher to the lower hydrate as shown by taking its *X*-ray diagram at intervals of several months or years. At one time we thought that both hydrates could exist in contact with solution at 25°, as there were indications of two solubility curves. The solution–moist solid tie lines do not support this view, however, and it seems clear that the appearance of two curves was caused by supersaturated conditions having persisted in some cases. There are indications that a more hydrated form of this salt $5Al_2O_3,6SO_3,60H_2O$ may be able to separate from very dilute solutions (see Note 8 to Table II).

The crystal structure of $5Al_2O_3,6SO_3.46H_2O$ is unknown, but there was a possibility of the existence

of stereoisomeric forms if the distribution of OH and H_2O was not random in any octahedral structures centred round aluminium ions which might be present (see p. 2252). This was tested for directly as follows. A solution (Al_2O_3, 8·6; SO_3, 13·0%) capable of depositing a considerable amount of $5Al_2O_3,6SO_3,46H_2O$ was prepared and allowed to stand without stirring at room temperature. Periodically the crystals which had separated from the solution were filtered off, washed, and air-dried. In this way seven fractions were obtained. The *X*-ray diagrams as well as the microscopic appearance of the first and the seventh fraction gave no indications of the separation of stereoisomers.

A precisely similar experiment was carried out with the compound $Al_2O_3,2SO_3,11H_2O$ since this might be a sort of double salt $[Al(H_2O)_6][Al(OH)_2H_2O)_4][SO_4]_2$, in which case there was also a possibility of the existence of stereoisomers. A solution containing Al_2O_3, 8·5; SO_3, 18·3% was used and five fractions of the solid were obtained. The first and the fifth fraction were identical as regards *X*-ray diagrams and optical properties.

With random distribution of hydroxyl groups in octahedral structures there would be no difference between $[AlOH(H_2O)_5][SO_4]_2$ and $[Al(H_2O)_6][Al(OH)_2(H_2O)_4][SO_4]_2$. When $Al_2O_3.2SO_3,11H_2O$ was treated at room temperature, or at 25°, with a concentrated solution of ammonium sulphate [1 g. of basic salt, 7·5 g. of $(NH_4)_2SO_4$, 10 c.c. of H_2O] separation of alum crystals began almost at once and was complete after a few days, being almost quantitatively that required by a reaction $2[AlOH(H_2O)_5]^{\cdots} \rightleftarrows [Al(H_2O)_6]^{\cdots\cdots} + [Al(OH)_2(H_2O)_4]$.

Small amounts of semi-colloidal basic products also separated but, after being stirred, they could be pipetted away, with the solution, from the alum crystals. Since $Al_2O_3,2SO_3,11H_2O$ dissolves readily in cold water, this formation of alum is most likely due to the above disproportionation occurring in the solution and is no indication that $Al_2O_3.2SO_3,11H_2O$ really has the structure $[Al(H_2O)_6][Al(OH)_2(H_2O)_4][SO_4]_2$; indeed, *X*-ray single-crystal work on this compound shows that this structure is impossible.

$5Al_2O_3,6SO_3,46H_2O$ also gave alum crystals quite rapidly when similarly treated with ammonium sulphate, almost exactly one-eighth of the aluminium of a preparation having $R = 0·8$ appearing as alum. Disproportionation in the above sense is hastened by the separation of alum.

The experiments just quoted were carried out originally to see whether any double salts of $Al_2O_3,2SO_3,11H_2O$ or of $5Al_2O_3,6SO_3,46H_2O$ with ammonium sulphate could be obtained and showed that they could not.

Characteristic crystals of $5Al_2O_3,6SO_3,46H_2O$, giving a good *X*-ray diagram have been obtained by the action of sulphuric acid upon aluminium hydroxide. 20 G. of $AlCl_3,6H_2O$ in 100 c.c. water were precipitated cold by 78 c.c. of 3·2N-ammonia. The washed precipitate was added to 120 c.c. of 1·02N-sulphuric acid. After 24 hours at room temperature with occasional shaking, much of the hydroxide had dissolved, and after another 10 days the undissolved portion was mainly crystalline. 5 C.c. of 2N-hydrochloric acid were added in the hope of dissolving a small amount of residual alumina but some of this becomes very insoluble in acid on standing, and even after the mixture had been kept for 3 months, some was still mixed with the coarse crystals of basic salt. The latter were separated by decantation and washing with cold water from most of the hydroxide, but some of this was almost certainly still present. The air-dry crystals contained Al_2O_3, 29·38; SO_3, 25·03%; $R = 0·92$; yield 0·59 g.

The solubility curve of any solid phase xAl_2O_3,ySO_3,zH_2O in the system Al_2O_3–SO_3–H_2O should be a closed curve enclosing the point representing the composition of the dry solid. It is probable that the two-liquid system I (see p. 2257) is metastable towards $5Al_2O_3,6SO_3,46H_2O$ until it, in its turn, becomes metastable towards $5Al_2O_3,3SO_3,32H_2O$. There would, in this case, be no stable point of intersection of the solubility curve of $5Al_2O_3,6SO_3,46H_2O$ with the curve of two-liquid system I. It is important to bear in mind that a solid phase xAl_2O_3,ySO_3,zH_2O can only separate from solutions or mixtures having compositions which fall within its closed solubility curve. All points outside the latter correspond to mixtures which are unsaturated towards the compound in question. The numerous cases, met with during the examination of two-liquid system I, in which $5Al_2O_3,6SO_3,46H_2O$ appeared as an additional phase, suggest that one part of the metastable portion of the solubility curve of $5Al_2O_3,6SO_3,46H_2O$ probably cuts through the solubility curve of two-liquid system I and would eventually join up with the stable portion of the solubility curve of $5Al_2O_3,6H_2O,46H_2O$ after passing round the point corresponding to the latter composition (see Fig. 2).

$5Al_2O_3,6SO_3,46H_2O$ can exist up to at least 50° and was obtained at this temperature in an attempt to prepare "aluminite." A solution (115 g.) prepared by method (iii) and containing approx. Al_2O_3, 8·6; SO_3 13·0% was heated in a small conical, tightly corked flask held partly immersed in a thermostat adjusted to 50°. The mixture was inoculated with a very small amount of "aluminite." Separation of solid phase was very slow, but there was a considerable quantity after 24 days in the form of small, well-formed prisms which extinguished at angles ranging between 16° and 34° to the length. As the solid did not seem to be increasing in amount, some of the clear solution was pipetted out for analysis (temp. 50·3°), and the solid was then filtered off on a Buchner funnel and washed with a small amount of water, followed by absolute alcohol. Wt. of air-dry solid 1·609 g.; it contained: Al_2O_3, 27·93; SO_3, 26·58%; $R = 0·824$, and the *X*-ray diagram showed it to be $5Al_2O_3,6SO_3,xH_2O$. The solution contained: Al_2O_3, 8·67; SO_3, 13·36%, and this is less acidic than the corresponding solution at 25°, whereas the reverse would be expected. This may indicate that the 46-hydrate is metastable towards the 40-hydrate at 50°. In this method of heating, considerable loss of moisture through the cork occurred and in this case separation of solid must have been mainly dependent upon such loss.

A lower hydrate, $5Al_2O_3,6SO_3,36H_2O$, was obtained as follows at approx. 88°. 2750 G. of solution (Al_2O_3, 7·8; SO_3, 11·6%) were heated in a large lipless beaker covered by a clock-glass and standing in an oil-bath heated to 90°. The solution was not inoculated but slowly deposited a solid in the form of minute prisms showing straight extinction. Separation appeared to have stopped after 12 days' heating, during which time the total volume of mixture had decreased by about 500 c.c. owing to evaporation. The solid was filtered off, washed with cold water, and air-dried. The yield was 260 g. (Found: Al_2O_3, 31·22; SO_3, 29·22%; $R = 0·838$. $5Al_2O_3,6SO_3,36H_2O$ requires Al_2O_3, 31·14; SO_3,

TABLE II.

$5Al_2O_3,6SO_3,xH_2O$ *at* 25°.

(*w* = wt. %; *m* = molecular %.)

Solution.				Moist solid.				Dry solid.		Equilibrated solid.		Time shaken at 25°			
Al_2O_3.		SO_3.		Al_2O_3.		SO_3.		Al_2O_3.	SO_3.	Al_2O_3.	SO_3.	(weeks).	*R* of solid.	*R* of solution.	Note.
w.	*m*.	*w*.	*m*.	*w*.	*m*.	*w*.	*m*.	*w*.	*w*.	*w*.	*w*.				
8·57	1·92	18·11	5·12	14·83	3·65	20·87	6·56	—	—	—	—	2	—	—	
7·25	1·56	15·20	4·16	—	—	—	—	27·45	26·84	27·03	26·43	4·5	0·802	0·375	
7·16	1·53	15·11	4·12	18·52	5·08	26·40	9·24	—	—	—	—	5	—	—	(1)
7·17	1·53	14·97	4·08	15·90	3·93	19·89	6·26	—	—	—	—	4	—	—	
6·51	1·35	12·49	3·31	22·46	6·23	23·14	8·19	—	—	—	—	5	—	—	
5·85	1·20	11·80	3·08	17·98	4·54	19·84	6·39	—	—	—	—	8	—	—	(2)
5·76	1·18	11·76	3·07	18·91	4·88	20·69	6·81	—	—	—	—	13	—	—	(2)
5·55	1·13	11·13	2·88	15·88	3·85	18·28	5·65	27·19	26·48	—	—	14	0·805	0·392	(3)
4·57	0·89	7·19	1·78	17·86	4·44	18·38	5·82	27·17	26·10	27·05	25·98	2·5	0·817	0·500	
4·55	0·90	9·04	2·28	—	—	—	—	28·55	27·71	—	—	9	0·808	0·395	(4)
4·40	0·87	8·70	2·18	16·84	4·13	18·34	5·73	29·13	28·35	—	—	6	0·806	0·399	(5)
4·27	0·84	7·92	1·97	20·91	5·59	21·64	7·38	—	—	—	—	7·5	—	—	
4·07	0·79	7·38	1·83	—	—	—	—	27·04	25·85	—	—	12	0·820	0·432	(4)
3·94	0·75	5·44	1·32	17·95	4·43	17·65	5·55	—	—	—	—	8	—	—	(6)
3·79	0·73	6·96	1·71	18·91	4·81	19·51	6·34	27·16	26·31	26·93	26·10	7·5	0·810	0·427	
3·76	0·72	6·27	1·53	19·78	5·11	19·82	6·53	—	—	—	—	11·5	—	—	
3·02	0·57	5·58	1·35	17·76	4·39	18·06	5·69	—	—	—	—	18 days	—	—	
2·97	0·56	5·70	1·38	—	—	—	—	26·93	26·13	—	—	16	0·809	0·406	
2·86	0·54	5·62	1·36	—	—	—	—	27·06	26·04	27·00	25·98	16	0·815	0·397	
2·91	0·55	5·34	1·29	—	—	—	—	27·31	25·83	—	—	7	0·829	0·426	(4) (7)
2·81	0·53	5·26	1·26	—	—	—	—	27·55	25·85	—	—	29	0·836	0·421	(4) (7)
2·65	0·50	4·84	1·16	19·32	4·93	19·36	6·30	—	—	—	—	19	—	—	
2·57	0·48	3·51	0·83	18·07	4·29	13·96	4·23	—	—	—	—	2	—	—	(8)
2·33	0·43	4·52	1·08	—	—	—	—	27·23	26·04	—	—	10	0·820	0·398	(4)
2·34	0·44	4·00	0·95	—	—	—	—	28·73	25·45	27·69	24·52	19	0·886	0·463	(9)
2·37	0·44	3·49	0·82	—	—	—	—	30·72	20·70	28·45	19·18	13·5	1·16	0·537	(10)
2·16	0·40	3·66	0·87	20·93	5·51	20·42	6·86	27·38	26·06	26·85	25·55	15	0·824	0·460	
2·08	0·38	3·74	0·88	—	—	—	—	27·10	25·90	—	—	13	0·821	0·432	(4)
1·55	0·28	2·54	0·59	16·21	3·78	14·10	4·19	—	—	—	—	23	—	—	(11)
—	—	—	—	—	—	—	—	29·38	25·03	—	—	—	0·92	—	(12)
1·24	0·23	2·19	0·51	—	—	—	—	29·03	24·00	26·52	21·76	15·5	0·949	0·451	(8)
—	—	—	—	—	—	—	—	29·88	24·65	—	—	—	0·951	—	(13)

Notes to Table II. The mixtures for all the experiments in Table II were prepared by Method (iii) (see p. 2240).]—(1) Two mixtures of suitable composition, on either side of the transition point, were prepared, inoculated with $Al_2O_3,2SO_3,11H_2O$ and $5Al_2O_3,6SO_3,46H_2O$, respectively, and shaken for 2 weeks at 25°. Good crops of each compound had by then separated from their respective mixtures which were then combined. Crystals of both compounds could be distinguished in the final mixture after a further 3 weeks' shaking.

(2) The same original mixture analysed after 8 and 13 weeks' shaking.

(3) Mixture kept for 70 months at room temperature after preparation, and some of it was then shaken for 14 weeks at 25° with the results shown.

(4) These mixtures had been inoculated with 0·01 g. of "aluminite" but the solid separating was entirely $5Al_2O_3,6SO_3,46H_2O$. As the amount of this ranged from 2 to 6·5 g., any effect due to the aluminite, if still present as such, on the analyses would be inappreciable. The mixture giving the solution of Al_2O_3, 4·07; SO_3, 7·38% had been heated considerably during the preparation (see p. 2257).

(5) After exposure of a weighed amount in a crucible to the air at room temperature for 3 weeks it had lost more water—the weight having apparently become constant—and then contained Al_2O_3, 29·48; SO_3, 28·70%.

(6) This mixture had been inoculated with Werner's supposed $[Cr(OH)_2(H_2O)_4]_2[SO_4]$ (see p. 2253).

(7) The same original mixture analysed after 7 and after 29 weeks.

(8) The same original mixture used for these two experiments inoculated with 0·5 g. of $5Al_2O_3,6SO_3,40H_2O$. After 2 weeks' shaking some of the mixture was used for the first analysis. The solution was then very supersaturated and the tie-line suggests that some glassy solid was present along with $5Al_2O_3,6SO_3,xH_2O$. The rest of the mixture was left at room temperature for 11 weeks and then shaken at 25° for 15·5 weeks before the second analysis. The solid phase of this experiment was relatively coarse with some good crystals of $5Al_2O_3,6SO_3,46H_2O$. There were, however, microscopic and *X*-ray indications of the probable presence of a considerable proportion of glassy solid. The glassy solid corresponding to a solution of composition Al_2O_3, 1·24; SO_3, 2·19% would contain about Al_2O_3, 30·2; SO_3, 17·5%. A mixture of one-third of this with two-thirds of $5Al_2O_3,6SO_3,46H_2O$ would contain Al_2O_3, 28·8; SO_3, 23·4%, which is very close to the composition of the dry solid of the present experiment. Now the solid had been washed with cold water only, and exposed to the air for 20 hours before analysis, so it may well have lost only adhering water. The gain of water on equilibration could be accounted for very closely if the $5Al_2O_3,6SO_3,46H_2O$ had absorbed water to form a new hydrate with $60H_2O$. We have no other evidence for such a hydrate, but the case of hydrobasaluminite (see p. 2265) shows that some of the basic aluminium sulphates readily form labile hydrates containing large amounts of water. The ease with which some of these hydrated basic salts gain and lose water is shown by the behaviour of the present specimen which had been kept in a corked tube. It gave quite a good *X*-ray diagram. This was first taken 9 weeks after preparation and was that of $5Al_2O_3,6SO_3,40H_2O$. Fresh *X*-ray examination 6 weeks later gave the diagram of $5Al_2O_3,6SO_3,46H_2O$, and a year later a new *X*-ray diagram showed that the solid had again lost water to form $5Al_2O_3,6SO_3,40H_2O$.

(9) The mixture (21 g.) was inoculated with 0·0124 g. of "aluminite." This had caused no crystallisation after 14 weeks' shaking at 25°, but much of the "glassy" solid of the two-liquid system I (see p. 2257) had separated among which the "aluminite" crystals were visible. After filtration, the "glassy" solid readily dissolved in a little dilute acid, leaving the crystals, which after being washed and air-dried weighed 0·0126 g., while the solution contained Al_2O_3, 5·25; SO_3, 6·38%, which gives a point on the curve of two-liquid system I. Aluminite used for inoculation can evidently remain unaltered for long periods. The aluminite crystals were returned to the solution (now about 14 g.), and the mixture shaken for a further 19 weeks at 25°. 1·12 G. of air-dry solid were then obtained on filtering the mixture, and it consisted of fairly large well-formed prisms of $5Al_2O_3,6SO_3,46H_2O$ mixed with a small proportion of what looked like the glassy solid of two-liquid system I. The equilibrated composition is near to that needed for such a mixture containing 20% of the glass.

(10) The solid phase in this experiment consisted mainly of the glassy solid of two-liquid system I, though the *X*-ray diagram showed that some $5Al_2O_3,6SO_3,46H_2O$ was present. Both solution and equilibrated solid points fit on the curve of two-liquid system I.

(11) See Note (6) to Table III (p. 2259).

(12) See p. 2249 for details of preparation.

(13) A solution from which glassy solid had separated at 25° was filtered and contained Al_2O_3, 4·88; SO_3, 5·77%. After standing at room temperature for 3 years a small amount of solid (0·22 g.) had separated consisting of a mixture of good prisms with a considerably smaller proportion of the glassy solid. The *X*-ray diagram was that of $5Al_2O_3,6SO_3,46H_2O$.

29·30%). This *compound* appears to be identical with $Al_2O_3,SO_3,6{\cdot}78H_2O$ (see p. 2252). The mother-liquors from the solid contained Al_2O_3, 6·63; SO_3, 11·4%; $R = 0{\cdot}455$.

Rammelsberg (*Pogg. Ann.*, 1838, **43**, 583) analysed crusts deposited on the sides of a glass bottle in which dilute sulphuric acid, saturated with aluminium hydroxide, had been kept for many years. He considered that they consisted of $3Al_2O_3,4SO_3,30H_2O$. It seems more likely that they were a mixture of $5Al_2O_3,6SO_3,46H_2O$ and $Al_2O_3,2SO_3,11H_2O$. An equimolecular mixture of these would have a composition corresponding to $3Al_2O_3,4SO_3,28{\cdot}5H_2O$.

Compounds with $Al_2O_3/SO_3 = 1{\cdot}0$ (Plate, Nos. 5—8).

(1) $Al_2O_3,SO_3,9H_2O$.—The best known and best defined of all the basic aluminium sulphate minerals is "aluminite," $Al_2O_3,SO_3,9H_2O$. This occurs in a number of localities, usually as white chalky-looking nodules, composed of minute well-formed prisms. These nodules generally occur in a clayey material, and the field indications are that the "aluminite" has resulted from

the action of sulphuric acid formed by oxidation of pyrities or in other ways on clay or marl at quite ordinary or moderate temperatures. In one specimen, of unknown origin, in our collection it occurs as soft powdery patches surrounded by crystals of gypsum. " Aluminite " is a perfectly definite compound of fixed composition and giving a characteristic *X*-ray diagram. We have taken the *X*-ray spectra of three specimens of " aluminite " of quite different origins, one from the British Museum collection and two from our own, and find them to be identical. This has been confirmed by Dr. M. Hey and Mr. F. A. Bannister who have examined some other specimens also with the same result. The specimens examined by us were : (i) " Aluminite " B.M. 425 from Halle, Saxony, bought by the Museum from H. Heuland in 1837. This is not " type material " although the original " aluminite " was discovered near Halle, Saxony, about 1730. (ii) " Aluminite " from Red Desert Region, Sweetwater County, Wyoming, U.S.A. (iii) " Aluminite " from an old collection of minerals presented to the University of Reading. It included many fine specimens from famous localities but many had lost their labels. This specimen which we identified was one of these, so the locality from which it came is unknown. The " aluminite " is associated with crystals of gypsum, $CaSO_4,2H_2O$, in the specimen as well as with some clayey or perhaps bauxitic material.

Specimens (ii) and (iii) were analysed : The former contained 1·76% of material insoluble in cold concentrated hydrochloric acid after 30 minutes (dried at 105°) ; this consisted chiefly of very well-rounded quartz grains together with a little clayey material. The composition of the rest of the mineral, free from insoluble matter, was Al_2O_3, 30·03 ; SO_3, 23·32% ; $R = 1·01$ (Calc. for $Al_2O_3,SO_3,9H_2O$: Al_2O_3, 29·65 ; SO_3, 23·26%). Specimen (iii) contained only 0·2% of material insoluble after digestion with 2*N*-hydrochloric acid ; the rest of the mineral contained Al_2O_3, 30·28 ; SO_3, 23·10% ; $R = 1·028$. Calcium, magnesium, and alkali metals were absent. The slight excess of alumina in both (ii) and (iii) is possibly due to extraction of a small amount from the associated clayey or bauxitic matter. There are no valid reasons for thinking that *R* of the pure mineral is other than 1·0 or that it is a solid solution.

Aluminite dissolves in acid much less readily than does $5Al_2O_3,6SO_3,xH_2O$.

Aluminite (iii) was interesting for a special reason. Material from one corner of the specimen gave an *X*-ray diagram entirely different from that of the aluminite with which it was first confused. Messrs. Bannister and Hey have clarified the situation by finding that material giving this new *X*-ray diagram is associated with aluminite on a number of specimens of this mineral from various localities. It has also been found in notable quantities in the Northamptonshire oolitic ironstone (Bannister and Hollingworth, *Nature*, 1948, **162**, 565). Its nature is discussed on p. 2265.

We have made many attempts to prepare aluminite at 25° by seeding with it a wide range of solutions from which $5Al_2O_3,6SO_3,46H_2O$ will crystallise. All these attempts were unsuccessful although the aluminite appeared to remain unaltered by such solutions for many weeks [see, *e.g.*, Note (9) to Table II]. Attempts to prepare it at higher temperatures have also failed, as have those in which dilute solutions of aluminium sulphate were treated with calcium carbonate.

