850. *The System* $Al_2(SO_4)_3-H_2SO_4-H_2O.$

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Improved analytical methods being used, the system $Al_2(SO_4)_3-H_2SO_4-$ H_2O has been investigated by phase-rule methods at 25°, 30°, 50°, and 60°, and the following solid phases have been found : $Al_2(SO_4)_3,16H_2O$, which habitually contains about half a molecule of additional water held by adsorption or in a zeolitic manner; $Al_2(SO_4)_3,14H_2O$; $2Al_2(SO_4)_3,H_2SO_4,24H_2O$; $Al_2(SO_4)_3,H_2SO_4,12H_2O$; $Al_2(SO_4)_3,H_2SO_4,8H_2O$ in two forms, the metastable one of which contains a slight excess of acid; $Al_2(SO_4)_3,H_2SO_4,2H_2O$, which contains a slight excess of acid and water. Anhydrous $Al_2(SO_4)_3$ with and without a slight excess of acid and water, $Al_2(SO_4)_3,H_2SO_4,2H_2O$, $Al_2(SO_4)_3,9H_2O$, and $Al_2(SO_4)_3,6H_2O$ have been prepared in other ways. All these solids have been isolated in the dry state for analysis, and in a search for isomorphism their X-ray powder photographs have been compared with those of the mineral coquimbite, of corresponding ferric sulphates, and of ferric ammonium sulphate and its tetrahydrate. Solubilities, microscopical appearances, and lattice spacings are recorded. The nature of the non-stoicheiometric solid phases and the application of Taylor's criteria (*J.*, 1952, 2370) for distinguishing between normal and acid sulphates are discussed. Certain results for the $Al_2(SO_4)_3-H_2O$ system are included.

THE investigation by phase-rule methods of systems of the type metal sulphate–sulphuric acid–water can furnish valuable data regarding the hydrates of the metal sulphate and the occurrence of acid sulphates (cf. Taylor, *J.*, 1952, 2370). In the case of aluminium sulphate, 13 hydrates of the normal sulphate containing from 2 to 27 molecules of water of crystallisation, together with six acid sulphates varying from 1,1,3

[$\equiv$Al$_2$(SO$_4$)$_3$,H$_2$SO$_4$,3H$_2$O, a convention which is used throughout this paper] to 1,3,12 have been reported, but it seems very doubtful if all of these are in fact distinct chemical individuals, and furthermore, little information is available regarding the conditions under which they are stable (Mellor, " Inorganic and Theoretical Chemistry," Longmans, 1924, **5**, p. 332). Recent ternary solubility work has failed to clarify this position. Henry and King (*J. Amer. Chem. Soc.*, 1949, **71**, 1142) have reported a complete isotherm at 60° showing the four solid phases Al$_2$(SO$_4$)$_3$,16H$_2$O, Al$_2$(SO$_4$)$_3$,9H$_2$O, 1,3,12, and Al$_2$(SO$_4$)$_3$, the one succeeding the other as the acid concentration increased. Collet (*Compt. rend.*, 1950, **230**, 951) has reported the following sequence at 20° : the 18-, 16-, 10-, and 6-hydrates of the normal sulphate followed by 1,1,4; while Funaki (*Bull. Tokyo Inst. Tech.*, 1950, Series B, No. 1, 66) has claimed the sequence 18-, 16-, 9-hydrates followed by 1,5,0 at 25°. On the other hand, very careful work by Bassett and Goodwin (*J.*, 1949, 2239) has shown that at 25° up to an acid concentration of 47·5% only the 16-hydrate of the normal sulphate occurs as stable solid phase.

In an attempt to clarify this situation, a full investigation of the ternary system from 25° to 60° was undertaken and also of some features of the Al$_2$(SO$_4$)$_3$–H$_2$O system. Certain aspects of the corresponding ferric sulphate system have also been examined and a comparison of the two has helped to elucidate some features of the aluminium sulphate system. For the latter, it is of prime importance that the solubility determinations should be of the highest possible accuracy, for in assessing tie-line convergence points on the usual triangular diagram quite small errors assume major significance. This arises in view of the large molecular weight of aluminium sulphate compared with those of water and sulphuric acid. All techniques and analytical procedures were therefore the subject of special investigation.

Preliminary results have already been reported by Taylor and Scott (*Nature*, 1951, **168**, 520) who (*a*) have shown by tracer technique, using radioactive cæsium sulphate and manganese sulphate as tracers, that the salt of composition 1,1,12 occurs as a stable phase in the 30—50° range, and (*b*) reported the occurrence of 1,1,8 (in two forms) and 1,1,2.

EXPERIMENTAL

Materials.—Wherever possible the reagents were of " AnalaR " grade. The aluminium sulphate was recrystallised by Smith's procedure (*J. Amer. Chem. Soc.*, 1942, **64**, 41) and dried in air overnight at room temperature. The resulting product was perfectly dry, neither deliquesced nor effloresced under ordinary atmospheric conditions, and dissolved completely in distilled water. Sodium and potassium salts, the most likely impurities, were shown to be present only in minute traces even in the unrecrystallised salt. For all solubility determinations at low acid concentrations the recrystallised salt was used; at high acid concentrations, the unrecrystallised material was used. The latter was justified by (*a*) the absence of impurities in the " AnalaR " salt apart from very small amounts of basic sulphate, (*b*) the agreement of solubility results when either material was used, and (*c*) the rapid conversion under highly acid conditions of any basic sulphate present. Different preparations of the recrystallised material contained between 16·5 and 16·8 molecules of water of crystallisation and no free acid. Ferric sulphate (B.D.H.) was used without further purification. It was shown by the procedure below to have the approximate composition 5,2,29, and an *X*-ray powder photograph showed that the majority of the acid was present as the 1,1,2 salt.

Methods of Analysis.—In all cases, the metal and either the total SO$_4$ radical or the free acid concentration were determined, the water being obtained by difference.

Aluminium was determined by precipitation with 8-hydroxyquinoline using a modification of Cumming and Kay's procedure (" Quantitative Chemical Analysis," Gurney and Jackson, 9th edn., 1945, p. 284). The greater part of any sulphuric acid present was neutralised with ammonia and the temperature raised to 90—95° before dropwise addition of the ammonium acetate solution. This avoided inconveniently large volumes of ammonium acetate and conferred a slightly improved physical form on the precipitate such that sintered-glass crucibles of grade 3 porosity could be used with confidence. With precipitates of less than 0·2 g., it was essential to cool slowly to room temperature before filtration, otherwise results were up to 2% low. Precipitates were washed with water at 30—40° and dried to constant weight at 120°. This procedure proved accurate for several total weights of aluminium sulphate and various acid : salt ratios, a Hilger high-purity sample of aluminium (99·98% pure) being used as standard.

