The relative abundances of the isotopes of zinc of masses 64, 66, 67, 68 and 70 were found to be 48.89, 27.81, 4.07, 18.61 and 0.620%, respectively. With a packing fraction of -7.0×10^{-4} and the conversion factor 1.000275, the computed chemical atomic weight is 65.40, whereas the International chemical value is 65.38.

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The System Aluminum Sulfate–Sulfuric Acid–Water at 60°

BY JACK L. HENRY[1] AND G. BROOKS KING

This report is part of a study of the more extensive system aluminum oxide–sulfur trioxide–water at 60° which is being investigated in connection with the development of an alumina-from-clay extraction process. The temperature 60° has been found most advantageous for the process as determined with laboratory scale and pilot plant extraction towers.[2] Although the leach operations are carried on within the basic region, it was felt desirable to conduct a study of the system in its entirety. In connection with the acid system presented in this paper, no complete ternary systems have been reported. F. Wirth[3] has studied the solubility of aluminum sulfate in sulfuric acid solutions of concentrations up to 75% at 25° and has reported but one solid phase, the 18 hydrate. At the same temperature Motida[4] has found the 16 hydrate in addition to the 18 hydrate, but presented no data for sulfuric acid concentrations above 48%. Kremann and Hüttinger[5] in their work on the solubility of freshly precipitated aluminum hydroxide in aluminum sulfate solutions report that the 16 hydrate exists as the solid phase in the less basic region at 20, 40 and 60°. This would seem to be in agreement with the views of P. M. Delacharlonny,[6] who favors the 16 hydrate. Horan and Skarulis,[7] however, failed to prepare the 18 hydrate and suggest the possibility of $Al_2(SO_4)_3 \cdot 17H_2O$ at the temperature 0°. Following this work, N. O. Smith,[8] by repeating at 25° the parts of three ternary systems which involve hydrated aluminum sulfate as the solid phase, showed further evidence in favor of the 17 hydrate. The following hydrates of aluminum sulfate have been found reported in the literature: 2, 3, 6, 9, 10, 12, 14, 16, 17, 18, 22, 24 and 27. That they are all true chemical individuals, however, seems questionable. The present paper treats the system over sulfuric acid concentrations up to 96.08% and shows the presence of the four solid phases at 60°: $Al_2(SO_4)_3 \cdot 16H_2O$, $Al_2(SO_4)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 12H_2O$ and $Al_2(SO_4)_3$.

Experimental

Materials and Apparatus.—Mallinckrodt analytical reagent aluminum sulfate and sulfuric acid were employed throughout the system. Aluminum sulfate was recrystallized from a solution of specific gravity about 1.33 as suggested by Horan and Skarulis.[7] Extensive solubility studies on the system at 60° showed, however, that any deviations caused by impurities present in the unrecrystallized reagent could not be detected by the analytical methods used. Because of the high percentage of waste involved in recrystallization and the large amount of aluminum sulfate used, the unrecrystallized salt was employed in more than half the studies.

An electrically controlled thermostat which held the temperature at 60 ± 0.1° was employed. Evaporation loss from the bath was limited by a fabricated sheet aluminum cover. Glass-stoppered Pyrex tubes of about 40-ml. capacity which held the solutions under investigation were fitted with cotton-filled caps and secured to a wheel which rotated continually beneath the water surface of the bath. Such tumbling action provided efficient agitation during the time required for the solutions to reach equilibrium.

Methods of Analysis.—Aluminum sulfate was determined gravimetrically as Al_2O_3 by ignition at 1150°. Sulfuric acid was titrated directly in the presence of aluminum sulfate with standard sodium hydroxide solution. The aluminum which was combined in a complex by use of an excess of sodium oxalate[9] did not interfere with the titration. In regions of low sulfuric acid concentration the titrations were carried out electrometrically, whereas phenol red indicator was used at higher concentrations. The volumetric method for sulfuric acid gave satisfactory checks against the gravimetric barium sulfate procedure and proved to be much more rapid.