Berzelius (" Lehrbuch der Chemie," Dresden, 1826, **2**, ii, 684) said that he got $Al_2O_3,SO_3,9H_2O$ by adding ammonia to a solution of aluminium sulphate to alkaline reaction, but Bley (*Annalen*, 1854, **89**, 174) said the product was more basic. Our experience shows that only gels of indefinite composition are obtained by such methods. The substance stated to be $Al_2O_3,SO_3,6H_2O$ by Böttinger (*ibid.*, 1888, **244**, 224) and obtained by heating an aqueous solution of aluminium sulphate and sodium chloride to 130—140° in a sealed tube would almost certainly have contained sodium and was probably an " alunite " (see p. 2254).

(2) Al_2O_3,SO_3,xH_2O (*possibly* $6Al_2O_3,6SO_3,40H_2O$).—This was obtained by heating to 70° 115 g. of a solution containing approx. Al_2O_3, 8·6 ; SO_3, 13·0% as in the experiment on p. 2249. Separation of solid was slow but after 15 days there was much of it in the form of small prisms showing straight extinction. The clear solution contained Al_2O_3, 7·00 ; SO_3, 12·36%. The solid, filtered on the pump and washed with cold water (50 c.c.) followed by alcohol (30 c.c.), weighed 7·8 g. after air-drying. A second crop of solid as small compact nodules of prisms was obtained after further 5 weeks' heating at 70° (Found, for 1st crop : Al_2O_3, 33·33 ; SO_3, 26·31% ; $R = 0·994$. For second crop : Al_2O_3, 33·76 ; SO_3, 26·28% ; $R = 1·008$. Calc. for $Al_2O_3,SO_3,6·78H_2O$: Al_2O_3, 33·56 ; SO_3, 26·31%). The *X*-ray diagram of this compound was found to be identical with that given by $5Al_2O_3,6SO_3,36H_2O$ (see p. 2251). Both preparations looked very good microscopically and had all the appearance of being pure compounds. Both consisted of small, clear, well-formed prisms and were indistinguishable. There were no signs of the presence of any amorphous material. The identity of their *X*-ray diagrams may arise in a similar way to that shown by members of the alunite group having widely different compositions. $Al_2O_3,SO_3,4H_2O$, $Al_2O_3,SO_3,6·78H_2O$, and $5Al_2O_3,6SO_3,36H_2O$ were all prepared in very much the same way at very similar concentrations, so that they may all have some structural similarity. The constitution of alunite is well established (see p. 2254). It dissolves in hydrochloric acid with considerable difficulty even when in a fine state of division. Of the other basic aluminium sulphates, $Al_2O_3,SO_3,4H_2O$ most resembles alunite in its resistance to acid. Similar chains of AlO_6 octahedra may be present in both compounds linked together criss-cross by the SO_4 ions, the proportions of which differ in the two compounds. On this basis $Al_2O_3,SO_3,4H_2O$ may perhaps be written $[Al_2(OH)_4]SO_4,2H_2O$, the $2H_2O$ being fitted into cavities in the lattice. Compounds with other formulæ are easily derived from a structure of the type $[Al_2(OH)_4]SO_4 + xH_2O$ by similar processes to those which appear to operate in the alunite group. Thus, starting with $[Al_{12}(OH)_{24}SO_4]_6 + 21H_2O$, if 2 of the 12 Al positions are vacant one gets $[Al_{10}(OH)_{18}(H_2O)_6][SO_4]_6 + 21H_2O$ which is $5Al_2O_3,6SO_3,36H_2O$. Compounds with higher *R* values can be derived from this not only by filling the vacant Al positions in the octahedral band kation but also by replacing SO_4'' by $[Al(OH)_4]'$. This

second method gives compounds containing a higher proportion of water. A product corresponding to $6Al_2O_3,6SO_3,40{\cdot}67H_2O$ would be given by admixture in the molar ratio 1 : 2 : 2 of $[Al_{11}(OH)_{22}(H_2O)_2][SO_4]_5[Al(OH)_4].21H_2O$, $[Al_{10}(OH)_{19}(H_2O)_5][SO_4]_5[Al(OH)_4],21H_2O$, and $[Al_{10}(OH)_{18}(H_2O)_6][SO_4]_6,21H_2O$, respectively, and this would contain Al_2O_3, 33·56; SO_3, 26·31%.

It is of interest that the loss of weight at 100° (see below) would correspond almost exactly to loss of the $21H_2O$ in the above formulation. The small difference in compositions between the first and the second crop of Al_2O_3,SO_3,xH_2O indicates that it was probably chance that gave a product with R so close to unity.

This case merits further investigation, but everything points to its being a genuine one of solid solution formation. It seems clear that $5Al_2O_3,6SO_3,40H_2O$ and $5Al_2O_3,6SO_3,46H_2O$ do not give rise to solid solutions (see p. 2248) although some relationship to $5Al_2O_3,6SO_3,36H_2O$ might reasonably be expected. This might well be due to instability being caused in the more hydrated lattices both by (*a*) vacant Al positions in the AlO_6 band kations and by (*b*) lowering the total charges on the kations and anions by any replacement of $[SO_4]''$ by $[Al(OH)_4]'$. The two higher hydrates may therefore be kept rigidly of the form $[Al_{10}(OH)_{18}(H_2O)_2][SO_4]_6 + 29$ or $35H_2O$. If this is correct it follows that $5Al_2O_3,6SO_3,36H_2O$ belongs to a somewhat different series from the two more hydrated salts, since its band kation contains 6 octahedra for $6[SO_4]''$ ions instead of only 5.

(3) $Al_2O_3,SO_3,4H_2O$.—Another *compound* $Al_2O_3,SO_3,4H_2O$ was readily obtained as follows. A solution in a silica beaker prepared by method (iii) and containing approx. Al_2O_3, 8·6; SO_3, 13·0% was placed in another beaker of water heated nearly to 100°. Separation of white solid began fairly soon, but at a slow rate which became more and more rapid as the amount of solid increased and was complete after a week. Water lost by evaporation was periodically replaced but 20% had been lost by the mixture and was not replaced when the experiment was stopped and the solid separated. The rather viscous filtrate gave no precipitate on dilution with water. The solid was washed on the pump with water and air-dried; yield 10·33 g. from 116 g. of original mixture. The mother-liquor contained Al_2O_3, 7·40; SO_3, 14·94%, and the air-dry solid, Al_2O_3, 40·14; SO_3, 31·39%; R = 1·003 ($Al_2O_3,SO_3,4H_2O$ requires Al_2O_3, 40·16; SO_3, 31·42%).

The solid is strongly doubly refracting though individual crystals are very minute and too small to examine; they are probably orthorhombic. Its X-ray diagram is quite different from that of aluminite and of $Al_2O_3,SO_3,7H_2O$ and $5Al_2O_3,6SO_3,xH_2O$. It dissolves with great difficulty in acid. Heating for about 20 minutes with concentrated hydrochloric acid diluted with an equal volume of water is required, and digestion for several hours is needed with 2N-acid. Some of the solid and mother-liquor were shaken at 25° for 3 months and again separated for analysis. There had been little change of composition. The solution then contained Al_2O_3, 7·34; SO_3, 14·51%, and the air-dry solid Al_2O_3, 40·09; SO_3, 31·41%. Owing to the slow rate of solution of this solid it is doubtful whether these figures give a point on its 25° solubility curve. The air-dry solid after equilibration over the solution for 6 weeks had absorbed 2·2% of moisture. No more was taken up after another period of 6 weeks. This was all lost again after a few days' exposure to the laboratory air.

It has been shown by X-ray examination that the initial precipitate thrown down on heating such solutions as the above is amorphous. It is the glassy phase of two-liquid system I. In preparing $Al_2O_3,SO_3,4H_2O$ heating must be continued long enough to cause all traces of this amorphous material to become fully crystalline.

(4) $Al_2O_3,SO_3,5H_2O$.—Aluminite (ii) (p. 2252) lost 21·83% when heated to constant weight at 100—115°, allowance being made for the 2% of impurity assumed to lose nothing. Aluminite (iii) lost 20·0%. This corresponds closely to the formation of the *hydrate* $Al_2O_3,SO_3,5H_2O$, for which the calculated loss would be 20·93%. The product gave a striking and distinctive X-ray diagram. There were indications of a further halt at about $Al_2O_3,SO_3,2{\cdot}5H_2O$ at 150°, and at 200° the weight became constant with a total loss of 36·88%. This would correspond to the formation of $Al_2O_3,SO_3,2H_2O$ (Calc.: loss, 36·63%), but the X-ray diagram showed that the product was amorphous.

The fact that aluminite on dehydration does not, apparently, pass through the $Al_2O_3,SO_3,4H_2O$ stage is striking and suggests some important structural difference.

$Al_2O_3,SO_3,6{\cdot}78H_2O$ after being heated to constant weight at 100° corresponded to $Al_2O_3,SO_3,3\frac{1}{4}H_2O$, but X-ray examination showed that the product was amorphous.

$Al_2O_3,SO_3,4H_2O$ on dehydration to approximately constant weight first at 150° then at 200° lost 10·01% by weight in all. X-Ray photos were taken after heating to 150° and to 200°, but gave no indication of the formation or any lower hydrate. The lines of the original compound gradually disappeared as more and more amorphous material was formed. Even in the final product a few of these lines were still faintly visible.

The existence of a compound $[Al(OH)_2(H_2O)_4]_2SO_4 = Al_2O_3,SO_3,10H_2O$ could be reasonably expected but we have failed to obtain it. Among other methods tried without success was inoculation of suitable solutions with the corresponding chromium compound which, according to Werner (*Ber.*, 1908, **41**, 3447), can be obtained as a bright green, silky-looking, crystalline material by the action of pyridine on a solution containing chrome alum and sodium sulphate. The product obtained by following Werner's directions as closely as possible did not look crystalline, but, after air-drying, it contained Cr_2O_3, 38·3; SO_3, 19·25% (Calc.: Cr_2O_3, 36·89; SO_3, 19·42%), so it may have been essentially the compound which Werner claimed it to be. His method when applied to ammonium aluminium alum gave no precipitate at all.

The "Alunite" Group of Minerals and Compounds (Plate, Nos. 9 and 10).

The first-discovered and still the best-known member of this group is the potassium compound, $K[Al_3(OH)_6][SO_4]_2$, to which the name "alunite" strictly belongs. It occurs as a well-crystallised mineral in a number of localities and often in large quantities. Its high content of potassium makes it of considerable technical interest. During the past 50 years it has

become apparent that " alunite " is only one of a large number of minerals which are isomorphously related (Schaller, *U.S. Geol. Survey Bull.*, 1912, **509**, 76; *Z. Kryst.*, 1912, **50**, 106; *Amer. J. Sci.*, 1911, **32**, 359).

Isomorphous replacement within the group can be of the ordinary simple kind where Na, NH_4, K, Rb replace each other or $[Fe_3(OH)_6]$ replaces $[Al_3(OH)_6]$, but compensatory replacement may also occur. Many of the alunite minerals are phosphates in which the higher valency of the PO_4 as compared with the SO_4 group is balanced by the presence of bivalent kations such as Pb, Sr, or Ba in place of alkali metals. The situation was greatly clarified by Hendricks's study of the crystal structure of alunite and the jarosites (*Amer. Min.*, 1937, **22**, 772). The crystal lattice contains endless bands of AlO_6 or FeO_6 octahedra in which each Al or Fe ion is surrounded by four hydroxyl ions and two oxygen atoms of SO_4 ions. The latter are in *trans*-positions in the octahedra. These are joined by their edges, two OH ions being shared by two octahedra. The unit cell of alunite contains the amount represented by the formula $K[Al_3(OH)_6][SO_4]_2$.

Hendricks showed that the alunite structure is retained when one of the six hydroxyl ions is replaced by a water molecule. The group $[Al_3(OH)_5(H_2O)]$ carries four positive charges, however, so that no potassium ion is required in order to balance the charges on the two $[SO_4]$ ions. The place of the potassium is therefore taken by another water molecule, and it was shown that the *X*-ray diagram of $H_2O[Fe_3(OH)_5H_2O][SO_4]_2$ was in fact very closely similar to that of jarosite, $K[Fe_3(OH)_6][SO_4]_2$. It is probable that the rhombs of $3Al_2O_3,4SO_3,9H_2O$ obtained by heating a 3% solution of aluminium sulphate to 250° (Athanescu, *Compt. rend.*, 1886, **103**, 271) correspond to this ferric compound.

According to our investigations other modifications of the alunite structure can occur. These are all, in a sense, an extension of Hendricks's replacement of one in six of the hydroxyl ions of the $[Al_3(OH)_6]$ or $[Fe_3(OH)_6]$ chain by H_2O. As our work has concerned aluminium compounds we shall refer only to these. Each OH of the chain ion which is replaced by H_2O corresponds to an extra positive charge on this ion. Survival of the alunite structure must be dependent upon the retention of the chain kation with 3 octahedra per unit cell and of two $[RO_4]$ ions.

Replacement of two out of six OH by H_2O would be possible if one $[SO_4]$ were replaced by $[PO_4]$ to give $H_2O[Al_3(OH)_4(H_2O)_2][PO_4][SO_4]$, but, as our experiments have related only to sulphates, we will not consider further this possibility.

Replacement of more than one of the six OH groups by H_2O without increasing the valency of the $[RO_4]$ ion beyond 2 is only possible if an aluminium ion is dropped from one of the octahedra. In this way the compounds $NH_4[Al_2(OH)_3(H_2O)_3][SO_4]_2$, $H_2O[Al_2(OH)_2(H_2O)_4][SO_4]_2$, and $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$ could originate. The empty octahedra and the OH and H_2O would doubtless occur in the octahedral chains with a statistical distribution. Assumption of these compounds in addition to those already mentioned as accepted by Hendricks has enabled us to account quantitatively and exactly for the composition of a number of preparations which give excellent *X*-ray diagrams although their composition differs widely from that usually attributed to alunite.

Empty octahedral positions are, of course, well known in aluminium compounds. In hydrargillite, $Al_2O_3,3H_2O$, one in three of such positions contains no aluminium ion. The octahedra in the chains of the alunite structure are held together strongly by the $[SO_4]$ ions, and this should facilitate the occurrence of empty octahedra.

Potassium, sodium, and ammonium alunites were first prepared by Mitscherlich (*J. pr. Chem.*, 1861, **83**, 455) by heating in sealed tubes to 230° solutions of the appropriate alum and additional aluminium sulphate to which the corresponding alkali hydroxide had been added to the point at which further addition would have caused a permanent precipitate. Ammonium alunite does not appear to be known as a mineral, though ammonio-jarosite $NH_4[Fe_3(OH)_6][SO_4]_2$ occurs naturally (Dana, " Text-book of Mineralogy," 4th edn., 1932, p. 769). Until about 20 years ago it was supposed that alunite had been formed in Nature at relatively high temperatures and pressures (Hintze, " Handbuch der Mineralogie," 1929, I, 3, ii, 4183). This may have been the case with some occurrences of the mineral, but Leonard (*Econ. Geol.*, 1927, **22**, 18) showed that alunite can be produced at atmospheric pressure and temperatures as low as 20°, and it is well known to those who handle quantities of hot, slightly basic, liquors of alums or aluminium sulphate that these deposit precipitates which are alunitic in nature.

It may be necessary, in order to prepare in the laboratory well-crystallised alunites with the composition required by the conventional formulæ, to use the sealed-tube technique, but preparations obtained at ordinary pressure and temperatures not above 100° are micro-, or even

more coarsely, crystalline and give *X*-ray diagrams like that of the mineral. Such preparations differ from the mineral in seldom, if ever, having a composition required by the simple formulæ. They are either more basic or less basic, and the water content is often very high, as can be seen from the preparations shown in Table IIA. These can all be explained satisfactorily in terms of mixtures of the compounds discussed above. This manner of representing the composition of the preparations is, of course, artificial. In reality there will be some sort of random distribution of all the ions which take part in the isomorphous replacement. The compound $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2 = 2Al_2O_3,9H_2O$ is not known. Since it is necessary to assume the presence of a small proportion of V in all the preparations of Table IIA, it would appear that a small concentration at least of $[Al(OH)_4]$ ions must have been present in all the solutions involved. Measurements of the *X*-ray diagrams of these alunites are recorded in Table X (Appendix) because of their possible interest in connection with replacements occurring in the group.

Löwigite (Löwig, *Z. deut. geol. Ges.*, 1856, **8**, 247; Mitscherlich, *op. cit.*, p. 474), a somewhat ill-defined mineral found associated with alunite, has been given the formula $K_2SO_4,3Al_2O_3,3SO_3,9H_2O$. It is probable that this is actually an alunite and the above formula would be given exactly by the mixture of alunites: 1·2 mols. of $K[Al_3(OH)_6][SO_4]_2$ + 0·8 mol. of $K[Al_2(OH)_3(H_2O)_3][SO_4]_2$ + 0·2 mol. of $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$. Mr. F. A. Bannister has taken the *X*-ray diagrams of the British Museum specimen of löwigite and reports that it does, in fact, given the alunite diagram.

Further, the solid obtained by autoclaving at above 150° a concentrated solution of potassium alum in the " Kalunite " process for extracting alumina from alunite (B.PP. 397407—397412, 1933; Fleischer, *Amer. Inst. Min. Met. Eng.*, 1944, Tech. Publ. 1713; *Brit. Chem. Abs.*,

TABLE IIA.

Alunites.

Analysis of air-dry solids, %.							Same composition given by mixture of the " molecular " proportions indicated.*	Note.
$(NH_4)_2O$.	K_2O.	Na_2O.	Al_2O_3.	Cl.	SO_3.	H_2O (diff.).		
3·73	—	—	35·41	0·83	30·98	29·32	1·0 IIc + 0·35 III + 0·535 V	(1)
2·91	—	—	35·42	0·34	30·10	31·31	1·0 IIc + 0·68 III + 0·71 V	(2)
6·44	—	—	34·80	1·25	39·96	17·83	0·55 Ic + 0·45 IIc + 0·05 V	(3)
5·46	—	—	32·81	—	39·96	21·77	0·38 Ic + 0·62 IIc + 0·19 III + 0·077 V	(4)
4·24	—	—	35·37	—	40·85	19·55	1·0 Ic + 0·566 III + 0·031 V	(5)
4·28	—	—	35·77	—	37·83	22·12	0·74 Ic + 0·26 IIc + 0·437 III + 0·163 V	(6)
—	11·33	—	29·46	—	38·77	20·44	0·17 Ib + 0·83 IIb + 0·007 IV + 0·052 V	(7)
—	9·62	—	29·52	—	38·62	22·24	0·16 Ib + 0·84 IIb + 0·185 III + 0·075 V	(8)
—	9·06	—	28·27	—	37·75	24·94	1·0 Ib + 0·23 III + 0·105 V	(4)
—	—	5·77	31·26	—	39·17	23·80	0·2 Ia + 0·8 IIa + 0·315 III + 0·115 V	(4)
—	—	5·97	33·69	—	37·65	22·69	0·4 Ia + 0·6 IIa + 0·225 III + 0·145 V	(9)
—	—	5·65	34·66	—	40·37	19·32	0·83 Ia + 0·17 IIa + 0·385 III + 0·035 V	(10)

* Key to the compounds referred to in this column:

Ia = $Na[Al_3(OH)_6][SO_4]_2$
Ib = $K[Al_3(OH)_6][SO_4]_2$
Ic = $NH_4[Al_3(OH)_6][SO_4]_2$
IIa = $Na[Al_2(OH)_3(H_2O)_3][SO_4]_2$
IIb = $K[Al_2(OH)_3(H_2O)_3][SO_4]_2$
IIc = $NH_4[Al_2(OH)_3(H_2O)_3][SO_4]_2$
III = $H_2O[Al_2(OH)_2(H_2O)_4][SO_4]_2$
IV = $H_2O[Al_3(OH)_5(H_2O)][SO_4]_2$
V = $H_2O[Al_2(OH)_4(H_2O)_2][Al(OH)_4]_2$

In calculating the mixtures of these compounds which gave the same compositions as those found for the various preparations listed in Table IIA it was found simplest to take NH_4, K, or Na as unity and to divide it among compounds I and II. Then, by inspection and trial, the amounts of the other compounds which must be present were readily deduced, the hydroxyl equivalent to any chlorine present having been first calculated (see Note 2).

All the preparations of Table IIA dissolved in acid with considerably more difficulty than any of the other basic sulphates with the exception of $Al_2O_3,SO_3,4H_2O$. The ease of solution varies considerably according to the state of division of the preparation, and for amounts of 0·2—0·4 g. of solid the time required for solution in nearly boiling hydrochloric acid varied from about 10 minutes in 2N-acid to an hour in 10N-acid.

Notes to Table IIA.—All the preparations quoted in this table gave *X*-ray diagrams characteristic of alunite. Careful measurements disclosed small differences in the spacings and intensities of some of the lines (see Appendix, Table X).

(1) This is the alunite preparation described on p. 2275.

(2) 2 G. of the preparation of Note 1 were washed slowly on a funnel with 30 c.c. of cold water, then with alcohol, and air-dried. The analysis of the washed solid shows that, if the chlorine originally present is supposed to have been due to contaminating ammonium chloride, then only 59% has been removed

by the washing together with 15% of ammonium sulphate. In view of this result and the coarsely crystalline nature of the solid, the only reasonable conclusion to draw appears to be that the chlorine must be a constituent part of the alunite structure, replacing hydroxyl. The chlorine is slowly removed by hydrolysis but not much more readily than the ammonium.

This is one of only two cases in Table IIA where there is not perfect agreement between the water content, as well as all other constituents, as found by analysis and calculated for the mixture given in the table. The analytical composition corresponds to 15·52 mols. of H_2O per NH_4 ion, whereas the calculated figure is only 14·93 mols. It is quite likely that a small portion of the hydrolysis product had failed to crystallise fully and had retained, in consequence, too much water.

It may be significant, in this connection, that the only other preparation of Table IIA which did not give perfect agreement for all constituents between found and calculated figures was the preparation of potassium alunite containing 9·06% of K_2O. The analytical figures gave 7·2 mols. of H_2O per K ion, whereas the calculated figure for the mixture shown in Table IIA is only 6·83 mols. of H_2O. The washing with *hot* water may have led to the formation of some amorphous hydrolysis product.

(3) This solid was prepared in a similar manner to that of Note 1, but a larger proportion of basic double salt I had separated (4·30 g. as compared with 3·51 g.), so the basicity of the filtrate which was heated was less. 4·58 G. of alunite were obtained from this, and after 24 hours' heating it looked crystalline under the microscope though it was too fine for any double refraction to be seen.

