

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Hydration of Aluminum Sulfate

BY NORMAN O. SMITH

Until recently it was the general belief that the form of aluminum sulfate which is in equilibrium with its saturated aqueous solution at 25° is the octodecahydrate. Failure to prepare a hydrate of this composition led Horan and Skarulis¹ to doubt the generally accepted formula, and they record having prepared hydrated aluminum sulfate the composition of which corresponded closely to the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ as shown by aluminum determinations. Similarly Hill, Smith and Ricci² express doubt of the existence of the octodecahydrate in contact with saturated solution at 25°, and state that the heptadecahydrate is the probable form at that temperature. It is the purpose of this report to present further evidence in confirmation of the existence of the heptadecahydrate at 25°.

It is well known that in a ternary system the composition of a solid phase in equilibrium with liquid can be determined by extrapolation from the compositions of the liquids and of the corresponding "wet residues." Using the (isothermal) data of previous workers on systems of the type $\text{MSO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ for ternary solutions in equilibrium with hydrated aluminum sulfate only, the writer has calculated the composition of the latter by algebraic extrapolation³ to 0% MSO_4 . The source of the data used and the calculated composition of the solids are shown in Table I. With one exception¹ the writers in all cases assumed the hydrate to be the octodecahydrate; but not overlooking the fact that extrapolation amplifies analytical errors, the scant support given to this assumption by their own figures is obvious; calculation shows that the octodecahydrate contains 51.34%, the heptadecahydrate 52.76% and the hexadecahydrate 54.27% aluminum sulfate.

As indications of degree of hydration then, these data, taken collectively at any one temperature, are of little use. The writer has therefore repeated, at 25° only, parts of some of these systems, namely those parts which involve hydrated aluminum sulfate as the solid phase, in an attempt to improve the agreement and accuracy

- (1) Horan and Skarulis, *THIS JOURNAL*, **61**, 2689 (1939).
- (2) Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).
- (3) Hill and Ricci, *ibid.*, **53**, 4306 (1931).

TABLE I

	Solid phase, wt. % $\text{Al}_2(\text{SO}_4)_3$ extrap.		Solid phase, wt. % $\text{Al}_2(\text{SO}_4)_3$ extrap.
Temp. 0°	59.8	Temp. 25°	56.4
M = Li ₂	54.68	M = Na ₂	52.52
Ref. 1	52.55	Ref. 7	
	57.2		
Temp. 0°	51.37	Temp. 30°	51.33
M = Li ₂	52.66	M = Cu	51.47
Ref. 4	52.00	Ref. 8	
Temp. 0°	55.8	Temp. 30°	49.54
M = Na ₂		M = Mn	56.26
Ref. 5		Ref. 8	52.82
Temp. 0°	53.9	Temp. 30°	53.49
M = Cu	52.65	M = Ni	51.18
Ref. 6	53.38	Ref. 9	
Temp. 25°	55.8	Temp. 30°	58.4
M = Fe	55.35	M = Na ₂	56.2
Ref. 6		Ref. 5	

of the extrapolated figures, thereby obtaining more reliable information concerning the extent of hydration of the aluminum sulfate at 25°. It was hoped that this could be accomplished by using improved analytical methods where possible and basing extrapolations on the compositions of the liquids and of the complexes—the complexes instead of the wet residues because the former are capable of measurement with more accuracy than the latter.³

Cupric Sulfate, Aluminum Sulfate, Water at 25°.—Complexes of known composition were made up from cupric sulfate pentahydrate, hydrated aluminum sulfate and water, the copper salt being dissolved before the aluminum salt was added. The cupric sulfate was a recrystallized Mallinckrodt chemical (reagent grade) which, on analysis for copper electrolytically, showed the theoretical composition. The aluminum sulfate (used throughout the present work) was the "Analar" grade of the British Drug Houses, which had been treated as follows: 500 g. was recrystallized from the minimum quantity of water acidified with 10 ml. of concentrated sulfuric acid between 80° and room temperature. The crystals were stirred in contact with the mother liquor for forty-five hours and then filtered, washed twice with water, later with a 3:1 acetone-water mixture, air dried, placed in a closed container and shaken until uniform in composition as shown by analysis

- (4) Sanders and Dobbins, *J. Phys. Chem.*, **35**, 3087 (1931).
- (5) Dobbins and Adleston, *ibid.*, **39**, 637 (1935).
- (6) Occlshaw, *J. Chem. Soc.*, **127**, 2598 (1925).
- (7) Dobbins and Byrd, *J. Phys. Chem.*, **35**, 3673 (1931).
- (8) Caven and Mitchell, *J. Chem. Soc.*, **127**, 527 (1925).
- (9) Caven and Mitchell, *ibid.*, **127**, 2549 (1925).

for aluminum by precipitation with 8-hydroxyquinoline.¹⁰ The analytical composition was used in calculating the composition of the complexes. The latter were contained in glass-stoppered bottles of about 35 ml. capacity and rotated for about a week in a thermostat at $25 \pm 0.05^\circ$. A piece of glass rod was placed in each solubility bottle in order to keep the solid well ground. At equilibrium the liquid samples were removed for analysis by means of a pipet furnished with a paper and cotton wool filter. Copper was determined electrolytically and aluminum was determined in the residual liquid, as mentioned above. The aluminum results were duplicated, but the copper results were based on only one analysis because of the small quantities of copper available. The results are shown in Table II together with the calculated compositions of the solid phase.