Solubility Determinations.—Various mixtures of aluminum sulfate, sulfuric acid and water were weighed out approximately and placed in the described tubes. The mixtures were brought to equilibrium from the supersaturated condition in most cases. Tubes were removed from the wheel at intervals and samples taken for analysis to determine the progress in attainment of equilibrium. Time for establishment of equilibrium conditions increased with increasing sulfuric acid concentration. Equilibrium was attained in the less acidic regions within forty-eight hours, but in no case did the time exceed six days. At lower sulfuric acid concentrations the crystals, although quite small, separated quickly and completely. Above 50% sulfuric acid the equilibrium mixture proved difficult to handle in that the resulting viscous slurries failed to separate well into liquid and solid phases. A constant temperature centrifuge was designed and built in which the samples could be centrifuged at 60 ± 0.1°. This incor-

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[1] Submitted in partial fulfillment of the requirements for the Ph.D. degree, the State College of Washington.

[2] *Ind. Eng. Chem.*, **38**, 1181 (1946).

[3] F. Wirth, *Z. anorg. Chem.*, **79**, 360 (1912).

[4] Motida, *Science Repts. Tohôku Imp. Univ.*, First Ser., **26**, 611–617 (1938).

[5] R. Kremann and K. Hüttinger, *Jahrbuch d. k. k. geol. Reichsanstalt. Wien*, **58**, 637 (1908).

[6] P. M. Delacharlonny, *Compt. rend.*, **96**, 844 (1883).

[7] Horan and Skarulis, THIS JOURNAL, **61**, 2689 (1939).

[8] N. O. Smith, *ibid.*, **64**, 41 (1942).

[9] M. F. Adams (not yet published), presented at American Chemical Society regional meeting, Seattle, Washington, 1945.

porated an air-bath electrically controlled by a bimetallic spiral thermoregulator and a space heater. Successful separations were achieved by this means up to concentrations of sulfuric acid in excess of 85%. Above this concentration the density of the mother liquor so closely approached that of the minute crystals that centrifuging for a permissible length of time failed to bring about complete separation. The few points treated in this region were separated by gravitational settling over a period of from one to two weeks.

The method of "wet residues"[10] was used in nearly all cases except in the establishment of isothermally invariant points. In these, accurately synthesized complexes were employed. It was found that glass-stoppered tubes properly sealed with DeKhotinsky cement were highly satisfactory for the work with complexes.

Results

The compositions of the solutions and residues are given in Table I and shown graphically in Fig. 1. Tie-lines are constructed to intersect at the probable solid phase.

TABLE I

THE SYSTEM $Al_2(SO_4)_3$–H_2SO_4–H_2O AT 60°

Solution, wt. %		Residue, wt. %		Solid phase	Error in % $Al_2(SO_4)_3$ by algebraic extrapolation
$Al_2(SO_4)_3$	H_2SO_4	$Al_2(SO_4)_3$	H_2SO_4		
31.83	0.00	...	...		
29.31	2.37	46.24	0.94	M	−3.11
27.87	4.55	44.68	1.74	M	−0.83
26.15	7.09	43.00	3.05	M	−1.47
23.82	11.03	37.89	6.14	M	−1.30
21.88	14.25	37.14	7.80	M	−1.34
19.29	19.57	38.51	8.90	M	−0.28
16.44	25.93	36.46	12.29	M	−0.24
14.59	32.52	37.52	13.83	M	−0.23
14.51	35.29	36.96	17.14	M + N	
14.79	35.00	21.50	29.50[a]	M + N	
14.70	35.27	18.00	32.50[a]	M + N	
10.41	39.61	19.00	34.00[a]	N	−3.21
7.67	43.95	34.59	24.81	N	−1.63
5.99	48.11	28.51	30.55	N	+0.18
5.04	50.95	32.02	28.56	N	+1.39
4.43	55.09	19.87	41.70	N	−0.12
4.09	56.86	9.92	51.75[a]	N	−1.12
3.82	59.02	23.04	41.29	N + O	
3.69	58.84	13.77	51.07	N + O	
4.25	60.82	17.48	48.50[b]	N	−1.72
0.92	65.61	12.08	56.44	O	+1.36
.63	69.94	8.95	62.36	O	+0.61
.63	72.82	7.89	65.77	O	+0.05
.99	76.18	9.43	67.27	O	−0.33
1.74	78.49	8.00	73.00[a]	O + P	
1.81	78.45	8.00	73.50[a]	O + P	
1.72	77.97	8.00	72.50[a]	O + P	
0.17	82.57	7.00	77.00[a]	P	−1.42
.17	86.84	10.67	77.54	P	+0.85
.09	90.89	6.25	85.25	P	+0.64
Trace	96.08	4.32	91.78	P	+3.47

[a] Complex made up against analytical balance. [b] Metastable. M = $Al_2(SO_4)_3 \cdot 16H_2O$, N = $Al_2(SO_4)_3 \cdot 9H_2O$, O = $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 12H_2O$, P = $Al_2(SO_4)_3$.