(4) A solution was prepared containing approx. 8·6% Al_2O_3; 13·0% SO_3, that is to say, of the same composition as that which yielded the compound $Al_2O_3,SO_3,4H_2O$ after long heating to nearly 100° (see p. 2253). 20-G. lots of this solution were placed in three large test-tubes; to one was added 2 g. of ammonium sulphate and 5 c.c. of water, to another 2·64 g. of potassium sulphate and 5 c.c. of water, and to the third 2·16 g. of sodium sulphate and 5 c.c. of water. The mixtures were then placed in a beaker of boiling water. Solid began to separate very soon from each mixture, first from that containing potassium sulphate and last from that containing ammonium sulphate. After 5½ hours' heating in the boiling water the ammonium solid, though fine, was obviously crystalline. The other two solids were finer but looked crystalline though it was difficult to be certain whether there was any double refraction. The solids were then filtered hot. The ammonium solid was washed with 80 c.c. of cold water only and air-dried; its hot mother-liquor on standing deposited a considerable amount of alum. The potassium solid was washed with 70 c.c. of hot water, 10 c.c. of 50% alcohol, and finally with absolute alcohol, and air-dried. The sodium solid was washed with 60 c.c. of water, 10 c.c. of 50% and 10 c.c. of absolute alcohol, and air-dried. Yields were: NH_4 solid 2·624 g.; K solid 4·95 g.; Na solid 3·71 g.

(5) 22·5 G. of ammonium alum in 140 c.c. of water gently boiled in a beaker for about 26 hours, water lost by evaporation being replaced at intervals. The solid which had separated was fine but crystalline and was filtered off from the hot solution, washed with cold water, and air-dried; weight 0·736 g.

(6) 20 G. of solution (8·6% Al_2O_3; 13·0% SO_3) had been boiled for 2 hours. 1 G. of ammonium sulphate in 5 c.c. of water was added, and mixture shaken at 25° for 9 days; 4·46 g. of alum crystals which had separated were filtered off. After standing at room temperature for 48 hours, some more alum had crystallised out. The decantate from these was heated nearly to 100° for 30 hrs., and the minutely crystalline solid was then filtered from the hot mother-liquor, washed with 60 c.c. of cold water, and air-dried; yield 2·42 g.

(7) 2·7 G. of potassium hydroxide in 25 c.c. of water were added to 15·28 g. of potassium alum in 150 c.c. of water slowly with vigorous stirring. The mixture was filtered from a small amount of undissolved precipitate into a silica beaker which was immersed in a beaker of water kept at about 60°. Precipitate soon began to separate. After 16 hours' heating some fair-sized crystals were present. These were in the form of a right-angled wedge, the hypotenuse being the thin edge. Extinction was parallel to the hypotenuse. As this is one of the forms in which $5Al_2O_3,3SO_3,xH_2O$ (see p. 2266) separates, it is likely that the crystals consisted of this substance. After a further 4 days' heating all these wedge-shaped crystals had disappeared but the whole finely granular solid was crystalline and sparkled brilliantly when rotated between crossed nicols. After being heated to 60—90° for 11 days in all, the hot mixture was filtered and the solid washed with about 20 c.c. of water followed by absolute alcohol; weight of air-dry solid 5·09 g.

(8) Carried out as in the experiment to which Note 7 refers except that only 1·3 g. of potassium hydroxide were used and the mixture was heated for 5 weeks in a corked conical flask immersed in a thermostat kept at 70°. The solid was too fine to be sure from microscopic examination whether it was all crystalline. *X*-Ray examination showed that it was; yield 3·03 g.

(9) 9·7 G. of $Al_2(SO_4)_3,16H_2O$ and 4·9 g. of sodium sulphate decahydrate were dissolved in 100 c.c. of water, and 2 g. of sodium hydroxide in 15 c.c. of water were gradually added with vigorous stirring. The filtered solution was heated to 50° for 4 days. The solid which had separated did not look crystalline, and was shown to be completely amorphous by *X*-ray examination. About half was filtered off, and the rest of the mixture heated to 65° for 2 days. Square crystals had appeared after 2 days at 65°. In the hope that the proportion of square crystals might be increased, an additional 2·45 g. of sodium sulphate were added, but this made no difference. After a further 9 days' heating the solid was filtered off, washed with much water, then absolute alcohol, and air-dried; weight of solid, 2·14 g. After standing for a fortnight much of the doubly refracting $Na_2SO_4,Al_2(SO_4)_3,22H_2O$ had crystallised from the mother liquors.

(10) A solution of aluminium sulphate approximately saturated at the boiling point was boiled with γ-$Al_2O_3,3H_2O$ in the form of the so-called "Bayer hydrate" (hydrargillite) which always contains some sodium as an impurity. When no further hydrate appeared to be dissolving, the mixture was diluted and filtered, and the filtrate boiled for a long time. Small thin, nearly square, plates or aggregates of these separated having $R = 0·674$.

By working as above with 150 g. of $Al_2(SO_4)_3,16H_2O$ only 0·368 g. of the basic salt was obtained. The mother-liquor contained Al_2O_3, 9·39; SO_3, 20·91%; $R = 0·352$.

B, 1945, 153) is also stated to be $K_2SO_4,3Al_2O_3,4SO_3,9H_2O$. This also may well be an alunite and with 10·5 instead of $9H_2O$ the composition would be exactly matched by the mixture of alunites: 1 mol. of $K[Al_3(OH)_6][SO_4]_2$ + 1 mol. of $K[Al_2(OH)_3(H_2O)_3][SO_4]_2$ + 0·5 mol. of $H_2O[Al_2(OH)_2(H_2O)_4][SO_4]_2$.

Two-Liquid System I. The "Glassy Solid."

Solutions in equilibrium at 25° with $5Al_2O_3,6SO_3,46H_2O$ and containing less than about 4·9% Al_2O_3 and 9·1% SO_3 become milky on sufficient dilution (at room temperature) owing to separation of a still more basic product. The same substance can be obtained by spontaneous separation, without any dilution, from solutions of suitable composition prepared by method (iii) (p. 2240). It is also formed by boiling crystals of $5Al_2O_3,6SO_3,xH_2O$ with water. By using these three methods of preparation the solubility curve of this more basic material has been traced. The results are recorded in Table III.

This more basic material is amorphous or glassy. It is obtained in the form of relatively large glassy spheres or discs where separation has occurred slowly from solutions prepared by method (iii), either spontaneously, or as a result of very gradual dilution, extending over several weeks, of suitable concentrated solutions. These spheres or discs break with a conchoidal fracture and are isotropic when examined in polarised light. The basic material which separates quickly on rapid dilution of fairly concentrated solutions is seen under the microscope to consist of aggregates of very minute transparent discs, while the precipitate obtained by dilution of dilute solutions shows very little structure under the microscope. The material is found to be amorphous by *X*-ray examination, whether it is in the form of the large glassy spheres or of the more or less structureless precipitates.

The composition of the "glassy" or amorphous phase is variable and depends upon that of the solution from which it separates. Its water content is very sensitive to the humidity of the air with which it is in contact, varying continuously with this.

The "glassy" phases were analysed after filtration and washing followed by equilibration over the mother-liquors as described on p. 2243. The results so obtained have led to the conclusion that the "glassy" material represents the more concentrated phase of a two-liquid system. This appears to form a closed curve when plotted in the ordinary triangular diagram, as shown in Fig. 1. Although the more concentrated phase is "glassy" over the greater part of the region, it may be liquid in the ordinary sense of the word at the dilute end of the region where its water content is very high. The equilibrium "solids" corresponding to the most dilute solutions in Table III are rather soft.

Separation of the glassy phase of the two-liquid system on dilution of previously clear solutions can only occur if this dilution brings the composition within the area of the closed curve of the two-liquid system. The diluted solution will then break up into the appropriate glassy and liquid solutions. Now the lines joining points on the 25° solubility curve of $5Al_2O_3,6SO_3,46H_2O$ to the water point just fail to cut the curve of the two-liquid system, at 25°. Dilution at 25° would not therefore cause any separation of glassy solid. The curve of the two-liquid system and the other solubility curves will doubtless shift to the left-hand (or SO_3) side of the triangular diagram (corresponding to decreased solubility) with fall of temperature. Dilution at room temperature of a solution which was saturated with respect to $5Al_2O_3,6SO_3,46H_2O$ at 25° may well bring the composition to within the area of the two-liquid system at room temperature, with resultant precipitation of glassy solid.

Some change in the composition of the "glassy" solid is liable to occur, owing to further hydrolysis, when adhering mother-liquor is removed by washing with water. The solid will tend to become more basic. Washing of the "glassy" solids must for this reason be restricted as far as possible when separating them in a dry state for analysis and equilibration. This effect of the washing is one reason why solution, moist solid, and equilibrated solid points do not always fall on one straight line when plotted on the triangular diagram (see, *e.g.*, Note 11 to Table III). The effect on the composition of the glassy solid due to this cause appears as a rule to be less than that caused by heating the mixtures (see pp. 2258, 2260). Heating the mixtures affects the *slope* of the solution–moist solid tie-line as well.

Method (iii) is only suitable for preparing mixtures in the more concentrated region. If used for the more dilute region, solid (*viz.*, "glassy" phase) separates before all the aluminium has dissolved and it is not possible to separate the finely divided mercury by filtration. This may happen even in the more concentrated region if an attempt is made to obtain too large a proportion of the "glassy" phase. Preparation by the method of dilution has to be used for the less concentrated region, and large quantities of diluted solution must be prepared in some cases in order to obtain sufficient of the "glassy" phase.

All solutions in equilibrium with "glassy" solid become milky or turbid on dilution, more or less rapidly, according to circumstances. This shows that the curve of the two-liquid system is concave to the lines joining any point on this curve to the water point. A solution represented by any point on one of these lines will tend to break up into a more dilute solution and a corresponding "glassy" solid. Equilibrium solutions containing less than 0·5% Al_2O_3; 1·0% SO_3 only become faintly opalescent after very great dilution because in this region the curve of the two-liquid system is almost a straight line which runs practically to the water point.

Separation of the second (or "glassy") liquid phase is associated with some tendency for supersaturation to persist which is small in dilute solutions but considerable in the more concentrated and viscous ones.

Since the two-liquid system is probably entirely metastable towards crystalline compounds (see pp. 2249, 2260, 2264) there is always some tendency for such crystals to separate and complicate the situation.

Even when this does happen, analyses of the filtered solutions will generally give points which fall on the true (*i.e.*, not supersaturated) curve of the two-liquid system. Separation of crystalline material chiefly causes trouble in the study of the more concentrated region of the two-liquid system. The

tie-lines for this system are approximately parallel to one another. If an odd one cuts the others this may be due to the presence of some crystalline solid along with the " glassy " phase, although it occasionally happens that, for some reason, there has been lack of proper adjustment between the solution and the glassy solid so that the latter is not of uniform composition.

We know of no case where a two-liquid system of this kind has been systematically examined. Jones (*Trans. Faraday Soc.*, 1939, **35**, 1484) observed an isotropic material, similar to our " glassy " solid, in the system CaO–Al_2O_3–$CaSO_4$–H_2O. It was prepared by the action of lime-water in the cold on solutions of aluminium sulphate and was considered by Jones to be aluminium hydroxide gel with some lime in solution. Jones records n as 1·525—1·54 in some parts of the system and 1·48—1·49 in others (see Note 6 to Table III).

If all the mixtures in the region of the two-liquid system are prepared with little or no heating, the tie-lines are found to run approximately parallel to one another, while the solution and corresponding equilibrated dry (glassy) solid points lie on an elongated, roughly elliptical, closed curve (Fig. 1).

Mixtures in the more dilute region of the two-liquid system will actually deposit glassy solid if heated, but this does not apply to mixtures in the more concentrated region. The solid which has separated on heating usually redissolves again fairly soon after cooling to the original temperature.

The latter mixtures after being heated to 100° or even less for some time remain supersaturated for a considerably longer time when shaken at 25° than do mixtures which have not been heated. When glassy solid does separate at 25° from such heated solutions, the aqueous liquid soon adjusts itself to a point on the normal curve of the two-liquid system, but the composition of the glassy solid is generally too basic and may require a very lengthy period for proper adjustment. This too basic solid (after equilibration) may or may not fall on the curve of the two-liquid system but gives a tie-line which cuts across those of experiments in which the mixtures had not been heated. The behaviour indicates that heating has altered in some way the nature or relative concentration of the ionic or other species in solution. The composition of the glassy solid which separates is bound to reflect this alteration. The outermost layer of the glassy particles after they have been shaken for some time at 25° will no doubt have the composition which should correspond to that of the aqueous solution, but adjustment of composition throughout the whole glassy particle is a very slow process so that even after long shaking at 25° the bulk composition of the glassy solid remains abnormal in such cases.

TABLE III.

Two-liquid system I at 25°.

Solution.		" Glassy " Solid.							
		Moist.		Air-dry.		Equilibrated.		Time of shaking at 25°	
Al_2O_3, %	SO_3, %	Al_2O_3, %	SO_3, %	Al_2O_3, %	SO_3, %	Al_2O_3, %	SO_3, %	(weeks).	Note.
13·60	12·82	—	—	—	—	25·1	18·6	—	(1)
10·38	9·79	22·49	13·66	—	—	—	—	4	
5·28	6·55	16·93	12·85	—	—	28·63	19·25	9	
4·38	5·46	—	—	34·19	22·34	29·55	19·30	9·5	(2)
4·32	5·28	13·38	10·33	—	—	—	—	2·5	
4·10	5·22	20·23	14·12	—	—	—	—	8	
2·94	4·03	13·19	9·86	—	—	—	—	7	
2·88	3·96	—	—	30·39	23·79	—	—	7	(3)
2·73	3·82	17·12	11·92	—	—	—	—	7	
2·68	3·73	13·90	10·05	—	—	—	—	7	
2·40	3·42	—	—	35·93	20·26	29·41	16·58	7	(4)
2·09	3·09	18·99	12·74	—	—	—	—	7	
1·78	2·76	19·19	12·04	—	—	—	—	9	(5)
1·55	2·54	16·40	14·10	—	—	—	—	23	(6)
1·29	2·11	14·76	9·90	—	—	—	—	7	(7)
1·26	1·87	12·65	8·54	—	—	—	—	8 (days)	(7)
1·24	2·11	25·59	15·05	36·48	21·12	30·24	17·51	32	(8)
1·16	1·95	18·54	12·05	—	—	—	—	8	
0·928	1·67	13·69	8·85	35·02	20·39	28·53	16·63	7	(9)
0·934	1·61	—	—	—	—	30·64	18·28	5	(10)
0·681	1·24	13·43	8·34	—	—	—	—	10	
0·680	1·24	15·39	9·36	—	—	29·74	16·42	13	(11)
0·502	1·00	—	—	—	—	30·12	17·85	12	(12)
0·212	0·436	17·20	9·89	—	—	28·49	15·79	9	(13)
0·102	0·209	15·95	8·74	—	—	—	—	—	(14)
0·0418	0·091	11·71	6·44	—	—	—	—	6	
0·037	0·084	10·69	5·88	—	—	—	—	3·5	
0·0354	0·0807	13·91	7·47	—	—	—	—	6	
0·0248	0·055	9·77	5·12	—	—	23·48	12·17	9	(15)
0·0143	0·033	16·82	8·31	—	—	—	—	11 (days)	(16)
0·0133	0·0308	—	—	—	—	23·25	11·86	3 (days)	(16)
0·0103	0·021	8·88	4·45	—	—	18·29	9·17	5	(17)

Notes to Table III.—(1) This was a special experiment made in an attempt to obtain a pair of points in the very concentrated region of the two-liquid system. A very viscous concentrated basic solution was prepared by method (iii). After filtration it was evaporated at room temperature over calcium

chloride and gave a brittle glass (containing 30·24% Al_2O_3; 24·76% SO_3). This was then equilibrated over another basic solution which it was thought might be related to the glass as the complementary liquid phase. The glass increased in weight by nearly 24% owing to water absorption during the first 12 days. A decrease in weight then began owing to devitrification of the glass, with formation of crystals of $5Al_2O_3,6SO_3,46H_2O$. The rate of decrease in weight gradually diminished and a plot of the weights at different times showed that a constant weight of 0·44 g. would have been reached after 120 days from the start of the experiment which, however, was stopped for analysis after 89 days when the weight was 0·4413 g. The composition of the equilibrated solid (referred to the 120-days final weight) was 26·26% Al_2O_3; 21·63% SO_3. It was an opaque hard lump, all the original pieces of glass having joined together. Examination with a lens during the solution in 2N-hydrochloric acid showed it to consist of small, but well-formed, prisms of $5Al_2O_3,6SO_3,46H_2O$ cemented together by (presumably) glassy material. During the course of the equilibration many crystals of $5Al_2O_3,6SO_3,46H_2O$ had also separated from the liquid solution. The latter was filtered from these and the composition found by analysis is given in Table III.

A line drawn from the $5Al_2O_3,6SO_3,46H_2O$ point on the triangular diagram through the point corresponding to the equilibrated solid was produced until it cut the curve drawn through the points for the solutions in Table III. This gave 25·1% Al_2O_3; 18·6% SO_3 as the probable composition of the "glass" in equilibrium with the solution containing 13·6% Al_2O_3; 12·82% SO_3.

(2) The mixture for this experiment was prepared by adding the air-dried precipitate obtained by three-fold dilution of a concentrated solution to some of the undiluted solution. The "glassy" solid, analysed after 9·5 weeks' shaking at 25°, had almost the *R* value to be expected (according to the majority of the results in Table III) for one in equilibrium with the concentrated solution and not with one a third of the concentration. The composition of the original glassy solid must have been adjusted during the shaking, which was possible because the particles were very fine. In this particular experiment equilibration was done at room temperature, which is the probable reason for the water content of the equilibrated solid being considerably higher than it should have been.

(3) Solid phase was a mixture of "glassy" solid and $5Al_2O_3,6SO_3,46H_2O$. The solution point falls exactly on the curve of the two-liquid system.

(4) This mixture was prepared by method (iii) and filtered, and the clear solution heated in boiling water for 6 hours, water lost by evaporation being replaced. Much glassy solid separated. This was allowed to settle, and half the solution removed by decantation. The rest of the solution and the solid were then shaken at 25° for 7 weeks. The solution and the equilibrated solid point fall on the curve of the two-liquid system, but the solid is considerably more basic than corresponds to the majority of the experiments in Table III. It was a mixture of fair-sized glassy discs and finer material, and its amorphous nature was confirmed by *X*-ray examination.

(5) The mixture of this experiment had been prepared without much heating by method (iii) to contain approx. 2·69% Al_2O_3, 3·25% SO_3. It was inoculated with a very small amount of crystals of both $5Al_2O_3,6SO_3,xH_2O$ and $5Al_2O_3,3SO_3,xH_2O$. After 2 days' shaking at 25° a small amount of solid phase was present which contained a large proportion of needles of $5Al_2O_3,6SO_3,46H_2O$. The rest seemed to consist of the glassy solid, but no crystals of $5Al_2O_3,3SO_3,xH_2O$ could be distinguished.

The mixture was then heated for some time. This destroyed the crystals of $5Al_2O_3,6SO_3,46H_2O$ and caused much glassy solid to separate. The mixture was again inoculated with some of the same two crystalline solids as had been previously used, but these had all dissolved when the mixture was examined after 3 weeks' shaking at 25°. After 9 weeks' shaking at 25° from the second inoculation the (silica) tube was opened and the contents separated for analysis. No crystals of either inoculant could then be detected. Much of the solid was in the form of irregular and disc-like glassy fragments with much finer material. The solution point and tie-line are absolutely typical of the two-liquid system.

The most remarkable feature of this experiment is that the solution which was originally supersaturated with respect to $5Al_2O_3,6SO_3,46H_2O$ became unsaturated with respect to it—temporarily at least—after heating. This indicates some important change in the nature of the aqueous solution caused by heating, as does the change in viscosity referred to on p. 2260.

(6) The solid phase was a mixture of prisms of $5Al_2O_3,6SO_3,46H_2O$ with a considerable proportion of relatively large discs of glassy solid. The aqueous solution was still somewhat supersaturated in all probability (see p. 2249). After only 9 weeks' shaking at 25° it had contained Al_2O_3, 1·85; SO_3, 2·76%. The refractive index of the "glassy" discs was 1·477 ± 0·003 (see p. 2258).

(7) The solution points for these two experiments fall on the curve of the two-liquid system I and give almost identical tie-lines. The mixture for the experiment giving a solution of *ca.* Al_2O_3, 1·29; SO_3, 2·11% was prepared by method (iii) followed by dilution, while the mixture for the other experiment was obtained by boiling 0·5 g. of $5Al_2O_3,6SO_3,xH_2O$ with 10 c.c. of water for an hour. This second solution was still slightly supersaturated owing to the short period of shaking.

(8) The solution had exactly the same composition after only 16 weeks' shaking. The solid was glassy, in characteristic bright groups of spherical particles. The points for solution and for moist and equilibrated solids fall exactly on a straight line. The *X*-ray diagram showed that, while the solid was essentially amorphous, there was a very small admixture of the crystalline $5Al_2O_3,3SO_3,xH_2O$. This experiment is also quoted in Table V.

(9) This mixture had been prepared from 4·49 g. of aluminium and 500 c.c. of 0·515N-sulphuric acid warmed to 30° for 3 days; reaction was then complete, much glassy solid having separated. Mercury globules were separated by decantation, and the mixture left in a tightly corked flask at room temperature for 68 months, after which period the "solid" still consisted entirely of glassy material. Some of the mixture was then shaken at 25° for 7 weeks, and solution and moist solid were then separated and analysed with the results shown. These give a tie-line which is perfectly normal in comparison with those given by the other experiments of Table III. It cuts the curve of the two-liquid system at a point corresponding to Al_2O_3, 30·60; SO_3, 18·25%, which should be the composition of the equilibrated glassy solid.

The rest of the mixture was filtered on the pump, and the solid washed with 50 c.c. of cold water and

air-dried (yield 8·6 g.). It was greyish owing to the presence of 0·8% of finely divided mercury. Analytical results quoted have been corrected for this. The composition of the solid before and after equilibration over the 25° equilibrium solution is shown in Table III. Its somewhat different composition and greater basicity as compared with that indicated by the tie-line passing through the point corresponding to the moist solid is probably due mainly to the fact that the 8·6 g. of filtered solid had been in equilibrium with solution, not at 25°, but at an average temperature which was about 10° lower.