The results recorded in Table 1 cover the actual concentration conditions encountered in solutions from solubility measurements.

TABLE 1. *Determination of aluminium.*

Taken { $Al_2(SO_4)_3$, g.	0·0326	0·0326	0·0816	0·1630
Wt. ratio, $H_2SO_4 : Al_2(SO_4)_3$	300	100	5	5
Found: $Al_2(SO_4)_3$, g.	0·0333	0·0327	0·0816	0·1628

Total sulphate was determined by direct precipitation with barium chloride without removal of aluminium. In accord with the results of Bassett and Goodwin (*loc. cit.*), no adsorption of aluminium on the barium sulphate precipitate (leading to low results) was observed, and distinct loss of sulphate occurred if the aluminium was previously removed by precipitation (and even re-precipitation) with ammonia. Some trouble arose from the poor physical form of the precipitate, and although the use of picric acid effected a moderate improvement, a complete remedy apart from the inadmissible removal of the aluminium was not found. Subsequently, a more rapid volumetric procedure for free sulphuric acid was developed from the method given by Scott and Furman (" Standard Methods of Chemical Analysis," Technical Press Ltd., 5th edn., 1939, p. 16), in which the sulphuric acid is titrated with alkali after addition of potassium fluoride to precipitate the aluminium as $AlF_3,3KF$. Experiment showed that this procedure gave results which were up to 3% low depending on the ratio $H_2SO_4 : Al_2(SO_4)_3$, the loss of acid being due presumably, as suggested by Graham (*Ind. Eng. Chem. Anal.*, 1946, **18**, 472), to its adsorption on the complex fluoride precipitate. To avoid this loss in special cases where the ratio $H_2SO_4 : Al_2(SO_4)_3$ was very high, Graham recommended delaying the addition of the fluoride until after 99·5% of the acid had been neutralised (cf. Glemser and Thelen, *Angew. Chem.*, 1950, **62**, 269), but the present research showed that in all cases virtually

TABLE 2. *Determination of H_2SO_4 in presence of Al.*

Taken			Found: *		Taken			Found: †
H_2SO_4, ml.	$Al_2(SO_4)_3$, g.	Wt. ratio, $H_2SO_4 : Al_2(SO_4)_3$	NaOH ml.	H_2SO_4, ml.	$Al_2(SO_4)_3$, g.	Wt. ratio, $H_2SO_4 : Al_2(SO_4)_3$		NaOH, ml.
0·905N			0·481N	0·905N				0·0993N
10·0	0·0	—	18·83	1·00	0·0	—		9·12
10·0	0·027	16	18·82	1·00	0·25	0·17		9·15
10·0	0·160	3	18·82	1·00	0·85	0·05		9·12
10·0	0·424	1	18·82					

* Calc.: 18·82 ml. † Calc.: 9·11 ml.

the complete neutralisation of the acid before addition of the fluoride was essential. A series of titrations was always carried out in which progressively larger amounts of alkali were added before the fluoride until no further increase in titre was observed. The results in Table 2 show this procedure to be reliable.

Repeated comparison of the oxine–barium sulphate and volumetric methods for free acid determination showed that they agreed to 2 parts in 1000 except when both the free acid concentration and the acid : salt ratio were low. In this range, the volumetric method gave results up to 3% higher, and is considered more accurate for it gives the acid concentration directly instead of as a small difference between two large quantities both of which may contain an experimental error.

Ferric sulphate compounds were analysed for iron either by direct ignition with blowpipe heating to ferric oxide or by reduction with aluminium followed by permanganate titration (Cumming and Kay, *op. cit.*, p. 395). Total SO_4 radical was determined by titration at the boil with sodium hydroxide to phenolphthalein end-point.

Ternary Solubility Measurements.—Solubility determinations were carried out in a manner analogous to that given by Taylor (*loc. cit.*) with the addition that all initial solids by careful heating were brought completely into solution before being stirred to equilibrium. Certain mixtures at very high acid concentrations required the use of oleum in place of " AnalaR " sulphuric acid. The time to attain equilibrium varied from a few hours at the low-acid side to several months at the high-acid side of the system. Seeding with the desired solid phase was frequently advantageous, and occasionally after the desired solid phase had been obtained from a mixture of known composition, the latter was adjusted to a different value by the addition of water or acid as required. Nevertheless, stubborn metastability was frequently encountered, particularly at high acid concentrations. At equilibrium, mixtures were filtered with suction either through a sintered-glass micro-filter stick of No. 3 porosity attached to a pre-heated pipette, or through a number 3 grade sintered-glass mercury filter suitably attached to a small receiver. The

open end of the mercury filter could be closed with a calcium chloride tube, and the whole unit immersed in the thermostat so that the very slow filtering mixtures encountered at the high acid side of the system could be filtered without disturbance of the equilibrium. After filtration, weighed samples of the solution and moist solids were diluted to a standard volume and analysed. Continuous use was made of microscopical examinations and of X-ray powder photographs in

TABLE 3. *The system* $Al_2(SO_4)_3$–H_2SO_4–H_2O.