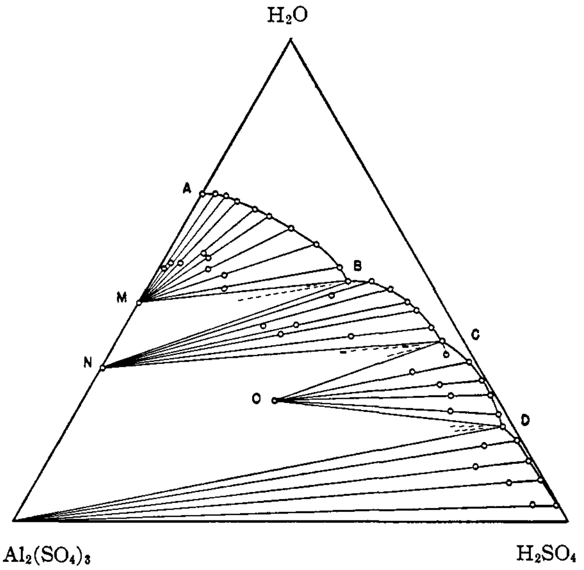

Fig. 1.—System $Al_2(SO_4)_3$–H_2SO_4–H_2O at 60°: M = $Al_2(SO_4)_3 \cdot 16H_2O$, N = $Al_2(SO_4)_3 \cdot 9H_2O$, O = $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 12H_2O$, P = $Al_2(SO_4)_3$.

Data were plotted and graphical extrapolations made on an accurately drawn triangular diagram with edge dimensions of 50 cm. To check the accuracy of the solid phases determined by such graphical means, algebraic extrapolations[11] were carried out for each of the four solids. By algebraic extrapolation of data on curve AB the points nearest the edge of the triangle would seem to favor the 15 hydrate of aluminum sulfate, whereas those data nearer point B show the 16 hydrate to be the probable solid phase. Extrapolations of data nearest point A appear more erratic, however. This might be expected since the tie-lines are so nearly parallel to the edge of the diagram. Such uncertainty in this region would suggest that more weight be placed on those data nearer point B on the curve. Algebraic extrapolations from the four points nearest B show an average error in per cent. $Al_2(SO_4)_3$ of −0.53 from the 16 hydrate and +1.09 from the 15 hydrate. The 18 hydrate reported by Motida[4] to exist over the range of sulfuric acid concentration up to 7.24% at 25° was not observed at this higher isotherm although the possibility of a transition near A was given careful consideration. Extension of the work into the basic region, not yet published, throws little light on the possibility of an 18 hydrate because the curve breaks soon after passing the $Al_2(SO_4)_3$–H_2O axis.

Since our value of 31.8% for the solubility of pure aluminum sulfate at 60° differs so greatly from the value 37.2% reported by Poggiale[12] it was felt that the binary system $Al_2(SO_4)_3$–H_2O should be re-investigated at least in part. Whereas the solubilities near 25 and 30° lie close to the values obtained by Poggiale, a large negative deviation is observed at higher temperatures. The

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(10) Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

(11) Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

(12) Poggiale, *Ann. Chim. Phys.*, [3] **8**, 467 (1843).

results reported by Poggiale are shown by the broken line in Fig. 2. Much work has been done on solubility studies of aluminum sulfate at 25 and 30°, but relatively little above these temperatures. The fact that Poggiale's binary study agrees with recent investigators in this more common range may explain why re-investigation of the system at elevated temperatures has not been conducted. Data for the binary study are given in Table II and shown graphically in Fig. 2. Equilibrium was established from both undersaturation and supersaturation in each case. No attempt was made to identify the solid phase, and although the curve is drawn as smooth the data do not rule out the possibility of a change in hydration in this range.