This experiment illustrates the remarkable persistence of the metastable " glassy " condition.

(10) This had been allowed to stand for 6 weeks at room temperature after preparation, and was then shaken for 5 weeks at 25°. The solid was shown to be amorphous by *X*-rays.

(11) The equilibrated solid is slightly too basic and so is not quite in line with the solution and moist solid points.

(12) This solid was in the form of fairly large glassy spheres, shown to be amorphous by *X*-rays, which had been formed by the gradual dilution of a much more concentrated solution over a period of about 2 months. It is rather less basic than it should be to fall into line with most of the experiments in Table III, owing probably to the inner portions of the spheres having separated from more concentrated solutions which were in equilibrium with more acidic glasses than the more dilute solutions.

(13) This mixture was prepared by method (iii), followed by tenfold dilution. The solid phase was shown to be amorphous by *X*-rays.

(14) This mixture had been prepared from 1·35 g. of aluminium and 500 c.c. of 0·103N-sulphuric acid warmed to 30° for 3 days; reaction was then complete, much glassy solid having separated. Mercury globules were separated by decantation, and the mixture was kept at room temperature, in a tightly corked flask, for 68 months. The solid phase was then seen to consist mainly of glassy solid with a small proportion of fairly large crystals. These were in the form of somewhat rounded St. Andrew's crosses seen, in polarised light, to be due to twinning or intergrowth of prisms. A portion of the mixture was shaken at 25° for 2 months, and solution and moist solid then analysed, with the results shown in Table III. The tie-line shows that R of the glassy solid was about 1·39. The rest of the mixture was stirred, allowed to settle for a short time, and the coarse crystals separated by decantation. To the settled mixture of crystals with about 5 c.c. of solution were added 5 c.c. of 2N-hydrochloric acid. After about 30 minutes at room temperature all glassy solid had dissolved, but the crystals appeared unaltered. The solution was opalescent from a trace of semi-colloidal mercury, from which the crystals were easily separated by decantation. They were then filtered off, well washed with cold water, and air-dried. The yield of crystals was only 0·0244 g., and they contained Al_2O_3, 45·97%; SO_3, 15·60%; $R = 2·31$, and gave a characteristic *X*-ray diagram. The crystals are those of a new compound $7Al_2O_3,3SO_3,xH_2O$ (see p. 2271). The original decantate from these crystals had been kept, and 3 years later a further very small amount of much smaller crystals was separated from the mixture by repeated settlement and decantation. There was not sufficient for analysis but only for *X*-ray examination. This showed that the crystals consisted of $5Al_2O_3,3SO_3,xH_2O$ after separation and air-drying. This suggests that the solution of this experiment gives a point very close to that at which the solubility curve of $5Al_2O_3,3SO_3,xH_2O$ cuts that of $7Al_2O_3,3SO_3,xH_2O$. The solution point actually found is on the curve of two-liquid system I, and probably very slightly supersaturated towards one or both of these two crystalline basic salts. The recorded results are explicable if the $7Al_2O_3,3SO_3,xH_2O$ first obtained was actually metastable towards $5Al_2O_3.3SO_3.xH_2O$.

It seems likely that the solubility curve of $7Al_2O_3,3SO_3,xH_2O$ will cut that of γ-$Al_2O_3,3H_2O$ (hydrargillite) before cutting that of the two-liquid system I, which is probably metastable towards some crystalline compound over the whole of its range (see Fig. 2).

(15) This mixture was prepared by pouring rapidly into 5 l. of distilled water at 25°, 20 g. of a clear solution containing approximately Al_2O_3, 4·3; SO_3, 5·3%. Solid began to separate after about 10 sec. After settling overnight, most of the clear liquid was decanted, and by repeating the settling process most of the rather bulky solid and about 60 c.c. of solution were transferred to a large silica tube in which it was shaken at 25°. The solid used for the equilibration experiment had been given one small wash with water and air-dried, and was in moderately hard lumps which remained in this condition at the end of the experiment, which took 6·5 weeks.

(16) In each of these experiments 0·11 g. of $5Al_2O_3,6SO_3,xH_2O$ was boiled with 65 c.c. of water in silica flasks for 2 hours. The one mixture after 11 days' shaking at 25° was filtered, and solution and moist solid were analysed. The second mixture was filtered after 3 days' shaking at 25°. The solution was analysed, and the solid washed with a little water, air-dried, equilibrated over some of the solution, and then analysed. The tie-lines are normal for the two-liquid system I. Equilibrium between solid and solution had adjusted itself quickly because of the small amount of solid present. *X*-Ray examination showed the solid to be amorphous.

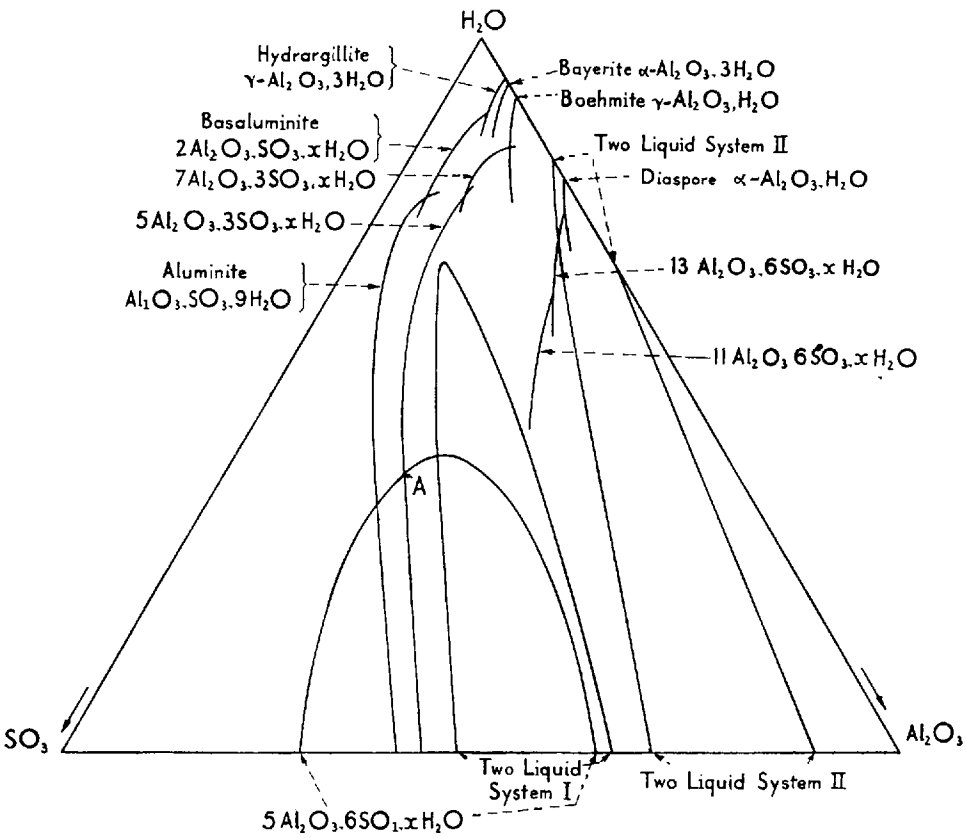
(17) The mixture was prepared and the experiment carried out as in Note (15) by pouring 20 g. of a solution containing approximately Al_2O_3, 4·6; SO_3, 7·2% into 10 l. of water. The equilibrated solid was soft but friable. Equilibration took only 4 weeks.

It was found on numerous occasions that, in the more concentrated region of two-liquid system I, if the basic solutions were heated to about 100° for some time, during or after preparation, their subsequent behaviour was considerably altered. The separation of crystals of $5Al_2O_3,6SO_3,46H_2O$, was hindered, but formation of crystals of the very basic $5Al_2O_3,3SO_3,32H_2O$ (see pp. 2266, 2267) appeared to be facilitated. The heating probably causes the formation of more basic complexes and leads to a complete readjustment of the equilibrium of the solutions which on cooling only slowly returns to that appropriate to the lower temperature. This means that solutions of the same percentage composition may at the same temperature and pressure have different ionic compositions. The case is analogous to that of solutions containing green and purple chromic salts or of solutions containing ortho- and pyro-phosphates. The existence of such differences in the case of basic aluminium sulphates is supported by experiments made at Billingham in 1935 which showed that the viscosity of

basic aluminium sulphate solutions, after 3 hours' heating to 100°, increased by an amount which, though small, was probably significant. It was 6% for a solution containing about Al_2O_3, 10; SO_3, 12%, but only 3% for a less basic one containing about Al_2O_3, 10; SO_3, 15%. A phosphate solution containing much pyrophosphate might similarly be unsaturated towards an orthophosphate to which it would be saturated if all the dissolved phosphate were in the form of orthophosphate.

Any change in the ionic composition of the solution would be reflected in the composition of glassy solid which separated from it. This would account for the results obtained in the experiment in Table III to which Note 5 refers. Other evidence for the effect of heating on the nature of basic aluminium sulphate solutions is considered later (p. 2273).

FIG. 2.



Key to Fig. 2.

Suggested probable relative positions of the solubility curves in the immediate neighbourhood of the water point on a much larger scale than that of Fig. 1. Some idea of the scale can be obtained from the concentrations at point A which are about Al_2O_3, 1·2; SO_3, 2·1%. *If the diagram could be drawn truly to scale all the points where curves cut the right-hand side of the triangle would probably appear within the very short range* 0—0·01% Al_2O_3, *except perhaps the lower point for the curve of two-liquid system II.*

Two-liquid System II.

The curds obtained from aluminium hydroxide sols by the action of sulphate ions and aluminium hydroxide precipitated by ammonia from sulphate solution contain considerable amounts of sulphate which it is almost impossible to remove by washing with water. These facts suggested some relationship to the "glassy" solid phase of the two-liquid system I, as did the general behaviour of hydroxide sols (Bassett and Durrant, *loc. cit.*, p. 280). Investigation of the matter appears to show that these hydroxide curds and precipitates represent the more concentrated phase of a second two-liquid system more basic than that already considered.

It is surprising how difficult it is to obtain an aluminium hydroxide precipitate which is truly amorphous to *X*-rays. This can only be done, in our experience, by precipitation in the cold with the minimum amount of alkali; we always used ammonia. Even when so obtained, most aluminium hydroxide precipitates, after being washed and dried at room temperature, give an *X*-ray diagram containing a few broad lines corresponding to the chief lines of boehmite or γ-Al_2O_3,H_2O. In many cases these are sharp enough to be referred to sub-crystalline (*i.e.*, particles of diameter 500—600 A.)

rather than amorphous (*i.e.*, less than 50 A.) material. In other cases, superimposed on this sub-crystalline boehmite pattern, are the two innermost lines of the bayerite (α-$Al_2O_3,3H_2O$) diagram. As a rule these are so sharp as to indicate the presence of truly crystalline rather than sub-crystalline material. As the proportion of this present in the specimen increases, the number of sharp lines due to bayerite also increases. This is important, as the two innermost lines of the bayerite (α-$Al_2O_3,3H_2O$) diagram are indistinguishable from the corresponding lines of γ-$Al_2O_3,3H_2O$. It is evident that the normal change is from sub-crystalline boehmite (γ-Al_2O_3,H_2O) to crystalline bayerite (α-$Al_2O_3,3H_2O$).

Precipitation in the cold with a large excess of ammonia favours the formation of α-$Al_2O_3,3H_2O$ with particles large enough to yield a very sharp *X*-ray pattern. Aluminium hydroxide precipitates obtained with ammonia seldom give *X*-ray diagrams indicative of the presence of amorphous or sub-crystalline hydrargillite (γ-$Al_2O_3,3H_2O$) but occasionally such precipitates are obtained.

Crystalline hydrargillite is best obtained from sodium aluminate solutions.

Precipitates formed at 100° are translucent and look very amorphous to the naked eye. They alway seem to give a boehmite (γ-Al_2O_3,H_2O) *X*-ray diagram, often with very sharp lines. This shows that the crystalline portion of the precipitatee is relatively coarse. The reluctance with which such precipitates dissolve in dilute acid seems to be chiefly due to this. It would seem that real ease of solution of aluminium hydroxide in acid is only found when much truly amorphous material is present and that the reactivity towards acid of the crystalline hydroxides is determined largely by crystal particle size, although there is some evidence that the α- and γ-monohydrates are less reactive that the α- and γ-trihydrates and dissolve more slowly in either acid or alkali (see, *e.g.*, Frary, *Chem. and Ind.*, 1946, **65**, 14). The chief difficulty in making any such comparison lies in obtaining the compounds in comparable conditions of particle size. When coarsely crystalline, they all dissolve with great difficulty even in concentrated hydrochloric acid.

The curds obtained by coagulation of aluminium hydroxide sols, even when they are very old, give *X*-ray photographs which are essentially similar to those given by ordinary aluminium hydroxide precipitates (compare Bassett and Durrant, *loc. cit.*, p. 289).

X-Ray diagrams of partially amorphous or glassy materials give a very uncertain indication of the proportion of non-crystalline matter which is present. Even a very small proportion of crystalline material may give rise to a number of quite sharp lines. It is probable that both the cold- and the hot-precipitated aluminium hydroxide, which look amorphous, contain a relatively large proportion of truly amorphous material. The proportion of this may be less in the hot-precipitated material, and this would be an additional reason for its lower reactivity towards acids. The boehmite lines when they first begin to appear in the *X*-ray diagrams are very diffuse but become sharper as the material becomes more crystalline, and this is an indication that boehmite is the first crystalline compound to separate. The lines due to bayerite are quite sharp right from the beginning even when only the two innermost lines of its diagram are present. This may well be due to the bayerite resulting from recrystallisation of the primary boehmite when this has already reached the sub-crystalline stage. Relatively large crystallites of the secondary compound are thus formed almost as soon as it begins to appear. The initial slow building up of a crystalline structure has been doen by the boehmite. This curious difference has already been noticed by Kraut, Flake, Schmidt, and Volmer (*Ber.*, 1942, **75**, 1357) though no reason for it was suggested.

It may be that diaspore is actually the first crystalline hydroxide to form, but that it is so unstable under the usual conditions of precipitation and changes so quickly into boehmite that it escapes notice. In any case we have never noticed diaspore lines in the *X*-ray spectra of any of our preparations. Laubengayer and Weisz (*J. Amer. Chem. Soc.*, 1943, **65**, 247) state that in the system Al_2O_3–H_2O corundum is stable above 450° ± 5°, diaspore (α-Al_2O_3,H_2O) between 280° and 450°, boehmite (γ-Al_2O_3,H_2O) between 155° and 280°, and hydrargillite (γ-$Al_2O_3,3H_2O$) below 155°. Bayerite (α-$Al_2O_3,3H_2O$) also occurs below 155° but is less stable than hydrargillite. γ-Alumina is metastable from 100° to 500° (see also Cooke and Haresnape, *Trans. Faraday Soc.*, 1947, **43**, 395).

" Bayer hydrate " is a name often used technically for the crystalline hydrargillite (γ-$Al_2O_3,3H_2O$) obtained in the ordinary Bayer process for purifying bauxite. It is better to avoid this name owing to the danger of confusion with bayerite (α-$Al_2O_3,3H_2O$).

TABLE IV.

Two-liquid system II at 25°.

Solution.		Equilibrated curd.			*n* value of curd (Bassett & Durrant, *loc. cit.*).*	Expt.	Note.
Al_2O_3, %.	SO_3, %.	Al_2O_3, %.	SO_3, %.				
0·0012	0·0017	30·12	8·82	Aluminium hydroxide precipitated by ammonia from sulphate	7·0	(*a*)	(1)
0·0006	0·0016	42·53	8·19		11·2	(*b*)	
Too little to detect		13·62	2·34		12·7	(*c*)	
,,	,,	8·13	1·36		13·1	(*d*)	
0·0011	0·0025	34·96	5·67	Curd precipitated from aluminium hydroxide sols. by $(NH_4)_2SO_4$	13·5	(*e*)	(2)
0·0005	0·0016	48·83	4·77		23·0	(*f*)	
0·0002	0·0005	44·98	3·32		30·9	(*g*)	
Too little to detect	0·02	38·23	2·66		32·8	(*h*)	

* n = equivs. of $Al(OH)_3$/equivs. of bound $Al^{\cdots}$, where bound $Al^{\cdots}$ is equivalent to the SO_4'' present (Bassett and Durrant, *loc. cit.*, p. 281).

Notes to Table IV.—(1) 2 G. of $Al_2(SO_4)_3,16H_2O$ were dissolved in 20, 60, 600, and 2000 c.c. of water, corresponding to experiments (*d*), (*c*), (*b*), (*a*) in Table IV, and each solution was treated in the cold with 6 c.c. of 3·2N-ammonia. Precipitates were well washed with cold water till they gave no reaction with Nessler's reagent, and then shaken with 20 c.c. of water in silica tubes at 25° for 6—8 weeks; the mixtures were then separated for analysis of the solutions and precipitates. The latter were washed with a few c.c. of water, air-dried for 48 hours, and then equilibrated over some of the corresponding solution before analysis. Equilibration took about 7 weeks. The more dilute the solution from which the precipitate had been originally formed, the larger the proportion of sulphate present in the precipitate.

The *X*-ray diagram of hydroxide (*a*) showed only the haloes characteristic of a glass. The hydroxides of experiments (*b*), (*c*), and (*d*) all gave *X*-ray patterns characteristic of incipient boehmite crystallisation and suggestive of the presence of particles with diameters of 50 A. or less.

(2) The procedure in the four aluminium hydroxide sol experiments was essentially similar to that described above except that the precipitates were obtained by the action of ammonium sulphate on the sols. The curds are not very easy to wash. Analyses of sols 7, 9, and 12 and details of their preparation are given by Bassett and Durrant (*loc. cit.*).

(2) Sol 4, when 8 days old, contained the following species in concentrations given in milligram-equivs. per litre :

Total Al.	Un-ionised Al.	Bound Al$^{\cdots}$.	Free Al$^{\cdots}$.	Cl′.	*n*.
1037·6	898	99	40·6	139·6	9·07

It had been prepared from hydroxide precipitated in the cold from $Al_2(SO_4)_3$ solution.

The ages of these sols at the date of the present experiments are shown below in parentheses. Details of each experiment are given below.

(*e*) Sol 9 (3½ yrs.). 80 C.c. of slightly opalescent non-thixotropic sol were pipetted away from a considerable sediment of bayerite (α-$Al_2O_3,3H_2O$) and curded with 0·2 g. of ammonium sulphate in 5 c.c. of water. *X*-Ray examination of the curd showed lines due to sub-crystalline boehmite together with a series of spots due to a small proportion (5% ?) of crystalline material. Comparison with the *X*-ray diagrams of the crystalline basic sulphates and hydrated aluminas showed that this crystalline material was almost certainly the basic sulphate with $R = 2·17$.

(*f*) Sol 4 (6½ yrs.). No sediment had separated from this sol, which was translucent and very thixotropic. 35 C.c. were curded with 0·2 g. of ammonium sulphate in 5 c.c. of water. The *X*-ray diagram indicated that the curd contained much sub-crystalline bayerite (α-$Al_2O_3,3H_2O$) plus a little much finer boehmite.

(*g*) Sol 7 (4 yrs.). This was translucent and rather viscous but not thixotropic and had not deposited any sediment. 80 C.c. were curded with 0·2 g. of ammonium sulphate in 5 c.c. of water. *X*-Ray diagram showed this curd to contain sub-crystalline boehmite.

(*h*) Sol 12 (2¾ yrs.). This translucent, very thixotropic sol had deposited no sediment. 55 C.c. were curded with 0·2 g. of ammonium sulphate in 5 c.c. of water. According to the *X*-ray diagram this curd contained sub-crystalline boehmite. The solution in this experiment was found to contain an excessive amount of sulphate (0·02%) but insufficient Al_2O_3 to be detected. The solution gave a strong reaction with Nessler reagent, so it is evident that in this case the curd had not been sufficiently washed. The results have been included in Table IV because they seem to fall into line with the others in spite of the presence of this ammonium sulphate.

There is still lack of agreement as to which forms are to be designated α- and γ-, and γ-forms are nowadays sometimes called β-forms, so it is best always to give the mineralogical name in addition to any alphabetical prefix. α-$Al_2O_3,3H_2O$ has not been found as a mineral but the name bayerite is often applied to it. The synthetic γ-Al_2O_3,H_2O is now generally called boehmite, bauxite being regarded as the name of a " rock " which, though often consisting mainly of γ-Al_2O_3,H_2O, may contain other hydrates of alumina and other constituents too.

The more basic two-liquid system was studied as described in the notes attached to Table IV, which summarises the results obtained.

The four experiments with precipitated aluminium hydroxide recorded in Table IV give a smooth curve as shown in Fig. 1 which is very similar to that given by the more acid two-liquid system I. The four experiments with curds from aluminium hydroxide sols give points displaced from this curve in the direction of the Al_2O_3 point. This may well be due to the proportion of crystalline or sub-crystalline material present in these curds, and from 25 to 33% of such material would be adequate to account for the displacement. The *X*-ray diagrams suggest that an amount of that order must be present. The initial amorphous precipitate of so-called aluminium hydroxide appears to behave as a liquid phase. It may contain $Al(OH)_3$ and AlO·OH molecules and aggregates of these, together with various basic aluminium kations and SO_4 ions. The AlO·OH is the first hydroxide to crystallise, but once the more stable crystals of $Al(OH)_3$ begin to form they grow more rapidly and larger crystals of α- or γ-$Al_2O_3,3H_2O$ appear to be normally obtained at 25° than of γ-Al_2O_3,H_2O. It cannot be supposed that either the crystalline or sub-crystalline hydroxides could dissolve sulphate in the same way as the amorphous " hydroxide " (*i.e.*, the liquid phase), but it is possible that considerable surface adsorption of sulphate and water by the crystalline and sub-crystalline hydroxide would occur. It is the resultants of these three effects due to amorphous, sub-crystalline, and crystalline material which lead to the figures shown in Table IV.