|	Solution: $Al_2(SO_4)_3$ %	H_2SO_4 %	Moist solid phase: $Al_2(SO_4)_3$ %	H_2SO_4 %	Solid phase		Solution: $Al_2(SO_4)_3$ %	H_2SO_4 %	Moist solid phase: $Al_2(SO_4)_3$ %	H_2SO_4 %	Solid phase
					At 25°						
	27·76	0·0	—	—	A	*	1·42	68·68	17·74	51·46	B
	27·74	0·0	—	—	A		0·67	65·66	23·73	43·69	B + C
	27·79	0·0	—	—	A		0·23	68·36	15·16	55·16	C
	23·89	4·78	38·59	2·48	A		0·59	69·32	20·27	51·77	C
	16·88	14·60	36·76	6·67	A		0·18	73·20	13·05	61·13	C
	5·23	36·12	29·93	17·58	A		0·19	73·93	—	—	C
	3·19	45·26	26·47	24·28	A		0·57	78·13	—	—	C
	3·05	45·99	30·31	21·54	A	*	0·77	79·77	16·70	62·41	C
	3·14	47·30	—	—	A	*	1·08	80·25	14·11	65·80	C
	3·13	47·53	24·77	27·16	A	††	0·6	78·5	—	—	C + E
	3·22	48·30	24·33	30·50	A + B	**	1·12	72·61	37·85	37·26	D
	2·50	49·55	27·98	31·61	B	*	0·36	74·60	—	—	D
	2·46	50·10	24·28	33·81	B	*	0·37	74·60	37·98	38·50	D
	0·95	56·21	14·73	44·54	B	**	1·31	75·33	30·97	44·65	D
	0·75	58·10	27·11	35·74	B		0·18	82·49	30·39	57·00	E
	0·62	58·89	20·78	41·43	B		0·12	83·90	—	—	E
	0·56	63·48	16·32	48·33	B		0·14	86·48	25·72	63·17	E
	0·64	65·32	17·50	48·44	B	†	0·01	92·71	7·62	85·09	E
*	0·68	66·20	—	—	B		<0·07	99·30	—	—	E
					At 30°.						
	3·98	45·24	—	—	A		3·01	49·71	—	—	B
	4·36	46·86	§ 51·25	14·12	A + B		0·93	57·89	38·35	26·75	B
	4·06	47·50	—	—	B						
					At 50°.						
	29·70	0·0	—	—	A		3·29	52·41	—	—	G
	25·53	5·28	—	—	A	††	3·30	53·90	—	—	G + B
	20·57	13·22	—	—	A	*	3·81	52·53	—	—	B
	11·67	31·27	—	—	A	*	3·48	53·61	—	—	B
	10·02	36·41	—	—	A		3·27	54·20	—	—	B
*	9·91	39·65	34·87	17·64	A		2·27	59·03	—	—	B
*	9·90	40·36	—	—	A	*	2·22	61·31	—	—	B
††	10·0	37·0	—	—	A + F	††	2·20	60·00	—	—	B + C
	8·93	39·40	—	—	F		0·77	64·90	—	—	C
††	8·2	41·5	—	—	F + G		0·43	72·70	—	—	C
*	9·91	38·90	—	—	A + G		0·71	76·73	—	—	C
	7·82	42·08	—	—	G	*	1·33	78·43	—	—	C
	7·47	42·60	—	—	G	††	0·80	77·00	—	—	C + E
	6·16	44·94	—	—	G		0·07	83·00	—	—	E
	5·61	46·26	49·23	14·40	G		<0·07	92·50	—	—	E
	3·54	51·40	40·29	22·60	G						
					At 60°.						
*	14·82	31·56	—	—	A	*	12·44	36·95	—	—	G
*	14·43	33·91	—	—	A	*	11·44	38·39	—	—	G
††	14·3	34·4	—	—	A + G	*	10·31	40·11	—	—	G
††	17·0	25·5	—	—	A + F	*	9·21	42·09	—	—	G
	12·56	32·80	—	—	F		6·76	46·61	—	—	G
	10·18	37·45	—	—	F	††	4·7	54·5	—	—	G + B
	9·59	39·23	—	—	F	*	6·52	49·74	—	—	B
†	8·00	44·00	—	—	F + G	*	5·27	52·43	—	—	B
*	12·62	36·60	—	—	G		3·96	57·53	—	—	B

* = Metastable. ** = May be supersaturated. † = Al estimated colorimetrically with alizarin. †† = Interpolated invariant points. § = Acetone-washed dry solids.

Solid phases:
A = $Al_2(SO_4)_3,16H_2O$.
C = $Al_2(SO_4)_3,H_2SO_4,8H_2O$, stable form.
E = " acidic " $Al_2(SO_4)_3,H_2SO_4,2H_2O$.
G = $2Al_2(SO_4)_3,H_2SO_4,24H_2O$.

B = $Al_2(SO_4)_3,H_2SO_4,12H_2O$.
D = $Al_2(SO_4)_3,H_2SO_4,8H_2O$, metastable form.
F = $Al_2(SO_4)_3,14H_2O$.

Further details are given on pp. 4434—4438.

recognising solid phases and invariant points and particularly in following the course of solid phase transitions. Results are given in Table 3 and Figs. 1 and 2. The position of all tie-lines was determined with the aid of mathematical extrapolation to eliminate drawing errors. Compositions are by weight.

FIG. 1. *System* $Al_2(SO_4)_3$–H_2SO_4–H_2O *at* 25°
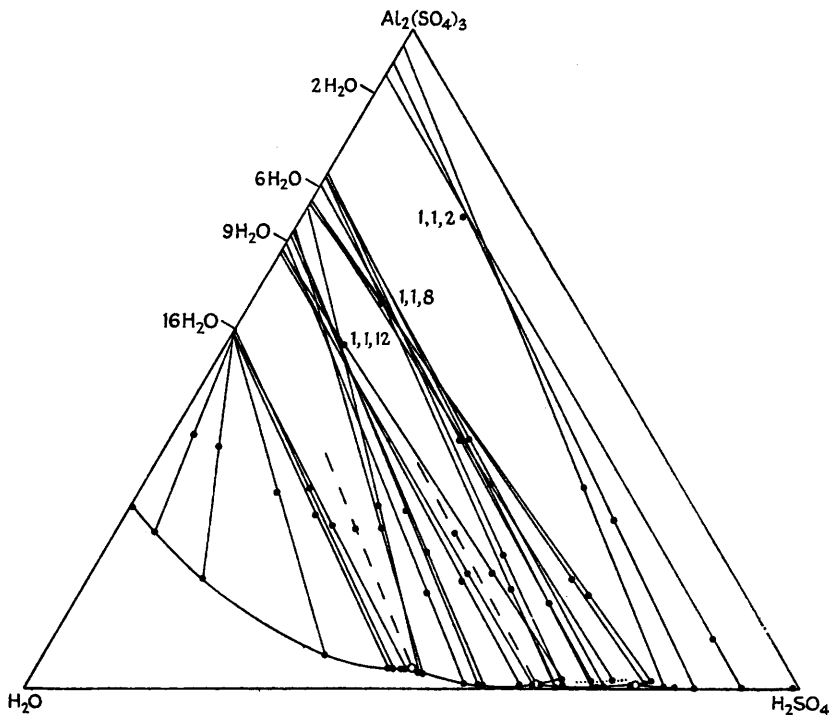
FIG. 2. *System* $Al_2(SO_4)_3$–H_2SO_4–H_2O *at* 25°, 30°, 50°, *and* 60°
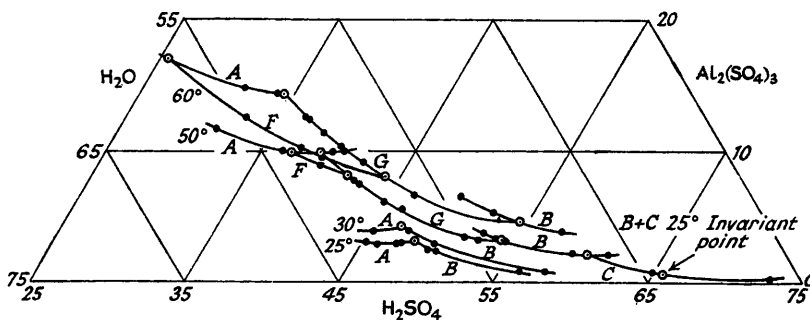
Solid phases indicated by capital letter as in Table 3.
Open circles denote isothermal invariant points.