TABLE II

CuSO ₄ -Al ₂ (SO ₄) ₃ -H ₂ O AT 25°				
Liquid solution,		Original complex,		Wt. %
CuSO ₄	Al ₂ (SO ₄) ₃	CuSO ₄	Al ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃ in solid (extrap.)
0.000	27.84U	0.000
0.000	27.85S	0.000
1.281	27.02	0.785	37.06	52.95
2.151	26.37	1.496	34.53	53.17
3.139	26.02	2.049	35.25	52.60
4.464	25.08	3.472	31.29	53.03
5.187	24.65	8	28	"

Mean 52.94

^a Isothermally invariant point. Solid phases present: Al₂(SO₄)₃·17H₂O and CuSO₄·5H₂O.

The solubilities of the pure hydrated aluminum sulfate determined from under- and oversaturation as indicated by the letters U and S, respectively, are averages of closely agreeing measurements.

Ferrous Sulfate, Aluminum Sulfate, Water at 25°.—

The ferrous sulfate employed was the "Analar" grade of the British Drug Houses, and its iron content was found to correspond to the theoretical value, iron being determined by titration with permanganate standardized with sodium oxalate. In order to prevent oxidation of iron, the complexes were made up in an atmosphere of hydrogen and using water which had been freshly boiled and cooled in a current of hydrogen according to the method of Occleshaw.⁶ The aluminum sulfate used was the same as that in the first system. In this case it was not convenient to dissolve the ferrous sulfate first, as was done with the cupric sulfate. The complexes were rotated for about a week and the liquids then analyzed for iron by permanganate, and for total iron and aluminum by oxidation of the iron by nitric acid and simultaneous precipitation of both by 8-hydroxyquinoline^{10,11}—a method which had been found satisfactory in previous work.² The results are given in Table III.

Nickel Sulfate, Aluminum Sulfate, Water at 25°.—Because of the difficulty of preparing solid nickel sulfate of constant composition, as noted by Hill and Taylor,¹² the complexes were made up using a solution of the British Drug Houses pure nickel sulfate, which had been stand-

TABLE III

FeSO ₄ -Al ₂ (SO ₄) ₃ -H ₂ O AT 25°				
Liquid solution,		Original complex,		Wt. %
FeSO ₄	Al ₂ (SO ₄) ₃	FeSO ₄	Al ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃ in solid (extrap.)
0.0000	27.85	0.0000
0.5447	27.33	0.3882	34.64	52.77
1.268	26.96	0.808	36.45	53.12
2.415	26.33	1.579	35.47	52.73
3.198	25.69	1.956	36.27	52.93
3.908	25.28	4.41	26.5	"

Mean 52.89

^a Isothermally invariant point. Solid phases present: Al₂(SO₄)₃·17H₂O and (according to Occleshaw) FeSO₄·Al₂(SO₄)₃·24H₂O.

ardized by determining the nickel content with dimethylglyoxime. After about five days of rotation in the thermostat, the liquids were analyzed as follows: nickel was determined with dimethylglyoxime in the presence of tartrate. Aluminum was determined with 8-hydroxyquinoline after removal of the nickel as just described; and it was found necessary also to destroy the tartrate by repeated digestion in a Kjeldahl flask with a mixture of concentrated nitric and sulfuric acids. The method was found by preliminary tests to be quite satisfactory. Table IV shows the results obtained.

TABLE IV

Measurements not carried up to any isothermally invariant point.

NiSO ₄ -Al ₂ (SO ₄) ₃ -H ₂ O AT 25°				
Liquid solution,		Original complex,		Wt. %
NiSO ₄	Al ₂ (SO ₄) ₃	NiSO ₄	Al ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃ in solid (extrap.)
0.000	27.85	0.000
0.846	27.09	0.578	35.29	52.98
1.743	26.70	1.043	37.07	52.52
3.982	25.22	2.170	37.68	52.60
6.023	23.74	3.332	36.75	52.86

Mean 52.74

Discussion of Results.—Figure 1 shows the above results graphically and also the data of Occleshaw⁶ for the copper and iron systems.