The view that amorphous precipitated aluminium hydroxide is a second, very concentrated liquid phase in equilibrium with a very dilute aqueous solution gives a reasonable explanation of the facts, and explains its peculiar properties, in particular, its capacity for " carrying down " and obstinately retaining other constituents of the solution. It is probable that many other amorphous precipitates have a similar nature. The curve of this second two-liquid system probably runs from a point on the

H_2O–Al_2O_3 side of the triangular diagram very close to the H_2O point and eventually returns to the same side of the triangular diagram at a point rather further from the H_2O point. These two points correspond to the aqueous solution free from sulphate and to the pure amorphous liquid hydroxide phase, also free from sulphate, with which it is in equilibrium. This two-liquid system will be metastable towards the crystalline hydroxides—hydrargillite (γ-$Al_2O_3,3H_2O$), bayerite (α-$Al_2O_3,3H_2O$), and boehmite (γ-Al_2O_3,H_2O)—and to the crystalline basic aluminium sulphates. Hydrargillite alone of the crystalline hydrated aluminas has a stable range of existence at 25° in contact with extremely dilute solutions in the immediate neighbourhood of the water point.

The composition of the aqueous solutions in Table IV is subject to considerable uncertainty owing to the very low concentrations and the minute weights of alumina and barium sulphate obtained in the analyses.

The values of n for the hydroxide phase of two-liquid systems II are shown in Table IV, where n is defined. Fig. 1 shows that the lowest n value corresponding to any point on the curve of two-liquid system II is about 7, and for the greater part of the curve the value does not rise above 13. It is evident that near where the curve cuts the H_2O–Al_2O_3 side of the triangular diagram the hydroxide phase may have very large n values (up to infinity !). It may be that the two-liquid system curve obtained with completely amorphous aluminium hydroxide would lie a little more to the SO_3 side of the diagram and correspond to a minimum n value of 6. It seems possible that no aluminium hydroxide sol can have micelles with a smaller n value than 6. This would correspond to complete conversion of the hydroxide into $7Al_2O_3,3SO_3,xH_2O$, the most basic sulphate for which there is any evidence. Bassett and Durrant's method (*loc. cit.*) does not enable the minimum value of n to be determined with any certainty owing to complications caused by the presence of basic kations in the aqueous solution as well as in the micelles.

The bivalent sulphate ion is not a satisfactory anion for positive aluminium hydroxide sols. Such sols would usually break up into the two-liquid system aqueous solution–curd. It may be presumed that any such sols, which are obtainable, will be represented by points which fall within the closed curve of two-liquid system II.

The *X*-ray diagrams of the " glassy " or amorphous phases of two-liquid systems I and II both show very faint indications of broad lines or haloes but are so similar as to be indistinguishable. The glass of two-liquid system I seems to be more stable than the amorphous phase of two-liquid system II but in course of time both begin to show lines in their *X*-ray diagrams which are clearly referable to definite crystalline compounds. In the case of two-liquid system II it is only exceptionally that the amorphous phase does not show from the start lines which are clearly due to incipient boehmite. Boehmite lines never appear in the *X*-ray diagrams of the glassy solid of two-liquid system I. Such lines as do eventually appear suggest incipient formation of either $5Al_2O_3,6SO_3,xH_2O$ or $5Al_2O_3,3SO_3,xH_2O$.

At Black Spring, Doughty Springs, Delta Co., Colorado, a precipitate has resulted from the mixing of an alkaline water with one containing aluminium sulphate. The " mineral " so formed has been called doughtyite [Headden, *Proc. Colorado Sci. Soc.*, 1905, **8**, 66; *J.*, 1906, **90** (Abs.), II, 37]. We have taken the *X*-ray diagram of the British Museum Specimen (B.M.1910.475) and find it to be typical of an amorphous material and just like that of the fully amorphous phases of two-liquid systems I and II. The specimen was collected by Headden at the same time as the sample he analysed. The strongest line of the quartz diagram—somewhat " spotty "—is seen, thus indicating the presence of a few fine grains of quartz in the specimen. Headden's analytical results correspond with those required by the formula $Al_2(SO_4)_3,5Al_2(OH)_6,21H_2O$ (40·8% Al_2O_3; 16·0% SO_3). This composition does not give a point on our curve for two-liquid system II—40·8% Al_2O_3 would require only about 10% SO_3 on our curve. It is not known at what temperature the doughtyite had been precipitated, and the material analysed had probably been air-dried for some considerable time. Both these factors would have a great effect on the composition : the solid in Table IV which contained, after equilibration, 30·12% Al_2O_3; 8·82% SO_3, had the much higher content of 41·02% Al_2O_3; 12·02% SO_3 before equilibration. It is suggested that doughtyite in its original condition had contained about 10% Al_2O_3, 4% SO_3, and represented a glassy phase of two-liquid system I. This had lost much water between the times when it was collected and analysed.

Crystalline Compounds covering the R *Range of* 1·67—2·33 (Plate, Nos. 11—14).

There are at least five compounds in this range with R values of 1·67, 1·83, 2·00, 2·17, and 2·33 with distinct *X*-ray diagrams.

The compound with $R = 2·00$ has, so far, only been found as a mineral, and the compounds with $R = 1·83$ and 2·17 have only been obtained by the sol method. Both $5Al_2O_3,3SO_3,xH_2O$ and $7Al_2O_3,3SO_3,xH_2O$ have been prepared by method (iii) from solutions containing only Al_2O_3, SO_3, and water. $5Al_2O_3,3SO_3,xH_2O$ can also be prepared by the sol method and, best of all, by a modification of the latter.

The extremely short range of stable (?) existence of these very basic compounds constitutes the major difficulty in their preparation. This range at 25° appears to be between the approximate concentration limits Al_2O_3, 1·2; SO_3, 2·1% and Al_2O_3, 0·0005; SO_3, 0·0015%. At the one end of this range $5Al_2O_3,6SO_3,46H_2O$ becomes the stable (?) solid phase, and at the other end hydrargillite.

It is not possible to say with certainty whether, in the three-component system at 25°, any of these compounds are entirely metastable, nor can it be stated which of them have definite ranges of stability in contact with solution or what the limits of the ranges are. If, however, as suggested on p. 2273, the compounds with $R = 1·83$ and 2·17 have structures based on that of diaspore, they would probably be metastable at 25° towards $5Al_2O_3,3SO_3,xH_2O$ and

$7Al_2O_3,3SO_3,xH_2O$ if these have a layer-lattice structure based on that of boehmite. $5Al_2O_3,3SO_3,xH_2O$ and $7Al_2O_3,3SO_3,xH_2O$ would in their turn be metastable towards basaluminite and aluminite if these have structures related to that of hydrargillite (see Fig. 2).

The sol method enables highly supersaturated solutions to be prepared from which by appropriate procedure the basic salts with $R = 1{\cdot}67$, $1{\cdot}83$, or $2{\cdot}17$ can be obtained in a well-crystallised condition and in reasonable amounts. Separation of amorphous matter causes no difficulty in the preparation of the compounds with $R = 1{\cdot}83$ or $2{\cdot}17$ by the sol method, but such trouble is met with when preparing the compound with $R = 1{\cdot}67$ by this method. It is evident that two-liquid systems analogous to those found in the system Al_2O_3–SO_3–H_2O also occur in the five-component system involved in the sol method of preparation.

It is interesting, and may have some significance, that the R values of all the known aluminium sulphates, other than double salts, can be expressed by the ratio $x/6$, where x can have most of the values from 1 to 14. The compound with $x = 1$ would be $Al_2(HSO_4)_6,xH_2O$. It is doubtful if it has been prepared. Salts with all other values of x up to 14 are dealt with in the present communication excepting those where x is 4, 7, 8, or 9. These are not known at present, but one is tempted to think that they may be found some day and so complete the series.

(1) $2Al_2O_3,SO_3,xH_2O$.—Steinberg (*J. pr. Chem.*, 1844, **32**, 495) gave the name paraluminite and the formula $2Al_2O_3,SO_3,15H_2O$ to a mineral from Halle, Saxony, the type locality for aluminite. This mineral has always been regarded as a doubtful species, and we found that the British Museum specimen (B.M. 54801) which came from Caden, Morbihan, Brittany, gave the X-ray diagram of alunite. Recent discoveries in Northamptonshire (see p. 2251) have thrown new light on the matter. A pure white crystalline mineral has been found in considerable amounts in cracks and fissures in the ironstone which has the same R value (2·0) as Steinberg's paraluminite. It occurs in two forms differing in their degree of hydration. The less hydrated form gives the X-ray diagram of the material found by the author and by Bannister and Hey associated with aluminite on many specimens of that mineral. The more hydrated form has quite a different X-ray diagram when in the wet state, as found, but on keeping it tends to lose water and then gives the X-ray diagram of the lower hydrate. It is of some interest that aluminite has not, so far, been found in the Northampton deposits. The author has been able to analyse a specimen of this new mineral (the less hydrated form) through the kindness of Messrs. Bannister and Hey. It was in soft lumps and the values found for two different lumps were :

	I.	II.		I.	II.
Al_2O_3	44·35%	43·93%	$CaCO_3$	0·45%	0·01%
SO_3	15·56%	16·24%	H_2O (diff.)	36·83%	38·29%
SiO_2	2·81%	1·53%			

Fe, Mg, Na, and K were absent unless in minute traces. The silica was present as a silicate which gelatinised readily with hydrochloric acid (there was no quartz present). This silicate was most probably allophane, $Al_2O_3,SiO_2,5H_2O$, which occurs in the Northamptonshire ironstone mines. Calculating the silica to allophane one gets for the mineral composition :

		I.	II.
Allophane		11·81%	6·43%
Calcite		0·45%	0·01%
As basic sulphate	Al_2O_3	39·57%	41·33%
	SO_3	15·56%	16·24%
	H_2O	32·61%	35·99%

The composition of the pure basic sulphate would be :

	I.	II.
Al_2O_3	45·10%	44·18%
SO_3	17·73%	17·36%
H_2O	37·16%	38·46%
$R =$	1·996	1·996

The results correspond to the formulæ: (I) $2Al_2O_3,SO_3,9{\cdot}25H_2O$, and (II) $2Al_2O_3,SO_3,9{\cdot}88H_2O$, which require (I) Al_2O_3, 45·28; SO_3, 17·76; H_2O, 36·96%, and (II) Al_2O_3, 44·17; SO_3, 17·33; H_2O, 38·50%. The more hydrated form of the mineral contains far more water than is required by the formula $2Al_2O_3,SO_3,15H_2O$. It has been established therefore that there is a mineral having $R = 2{\cdot}0$, but the precise relationship of the two different hydrates of this mineral to Steinberg's paraluminite remains obscure.

The new mineral $2Al_2O_3,SO_3,xH_2O$ (where x is probably 10) has been given the name "basaluminite," while the much more hydrated form has been called "hydrobasaluminite" (Bannister and Hollingworth, *loc. cit.*).

The story of this mineral illustrates the difficulty of attempting to identify minerals of the

nature of the basic aluminium sulphates merely from the appearance or from their locality and mode of occurrence. It would seem that all basic aluminium sulphate minerals require a thorough overhaul, *X*-ray and analytical.

(2) $5Al_2O_3,3SO_3,xH_2O$.—Crystals of $5Al_2O_3,3SO_3,xH_2O$ will separate spontaneously from suitable dilute solutions which have been only moderately heated during preparation by method (iii), but they can also be obtained at 25°, either spontaneously or after inoculation, from more concentrated solutions if these have been heated to from 80° to 100° for some time before being shaken at 25°. Such heating delays separation of $5Al_2O_3,6SO_3,46H_2O$, but does not appear to be necessary in the way that it is when preparation by the sol method is employed (see p. 2267).

The crystals are either small rectangular plates, sometimes with numerous facets, showing straight extinction, or four-sided platelets with angles of 80° and 100°, generally in characteristic doublets, the plates being joined at the acute angles. These doublets extinguish at 40° to one of the sides. Sometimes separate prisms with this extinction angle occur. The two types of crystal appear to be different habits of the same crystal form. A third variant is often obtained when the salt crystallises from solution on the sides of the containing vessel. It is in the form of a wedge looking almost like a right-angled isosceles triangle, the hypotenuse being the thin edge of the wedge and extinction parallel to this.

Solubility data relating to $5Al_2O_3,3SO_3,xH_2O$ at 25° are given in Table V. All the mixtures there recorded were prepared by method (iii).

TABLE V.

$5Al_2O_3,3SO_3,xH_2O$ *at* 25°.

Solution.		Moist solid.		Dry solid.		Equil. solid.		Shaken at 25° for	*R* of	
Al_2O_3, %	SO_3, %	Al_2O_3, %	SO_3, %	Al_2O_3, %	SO_3, %	Al_2SO_3, %	SO_3. %	(weeks).	solid.	Note.
9·03	9·33	25·03	15·02	—	—	—	—	4	—	(1)
7·71	8·58	17·72	13·04	—	—	—	—	3	—	(2)
6·98	9·18	24·88	14·55	—	—	—	—	7	—	(3)
7·01	8·44	—	—	37·67	18·44	—	—	1	1·60	(3*a*)
6·87	7·75	25·33	16·04	—	—	—	—	2·5	—	(1)
6·59	6·85	24·10	13·38	—	—	—	—	12 (days)	—	(4)
5·66	7·07	—	—	35·37	18·81	35·17	18·70	12	1·47	(5)
5·46	6·59	—	—	38·24	19·07	35·63	17·77	4·5	1·57	(6)
4·73	6·17	—	—	35·32	20·37	31·94	18·42	8	1·36	(6)
4·00	5·27	—	—	35·73	19·50	33·22	18·12	9·5	1·44	(7)
2·15	3·21	—	—	35·25	19·55	{30·88 29·68	{17·13 16·48	14	1·41	(8)
1·76	2·74	—	—	38·49	19·05	36·58	18·10	5·5	1·58	(9)
1·24	2·11	25·59	15·05	36·48	21·12	30·24	17·51	32	1·36	(10)
1·25	2·10	—	—	38·42	18·36	36·30	17·35	6	1·64	(11)
0·418	0·808	—	—	34·49	20·03	—	—	9	1·35	(12)
0·421	0·822	—	—	36·84	18·04	—	—	15	1·60	

Notes to Table V.—(1) Solid seen under microscope to consist of a mixture of prisms of $5Al_2O_3,6SO_3,46H_2O$ and the characteristic double platelets of $5Al_2O_3,3SO_3,xH_2O$. The mixture had been inoculated with the latter. No glassy solid could be seen, though some had separated at the start of the experiment.

(2) Mixture had been heated to 80° for an hour before being shaken at 25° to destroy prisms of $5Al_2O_3,6SO_3,46H_2O$. Solid phase consisted of a mixture of glassy solid and of well-formed small rectangular (nearly square) crystals showing straight extinction.

(3) Mixture had been heated in boiling water for an hour, which caused glassy solid to separate. After the shaking at 25° all of this had gone and there were only a few fairly large double platelets which were analysed in the moist condition. The tie-line runs very close to the point for $5Al_2O_3,3SO_3,32H_2O$, and nearly as close to that for $5Al_2O_3,3SO_3,35H_2O$. The solution point appears to lie on the true solubility curve of $5Al_2O_3,3SO_3,xH_2O$, which is very metastable in this region towards $5Al_2O_3,6SO_3,46H_2O$.

(3*a*) Solution of aluminium effected quickly by heating, and completed by standing overnight; inoculated with $5Al_2O_3,3SO_3,xH_2O$; after 7 weeks' shaking at 25° crystals of latter had separated, but after further 3 weeks needles of $5Al_2O_3,6SO_3,46H_2O$ were coming out. The bottle was opened and heated in boiling water for 10 minutes to destroy these. After a further 2 days at 25°, only $5Al_2O_3,3SO_3,xH_2O$ and probably a little glassy solid could be seen. The mixture was filtered for analysis. As water caused immediate separation of solid from the mother-liquor, the crystals were first washed rapidly with a few c.c. of 0·4N-hydrochloric acid, then with water, and air-dried. The *X*-ray diagram was typical of $5Al_2O_3,3SO_3,xH_2O$ with probably a very little glassy solid. The solution point lies either on or only just off the curve of two-liquid system I.

(4) The solid consisted mainly of small square plates, and the tie-line runs to a point close to that for $5Al_2O_3,3SO_3,32H_2O$. The solution is considerably supersaturated, and the solid probably contained some glassy solid.

(5) The solid was largely crystalline, apparently very minute square crystals, but the *X*-ray diagram shows that much glass was present also.

(6) The mixture was heated in boiling water for 7 hours, which caused much glassy solid to separate. Nearly all of this had redissolved after 15 hours' shaking at 25°. When the experiment was stopped, the solid consisted largely of the small square crystals, but there was some glass as well.

(7) The solid consisted chiefly of the double platelets of $5Al_2O_3,3SO_3,xH_2O$. No glassy solid could be seen, but the *X*-ray diagram indicates the presence of a considerable amount.

(8) This mixture had been heated considerably, which caused much glass to separate initially. After the long shaking at 25°, the fine solid which must have been mainly glassy contained many small but well-formed double platelets which were large enough for optical measurements. The equilibration curve of this solid showed two breaks, giving the two compositions for the equilibrated solid shown in Table V; water adsorption by the glassy solid continues after that by the partially dehydrated crystals has ceased.

(9) The mixture had been heated to the boil for a long time. The solid analysed was seen to be a mixture of glassy solid and well-formed square plates, showing straight extinction, of $5Al_2O_3,3SO_3,xH_2O$.

(10) The mixture was heated very little during preparation, and not above 25° subsequently. The composition of the solution was exactly the same after 16 weeks' shaking at 25° as after 32 weeks'. The *X*-ray diagram showed that the solid was mainly glassy, but most of the strong lines of $5Al_2O_3,3SO_3,xH_2O$ were showing up. This experiment is also quoted in Table III.

(11) The mixture was only gently heated during preparation, and was filtered before the 6 weeks' shaking from small amount of white solid which had separated during preparation. The solid analysed consisted of small nodular groups of crystals, some of which showed the double platelet form with angles of 100° and 80°. The microscopic appearance showed plainly that the solid was essentially crystalline, but a few thin discs of the glassy solid would have been undetectable among the crystals in the aggregates. The composition of the air-dry solid corresponds very closely to a mixture of 95% of $5Al_2O_3,3SO_3,32H_2O$ with 5% of an air-dry glassy solid of the same composition as that separated from the solution in Table V to which note 10 relates, while the composition of the equilibrated solid corresponds to a mixture of 95% of $5Al_2O_3,3SO_3,35H_2O$ with 5% of the corresponding equilibrated glass. This result is important as indicating that it is the 35-hydrate rather than the 32-hydrate which is in equilibrium with solutions at 25°. The tie-line evidence is so scanty that it cannot decide the precise nature of the solid phases in this part of the diagram.

(12) The mixture for this experiment had not been heated much but it had been inoculated with a little of the square crystals of $5Al_2O_3,3SO_3,xH_2O$. After 9 weeks' shaking the mixture was filtered and analysed; *R* of the solid phase was 1·35, and microscopically it consisted mainly of the glassy solid with a small amount of the square crystals. The solution point falls on the curve of the two-liquid system I. The rest of the filtered solution, after being kept at room temperature for 2½ years in a stoppered bottle, had given a small deposit consisting mainly of fair-sized prisms, extinguishing at 40° to the length when lying flat on the slide, together with a small proportion of characteristic clusters of the discs of glassy solid. This solid together with about half of the mother-liquor was transferred to a small solubility bottle and shaken at 25° for 15 weeks, and solution and solid were then analysed. The solid now seemed to consist only of the prisms; no glass could be distinguished under the microscope, having apparently dissolved with the rise of temperature to 25°. There was plenty of solution for analysis and its composition suggests that it no longer corresponds to a point on the two-liquid system I but that it may represent a point on the true solubility curve of $5Al_2O_3,3SO_3,xH_2O$—slightly on the acid side of the curve of the two-liquid system. The total weight of solid was only 3·8 mg. and the whole analysis had to be done on this small amount, so the experimental error may be considerable.

X-Ray diagrams were taken of all the solids in Table V which were separated in the dry state. The presence of some amorphous material was indicated in most cases, especially when *R* was much below 1·67. The lines in the diagrams were always in the same positions and of similar relative intensities.

The results obtained by method of preparation (iii) and summarised in Table V are important because the mixtures contain only Al_2O_3, SO_3, and H_2O and so enable the solubility curve of the salt $5Al_2O_3,3SO_3,xH_2O$ to be located with some degree of exactness. This curve is found to run very close to the curve of two-liquid system I towards which it is stable, but it cuts the curve of $5Al_2O_3,6SO_3,46H_2O$ at about Al_2O_3, 1·24; SO_3, 2·11%, so that in contact with more concentrated solutions than this it is metastable. It is difficult to obtain $5Al_2O_3,3SO_3,xH_2O$ free from $5Al_2O_3,6SO_3,46H_2O$ from such more concentrated solutions since the more acid salt tends to separate more readily and rapidly from solution. The method allows only small amounts of the salt to be obtained in any reasonable purity. This is chiefly owing to the ease with which contamination by the glassy solid of two-liquid system I can occur owing to the proximity of the two solubility curves and to the ease of separation of $5Al_2O_3,6SO_3,46H_2O$ first referred to.

Large amounts of $5Al_2O_3,3SO_3,xH_2O$ can be obtained in fair-sized crystals by the sol method (v) of p. 2240. It is important to heat the sol to about 100° for at least an hour before addition of the ammonium sulphate in order to obtain good yields and to avoid separation of the compounds with $R = 2·17$ or 1·83 or one of the double salts of the latter with ammonium sulphate.

The conditions of preparation by the sol method are much more complex than was realised by Bassett and Durrant. They failed to notice the presence of ammonia in the five preparations with $R = 1·64$ and 1·67 quoted in their paper [*loc. cit.*, expts. (IV), (V), and (VI), p. 292]. The corrected analysis of one of these preparations is given as an example. No. (i) of preparation (VI) contained Al_2O_3, 40·11; SO_3, 18·96; NH_3, 0·92 [= 3·57% $(NH_4)_2SO_4$]. Now [40·11/102]/[18·96/80] = 1·66, but after deducting SO_3 equivalent to the NH_3, the ratio becomes 1·86. These preparations actually consist of a new double salt (referred to as basic double salt I) $(NH_4)_2SO_4(11Al_2O_3,6SO_3,xH_2O)$ which is considered later. Its *X*-ray diagram differs from that of $5Al_2O_3,3SO_3,xH_2O$.