TABLE II

SOLUBILITY OF HYDRATED ALUMINUM SULFATE

Temp., °C.	Solubility $Al_2(SO_4)_3$ (wt. %) Undersaturation value	Supersaturation value	Average
25	28.3	28.3	28.3
30	28.6	28.6	28.6
35	28.9	28.9	28.9
40	29.5	29.7	29.6
45	29.9	30.1	30.0
50	30.8	30.3	30.6
55	31.1	31.3	31.2
60	31.8	31.8	31.8
65	33.0	32.8	32.9

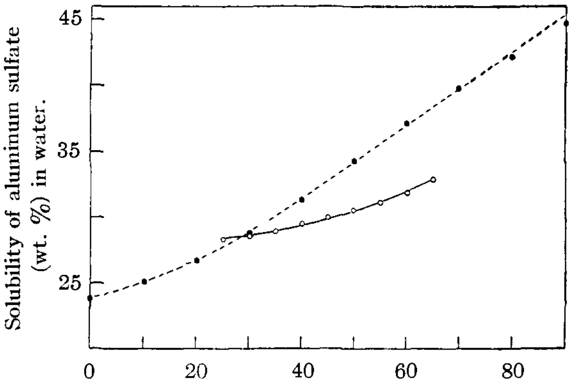

Fig. 2.—Solubility of hydrated $Al_2(SO_4)_3$ in H_2O given as percentage by weight. Broken-line curve represents the values reported by Poggiale.[11]

The solubility curve BC, Fig. 1, shows $Al_2(SO_4)_3 \cdot 9H_2O$ to be the probable solid phase. The average deviation in per cent. $Al_2(SO_4)_3$ by algebraic extrapolation is +0.89. Metastability was encountered in this region as shown by the broken line extending beyond 60.8% sulfuric acid. Behavior of several samples prepared in the range of curve CD indicated that this metastable condition extends to about 65% sulfuric acid.

The curve CD represents solutions in equilibrium with the acid salt $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 12H_2O$. Average deviation in per cent. $Al_2(SO_4)_3$ from the composition of this solid phase as determined by algebraic extrapolation is +0.42. Three acid salts have been reported, $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 3H_2O$ by E. Baud,[13] $Al_2(SO_4)_3 \cdot 2H_2SO_4 \cdot 10H_2O$ by F. Jeremin,[14] and $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 7H_2O$ by R. Silberberger.[15] The later bisulfate was reported to have been prepared by the addition of aluminum sulfate to cold concentrated sulfuric acid and warming. The acid salt described in the present paper is very similar in physical properties to that reported by Silberberger but differs as to degree of hydration. When filtered and washed with ether the acid sulfate appears as a fine white powder. In contact with water it remains for several hours as a "silky" precipitate gradually decomposing and going into solution. The white powder appears to be slightly deliquescent and changes in moist air to form a paste-like mass which is readily soluble in water.

Beyond the isothermally invariant point *D* anhydrous aluminum sulfate is found to be the solid phase. The average error in per cent. $Al_2(SO_4)_3$ is +0.88. The highest concentration of sulfuric acid studied shows only a trace of dissolved aluminum sulfate. This may be compared with the work of Kendall and Davidson,[16] who report the molar solubility of anhydrous aluminum sulfate in anhydrous sulfuric acid at 25° to be less than 0.01. The amplification of analytical errors caused by failure to obtain a more complete separation of the residue from the solution has contributed greatly to the deviations in the extrapolations. The relatively large range of extrapolations may cast some doubt upon the degree of hydration of phases N and O as stated.

Summary

The ternary system $Al_2(SO_4)_3$–H_2SO_4–H_2O has been investigated at 60°. The four solid phases, $Al_2(SO_4)_3 \cdot 16H_2O$, $Al_2(SO_4)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 12H_2O$, and anhydrous $Al_2(SO_4)_3$ have been found.

Investigation of the binary system $Al_2(SO_4)_3$–H_2O from 25 to 65° shows lower values of solubility in the higher temperature range than have been previously reported.

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[13] E. Baud, *Compt. rend.*, **137**, 494 (1903).

[14] F. Jeremin, *J. Russ. Phys.-Chem., Soc.*, **13**, 468 (1888).

[15] R. Silberberger, *Monatsh.*, **25**, 220 (1904).

[16] Kendall and Davidson, THIS JOURNAL, **43**, 979 (1921).