In view of the large scale of the diagram the agreement with Occleshaw's figures in the case of the copper system is satisfactory, the present results showing a slightly lower concentration of dissolved salts than his. The figure for the solubility of hydrated aluminum sulfate (27.85%) agrees well with that of Occleshaw⁶ (27.80%), and of Hill, Smith and Ricci² (27.83%). Similarly the concentration of the isothermally invariant liquid confirms Occleshaw's results.⁶ The same remarks apply to the iron system although Occleshaw's data are too few in number for proper comparison.

The solubility curve for aluminum sulfate heptadecahydrate in the nickel system has not been determined previously at 25°.

(10) Kolthoff and Sandell, *THIS JOURNAL*, **50**, 1900 (1928).

(11) Berg, *Z. anal. Chem.*, **76**, 193 (1929).

(12) Hill and Taylor, *THIS JOURNAL*, **60**, 1099 (1938).

Comparison of the last column of Tables II, III and IV with the last column of Table I shows that the agreement in any one system has been considerably improved. Improvement is apparent also in the agreement among different systems at a single temperature. Further comparison might be made of the present extrapolated figures with those of Caven and Mitchell^{8,9} for the copper and nickel systems, but the fact that they were obtained under different conditions of temperature partly invalidates such comparison.

Concerning the actual value of the extrapolated composition it is evident that the probable figure is much nearer that for the heptadecahydrate (52.76%) than that for either the octo- (51.34%) or hexadecahydrate (54.27%).

The validity of the above extrapolations depends to a considerable extent on the purity of the aluminum sulfate used for the complexes, the preparation of which is described above. As no precautions had been taken against efflorescence, the composition of this material was inconclusive as a means of indicating hydration; however, since aluminum analysis had shown 53.15% $\text{Al}_2(\text{SO}_4)_3$, and sulfate analysis (precipitation of barium sulfate in the presence of 0.1 *N* hydrochloric acid) 53.36% $\text{Al}_2(\text{SO}_4)_3$, and bearing in mind the usual inaccuracy of barium sulfate precipitation, one may conclude that the product, apart from efflorescence, had been contaminated only by a small amount of free sulfuric acid. The presence of such acid was substantiated by the somewhat sticky consistency of the preparation. Contamination by difficultly removable alkali sulfates was considered improbable because no indication of them had been found in flame tests, and tests for ammonium.

Preparation of $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$.—Horan and Skarulis¹ had succeeded in preparing $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ by gradual hydration, in a desiccator over saturated sodium bromide dihydrate solution, of previously partially dehydrated aluminum sulfate, although their preparation was analyzed for aluminum content only. The writer has been able to prepare the same substance by the reverse process of drying the wet hydrate, thus showing that water, if it is occluded as Horan and Skarulis suggest, can still be removed by this method. The procedure was as follows. The clear mother liquor from the main recrystallization described above was allowed to stand in a flask in sub-zero weather with frequent shaking till it turned solid.

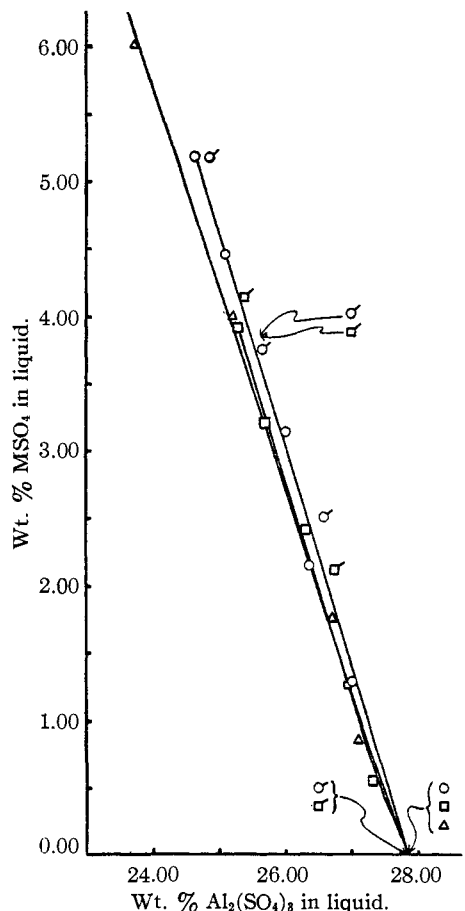


Fig. 1.—Solubility curves of $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ at 25°: O, $\text{CuSO}_4\text{-Al}_2(\text{SO}_4)_3$; □, $\text{FeSO}_4\text{-Al}_2(\text{SO}_4)_3$; △, $\text{NiSO}_4\text{-Al}_2(\text{SO}_4)_3$; Occlshaw's results—σ', $\text{CuSO}_4\text{-Al}_2(\text{SO}_4)_3$; σ'', $\text{FeSO}_4\text{-Al}_2(\text{SO}_4)_3$.