Bassett and Durrant's "Maltese-cross twins" with $R = 1·70$—1·72 really consist of $5Al_2O_3,3SO_3,xH_2O$,

probably contaminated with $7Al_2O_3,3SO_3,xH_2O$, but only very small yields were obtained in their experiments since the solutions had not been heated long enough. Even the yield of 0·68 g. given at the top of p. 293 of their paper is an error. The yields of fine and coarse material in that experiment have been transposed : that of the coarse was only 0·25 g. and that of the fine 0·68 g. The latter has since been shown to be glassy by *X*-rays.

Details of a number of well-crystallised preparations of $5Al_2O_3,3SO_3,xH_2O$ obtained by the sol method are given in Table VI. All these preparations gave *X*-ray diagrams typical of $5Al_2O_3,3SO_3,xH_2O$. The data given for each experiment relate to 10 g. of $AlCl_3,6H_2O$. In each case the ammonia was added to the chloride solution at room temperature with constant stirring. The mixture was then heated, for the time mentioned, to about 100° and then filtered before dilution and addition of ammonium sulphate. Ammonia was absent from all these preparations. Analyses refer to the air-dry solids.

It is clear that even when prepared by the sol method the conditions for separation of amorphous or glassy solid are very similar to those required by $5Al_2O_3,3SO_3,xH_2O$. The two tend to separate together but, as much larger quantities can be prepared by this method and in larger crystals, the latter are readily separated from the bulk of the amorphous material by treatment with dilute hydrochloric acid : good crystals so prepared still give somewhat hazy *X*-ray diagrams, possibly owing to glassy inclusions in the crystals.† It must be emphasised that this glassy solid which separates from the heated sol mixtures is not a gel obtained by curding a sol but is of exactly the same character as the glassy phase of two-liquid system I of the three-component system Al_2O_3–SO_3–H_2O. A true gel is obtained if the sols have not been heated for a sufficient time before addition of the ammonium sulphate. These gels correspond to the amorphous phase of two-liquid system II of the three-component system. In the simple Al_2O_3–SO_3–H_2O system, $5Al_2O_3,3SO_3,xH_2O$ often seems to form from the two-liquid system I which is metastable towards it, but this change is very slow. Much the same appears to happen in the sol method of preparation, but the presence of ammonium chloride accelerates the change. The amorphous solid which so often, but not always, is the first substance to separate in preparations by this method must be regarded as the amorphous or glassy phase of two-liquid system I. In such cases the major portion of $5Al_2O_3,3SO_3,xH_2O$ obtained results from the transformation of this amorphous phase, but quite a lot also separates from the aqueous liquid phase on the sides of the containing vessel in curious wedge-shaped crystals.

TABLE VI.

$5Al_2O_3,3SO_3,xH_2O$ *prepared by the sol method* : 10 *g. of* $AlCl_3,6H_2O$ *used in each experiment.*

3·2N-NH_3, c.c.	Time sol was boiled, mins.	Vol. of sol boiled, c.c.	$(NH_4)_2SO_4$, g.	Total vol., c.c.	Wt. of solid obtained, g.	Actual *R* value found.	Composition of crystals, %. Al_2O_3.	SO_3.	Note.
20	10	40	3	450	1·6	1·59	35·19 33·89	17·34 16·70	(1)
16·9	15	92	2·5	400	0·68 0·252	1·64 1·72	35·72 39·16	17·06 17·85	(2)
22·5	15	42	3	453	0·49	1·69	38·00	17·64	(3)
10	60	60	2	70	0·502	1·74	39·17	17·69	(4)
15	60	65	2	70	0·822	1·73	38·55	17·45	(5)
22·5	60	97	2·5	120	1·95 1·33	1·70 1·63	38·55 37·20	17·82 17·88	(6)
A*22·5	60	42	3	453	3	1·67	37·44	17·62	(7)
32·7	90	110	20	217	3·91 1·10	1·74 1·67	29·74 38·26	13·38 17·97	(8)
25·9	5 days	46	3	57	3·65	1·68	38·62	18·05	(9)
			Calc. for $5Al_2O_3,3SO_3,31H_2O$:				39·00	18·35	
			,, $5Al_2O_3,3SO_3,32H_2O$:				38·47	18·10	
			,, $5Al_2O_3,3SO_3,34H_2O$:				37·45	17·63	
			,, $5Al_2O_3,3SO_3,35H_2O$:				36·96	17·39	

* See p. 2273.

Notes to Table VI.—(1) Separation of solid began 10 minutes after dilution and addition of ammonium sulphate. After 3 weeks, some of finer portion of solid was separated and found to contain Al_2O_3, 35·95; SO_3, 17·58% in the air-dry state; $R = 1·60$. The rest of solid was separated by decantation, and 7 c.c. of 2N-hydrochloric acid were added to the 70 c.c. of solid plus solution to dissolve any amorphous solid. After 10 minutes' shaking the coarse crystals were filtered off and easily washed free from Cl and NH_3 and then air-dried. The *X*-ray diagram was only taken for the coarse crystals and was characteristic of $5Al_2O_3,3SO_3,xH_2O$. The lower values for Al_2O_3 and SO_3 in the table are for coarse crystals equilibrated over some of the mother-liquor at 25°.

100 C.c. of mother-liquor decanted from the crystals had been treated with a further 1 g. of ammonium sulphate, and after 7 months' standing in a covered beaker had shrunk to 35 c.c. A few small clear alum crystals and some small doubly refracting crystals of $5Al_2O_3,3SO_3,xH_2O$ had separated. The alum crystals were removed but, although they looked pure it was found, on dissolving them in warm water, that they contained a fairly large number of inclusions of crystals of $5Al_2O_3,3SO_3,xH_2O$. This supports the view that many of the apparently good crystals of $5Al_2O_3,3SO_3,xH_2O$ may have contained numerous inclusions of the glassy solid.

(2) Expt. (vii) quoted by Bassett and Durrant (*loc. cit.*, pp. 292, 293) but see p. 2267.

† See p. 2271 for a more probable explanation of the poor *X*-ray diagrams.

(3) Behaviour much as in (1). After 5½ weeks, the mother-liquors were removed by decantation, and 50 c.c. of approx. N-hydrochloric acid were added to the residue. This dissolved amorphous material at once and possibly some of the crystals. The latter were filtered off and washed.

(4) Small crystal deposit first seen a week after admixture. After 8 weeks' standing the volume had shrunk to about 50 c.c., and the solid seemed to consist entirely of the Maltese-cross twins. It was then separated and filtered off and washed easily.

(5) This mixture was quite undisturbed during the fortnight's crystallisation. The solid consisted of clear crystals which behaved like aggregates of plates.

(6) The second crop of crystals with $R = 1{\cdot}63$ had separated during 22 weeks' standing at room temperature of the filtrate from the first crop; about 20 c.c. of water had been lost by evaporation. No amorphous material was visible under the microscope in either lot of crystals.

(7) Much solid was present after 3 days and appeared to be amorphous. After 2 days more it began to show double refraction, and after 8 weeks' standing at room temperature with occasional stirring it looked entirely crystalline. The composition of the air-dry solid corresponds exactly to $5Al_2O_3,3SO_3,34H_2O$.

(8) The ammonia caused a permanent precipitate, so 9 c.c. of 2N-hydrochloric acid were stirred in to dissolve it before the heating. Addition of the ammonium sulphate soon caused a precipitate, and in the hope that this would dissolve, the whole mixture was heated to nearly 100° for some time. This seemed to increase precipitation. The precipitate settled rapidly and after washing and air-drying weighed 3·91 g. It was free from ammonia and amorphous to *X*-rays. After 4 days at room temperature the filtrate had deposited a smaller amount of fair-sized clear crystals free from NH_3 which were interpenetrating twins. After separation from the solution and air-drying they gave the *X*-ray diagram of $5Al_2O_3,3SO_3,xH_2O$. They were equilibrated over a solution which contained Al_2O_3, 1·27; SO_3, 2·00%, after the equilibration. Table V shows that such a solution should be in approximate equilibrium with $5Al_2O_3,3SO_3,xH_2O$. The equilibrated crystals contained Al_2O_3, 37·74; SO_3, 17·74%, approximating to $5Al_2O_3,3SO_3,34H_2O$. The experiment shows how very basic the amorphous solids can be which separate from the solutions on heating, and shows also that $5Al_2O_3,3SO_3,xH_2O$ has no tendency to form a double salt with ammonium sulphate in spite of the high concentration of this.

(9) The ammonia added was just that required to form $[Al(OH)_2]^+$. The 5 days' heating was done in a counterpoised silica beaker and the temperature varied between 50° and 100°. Water lost by evaporation was periodically replaced. Addition of ammonium sulphate caused no immediate precipitate, but after standing overnight at room temperature there was a slight prismatic deposit. The mixture was well stirred, and separation of solid seemed complete after 3 days. The solid was easily washed free from chloride and ammonia. The mother-liquor contained 0·85% Al_2O_3. No alum crystals were present. The experiment is important in showing that, after long heating, pure ammonia-free $5Al_2O_3,3SO_3,xH_2O$ can be obtained from very concentrated solutions.

TABLE VII.

$5Al_2O_3,3SO_3,xH_2O$ *prepared at* 70° *and at* 50°.

Solution.		Air-dry solid.			Time of heating,		
Al_2O_3, %.	SO_3, %.	Al_2O_3, %.	SO_3, %.	Temp.	(weeks).	*R*.	Note.
0·82	1·56	39·20	18·44	70°	4	1·68	(1)
0·022	0·049	37·98	16·82	70	6	1·77	(2)
0·494	0·977	37·41	18·32	50	5	1·60	(3)

Notes to Table VII.—(1) 3 G. of a slightly acid preparation of $5Al_2O_3,6SO_3,xH_2O$ (containing 26·6% Al_2O_3; 26·6% SO_3; $R = 0{\cdot}784$) and 50 c.c. of water were put in a 100-c.c. resistance-glass conical flask which was immersed up to the neck in a thermostat at 50°. The flask was then corked and occasionally shaken. After 16 hours' heating the solid had been converted entirely into amorphous pseudomorphs of the original crystals. The appearance of these was unaltered after a week when the temperature of the thermostat was raised to 70°. After 12 hours at this temperature, about half of the solid had become fairly coarsely crystalline and after a fortnight all amorphous material seemed to have disappeared. Heating was continued for another fortnight before separating solution and dry solid for analysis. Some of the clear solution was pipetted into weighing bottles. The rest of the solution with some of the finest solid was decanted and the remainder of the mixture filtered off on a small Buchner funnel and washed with 3·5 c.c. of water and then 3·5 c.c. of absolute alcohol. The weight of air-dry solid was 1·153 g. The solid was fairly coarsely crystalline in rectangular, nearly square, prisms showing straight extinction, with the roughish appearance described on p. 2271. It dissolved fairly easily on warming with 2N-hydrochloric acid and gave one of the best and clearest *X*-ray diagrams of $5Al_2O_3,3SO_3,xH_2O$ which we have obtained.

(2) Approx. 2 g. of a basic solid (*R* approx. 1·7) prepared by the sol method (and consisting apparently mainly of amorphous material with some crystals of $5Al_2O_3,3SO_3,xH_2O$ was placed in a resistance-glass conical flask with 50 c.c. of water. After an hour at 70° the solid had become largely converted into characteristic nodular and prismatic aggregates, and after 3 days about half seemed to be in this form. The remainder was very fine and might possibly have been amorphous. After a further 5½ weeks at 70° the appearance of the solid was essentially the same, so the mixture was filtered for analysis. The *X*-ray diagram was precisely like that of the previous preparation at 70°.

(3) 0·998 G. of the same basic solid (*R* about 1·7) referred to in Note (2) together with 0·803 g. of crystalline $Al_2O_3,2SO_3,11H_2O$ and 25 c.c. of water were heated at 50° in a Hysil-glass flask. After 20 hours' heating the solid was mainly crystalline and appeared to be entirely so after 5 weeks' heating, whereupon the mixture was separated for analysis. It gave a good *X*-ray diagram of $5Al_2O_3,3SO_3,xH_2O$.

Comparison of the figures in Table V and VII shows that, in the case of dilute solutions, the position of the solubility curve of $5Al_2O_3,3SO_3,xH_2O$ hardly changes between 25° and 70°.

The best and clearest crystals of $5Al_2O_3,3SO_3,xH_2O$ are most easily obtained by a modification of the sol method. It involves the initial preparation of a dilute basic aluminium chloride solution of controlled composition and containing no ammonium salts, unlike that prepared by the sol method. This solution is then precipitated by the addition of suitable amounts of ammonium sulphate. The initial basic chloride solution can be prepared by the solution of either aluminium *iso*propoxide or preferably of aluminium in a concentrated solution of aluminium chloride. The following preparations show the method of operation and the results obtained. 10 G. of $AlCl_3,6H_2O$ in about 20 c.c. of water were treated gradually with 17 g. of aluminium *iso*propoxide (containing 25% Al_2O_3). Solution was very slow in the cold but was hastened by boiling, which was continued under reflux for 5 days. This long boiling was given in the hope that it might establish a hydrargillite lattice structure in any " micelles " present in the solution which might facilitate the eventual precipitation of either aluminite or basaluminite should these have structures based on that of hydrargillite (see p. 2273). A small amount of hydroxide had separated from the solution during the boiling and this was filtered off. The clear filtrate was diluted to 500 c.c., and a solution of 5 g. of ammonium sulphate in 50 c.c. of water gradually added. A precipitate began to form after about three-quarters of the sulphate had been added. This appeared to be amorphous. After standing overnight, crystallisation in prisms and rosettes of prisms had begun, and appeared to be complete after 9 days, whereupon the solid was collected on a Buchner funnel and washed with 25 c.c. of cold water which was enough to remove all chloride. Weight of air-dried solid, 3 g., containing Al_2O_3, 38·56; SO_3, 18·00%; $R = 1·68$. The mother-liquor contained Al_2O_3, 0·11; SO_3, 0·49% by weight. The crystals evidently consisted of $5Al_2O_3,3SO_3,32H_2O$, but the important observation was made that during the air-drying of the washed crystals considerable loss of weight continued long after the crystals were dry in the ordinary sense. The crystals were weighed at frequent intervals during 9 days. There was a change in the rate of loss of water which indicated a loss of weight of 3·86% after the ordinary dry stage had been reached which would correspond to a loss of $3H_2O$ from $5Al_2O_3,3SO_3,35H_2O$ (Calc. loss for this change : 3·91%).

A second preparation was carried out in essentially the same way, but the aluminium *iso*propoxide was added more quickly which gave a much more colloidal solution. After the 35 c.c. had been boiled under reflux for 6 days much gelatinous solid had separated. After dilution with 25 c.c. of water the milky mixture gave a clear filtrate after passage through a Whatman No. 41 followed by a No. 42 filter-paper. The filtrate was made up to 100 c.c. and this diluted solution was analysed and found to contain Al_2O_3, 2·56; Cl, 1·93% (w/v). The remaining 95 c.c. of solution were poured into 2600 c.c. of water containing 3·44 g. of ammonium sulphate (the amount equivalent to the chlorine). There was no immediate precipitate but an appreciable amount had formed after 45 hours in the form of minute nearly circular transparent discs or spheres, probably of glassy solid. After 5 days there was much more solid, obviously crystalline in aggregates probably of platy crystals. Separation of solid seemed to be complete after further 3 days, and it was then separated as in the previous preparation. The behaviour of the crystals on drying was the same as in that experiment. Weight of air-dry solid, 2 g., containing: Al_2O_3, 39·46; SO_3, 17·87%; $R = 1·73$. The mother-liquor contained Al_2O_3, 0·04; SO_3, 0·075% by weight. It is thought that the solid was a mixture of 88% of $5Al_2O_3,3SO_3,32H_2O$ with 12% of the more basic $7Al_2O_3,3SO_3,33H_2O$, which requires Al_2O_3, 39·40; SO_3, 17·71%.

In a third preparation 0·9114 g. of aluminium was dissolved in 45·3 c.c. of N-hydrochloric acid by digestion for 5½ hours just below the boiling point, but as solution of the metal was still not complete a globule of mercury was added, and the mixture left overnight over a small flame. The mercury was then filtered off, and the solution poured into a dilute solution of 2·99 g. of ammonium sulphate, the volume of the mixed solution being made up to 2 l. There was no immediate precipitate but a considerable amount after 45 hours' standing. This was found to be relatively coarsely crystalline in separate clear crystals which were fairly thick rectangular plates. These were separated as before and showed the same behaviour on air drying. Weight obtained, 2 g., containing: Al_2O_3, 39·10; SO_3, 17·84%; $R = 1·72$. The mother-liquor contained: Al_2O_3, 0·033; SO_3, 0·068%.

A fourth preparation was carried out in an essentially similar manner from 6·83 g. of aluminium, 536·6 c.c. of N-hydrochloric acid, 35·42 g. of ammonium sulphate, and a final volume of 1 l. A yield of 1·4 g. of air-dry crystals was obtained of composition Al_2O_3, 38·39; SO_3, 17·91%; $R = 1·68$. The composition of the mother-liquor was : Al_2O_3, 1·22; SO_3, 2·07%. This gave a further crop of 1·15 g. of crystals after 5 weeks' standing at room temperature (Found : Al_2O_3, 38·50; SO_3, 18·07%; $R = 1·67$).

Still another solution was made from 0·683 g. of aluminium and 22·65 c.c. of N-hydrochloric acid, and after filtration and dilution to 50 c.c. this was added to a solution of 1·007 g. of ammonium sulphate in 950 c.c. of water. After standing with occasional stirring for a month, solution and solid were separated and analysed. Yield of solid after air drying, 1·9 g. The solution contained Al_2O_3, 0·0266; SO_3, 0·0169%, and the air-dry solid Al_2O_3, 40·77; SO_3, 17·66%; $R = 1·81$. The compositions of the latter corresponds exactly to that of a mixture of 75% of $5Al_2O_3,3SO_3,31H_2O$ and 25% of $7Al_2O_3,3SO_3,33H_2O$.

Since the air-drying had extended over 8 days under conditions of low humidity, the $5Al_2O_3,3SO_3,xH_2O$ may well have lost rather more water than usual. It is to be noted that the most basic " glassy solid " of two-liquid system I of which we have any knowledge had R about 1·74 (see note 8 to Table VI). It is also certain from the microscopic appearances of the present solid and all those prepared in a similar way that it was essentially, if not entirely, crystalline, so that admixture with the $R = 2·33$ salt appears to be the only way of accounting for preparations having $R = 1·7$ or above This applies to preparations made by the usual sol process also. It must be remembered that owing to the presence of ammonium salts the system has more than 3 components. If the NH_4 were equivalent to the Cl, as was approximately the case, the system would be one of 4 components, so that instead of there being only one solution in equilibrium with both of the salts with $R = 1·67$ and 2·33 at a given temperature, there would be a number of such solutions represented by a line on the isothermal diagram. This may be one reason for the difficulty in preparing pure $7Al_2O_3,3SO_3,xH_2O$.

When $5Al_2O_3,3SO_3,xH_2O$ has been air-dried the value of x is very close to 32. Crystals of the compound which have been washed only with water take an unexpectedly long time to reach constant weight when exposed to the air at room temperature. The weights at different times when plotted suggest that a rapid loss of weight due to free water is followed by a very much slower loss which ends when the composition corresponds to $5Al_2O_3,3SO_3,32H_2O$. The behaviour might be due to simple adsorption, to a zeolitic effect, or to the presence of a very unstable hydrate. The last possibility is ruled out because the original crystals still in their mother-liquor give the same X-ray diagram as the air-dry solid. Since the crystals are relatively large, it is more likely that the slow loss of water in the middle stage of the air-drying is due to zeolitic water rather than to surface adsorbed water, and the drying curves suggest that 3 or even more molecules of water may be involved in this way. Several equilibration experiments have indicated that two or three molecules of additional water can be taken up readily by the $5Al_2O_3,3SO_3,32H_2O$. It may be that the poor X-ray diagrams given by this compound are due to its zeolitic nature, since zeolitic water sometimes causes this sort of effect with compounds having layer-lattice structures.

The water in the wet crystals or the zeolitic water in the dry crystals gives rise to an amorphous " pattern " which is not visible against the lines of the crystalline framework but causes the photographs to have a dirty background just as those in question have. Even in $5Al_2O_3,3SO_3,32H_2O$ it is probable that some of the water is zeolitic, for a preparation of this salt obtained at 70° (see Table VII) contained rather less than $31H_2O$. The much clearer X-ray diagram which it gave corresponds to its much lower content of zeolitic water. On equilibration over the mother-liquors the air-dried solid regains some at least of the zeolitic water which has been lost. The air-dried crystals of this basic salt generally have a roughened, damaged appearance.

(3) $7Al_2O_3,3SO_3,xH_2O$.—This basic salt, with $R = 2{\cdot}33$, the most basic of all those obtained by us, was first obtained in very small amounts in the experiment quoted in Table III and discussed in Note 14 to that table. It is evidently closely related to $5Al_2O_3,3SO_3,xH_2O$ and probably has a similar type of structure. It is also formed from the glassy solid of two-liquid system I just as is $5Al_2O_3,3SO_3,xH_2O$. The X-ray diagrams of the two basic salts are also somewhat similar as regards both character and quality. This suggests that the air-dry $7Al_2O_3,3SO_3,33H_2O$ may result by loss of zeolitic water from a higher hydrate just as $5Al_2O_3,3SO_3,32H_2O$ appears to do.

$7Al_2O_3,3SO_3,xH_2O$ seems to be stable only in contact with solutions containing very low concentrations of Al_2O_3 and SO_3, which makes its preparation difficult. We have not yet succeeded in reproducing it in quantity at will. The composition found (Al_2O_3, 45·97; SO_3, 15·60%) is very close to that required by the formula $7Al_2O_3,3SO_3,33H_2O$ (Calc.: Al_2O_3, 46·13; SO_3, 15·51%).

The Basic Salts with R = 2·17 *and* 1·83 *and Double Salts of the Latter with Ammonium Sulphate* (Plate, Nos. 13—16).