Indicator Experiments in the Ternary System.—Three indicators were used : radioactive cæsium sulphate, manganese sulphate, and hydrogen chloride. Details for the radioactive tracer work at 30° have been given elsewhere (Taylor and Scott, *loc. cit.*), and the manganese (one drop of 30% sulphate solution per 50 g. of ternary mixture) was used in essentially the same manner at 25°, the indicator being determined colorimetrically as permanganate after oxidation with potassium periodate in presence of phosphoric acid (Cumming and Kay, *op. cit.*, p. 270). It was essential to add the manganese sulphate after the ternary mixture had been brought to equilibrium, otherwise the manganese was completely co-precipitated with the solid phase. In addition to experiments on acidic solid phases, a test of the whole procedure was carried out

with a mixture known to contain $Al_2(SO_4)_3,16H_2O$ as solid phase, the free acid concentration being about 46%, *i.e.*, as high as conveniently possible without causing the solid to be transformed into 1,1,12. Experiments at very high acid concentrations were unsuccessful owing partly to precipitation of the indicator and partly to its adsorption on the very finely divided solid phases occurring at such acid concentrations. In the case of hydrogen chloride at 25°, the indicator was added at the outset and determined after equilibrium was reached by electrometric titration with N/100-silver nitrate. The presence of aluminium and sulphate was shown not to influence the chloride determination. The use of hydrogen chloride was limited by its low solubility in concentrated sulphuric acid solutions at atmospheric pressure. Results are given in Table 4.

TABLE 4. *Indicator experiments.*

			Composition :			
			Calc. :		Found :	
Indicator	Temp.	Solid phase	$Al_2(SO_4)_3$, %	H_2SO_4, %	$Al_2(SO_4)_3$, %	H_2SO_4, %
$MnSO_4$	25°	A	54·3	0·0	58·4	−3·7
Cs_2SO_4	30	B	52·1	14·9	51·3	15·9
$MnSO_4$	25	B	52·1	14·9	51·5	15·1
HCl	25	B	52·1	14·9	48·1	17·8
$MnSO_4$	25	D	58·5	16·8	55·5	21·6

Solid phases as in Table 3.

Pure Dry Solid Phases.—Samples of all the solid phases listed in Table 3, together with several others not directly encountered in the solubility work, were prepared and analysed, and X-ray powder photographs were taken with a Unicam 9-cm. camera. A number of similar ferric compounds, whose compositions have been reliably established by Posnjak and Merwin (*J. Amer. Chem. Soc.*, 1922, **44**, 1965), were also prepared and examined for isomorphism with corresponding aluminium compounds. In cases involving the separation of a solid from a mother-liquor the simple procedure was adopted of washing the moist solids thoroughly with " AnalaR " acetone containing 1% of water, followed by drying at room temperature in a current of dry air and finally for five minutes at a pressure of less than 1 mm. of mercury. Microscopical appearances are recorded below, compositions in Table 5, and lattice spacings in the Appendix.

$Al_2(SO_4)_3,16H_2O$ (*A in Tables* 3, 4 *and* 5). As a test of the washing procedure in removing acidic liquid, the hydrate was separated at 25° from a saturated mother-liquor containing approximately 46% of free acid. The resulting dry solid contained 16·2 molecules of water of crystallisation and zero free acid. When grown very slowly from dilute solution, the hydrate was obtained as extremely thin elongated hexagons with vertical angle 92° 40′ (cf. Delacharlonny, *Compt. rend.*, 1883, **96**, 844) and symmetrical extinction, but in solubility experiments the usual habit was long thin laths extinguishing at an angle of about 43° with the length. The lattice spacings corresponded exactly with those given by Bassett and Goodwin (*loc. cit.*).

$Al_2(SO_4)_3,14H_2O$ (*F in Tables* 3 *and* 5). This hydrate was obtained only from solubility experiments at 50° and 60°, and was formed always as the result of a very slow transformation of either the 16-hydrate or the 2,1,24 phase. Its precipitation from solutions metastable with respect to 2,1,24 was sometimes assisted by addition of a little water. Washing was with warm acetone, the resulting solid containing only a trace of free acid. The crystals occurred as long narrow laths with a single oblique end-face, some showing parallel extinction and some not. It was distinguished from the 16-hydrate most reliably either by analysis of the dry solid or by its X-ray powder photograph.

$Al_2(SO_4)_3,9H_2O$. Recrystallised 16-hydrate was dried in air at 100° till it contained 8·7 molecules of water of crystallisation and then heated in a small sealed Pyrex tube at 160° for 9 weeks, during which time the solid underwent a visible recrystallisation. X-Ray powder photographs showed that the solid was practically structureless before heating but gave a characteristic diagram afterwards, such that the crystals obtained are thought to be essentially the 9-hydrate. They were highly birefringent, biaxial positive, with irregular shapes.

$Al_2(SO_4)_3,6H_2O$. This was prepared in the same way as the 9 hydrate starting from an amorphous solid containing 6·7 molecules of water of crystallisation. Small birefringent needles with oblique extinction were obtained which gave a good X-ray diagram.

Anhydrous $Al_2(SO_4)_3$. Heating of recrystallised 16-hydrate in air at 500° for 150 hours gave a product which analysis showed to be $Al_2(SO_4)_3$ apart from a slight loss of SO_3 and a very little residual water. The X-ray diagram showed the product to be well crystallised.

" *Acidic* " *anhydrous* $Al_2(SO_4)_3$. By dissolving 3 g. of " AnalaR " salt in 25 ml. of 70—80% acid and gently boiling the solution till fuming occurred, small thin hexagonal plates were first

precipitated (see below under 1,1,2), which on further heating were transformed into dense birefringent small square tablets (*d* 2·7). Although the *X*-ray diagram was identical with that of anhydrous Al$_2$(SO$_4$)$_3$, the square tablets contained about 1% of water and 7% of free acid. The presence of the latter on the surface of the crystals would indicate failure of the acetone washing procedure but this was shown not to be the case as follows. After immersion of the tablets in distilled water with intermittent stirring for 10 minutes and filtering, the filtrate contained only 15% of the free acid present in the crystals and a small quantity of aluminium ion. Furthermore, although the excess of acid varied a little from one preparation to another, yet it was independent of the volume of wash liquid.