The flask was then allowed to warm to about 0°, the crystals of aluminum sulfate filtered off, washed twice with ice water, centrifuged and placed at room temperature in a vacuum desiccator over some of the partly dehydrated salt which analyzed 53.69% $\text{Al}_2(\text{SO}_4)_3$. From time to time both the wet and partially dehydrated materials were well stirred and a record of their weight kept. The former was found to lose and the latter to gain weight as usual. When weight constancy was reached (in about two weeks) analysis of the former showed a composition of 52.79% $\text{Al}_2(\text{SO}_4)_3$ by aluminum and 53.06% $\text{Al}_2(\text{SO}_4)_3$ by sulfate determinations. Of course, the above procedure, while eliminating the possibilities of efflorescence and hydrolysis, actually gives no definite information concerning the degree of hydration of the salt in equilibrium with solution at 25°. Nor does this prove the state of hydration at 0° since the temperature of crystallization was not accurately maintained.

Summary

1. Previous data in the literature have been reviewed and shown to lend little support to the generally accepted formula for hydrated aluminum sulfate, namely, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

2. Parts of ternary systems have been repeated at 25° and evidence presented which indicates that the heptadecahydrate is the stable form of aluminum sulfate in equilibrium with

its saturated aqueous solution at this temperature.

3. Part of the solubility curve of $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ in the system $\text{NiSO}_4\text{--Al}_2(\text{SO}_4)_3\text{--H}_2\text{O}$ at 25° has been determined.

4. A substance of composition corresponding to the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ has been prepared by crystallization at a low temperature.

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Thermodynamic Properties of Nitrogen at High Pressures as Analytic Functions of Temperature and Pressure

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Introduction

Accurate P - V - T data for nitrogen were determined by Bartlett and co-workers¹ in 1928 over the temperature range -70 to 600° and up to pressures of 1000 atmospheres. Utilizing these data, Deming and Shupe² evaluated Beattie-Bridgeman constants which, in conjunction with the Beattie-Bridgeman equation of state, reproduced the P - V - T relations of this gas with an accuracy of 2% down to volumes of 84 cc. per mole. At the lowest temperature, -70° , this volume corresponds to a pressure of about 200 atmospheres, while at the highest temperature, 600° , about 1000 atmospheres. Later, employing graphical methods, Deming and Shupe³ evaluated from these same data a number of the thermodynamic properties of nitrogen at various temperatures and pressures, but made no attempt to express these properties as analytic functions of temperature and pressure.

The Beattie-Bridgeman equation of state, as ordinarily formulated, gives the pressure as an explicit function of volume and temperature. In order to obtain the thermodynamic properties as functions of pressure and temperature, it is convenient to have the volume as an explicit function of these two variables. By setting the actual volume equal to the ideal in all terms of the Beattie-Bridgeman equation beyond the first,

Beattie⁴ was able to formulate an equation explicit in volume, still retaining the ordinary constants. In preceding papers⁵ the authors tested this modified Beattie-Bridgeman equation by calculating the activity coefficients (*i. e.*, ratios of fugacity to pressure) of nitrogen, and showed that the equation yields satisfactory results up to pressures of 300 to 500 atmospheres over the entire temperature range, but is not satisfactory for pressures higher than these. They also went on to show⁶ how it is possible, knowing the Beattie-Bridgeman constants for nitrogen, to evaluate from these the Beattie-Bridgeman constants for any other gas.

Since the treatment employed in these papers is not limited to the equation used, but should be applicable to any equation of state explicit in volume, it should be possible to extend the pressure range of the analytic equations for the thermodynamic properties of a gas as soon as an equation of state of some gas is available which is more accurate at the high pressures than the modified Beattie-Bridgeman equation. It is the purpose of this paper (1) to present an equation of state for nitrogen explicit in volume and covering the temperature range -70 to 600° up to 1000 atmospheres pressure; (2) to deduce from this equation analytic expressions for the thermodynamic properties of the gas at high pressures; (3) to compare the quantities calculated from these

(1) Bartlett, Cupples and Tremearne, *THIS JOURNAL*, **50**, 1275 (1928).

(2) Deming and Shupe, *ibid.*, **52**, 1382 (1930).

(3) Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931); **45**, 111 (1934); **48**, 448 (1935).

(4) Beattie, *Proc. Natl. Acad. Sci.*, **16**, 14 (1930).

(5) Maron and Turnbull, *Ind. Eng. Chem.*, **33**, 69 (1941); **33**, 246 (1941).

(6) Maron and Turnbull, *ibid.*, **33**, 408 (1941).