These have only been obtained by the sol method and the procedure required is essentially the same in all cases. An aluminium chloride solution is treated gradually with ammonia with stirring so long as the precipitate first formed will redissolve owing to peptisation. It is best to use a fairly concentrated solution of aluminium chloride such as 10 g. of $AlCl_3,6H_2O$ in 20 c.c. of water, as the peptisation then occurs more readily and, for this quantity, one cannot in practice add more than about 31 c.c. of 3·2N-ammonia, which is four-fifths of that theoretically required to form $Al(OH)_3$. Use of rather less ammonia merely results in smaller yields of basic salt being obtained but does not affect its nature. It is not necessary to wait until peptisation is complete at room temperature. It is completed readily whilst the temperature is being raised to 100°. After addition of the ammonia the sol is boiled gently for 10 minutes. This converts the sol into a solution which no longer gives a curd of hydroxide on addition of ammonium sulphate. 5 Minutes' boiling is insufficient for this and gives a solution which produces about half as much curd with ammonium sulphate as is given by the unboiled sol, mixed with a correspondingly smaller amount of crystalline basic salt. Longer boiling than 10 minutes should generally be avoided as it lowers the yields of the compounds having $R = 2{\cdot}17$ or 1·83 owing to gradual formation of $5Al_2O_3,3SO_3,xH_2O$, a change which is usually complete after about an hour's boiling. After the 10 minutes' boiling the solution is filtered, if necessary, and stirred into a cold aqueous solution of ammonium sulphate. The nature of the crystalline compound which separates spontaneously on standing depends mainly upon the relative proportion of aluminium chloride and ammonium sulphate and only to a minor extent upon the actual concentrations. Special series of experiments showed that time of boiling and the basicity of the sols only altered the amount of the compound with $R = 2{\cdot}17$ or 1·83 which could be obtained but did not determine which of these actually separated. Neither could this be influenced by inoculation. It is clear that separation of these two basic salts, or the double salt with ammonium sulphate, does not depend upon the presence in the boiled solutions of two different ions or complexes one of which yields with sulphate ions the 2·17 compound while the other yields the 1·83 compound. All the evidence indicates that these two compounds are derived from one and the same ion or complex which is formed from the micelles of the sol by short boiling but is slowly converted by continued boiling into some other ion or complex which yields with sulphate ions $5Al_2O_3,3SO_3,xH_2O$.

With high concentrations of ammonium sulphate the 1·83 compound gives double salts, but apart from these it has not been possible to obtain any other very basic salts from the lightly boiled sols.

That a sol with different heat treatments can given two solutions giving two entirely different types of crystalline compound is of great interest. The solutions are not colloidal, but the very high basicity of the compounds which separate from them suggests that they must contain micelles approaching colloidal dimensions. They should repay further study.

Table VIII gives details of a number of preparations of the compounds with $R = 2{\cdot}17$ and 1·83 and the basic double salts I and II derived from the latter.

The Structures of the Basic Aluminium Sulphates.

Many basic salts are known to have layer-lattice structures which are related to those of the corresponding hydroxide and such, or related structures, seem far more probable for the very basic aluminium sulphates than those previously suggested (Bassett and Durrant, *loc. cit.*, p. 285). Aluminium hydroxide occurs in four different crystalline forms, and the rather

TABLE VIII.*

Preparations of compounds with R = 2·17 *and* 1·83 *and of basic double salts I and II* (Plate, Nos. 13—16).

(10 G. of $AlCl_3,6H_2O$ were used in each experiment.)

3·2N-NH_3, c.c.	Time sol was boiled, mins.	Vol. of sol boiled, c.c.	$(NH_4)_2SO_4$, g.	Total vol., c.c.	Wt. of solid obtained, g.	Actual *R* value found.	Composition of solid (air-dry), %. Al_2O_3.	SO_3.	NH_3.	Cl.
25·9	10	46	3	460	1·93	1·85	39·63	16·80	0·07	0·05
† 30	15	50	3	500	1·415	1·86	38·87	16·36	—	—
B30	10	130	5	1030	4·42	1·823	39·94	17·19	—	—
30	10	130	4	1030	4·36	1·87	39·63	16·66	—	—
30	10	130	3	1030	4·36	1·90	39·51	16·33	—	—
25	10	125	6	1025	2·80	‡ 1·844	39·13	17·42	0·33	—
30	10	130	6	1030	3·81	‡ 1·88	39·69	17·49	0·39	—
				Calc. for $11Al_2O_3,6SO_3,66H_2O$:			40·22	17·20		
				,, $11Al_2O_3,6SO_3,68H_2O$:			39·70	16·98		
25	0	100	1	900	Only curd obtained					
25	5	,,	1	,,	Half as much curd + salt with *R* = 2·17					
25	10	,,	1	,,	2·5	2·176	41·61	15·00		
25	20	,,	1	,,	2·02 } Not analysed but appearance showed that					
25	30	,,	1	,,	1·26 } both preps. consisted of salt with *R* = 2·17					
25	45	,,	1	,,	1·66	2·162	42·21	15·31	—	—
30	10	50	2	1000	1·76	2·17	42·68	15·42	—	—
Inoculated with 2·17-salt										
30	10	50	2	1000	1·75	2·15	42·34	15·45	—	—
Inoculated with 1·83-salt										
30	10	50	2	1000	1·87	2·15	41·04	14·95	—	—
Inoculated with $5Al_2O,3SO_3,xH_2O$										
30	10	50	2	1000	1·68	2·18	41·57	14·97	—	—
Inoculated with basic double salt I										
25 * ‖	10	125	1	1025	2·08	2·165	40·97	14·84	—	—
C30 * ‖	10	130	1	1030	3·22	2·176	41·40	14·92	—	—
30	10	50	1	2000	1·95	2·19	41·41	14·83	—	—
30	10	50	0·86	250	1·15	2·18	42·37	15·25	—	—
30	10	50	0·86	250	1·39	2·17	42·33	15·33	—	—
Inoculated with basaluminite										
				Calc. for $13Al_2O_3,6SO_3,76H_2O$:			41·77	15·12	—	—
				,, $13Al_2O_3,6SO_3,83H_2O$:			40·13	14·54	—	—
32	About 60 mins. at 70—80°.	132	3	530	3·58	1·68	40·22	18·76	0·84	—
D25·9	10	46	3	57	1·75	1·577	39·06	19·43 (air-dry)	1·33	0·38
							38·44	19·12 (equilibrated) on NH_4Cl-free basis	1·31	0·37
							38·65	19·22	1·14	—
				Calc. for $(NH_4)_2SO_4\{11Al_2O_3,6SO_3,66H_2O\}$:			38·40	19·17	1·16	—
E30	10	50	50	100	3·703	—	30·41	25·87	5·64	0·26
					on NH_4Cl-free basis		30·44	25·90	5·52	—
				Calc. for $6(NH_4)_2SO_4\{11Al_2O_3,6SO_3,72H_2O\}$:			30·41	26·02	5·53	—

* For B, C, D, and E, see p. 2273.

† About half of the original solid seemed to be amorphous. 50 C.c. of 2N-HCl were stirred in which dissolved amorphous part almost at once; the liquid was decanted, and the residue washed. A lot of washing was required to remove all NH_3 (200 c.c.), which suggests that some of basic double salt I was present originally.

‡ These *R* values are obtained after deduction of SO_3 equivalent to the NH_3.

‖ See note (p. 2276) about the separation of $5Al_2O_3,3SO_3$ from these mixtures.

peculiar conditions needed to obtain the several basic sulphates suggest very strongly that these are derived from different forms of the hydroxide and that establishment of the appropriate hydroxide structure is a principal necessity in the preparation of the different basic salts, which could only exist in a very restricted sense, if at all, in solution. Now diaspore, α-Al_2O_3,H_2O, can be regarded as built up of infinite strips each formed by the parallel linkage of two chains of AlO_6 octahedra with one-third of the octahedral holes unoccupied by aluminium. In boehmite, γ-Al_2O_3,H_2O, the diaspore bands are linked together into sheets (see Wells, "Structural Inorganic Chemistry," 1945, pp. 356, 357, and Fig. 97). Hydrargillite, γ-$Al_2O_3,3H_2O$, is built up of layers of $Al(OH)_6$ octahedra with one-third of the octahedral holes unoccupied. The structure of bayerite, α-$Al_2O_3,3H_2O$, has not been determined but it seems likely that the same layers of $Al(OH)_6$ octahedra are present. Although we have never observed the actual formation of diaspore in our experiments, it is reasonable to suppose that the irregular micelles of aluminium hydroxide sols are converted into bands or strips of the type characteristic of diaspore during the 10 minutes' boiling of the sols which is required for the preparation of the basic salts with R values of 1·83 and 2·17 and that these compounds have lattice structures derived from diaspore. The same change could probably occur slowly at room temperature, which would account for the fact that these basic salts can also be obtained in small amounts from sols which have not been boiled at all (Bassett and Durrant, *loc. cit.*, p. 291). The lattices derived from the diaspore structure appear to be saturated with sulphate in the compound $11Al_2O_3,6SO_3,xH_2O$, although the compound $13Al_2O_3,6SO_3,xH_2O$ is also stable in presence of a considerably smaller proportion of sulphate. This more basic compound is, however, readily converted into $11Al_2O_3,6SO_3,xH_2O$ by increasing the proportion of sulphate, and this is why the double salts formed with ammonium sulphate are always derived from $11Al_2O_3,6SO_3,xH_2O$ and not from $13Al_2O_3,6SO_3,xH_2O$. The ease with which $11Al_2O_3,6SO_3,xH_2O$ gives these double salts is a good reason for thinking that simple basic salts having the diaspore bands in their lattice do not exist with R smaller than 1·83. Formation of the boehmite structure is slow at room temperature, but much more rapid at 100°. This change would occur during the hour's boiling of the sols which is normally required for good yields of $5Al_2O_3,3SO_3,xH_2O$ to be obtained. This suggests that this salt has a structure based on that of boehmite. Since unheated basic aluminium sulphate solutions formed by method (iii) can yield crystals of $5Al_2O_3,3SO_3,xH_2O$, it would appear that their nature is essentially similar to that of solutions obtained by boiling the sols. Action of excess of alkali leads to formation of hydrargillite or bayerite. The latter is usually obtained by the use of ammonia, and the former by means of sodium hydroxide. Sheets having the hydrargillite structure are present in kaolinite. The field evidence suggests that aluminite and basaluminite, which are frequently associated in their occurrences, have been formed by the action of sulphuric acid or aluminium sulphate solutions upon clay or marl. A reasonable inference is that these two minerals probably have layer-lattice structures derived from hydrargillite.

The basic sulphates with R equal to unity or less may contain either chains of AlO_6 octahedra or even simpler structures (see pp. 2246, 2252, 2254).

The maximum theoretical yield obtainable by the sol method from 10 g. of $AlCl_3,6H_2O$ would be 5 g. of the salt with $R = 1·83$ or rather less than 4 g. of the salt with $R = 2·17$. The variation in yields obtained in the various experiments summarised in Table VIII is due to some extent to such factors as time of standing and amount of stirring between addition of ammonium sulphate and filtration of the basic salt. The supersaturation of the mixtures only breaks down slowly and the rate of separation of the various basic salts depends a great deal upon the number of nuclei of the separating salt which are present and the extent to which they are stirred up. An endeavour was made to keep these factors as similar as possible in any one set of experiments and not to filter off the product until separation seemed to be complete. Apart from variations due to such causes the tabulated results indicate that (in addition to the conclusions already drawn on p. 2271) an increased proportion of ammonia improves the yield of any one compound when other factors remain constant. It also appears that the lower the basicity and the more concentrated the sols the shorter the boiling which is needed to cause the changes which produce $5Al_2O_3,3SO_3,xH_2O$.

The ratio of $AlCl_3,6H_2O$ to $(NH_4)_2SO_4$ as well as the final concentration of the latter both seem to have some influence on the nature and yield of the compound obtained. There is considerable latitude allowable in the conditions of preparation of all the compounds but those employed in the experiments marked A, B, C, D, E in Tables VI and VIII seem on the whole to be the most satisfactory.

The compound with $R = 2·17$ is the easiest to obtain in the pure state owing to its

insolubility and inability to give double salts with ammonium sulphate. The compound with $R = 1{\cdot}83$ is more difficult to get pure because the conditions under which the pure compound or basic double salt I can separate from solution do not differ greatly.

The chief difficulty in the case of $5Al_2O_3,3SO_3,xH_2O$ is to get it quite free from amorphous material, as has been mentioned on p. 2267.

The compound with $R = 1{\cdot}83$ was obtained in good yield as follows: 10 G. of $AlCl_3,6H_2O$ in 200 c.c. of water were precipitated cold with a small excess of ammonia. Hydroxide was filtered off at the pump on a hardened filter-paper and washed with 200 c.c. of water to remove most of the ammonium chloride. The fairly hard cake was then well mixed with a spatula into 5 g. of $AlCl_3,6H_2O$ in 50 c.c. of water. Most of it peptised fairly quickly and after standing overnight had given a clear sol. This was boiled for 10 minutes, cooled by standing in cold water, and filtered from a trace of insoluble matter. A solution of 6·52 g. of " AnalaR " $Al_2(SO_4)_3,16H_2O$ (*i.e.*, the amount equivalent to 5 g. of $AlCl_3,6H_2O$) in 20 c.c. of water was then stirred fairly quickly into the sol. At first the mixture remained clear, but as the addition of sulphate proceeded it began to get milky and then rapidly became semi-solid after 15 c.c. of the sulphate solution had been added. 25 C.c. of water were added before completing the addition of sulphate. The precipitated solid was found to consist entirely of very minute needle-like prisms, so small and thin that it was difficult to see any double refraction. After 4 hours' standing it filtered off quickly and well on a Buchner funnel and was washed with 32 c.c. of cold water, followed by 10 c.c. of absolute alcohol and air-dried. Yield 3·7 g. (Found : Al_2O_3, 39·05; SO_3, 16·27%; $R = 1{\cdot}88$). It also contained 0·06% of NH_3. The *X*-ray diagram was exactly like other preparations having *R* of about this value [compare the experiments (i) and (ii) quoted by Bassett and Durrant (*loc. cit.*, pp. 290, 291)]. In those experiments the sols had not been heated at all, and it would seem that the amorphous (curd) phase of two-liquid system II is related to the crystalline basic salts with $R = 2{\cdot}17$ and $1{\cdot}83$ in much the same way that the glassy phase of two-liquid system I is related to the salt with $R = 1{\cdot}67$.

The compound having $R = 1{\cdot}83$ forms at least two double salts with ammonium sulphate. These are $[(NH_4)_2SO_4][11Al_2O_3,6SO_3,xH_2O)$ (x = about 66) and $6(NH_4)_2SO_4[11Al_2O_3,6SO_3,xH_2O])$ (x = about 72) and will be referred to as " basic double salt I " or " II ." The first of these forms well-developed flat prisms with square ends extinguishing at an angle of 12° to the sides of the prism. This enables it to be distinguished readily from the compounds having $R = 1{\cdot}83$ or 2·17, as well as from $5Al_2O_3,3SO_3,xH_2O$ since all of these form prisms showing straight extinction.

Two prisms of double salt I are often twinned or intergrown at right angles to their length, giving a characteristic Maltese cross.

" Basic double salt II " forms very well-developed and often large, transparent octahedra and tetrahedra. The angles of these are about those of the cubic system but these crystals show strong double refraction and are probably orthorhombic.

" Basic double salt I " is obtained very readily in good crystals and in good yield by the sol method from similar solutions to those which yield the compounds mentioned above. If the double salt is desired it is better to use a more concentrated solution and a higher proportion of ammonium sulphate. If it is not wanted it is better to use a more dilute solution with less ammonium sulphate though, even then, there is always a possibility of some of the double salt separating. This appears to be the case more particularly with preparations of the salt having $R = 1{\cdot}83$—probably because this is one constituent of basic double salt I.

By long-continued washing of basic double salt I with cold water the whole of the ammonia can be removed as sulphate from this double salt, but there occurs at the same time further hydrolysis of the basic sulphate so that the final, ammonia-free residue has $R = 2{\cdot}17$ and gives a sharp *X*-ray diagram identical with that of crystals having this value of the ratio but prepared directly. In the early stages of the washing it is probable that the ammonia-free basic salt which results is in an amorphous state, for a considerable proportion of the ammonium sulphate can be removed with little or no effect on the *X*-ray diagram which remains that of the basic double salt. Considerable solution of basic salt occurs during this hydrolytic washing, and if the washings are allowed to stand for some days a small amount of well-formed prisms of the compound with $R = 2{\cdot}17$ separates.

This decomposition and hydrolysis on washing of basic double salt I, slow though it is, makes the determination of its precise formula a little difficult. Prepared as in the experiments quoted by Bassett and Durrant and washed with about 50 c.c. of cold water, its *R* value is usually very close to 1·67 or, after deduction of SO_3 equivalent to the NH_3, to 1·86. Further washing increases both these ratios. This disturbance was minimised as far as possible in the following preparation: 20 g. of $AlCl_3,6H_2O$ in 40 c.c. of water were treated slowly and with stirring with 51·8 c.c. of 3·2N-ammonia, heated for 10 minutes to approximately 100°, and filtered from a little insoluble matter. 6 G. of ammonium sulphate in 20 c.c. of water were added. After standing undisturbed for 21 hours, there was a considerable crystalline deposit which adhered to the sides and bottom of the beaker so that the solution could be decanted with practically no loss of solid. The latter was washed by decantation in the beaker with several very small amounts each of 20%, 50%, 75%, and absolute alcohol. Even the 20% alcohol threw down a slight white precipitate (though small amounts of water did not) but by decanting this away the washed solids was not contaminated. The solid was finally detached from the beaker with a nickel spatula and air-dried; yield, 3·51 g. Some of the air-dried solid was equilibrated over some of the mother-liquor but only increased in weight by 1·7%.

		Al_2O_3, %.	SO_3, %.	NH_3, %.	Cl, %.
Found	air-dry	39·06	19·43	1·33	0·38
	equilibrated	38·44	19·12	1·31	0·37

The composition of the double salt on the ammonium chloride-free basis is :

	$(NH_4)_2SO_4$, %.	Al_2O_3, %.	SO_3 (total), %.
	4·48	38·65	19·22
Calc. for $(NH_4)_2SO_4[11Al_2O_3,6SO_3,66H_2O]$:	4·52	38·40	19·17

The *R* value for the double salt is 1·58, or 1·835 after deduction of SO_3 equivalent to NH_3 not balanced by Cl. The presence of the ammonium chloride is to be attributed to the somewhat inefficient washing. The latter has avoided any decomposition of the double salt, and the experiment shows that the basic constituent really has a relatively simple formula, which at first seemed doubtful.

The mother-liquors from the above preparation of basic double salt I, after 41 hours' heating at about 80°, had given a large deposit consisting of fairly large crystals of a rough appearance and apparently showing straight extinction. These crystals filtered easily and were washed with a very little water, then with 50%, 75%, and absolute alcohol and air-dried; yield 5·49 g. They gave a good "alunite" *X*-ray diagram in spite of a very abnormal composition. This case is discussed under "alunite" (see p. 2255, Notes 1 and 2).

Basic double salt I can also be prepared by the action of ammonium sulphate on previously prepared $11Al_2O_3,6SO_3,xH_2O$. This is best done in presence of some of the mother-liquor from which the 1·83-compound has crystallised since, if plain water is used, there is some hydrolysis with formation of small amounts of amorphous matter which make it difficult to obtain a pure preparation of the basic double salt.

Basic Double Salt II : $6(NH_4)_2SO_4[11Al_2O_3,6SO_3,xH_2O]$.

There are three methods by which this double salt can be prepared : (i) by the sol method directly, boiling for only 10 minutes and using a high concentration of ammonium sulphate; (ii) by the action of a solution of ammonium sulphate on basic double salt I; (iii) by the action of a concentrated solution of ammonium sulphate on the compound $11Al_2O_3,6SO_3,xH_2O$.

Method (i) is by far the best and simplest, but the other two are of interest as showing the close relationship of the three compounds. It is difficult to get quite pure preparations owing (*a*) to the ease with which ammonium sulphate is leached from the crystals and (*b*) to the formation of small amounts of amorphous basic products of hydrolysis which contaminate the crystals. This is due to the fact that, since none of the basic aluminium sulphates can form congruent solutions, any one of them is further hydrolysed to some extent by water or salt solutions. It is a serious cause of trouble when using methods (ii) and (iii) above. It could be avoided by using a solution of ammonium sulphate not in plain water but in the mother-liquor from which either of the salts $11Al_2O_3,6SO_3,xH_2O$ or $(NH_4)_2SO_4[11Al_2O_3,6SO_3,xH_2O]$ has crystallised. Difficulty (*a*) can be entirely overcome by restricted washing with suitable wash-liquors but the final product is usually contaminated with a trace of ammonium chloride. Method (i) was carried out as follows : To 10 g. of $AlCl_3,6H_2O$ in 20 c.c. of water were added fairly quickly with stirring 30 c.c. of 3·11N-ammonia. The mixture was heated quickly and peptisation was complete before it started to boil. It was boiled gently for 10 minutes and then cooled by standing the beaker in a trough of cold water. After filtration from traces of insoluble matter and dilution to 100 c.c., 50 g. of ammonium sulphate were added and dissolved by warming; the clear solution was then left undisturbed at room temperature. Crystallisation began after an hour, and a large deposit of fair-sized brilliant tetrahedra gradually formed on the sides and bottom of the beaker. Crystallisation appeared to be complete after 88 hours, and the whole of the mother-liquor was then removed by decantation. The loosely adherent crystals were then scraped on to a disc of hardened filter-paper on a small conical filter-funnel. After thoroughly draining on the pump, they were washed in succession with 3 c.c. of water, 50% and 75% alcohol, all three-quarters saturated with ammonium sulphate, and finally with absolute alcohol. The yield of air-dried crystals was 3·7 g. They consisted entirely of clear, fairly large (1—2 mm.) and well-formed doubly refracting tetrahedra quite free from alum crystals. Analysis gave the following results (in %) :

	Al_2O_3.	SO_3 (total).	NH_3.	Cl.	$(NH_4)_2SO_4$.
Found	30·41	25·87	5·64	0·26	—
On NH_4Cl-free basis this become	30·44	25·90	5·52	—	21·42
Calc. for $6(NH_4)_2SO_4[11Al_2O_3,6SO_3,72H_2O]$	30·41	26·02	5·53	—	21·47

The decantate from the double salt had by the next day deposited a little more of the double salt, but this was mixed with much ammonium alum, and in preparing this double salt it is necessary to be on one's guard against contamination with alum.