2Al$_2$(SO$_4$)$_3$,H$_2$SO$_4$,24H$_2$O (*G in Tables 3 and 5*). This phase was obtained as well-formed 0·5-mm. six-sided plates, biaxial negative, in solubility experiments at 50° and 60° by slow transformation of previously precipitated 16-hydrate or 1,1,12, and over appreciable ranges remained metastable with respect to the 14-hydrate for long periods. Whether it was isolated by acetone or by absolute alcohol washing, the composition was the same and the dry crystals appeared completely unchanged. Although the two tie-lines could indicate a composition of 2,1,22, analyses for three different preparations were very close to the composition 2,1,24, and the latter is therefore preferred.

Al$_2$(SO$_4$)$_3$,H$_2$SO$_4$,12H$_2$O (*B in Tables 3, 4, and 5*). Crystals of this composition were obtained very easily at all temperatures in the solubility work. The habit was small, very thin, birefringent plates, almost square, many of which had one or both pairs of opposite corners truncated.

TABLE 5. *Dry solid phases.*

Temp. of preptn.	Solid phase	Composition ·			
		Calc. :		Found :	
		Al$_2$(SO$_4$)$_3$, %	H$_2$SO$_4$, %	Al$_2$(SO$_4$)$_3$, %	H$_2$SO$_4$, %
Aluminium sulphate compounds.					
25°	A	54·3	0·0	53·16 53·41 54·00	0·0 0·0 0·0
60	F	57·57	0·0	58·23 58·29 57·20	<0·2 <0·1 <0·1
25	B	52·1	14·94	51·45	15·02
50	B	52·1	14·94	51·29 51·41	15·36 15·14
50	G	56·30	8·07	56·51 56·47 56·20	8·63 8·48 8·39
25	C	58·50	16·78	57·24	18·01
50	C	58·50	16·78	58·19	17·42
25	D	58·50	16·78	57·35 56·20 56·36	17·91 18·84 18·92
25	E	71·9	20·6	63·97 64·85 64·80	23·28 23·20 22·29
50	E	71·9	20·6	67·20	24·08
~190	1,1,2	71·9	20·6	71·15	20·38
~300	" Acidic " anhyd.	100·0	0·0	91·31 93·27	7·88 5·87
500	Anhydrous	100·0	0·0	100·9	−2·57

Solid phases as in Table 3.

		Fe$_2$(SO$_4$)$_3$, %	H$_2$SO$_4$, %	Fe$_2$(SO$_4$)$_3$, %	H$_2$SO$_4$, %
Ferric sulphate compounds.					
25	8-Hydrate	73·52	0·0	73·0	0·08
25	1,1,8	62·27	15·28	62·6	14·5
50	1,1,2	74·87	18·36	74·4	17·67
~300	Anhydrous	100·0	0·0	99·98	0·0

Al$_2$(SO$_4$)$_3$,H$_2$SO$_4$,8H$_2$O, *Stable form* (*C in Tables 3 and 5*). Several days' stirring were required even with seeding to induce precipitation of this solid as extremely small birefringent needles.

Al$_2$(SO$_4$)$_3$,H$_2$SO$_4$,8H$_2$O, *Metastable form* (*D in Tables 3, 4, and 5*). At 25° in the middle of the 1,1,8 range, a metastable form was obtained in quantity provided the solution initially was highly supersaturated; from less supersaturated solutions both forms frequently appeared

together. The crystals were in the form of rectangular blocks with bevelled end-faces, biaxial positive, a habit which was completely unchanged after acetone washing. The composition of different preparations varied slightly, having 1—2% of acid in excess of the composition 1,1,8. Doubling the quantity of wash liquid did not alter the composition. The crystals proved too unstable in air to give a reliable X-ray diagram, but a photograph of a mush of crystals and mother-liquor gave sufficient spacings to show that the two forms probably had different structures.

$Al_2(SO_4)_3,H_2SO_4,2H_2O$. The hexagonal plates referred to on p. 4436 in the preparation of " acidic " anhydrous $Al_2(SO_4)_3$ gave analyses very close to the composition 1,1,2. The hexagons were regular and isotropic normal to the six-fold axis, and the crystals thus belong to the hexagonal class. Observations during six months showed that transition to the square tablets phase did not occur below about 200°.

" *Acidic* " $Al_2(SO_4)_3,H_2SO_4,2H_2O$ (E *in Tables* 3 *and* 5). From supersaturated solutions containing more than 80% of free acid, small, roughly spherical, random aggregates of birefringent crystals were precipitated on prolonged stirring. Although these aggregates contained several units % more sulphuric acid and water (quantities which varied slightly from one preparation to another) than 1,1,2, the X-ray powder photographs were very similar, showing that both substances had essentially the same lattice structure. The composition was not dependent on the volume of wash-liquid used.

Alunite. About 2% of the 9-hydrate preparation was very slow to dissolve in boiling dilute sulphuric acid. This residue, after being washed with water and dried (P_2O_5) in a desiccator, was found to have an X-ray powder photograph characteristic of the alunite group. It contained only Al and SO_4 apart from water and may. therefore have the composition $H_2O[Al_3(OH)_5H_2O](SO_4)_2$, which is one member of the alunite series (Bassett and Goodwin, *loc. cit.*; Bassett, *J.*, 1950, 1460).

Coquimbite. A Royal Scottish Museum specimen, number 1875/9/9, was made available through the kind co-operation of Dr. C. D. Waterston. With assistance from Mr. A. R. Chalmers, the mineral was shown to have the composition $Fe_{1.54}Al_{0.46}(SO_4)_3,9H_2O$.

$Fe_2(SO_4)_3,8H_2O$. From a saturated solution containing 2—3% of free acid, after partial evaporation over phosphoric oxide followed by several days' stirring at 25°, minute fawn needles were obtained. After filtration, the hydrate was washed with a few drops of ice-cold water and then with acetone. It was found that transition to the 1,1,8 compound commenced in solution at a free acid concentration of about 5%, which is contrary to the published data (collected refs. in Seidell, " Solubilities of Inorganic and Metal Organic Compounds," Van Nostrand, 3rd edn., 1940).

TABLE 6. *The system* $Al_2(SO_4)_3–H_2O$ [solid phase : $Al_2(SO_4)_3,16H_2O$).

Temp.,°c	50·5	73·4	75·0	76·7	82·0	88·0	95·1	99·2	103·2	110·4	112·2
Solution : $Al_2(SO_4)_3$, %	30·09	33·33	33·63	34·28	36·60	38·74	41·86	43·90	46·85	52·0	53·0

$Fe_2(SO_4)_3,H_2SO_4,8H_2O$. Baskerville and Cameron's phase equilibria data (*J. Phys. Chem.*, 1935, **39**, 769) being used, pale fawn six-sided plates were obtained at 25°. They were biaxial with the acute bisectrix almost perpendicular to the plane of the crystal.

$Fe_2(SO_4)_3,H_2SO_4,2H_2O$. Very irregular fawn birefringent plates were obtained at 50°, Posnjak and Merwin's phase data (*loc. cit.*) being used.

Anhydrous $Fe_2(SO_4)_3$. Pale fawn, square and rectangular tablets, some with extra faces, were obtained by boiling 2 g. of B.D.H. ferric sulphate in 20 ml. of 80% acid till the mixture fumed very strongly. The anhydrous compound was found to be the only equilibrium solid phase under such conditions (cf. Posnjak and Merwin, *loc. cit.*)..

$(NH_4)_2SO_4,Fe_2(SO_4)_3$. This was prepared as well-formed nearly colourless hexagonal plates by low-temperature dehydration of ferric alum, and its composition checked by analysis.

$(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$. This was obtained as pale violet, tetragonal bipyramids by crystallisation at 25—30° of a solution of ferric alum strongly acidified with sulphuric acid. This *compound* does not appear to have been recorded previously [Found : Fe_2O_3, 26·4; $(NH_4)_2O$, 8·7; SO_3, 52·7. $(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$ requires Fe_2O_3, 26·4; $(NH_4)_2O$, 8·6; SO_3, 53·0%. The mother-liquor contained 4·5, 1·6, and 33·4%, respectively].

With the exception of the metastable aluminium 1,1,8 compound which dissolved readily, all solid phases with 9 or less molecules of water of crystallisation dissolved in water extremely slowly. Coquimbite and $Fe_2(SO_4)_3,8H_2O$ hydrolysed in water with the formation of a brown precipitate, but dissolved readily and completely in dilute acid.

Some Features of the Al$_2$(SO$_4$)$_3$–H$_2$O *System.*—(1) In a search for lower hydrates, solubility experiments by the synthetic method (cf. Taylor and Vincent, *J.*, 1952, 3218) were carried out in sealed tubes. Up to 112·2° (Table 6) the solid phase was the 16-hydrate and this probably just fails to have a congruent m. p. Above 112° two different solid phases appeared, but results were so erratic owing to the extreme slowness with which equilibrium was established in the highly viscous solutions that no estimate of the composition of the new phases could be made. At a composition corresponding to the 12-hydrate, the temperature of complete solution was about 200°. Since the 16-hydrate is only just able to give a congruent solution at 25°, and since hydrolysis may be expected to increase with rising temperature, some of the solutions in Table 6 may have been metastable with respect to a basic salt.

(2) At 25°, measurement of dissociation pressures, a McBain–Bakr silica spring balance and mercury manometer in an all-glass vacuum system being used, confirmed (*a*) the occurrence of the 14-hydrate, and (*b*) the ability of the 16-hydrate to absorb up to 0·8 molecule of water without the appearance of a liquid phase. The dissociation pressure for the reaction 16-hydrate $\rightleftharpoons$ 14-hydrate $+$ 2H$_2$O was 10·5 mm. of mercury, and the vapour pressure of saturated aluminium sulphate solution 21·3 mm. For hydrates containing less than 14 molecules of water, dissociation pressures are less than 3 mm.

(3) Orthobaric dehydration of the 16-hydrate in air saturated at 25° with water vapour (cf. Milligan and Weiser, *J. Phys. Chem.*, 1934, **38**, 513) confirmed the observations made in (2) above, but gave no information regarding hydrates lower than 14 owing to the prohibitive time to reach equilibrium.

DISCUSSION

The stable solid phase up to moderate acid concentrations in the 25—60° range is normal aluminium sulphate containing between 16 and 17 molecules of water of crystallisation. This phase is best regarded as a true 16-hydrate with the extra approximate 0·5 H$_2$O held by adsorption or in a zeolitic manner because (*a*) there is no evidence from any section of the work for a 16·5 $\longrightarrow$ 16-hydrate transition, and (*b*) the system solid 16-hydrate–water vapour was observed to be univariant over the composition range from 16 to 16·8 molecules of water per molecule of aluminium sulphate in the isothermal and orthobaric dehydration experiments. As far as tie-lines are concerned, the extra water is indistinguishable from true water of crystallisation and may therefore be held by relatively strong forces. This view is further supported by the facts that the extra water is invariably present in the solid no matter what its source, and the hydrate is not efflorescent in air.

In spite of the attention given to all analytical procedures, Fig. 1 shows that, with the exception of the 16-hydrate, the tie-line information, although clearly differentiating one solid phase from another, gave little more than suggestions as to their composition : following the 16-hydrate, a succession of highly hydrated acidic phases was favoured, but a sequence of lower hydrates of the normal sulphate was not ruled out. Recourse was therefore made to (1) indicator experiments, (2) isolation and analysis of dry solid phases, and (3) establishment by *X*-ray methods of isomorphism with corresponding ferric compounds of known composition.

The severe conditions which the ideal indicator in phase equilibria work must fulfil have been outlined by Taylor and Scott (*loc. cit.*), and it is seldom that such experiments yield more than suggestions as to solid-phase compositions. The unusual success with radioactive cæsium sulphate and manganese sulphate was due to both the minute quantity required and the accuracy with which they could be detected. Their use showed very definitely (Table 4) that phase B had the composition 1,1,12. The result for the hydrogen chloride indicator was less definite, but even so the acidic nature of the solid phase was clearly suggested. For the metastable phase D, manganese being used as indicator, the preferred composition was again that of 1,1 acidic solid. The fact that an experiment on the 16-hydrate with manganese as indicator definitely showed the absence of free acid from the solid phase, confirmed that the indicator procedure was trustworthy.