Basic double salt II is the compound obtained by Bassett and Durrant (*loc. cit.*, p. 293) in very small yield in the form of bright doubly refracting octahedra. The formula suggested by them, *viz.*, $2(NH_4)_2SO_4,5Al_2O_3,3SO_3,34H_2O$, from analysis of only 0·037 g. of the crystals is certainly incorrect.

The double salt is sometimes obtained in doubly refracting tetrahedra and sometimes in doubly refracting octahedra. Any one preparation generally consists entirely of either the one or the other but not of a mixture of the two types of crystals. The *X*-ray diagrams of the tetrahedral and octahedral forms are identical.

A preparation of basic double salt II from basic double salt I was carried out as follows : 1 G. of basic double salt I, 5 g. of ammonium sulphate, and 5 c.c. of water were shaken at 25°. After 18 days the prisms of the original double salt had all been converted into small doubly refracting octahedra of basic double salt II but much solid ammonium sulphate was also present. A further 5 c.c. of water had to be added before the latter had all dissolved after further shaking at 25°. A small amount of amorphous flocculent material was also present, which accounts for the rather high Al_2O_3 content of the preparation. The octahedral crystals were separated by decantation to remove as much as possible of the amorphous material and were then filtered off on the pump, washed with 2 c.c. of 60% and then 1 c.c. of absolute

alcohol and air-dried. Weight 1·13 g. [Found : Al_2O_3, 31·03; SO_3, 26·04; NH_3, 5·59% (= 21·70% $(NH_4)_2SO_4$)].

In another somewhat similar experiment the basic double salt I was not converted into the basic double salt II when shaken at 25° with a solution of 3·75 g. of ammonium sulphate in 12·5 c.c. of water but was converted by one containing 6·25 g. in 12·5 c.c. of water. A sample of $5Al_2O_3,3SO_3,32H_2O$ with $R = 1·67$ remained unaltered and gave no crystals of basic double salt II when shaken for a month at 25° with a saturated solution of ammonium sulphate. This is additional evidence that the structure of $5Al_2O_3,3SO_3,xH_2O$ must differ fundamentally from that of the compounds having $R = 1·83$ and 2·17. On the other hand, the sol obtained from 10 g. of $AlCl_3,6H_2O$ in 85 c.c. of water and 29 c.c. of 3·2N-ammonia after being heated to 100° for 40 minutes gave a good yield, 3·4 g., of basic double salt II after addition of 50 g. of ammonium sulphate in 100 c.c. of water. This result indicates that 40 minutes' heating to 100° of the very basic sol has been insufficient to destroy the condition which leads to precipitation of the compounds with $R = 1·83$ or 2·17 or their double salts and to give rise to one which permits $5Al_2O_3,3SO_3,xH_2O$ to separate. The less basic the sol the shorter appears to be the time of heating needed for this change to occur.

The change occurs to a very small extent, however, even after only 10 minutes' heating of very basic sols. The two mixtures marked with asterisks in Table VIII from which good yields of the salt with $R = 2·17$ had been separated had deposited, after 6 weeks' standing, a considerable amount of amorphous material in which were numerous small transparent square crystals. These were twins. They were bright between crossed nicols when the sides of the square were parallel to the cross-wires, and extinguished in hour-glass fashion when the diagonals of the square were parallel to the cross-wires. The clear liquid was decanted from the solid sediment. The two lots of the latter were combined, and 14 c.c. of 2N-hydrochloric acid were stirred into the total volume of 120 c.c. The amorphous solid dissolved, and the crystals were filtered off on the pump, washed with 15 c.c. of water and then 8 c.c. of alcohol and air-dried. The crystals (0·11 g.) gave the *X*-ray diagram of $5Al_2O_3,3SO_3,xH_2O$. It is quite clear that in all these basic aluminium sulphate solutions complex equilibria exist between many ionic, molecular, and even micellar species. These equilibria can be shifted and modified by heating or other treatment, but their existence tends to make the preparation of individual pure compounds a matter of considerable difficulty.

The fact is important that, in the case of both basic double salt I and II, the basic aluminium sulphate part of the double salt corresponds exactly to $11Al_2O_3,6SO_3,xH_2O$ when due precautions are taken to avoid decomposition. This makes it practically certain that the variation in the value of R between the limits 1·83 and 1·90 for the ammonia-free basic salt is due to the presence of small amounts of basic products of hydrolysis. As these products are amorphous they have practically no effect on the *X*-ray photographs. They result either from decomposition of small amounts of basic double salt I originally present as an impurity in the salt with $R = 1·83$ or by decomposition of the latter salt itself. 0·5 G. of this salt which had $R = 1·88$ was washed exhaustively with 200 c.c. of water on an ordinary conical funnel and filter-paper. The residue on the paper then had $R = 1·99$ and could be seen under the microscope to consist of a mixture of amorphous material and well-formed prisms of the compound having $R = 2·17$. The latter had clearly crystallised from solution in the funnel during the washing, and some more had crystallised from the filtrate. A small quantity of this salt (0·0453 g.), crystallised from solution in this way, was equilibrated at 25° over the solution from which it had separated. It absorbed 3·2% of water during this process and then gave on analysis Al_2O_3, 40·04; SO_3, 14·75% (Calc. for $13Al_2O_3,6SO_3,83H_2O$: Al_2O_3, 40·13; SO_3, 14·54%).

The compound with $R = 2·17$ is very resistant to further hydrolysis. 0·5686 G. of this salt with $R = 2·14$ was washed slowly with 400 c.c. of water (at room temperature). The washings contained in all 0·0038 g. Al_2O_3 and 0·0041 g. SO_3; $R = 0·725$. The removal of these amounts of Al_2O_3 and SO_3 would have raised the R value of the residue to 2·22. The *X*-ray diagram of the washed material was almost identical with that of the original apart from a slight blurring of the central lines owing to formation of amorphous material.

There is no evidence that $5Al_2O_3,3SO_3,xH_2O$ or the compounds with $R = 1·83$ and 2·17 or any double salts derived from these have ever been found as minerals. Bassett and Durrant (*loc. cit.*, p. 292) thought that the 2·17-compound might correspond to a mineral which had been recorded under the name of felsöbányite. This view is not tenable, however, for we have been able to determine the *X*-ray diagram of a British Museum specimen (B.M. 40280) of this rare mineral from Felsöbánya, Szatmár, Hungary (= Baia Sprie, Crisana şi Maramures, Romania). It occurs in this specimen as an incrustation on stibnite and appears to consist of radial groups of prisms. The *X*-ray diagram indicates the presence of some amorphous material but according to Mr. Bannister it is essentially that of allophane, $Al_2SiO_5,5H_2O$.

This work was started at the end of 1935 at the suggestion of Dr. M. P. Applebey who has taken a continued interest in it; further, various members of his staff at Billingham, and in particular Messrs. A. M. Clark and H. N. Wilson, gave information and assistance. Although most of the *X*-ray work connected with the investigation was carried out by one of the authors (T. H. G.), a considerable amount was done by Dr. G. H. Cheesman at Reading, and also by Mr. D. Clark of the Research Dept., Billingham. Dr. F. A. Bannister and Dr. M. Hey of the British Museum gave invaluable help in connection with the mineralogical bearings of the research. It is a pleasure to thank all of these for their assistance and Imperial Chemical Industries Ltd. and Messrs. Peter Spence & Sons Ltd. for generous apparatus and money grants.

Practically the whole of the experimental work recorded in this paper was carried out in the Chemical Dept. of the University of Reading, but a few of the last experiments have been done at Widnes.

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Appendix.

The *X*-ray photographs to which the data in Table IX relate were taken with a 6-cm. camera, using Cu-*K*α radiation, some by Dr. T. H. Goodwin and some by Dr. G. H. Cheesman. The measurements of the lines were made by Miss M. Kolasa in Dr. Goodwin's laboratory at the University of Glasgow. Only the first 10—15 lines are recorded though from 40 to 56 lines were actually measured in different cases down to spacings of about 1 A. Intensities were measured visually the value 10 being given to the strongest line, and ½ to one only just visible. Proportional values were assigned to other lines. *b*, *bb*, or *bbb* signifies broad or diffuse, *u* uncertain.

Table X relates to the *X*-ray diagrams of the series of alunites of Table IIA. These photographs were taken by Mr. D. Clark of the I.C.I. Research Department, Billingham with a 19-cm. camera using Cu-*K*α radiation. He also measured the lines. Intensities were measured visually; *s* signifies strong, *m* moderate, *w* weak, (*b*) broad, (*d*) diffuse. In these tables the spacings are recorded down to about 1·5 A., but all which were fainter than very weak (*vw*) are omitted. Far more spacings were actually measured, and reflections down to 5° could be observed.

In all the tables the spacings, *d*, are given in Ångström units.

TABLE IX.

(1) $Al_2(SO_4)_3,16H_2O$, alunogen, from Chile (see p. 2246 for analysis). No. 1 on Plate.*

d.	*I.*	*d.*	*I.*
13·96	8	4·37	10 *b*
9·41	2 *bbb*	3·91	9
7·11	7	3·62	7
6·49	3	3·42	5 *u*
5·96	3	3·32	6 *u*
4·83	4	2·97	8 *bb*

(2) $Al_2O_3,2SO_3,11H_2O$. No. 2 on Plate.

d.	*I.*	*d.*	*I.*
6·99	9	4·23	4
5·80	7	4·00	10
5·36	4 *u*	3·87	5 *u*
4·98	8	3·73	10
4·53	8	3·52	3

(3) $5Al_2O_3,6SO_3,46H_2O$. Specimen with $R = 0·805$ (see Table II). No. 3 on Plate.

d.	*I.*	*d.*	*I.*
12·96	8	4·48	8
10·85	9	4·08	10
9·69	6 *u*	3·80	4 *u*
8·33	10	3·61	6
7·24	8	3·33	7
5·92	6	3·16	5 *u*
5·55	7	2·99	8
4·93	6		

* The *X*-ray diagrams of very pure synthetic $Al_2(SO_3)_4,16H_2O$ and of the mineral alunogen appear to be identical in all respects. There are indications of a faint and fuzzy line of spacing 9·41 A. but it is considered unlikely that this belongs to $Al_2(SO_3)_4,16H_2O$.

(4) $5Al_2O_3,6SO_3,40H_3O$. Specimen with $R = 0·824$ (see Table II). No. 4 on Plate.

d.	*I.*	*d.*	*I.*
14·21	10	4·22	7
10·85	4	3·90	5
8·23	7	3·57	6 *bb*
7·38	7	3·08	4
6·67	3	2·91	6
6·23	4	2·77	6
5·19	6 *b*	2·55	4
4·62	7		

(5) $Al_2O_3,SO_3,9H_2O$, aluminite, from Halle, Saxony (see p. 2252). No. 5 on Plate.

d.	*I.*	*d.*	*I.*
9·25	9	3·80	10
7·72	10	3·49	6
6·45	8	3·23	4
5·49	6	3·12	7
4·98	7	2·93	5
4·69	7	2·75	6
4·35	9	2·53	3

(6) $Al_2O_3,SO_3,6·78H_2O$. No. 6 on Plate.

d.	*I.*	*d.*	*I.*
11·88	7 *bbb*	3·62	8
7·67	9	3·22	8 *b*
6·63	7	3·03	7
6·01	6 *bbb*	2·75	7 *b*
4·64	9	2·59	5
4·27	10	2·45	5

(7) $Al_2O_3,SO_3,5H_2O$. No. 7 on Plate.

d.	*I.*	*d.*	*I.*
7·72	8	5·00	4
7·04	7	4·44	5
6·58	4	4·21	4
6·18	4	4·00	10
5·89	4	3·77	3
5·27	3	3·65	3

(8) $Al_2O_3,SO_3,4H_2O$. No. 8 on Plate.

d.	*I.*	*d.*	*I.*
9·60	10 *b*	2·77	5
7·05	6	2·65	4
5·96	5	2·56	½
4·78	10 *bb*	2·48	3
3·83	9 *b*	2·34	7
3·45	6	2·19	7
3·18	7	2·11	½
2·95	10 *bb*		

(9) Australian alunite (see section 17 for analysis). No. 9 on Plate.* †

d.	*I.*‡	*d.*	*I.*‡
10·24	4 *u*	2·45	3
7·32	4 *u*	2·30	2
5·62	5	2·26	7
4·92	7	2·20	4
3·46	6	2·01	2
3·28	1 *bu*	1·89	7
2·99	10 *b*	1·82	½
2·85	3		

* The lines with spacings 10·2 and 7·3 A. were undoubtedly present in the *X*-ray photos of both Australian alunite and one preparation of synthetic potassium alunite which were taken at Reading. As other workers have failed to detect these two lines, they are probably not due to alunite.

† No. 10 on Plate is the diagram of synthetic ammonium alunite, the first preparation given in Table IIA. The measurements of this diagram are given in section 18.

‡ See also Pabst (*Amer. Min.*, 1947, **32**, 29).

TABLE IX (*continued*).

(10) $7Al_2O_3,3SO_3,33H_2O$ (measured by T.H.G.). The photograph was not considered good enough for reproduction.

d.	*I.*	*d.*	*I.*
13·8	8	3·64	4
11·6	10	3·51	4
8·73	8	3·28	— †
6·71	6	2·77	4 †
5·96	4	2·500	4
5·05	4 *	2·400	2
4·60	— *	2·306	2
4·23	6	2·400	2
3·86	4		

(11) $2Al_2O_3,SO_3,xH_2O$, Basaluminite (see pp. 2251 and 2265).‡ No. 11 on Plate.

d.	*I.*	*d.*	*I.*
12·15	10	3·81	6 *bb*
9·05	9	3·58	7
7·01	5 *bbb*	3·41	6
5·82	6	3·19	5
5·25	6	3·03	5 *bbb*
4·64	9 *b*	2·78	4

(12) $5Al_2O_3,3SO_3,32H_2O$. Specimen with $R = 1·60$ (see Table VII). No. 12 on Plate.

d.	*I.*	*d.*	*I.*
14·66	9	4·98	4
11·69	10	4·64	1 *u*
8·86	7	4·41	1 *u*
7·26	5	4·27	6
5·65	3	3·98	5
5·28	2	3·77	6

* Limits of a band of lines, 2 lines. † Limits of a band of lines.

‡ The *X*-ray diagram and these measurements relate to the material associated with aluminite (iii).

(13) $11Al_2O_3,6SO_3,xH_2O$. No. 13 on Plate.

d.	*I.*	*d.*	*I.*
11·25	10	3·89	6
9·39	6	3·52	4
7·10	5	3·35	3
5·68	½	3·17	5
5·27	2	2·94	½
4·68	8	2·86	6
4·29	3 *u*	2·73	4

(14) $13Al_2O_3,6SO_3,xH_2O$. No. 14 on Plate.

d.	*I.*	*d.*	*I.*
12·15	10	3·80	5
9·89	9	3·56	5
8·77	6	3·29	5 *b*
7·00	3	3·01	4
5·88	4	2·86	3
5·25	3 *b*	2·67	6
4·45	7 *b*	2·43	2 *b*
4·12	6		

(15) $(NH_4)_2SO_4[11Al_2O_3,6SO_3,xH_2O]$. No. 15 on Plate.

d.	*I.*	*d.*	*I.*
11·08	10	3·96	7
8·62	6	3·69	3
7·05	5	3·53	3
5·79	5	3·41	3
4·80	7 *b*	3·24	6
4·24	7	3·10	3

(16) $6(NH_4)_2SO_4[11Al_2O_3,6SO_3,xH_2O]$. No. 16 on Plate.

d.	*I.*	*d.*	*I.*
11·29	10	3·97	5
9·59	5	3·75	2
5·91	5	3·45	3
5·55	2 *u*	3·29	6
4·91	4	3·08	2
4·41	7	2·96	5

TABLE X.

Alunites of Table IIA.

Sections 18 and 24 relate to photographs taken with a 6-cm. camera and measured by Miss Kolasa

(17) Australian alunite * from Bulladelah, near Newcastle, N.S.W.†

d.	*I.*
5·723	*mw*
4·975	*ms*
3·491	*m* +
2·984	*s*
2·871	*w*
2·473	*vw*
2·280	*ms*
2·190	*w*
1·897	*ms*
1·741	*ms*
1·643	*vw*
1·564	*vw*
1·498	*m* +

(18) Ammonium alunite of Note 1. No. 10 on Plate.

d.	*I.*
5·73	4 *u*
4·93	9
4·18	3 *u*
3·80	2 *u*
3·61	1 *u*
3·46	5
3·25	2 *u*
2·97	10
2·85	1
2·48	1
2·28	4
2·19	2
1·92	1
1·90	6
1·73	5
1·64	2
1·56	2 *b*
1·49	4 *b*

(19) Ammonium alunite of Note 2.

d.	*I.*	*d.*	*I.*
8·819	*m*	2·305	*ms*
7·479	?	2·217	*mw*
6·819	*w*	2·133	*vw*
5·825	*mw*	2·104	*vw*
5·001	*vs*	2·060	*vw*
4·619	*w*	2·007	*w*
4·343	*m* +	1·946	*vw*
4·202	*m*	1·909	*vs*
3·859	*m*	1·874	*vw*
3·666	*m*	1·848	*w*
3·512	*s*	1·818	*w*
3·325, 3·253	*mw(b)*	1·750	*s*
		1·674	*vw*
2·999	*vvs*	1·652	*m*
2·912	*w*	1·581	*mw*
2·862	*w*	1·568	*mw*
2·797	*w*	1·513	*ms*
2·661	*vw*	1·498	*m(d)*
2·491	*mw*		

* Analysis of Australian alunite (by J. Anderson): Al_2O_3, 38·2; Fe_2O_3, 0·03; K_2O, 10·0; Na_2O 1·55; CaO, 0·12; TiO_2, trace; SO_3, 37·8; P_2O_5, 0·38; SiO_2, 1·5; H_2O (direct determination), 11·0; total 100·58% [H_2S and $(NH_4)_2S$ groups absent; MgO absent].

† See note to section 9 of Appendix.

TABLE X (*continued*).

(20) Ammonium alunite of Note 3.

d.	*I*.
5·836	*mw*
5·001	*vs*
3·504	*m* +
3·005	*vvs*
2·921	*vw*
2·865	*vw*
2·493	*vw*
2·322	*m* +
2·215	*w*
1·952	*mw*
1·908	*s*
1·750	*ms*
1·651	*mw*
1·585	*w*
1·570	*w*
1·520	*m*
1·502	*mw*

(21) Ammonium alunite of Note 4.

d.	*I*.
5·859	*w*
5·017	*s*
3·512	*m* +
3·008	*vs*
2·929	*vw*
2·868	*vw*
2·495	*vw*
2·321	*m* +
2·221	*w*
1·949	*mw*
1·914	*ms*
1·752	*m* +
1·654	*mw*
1·586	*w*
1·572	*vw*
1·519	*m*
1·503	*w*

(22) Ammonium alunite of Note 5.

d.	*I*.
5·813	*mw*
5·009	*s*
3·508	*m* +
3·002	*vs*
2·800	?
2·497	*vw*
2·328	*m*
2·300	*m*
2·220	*w*
1·958	*vw*
1·911	*ms*
1·752	*m* +
1·652	*mw*
1·586	*vw*
1·571	*vw*
1·523	*m*
1·506	*m*(*b*)

(23) Ammonium alunite of Note 6.

d.	*I*.
5·859	*w*
5·017	*s*
3·512	*m* +
3·008	*vs*
2·929	*vw*
2·868	*vw*
2·495	*vw*
2·321	*m* +
2·221	*w*
1·949	*mw*
1·914	*ms*
1·752	*m* +
1·654	*mw*
1·586	*w*
1·572	*vw*
1·519	*m*
1·503	*w*

(24) Potassium alunite of Note 7.*

d.	*I*.
10·10	5 *bbw*
7·37	4 *bbb*
5·49	5
4·97	5
4·78	7
4·03	4 *bbb*
3·51	4
3·41	6
2·94	10
2·79	3
2·43	1
2·23	7
2·17	4
1·98	1
1·88	8
1·72	6
1·62	3
1·54	3
1·49	1

(25) Potassium alunite of Note 8.

d.	*I*.
5·734	*mw*
4·950	*s*
3·508	*ms*
2·984	*vvs*
2·846	*w*
2·469	*vw*
2·263	*ms*
2·210	*mw*
1·904	*s*
1·752	*ms*
1·647	*w*
1·562	*w*
1·508	*w*
1·489	*ms*

(26) Potassium alunite of Note 4.

d.	*I*.
5·756	*mw*
4·975	*s*
3·516	*ms*
2·987	*vvs*
2·841	*w*
2·473	*vw*
2·258	*ms*
2·217	*mw*
2·018	*vw*(*b*)
1·907	*ms*
1·753	*m* +
1·651	*vw*
1·561	*w*
1·509	*w*
1·491	*w*

(27) Sodium alunite of Note 4.

d.	*I*.
5·679	*w*
4·901	*vs*
3·496	*s*
3·428	*vw*
2·958	*vvs*
2·915	*m*
2·844	*w*(*b*)
2·775	*m*
2·445	*vw*
2·212	*vs*
1·896	*vs*
1·870	*w*
1·848	*m*
1·746	*s*
1·644	*m*
1·554	*mw*
1·538	*m*
1·505	*w*

* See note to section 9 of Appendix.

(28) Sodium alunite of Note 9.

d.	*I*.	*d*.	*I*.
5·690	*mw*	1·867	*w*
4·909	*vs*	1·846	*m*
3·845	*vw*?	1·745	*s*
3·496	*s*	1·712	*vw*
3·005 }	*vvvs* (*b*)	1·665	*vw*
2·935 }		1·643	*m*
2·904	*w*	1·602	*vw*
2·841	*vw*	1·554	*mw*
2·775	*m*	1·537	*m*
2·439	*w*	1·504	*w*
2·209	*vs*	1·497	*w*
1·891	*vs*		

(29) Sodium alunite of Note 10.

d.	*I*.	*d*.	*I*.
7·186	*vvw*?	2·453	*w*
5·690	*m*	2·228	*s*
4·901	*vs*	1·900	*s*
4·486	*m*	1·861	*m*
4·343	*m*	1·747	*s*
3·925	*w*	1·647	*m*
3·508	*ms*	1·559	*mw*
2·973	*vvs*	1·544	*m*
2·852	*vw*	1·505	*mw*
2·797	*m*	1·482	*m*