In the absence of radioactive indicator experiments at high acid concentrations, and the failure of the manganese and hydrogen chloride indicators under such conditions, attempts were made by washing with acetone to isolate all the solid phases including the ferric com-

pounds in the dry state for analysis. Such a procedure involves the possibility of (*a*) decomposition by loss or gain of water, acid or solvent, and (*b*) precipitation of unwanted solids from the mother-liquor. Point (*a*) is considered unimportant since (1) both the 16-hydrate and the 1,1,12 phase after isolation had compositions very close to those required by their formulæ, (2) the crystal habit of several of the phases appeared unchanged after the washing procedure, and (3) compositions were independent of the volume of wash liquid used. Furthermore, a number of the phases in Table 5 have to within close limits stoicheiometric compositions, and this would have been most unlikely if significant decomposition had occurred. Point (*b*) was eliminated by the fact that addition of acetone to the mother-liquors in the proportions used in the washing procedure gave no precipitates in the time interval required to complete the washing. For these reasons, the compositions assigned to the solid phases in Tables 3, 4, and 5 are believed correct. The nature of the three phases D, E, and "acidic" anhydrous $Al_2(SO_4)_3$, whose compositions were not truly stoicheiometric, will be discussed below.

Further confirmation of the acidic nature of the solid phases was obtained by comparison of the *X*-ray powder photographs of corresponding aluminium and ferric compounds. In making these and subsequent comparisons, it was essential to compare the actual photographic films and not sets of calculated lattice spacings, for with the latter, important similarities and differences could be overlooked. In the case of the 1,1,8 compounds, the photographs were practically identical, showing that the two solids were isomorphous and therefore had the same atomic composition. For the 1,1,2 and anhydrous pairs of compounds, the photographs were sufficiently similar to indicate distinct possibilities of isomorphism. It is noteworthy that the characteristic features of the photographs of the 1,1,2 pair were also found in $(NH_4)_2SO_4,Fe_2(SO_4)_3$, showing that the oxonium ion may be replaced isomorphously by the ammonium ion (cf. Shiskin, *Zhur. Obs. Khim.*, 1951, **21**, 456; *Chem. Abs.*, 1951, **45**, 6115). Lattice dimensions and space-groups already known for $K_2SO_4,Al_2(SO_4)_3$, $(NH_4)_2SO_4,Al_2(SO_4)_3$, and $(NH_4)_2SO_4,Fe_2(SO_4)_3$ ("Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 31st edn., 1949, p. 2056, 2062) show that these also are isomorphous and belong to the hexagonal class as does the aluminium 1,1,2 compound. This is convincing evidence that the last compound (*a*) has the composition denoted by 1,1,2, (*b*) is an oxonium salt, and (*c*) is not the dihydrate of the normal sulphate. The *X*-ray diagram of $(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$ showed no resemblance to any of the other compounds dealt with in this paper.

In the case of coquimbite and the 9-hydrate of aluminium sulphate, less resemblance could be traced between the photographs than was expected, for it is well known that up to 50% of the iron in coquimbite can be replaced by aluminium. The lack of resemblance may cast doubt on the nature of the aluminium compound, but on the other hand it is known that coquimbite, and probably therefore the corresponding aluminium compound also, is polymorphous, and since the aluminium compound was prepared at 160°, the photographs may be those of structurally unrelated polymorphs.

The determination of numerous invariant points, either directly or by extrapolation of solubility curves (Table 3), allowed the direction of the univariant lines for the transitions 16-hydrate $\longrightarrow$ 1,1,12, 16-hydrate $\longrightarrow$ 2,1,24, and 1,1,12 $\longrightarrow$ 1,1,8 to be fixed on the polythermal projection diagram with certainty, so the empirical criteria suggested by Taylor (*loc. cit.*) for distinguishing between normal and acid sulphates could be applied. According to these criteria, for the first two transitions where an increase in acid content occurs in the direction from left to right, points on the univariant lines would be expected to show an increase in sulphuric acid concentration with rising temperature, while for the third transition, where dehydration occurs from left to right, an increase in water concentration could be expected. It should be noted that the first two transitions also involve dehydration from left to right, and depending on whether the hydrate or acid sulphate characteristics of the phases on the right-hand side are predominant, the direction of the univariant lines may follow either the water of the acid criteria respectively. In fact, all three transitions do conform to the hydrate–lower hydrate case, and it may therefore be that the hydrate nature of the phases is the more important, a view which is not unreasonable in view of their high degree of hydration. Owing to very stubborn metastability, invariant points and

univariant lines for the transitions 16-hydrate $\longrightarrow$ 14-hydrate, 14-hydrate $\longrightarrow$ 2,1,24, and 2,1,24 $\longrightarrow$ 1,1,12 were obtained only by considerable extrapolation of solubility curves and are therefore less reliable. Nevertheless, Fig. 2 suggests that the first transition does conform to the hydrate–lower hydrate case, and the second and third to the hydrate–acid sulphate criterion. According to Posnjak and Merwin's data (*loc. cit.*), transitions which involve simultaneously dehydration and an increase in the acid content of the solid phases do not occur in the corresponding ferric sulphate system; all transitions conform without ambiguity to Taylor's criteria although the position is complicated by retrograde solubility.

The nature of the non-stoicheiometric solid phases can be considered as follows. Since the *X*-ray powder photograph of " acidic " anhydrous $Al_2(SO_4)_3$ was identical even in the high-order lines with that of the true anhydrous salt, the two must have the same lattice structure. Since the extra acid and water in the former were present in roughly the same proportions as in the mother-liquor and were shown to be contained within the crystals and not on the surface, the presence of inter-crystallite liquid is indicated. The relationship between the 1,1,2 and the " acidic " 1,1,2 phase is not so simple, for although the powder photographs showed that they were both essentially the same chemical individual, yet the absence from the " acidic " 1,1,2 photograph of two or three of the low-order lines of moderate intensity pointed to slight differences in lattice structure. The latter, it is suggested, may be the result of lattice defects caused by the occasional absence of an aluminium ion, electrical neutrality being preserved by the substitution of three hydrogen ions in its place. The " holes " would be distributed on a statistical basis and the hydrogen ions would be associated with oxygen atoms of SO_4^- ions. Such a substitution process would be analogous to that known to occur in the alunite series (Bassett and Goodwin, *loc. cit.*), and would result in the " acidic " phase's varying slightly in composition from one preparation to another, as was in fact observed. The substitution on the average of one aluminium ion in every 16 transforms the composition 1,1,2 into 1,1·27,2·14 which would account very well for the acid concentration of the " acidic " phase. The latter's water content however varied between 2·46 and 3·68 molecules, which suggests that inclusion of acidic liquid had occurred in addition to a degree of substitution less than one in 16. Considering the habit of the " acidic " phase, inclusion of liquid would be very probable. Since the points representing the dry solid lay significantly on the water side of the corresponding group of tie-lines, absorption of a small quantity of liquid richer in water than the mother-liquor may have occurred during the washing procedure. Comparison of powder photographs showed that other transformations such as 9-hydrate $\longrightarrow$ 1,1,12 and 6-hydrate $\longrightarrow$ 1,1,8, caused by the substitution of one aluminium ion in every four, had not occurred. In view of the composition, tie-line and indicator experiment data for the metastable phase D, the latter is best regarded as a second form of the 1,1,8 compound. The *X*-ray data showed that the structures of the two forms were probably unrelated, and the extra sulphuric acid in the metastable form may therefore arise from occluded liquid.

The divergence of opinion of previous authors regarding the nature of the solid phases is probably due to the two factors : (*a*) too great reliance being placed on apparent tie-line convergence and (*b*) the existence of metastable equilibria. For example, it would be difficult on the basis of tie-line data alone to distinguish with certainty between the solid phases 1,1,8, 1,2,10, and 1,3,12, and although Henry and King (*loc. cit.*) have reported the solid 1,3,12, their description of the phase corresponds almost exactly with the stable form of our 1,1,8 substance. Similar difficulties apply to the two trios 9-hydrate–1,1,12–2,1,24 and anhydrous–dihydrate–1,1,2. Henry and King also report at 60°, following the acidic 1,3,12 (or more probably 1,1,8) with increasing acid concentration, the surprising appearance of the anhydrous normal sulphate. This phase may, as mentioned above, have been mistaken for the 1,1,2 compound, or their solutions may have been metastable with respect to 1,1,2, for we have observed the " acidic " anhydrous phase (prepared separately) to persist with the " acidic " 1,1,2 phase in contact with saturated solution (*ca.* 80% of free acid) for twelve months at 25—60° without showing any signs of approach to true equilibrium. On the other hand, we have never observed the formation of the " acidic " anhydrous phase in solution below about 200°.

13 E

APPENDIX

The X-ray photographs were taken with a 9-cm. camera, Cu-$K\alpha$ radiation being used for the aluminium compounds, and Co-$K\alpha$ for the ferric compounds. Only the first 10—15 lines are recorded, though many more were visible in different cases. Intensities were estimated visually; s signifies strong, m moderate, w weak. In Table 7, the spacings d are given in Ångström units. The spacings for $Fe_2(SO_4)_3,H_2SO_4,8H_2O$ agree with, but are more complete than, those given by Amiel, Gourdonneau, and Vauthier (*Compt. rend.*, 1945, **220**, 402). Their results for $Fe_2(SO_4)_3,9H_2O$, prepared by Recoura's method (*Ann. Chim. Phys.*, 1907, **11**, 264), differ appreciably from those given below for $Al_2(SO_4)_3,9H_2O$ or coquimbite.

TABLE 7. *Lattice spacings.*

$Al_2(SO_4)_3,14H_2O$		$Al_2(SO_4)_3,9H_2O$		$Al_2(SO_4)_3,6H_2O$		$Al_2(SO_4)_3$		Alunite		Al, 1,1,12	
d	I	d	I	d	I	d	I	d	I	d	I
7·37	w	7·56	m	7·74	w	5·72	m	4·95	m	8·28	w
5·62	w	5·50	·w	6·70	m	4·19	m	3·57	w	7·40	w
5·15	w	4·64	s	5·58	w	3·47	s	3·01	s	6·12	w
4·55	s	4·26	s	4·73	s	2·88	m	2·79	w	4·74	m
4·26	m	3·80	s	4·03	w	2·63	m	2·25	m	4·32	s
3·91	m	3·48	s	3·80	m	2·58	m	1·91	m	4·08	m
3·63	m	3·14	m	3·59	m	2·33	w	1·87	w	3·86	w
3·29	w	2·98	m	3·29	m	2·29	w	1·75	m	3·68	m
2·98	w	2·71	m	3·01	m	2·19	m	1·65	w	3·55	w
2·78	w	2·64	w	2·67	w	2·02	m	1·55	w	3·27	w
2·66	w					1·98	w	1·48	w	3·14	w
2·59	w					1·92	m	1·46	m	2·99	m
2·53	w									2·80	m
										2·66	w
										2·56	m

Al, 1,1,8, stable		Al, 1,1,8, metastable		Al, "acidic," 1,1,2		Al, 1,1,2		Coquimbite		$Fe_2(SO_4)_3,8H_2O$	
d	I	d	I	d	I	d	I	d	I	d	I
9·40	s	6·27	w	8·28	m	10·48	s	9·63	w	10·54	m
8·96	s	5·19	w	4·06	m	7·82	m	8·58	s	7·23	w
5·12	w	4·68	s	3·93	m	4·04	w	5·53	m	6·87	s
4·68	s	4·16	w	3·74	w	3·86	m	4·65	m	5·26	w
4·40	w	3·97	w	3·40	s	3·70	m	3·64	m	4·84	w
3·99	m	3·89	w	3·14	w	3·57	m	3·49	w	4·45	m
3·65	w	3·74	m	2·90	m	3·34	s	3·36	m	4·22	w
3·46	m	3·61	m	2·64	m	3·09	w	3·03	w	4·01	w
3·26	m	3·48	m	2·37	m	2·95	w	2·77	s	3·58	m
3·04	s	3·14	w	2·26	m	2·85	w	2·54	w	3·35	w
2·69	w	2·99	w	2·03	w	2·73	w	2·31	w	3·22	w
2·66	w	2·89	w	1·94	w	2·58	m				
2·59	w	2·80	w			2·35	m				
2·56	w	2·76	w			2·31	w				
2·49	w	2·61	w			2·26	m				

Fe, 1,1,8		Fe, 1,1,2		$Fe_2(SO_4)_3$		$(NH_4)_2SO_4,Fe_2(SO_4)_3$		$(NH_4)_2SO_4,Fe_2(SO_4)_3,4H_2O$	
d	I	d	I	d	I	d	I	d	I
9·22	s	10·28	m	6·08	m	8·10	s	6·91	w
8·81	s	9·01	m	5·32	w	4·49	w	5·77	s
5·19	w	7·72	m	4·40	m	4·10	w	5·15	w
4·79	w	4·05	w	4·14	m	3·67	w	4·55	w
4·68	m	3·90	w	3·71	w	3·41	m	3·80	s
4·18	w	3·71	w	3·59	s	2·69	w	3·27	s
4·01	m	3·59	w	3·26	w	2·39	m	2·88	w
3·50	m	3·35	s	3·16	w	2·07	w	2·77	w
3·26	m	3·26	w	2·99	m	1·96	w	2·67	w
3·08	m	3·08	w	2·90	w				
2·75	w	2·57	w	2·74	m				
2·64	w	2·39	m	2·69	w				
2·57	w	2·27	w	2·63	w				
2·49	w	2·02	w	2·42	w				