large tetrabutylammonium cation, and spectral differences should vanish as they do.

Analogous solvent dependence of the stability of the trihalide ion is found in the literature on tribromide ion.[27–33] This is consistent with the literature on solvent complexes of bromine which is parallel to that for iodine.[34]

The acid effect noted on the triiodide equilibrium, in the region of acidity 1 *M* $HClO_4$ is apparently the first evidence for a difference in the dissociation constants for HI and HI_3. The temperature variation in the peak extinction coefficient of triiodide is probably related to the origin of the absorption. This is a modified absorption of the iodide ion, which will be discussed elsewhere.

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Dissociation Pressures and Related Measurements in the System Aluminum Sulfate–Water[1]

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Published data on the system aluminum sulfate–water are incomplete and contradictory. A static manometric method was used to measure the vapor pressures of known aluminum sulfate–water compositions at fixed temperatures as known quantities of water were withdrawn. Measurements were made at 25, 14 and 0°, and the sample size was varied. Equilibrium could be reached only for the higher hydrates. Within the range of conditions studied both of the compounds $Al_2(SO_4)_3\cdot 16H_2O$ and $Al_2(SO_4)_3\cdot 17H_2O$ appear to exist and are, furthermore, mutually soluble. The $17H_2O$ is thus capable of losing up to one mole of zeolitic water. Dissociation pressures for the systems vapor–liquid–$17H_2O$ and vapor–$16H_2O$–lower hydrate, and for a metastable system, were obtained at each temperature. A log *P* *vs.* $1/T$ plot was linear for each. The ice curve and eutectic point were redetermined giving results markedly different from the only previous values. The solubility curve of the $17H_2O$ was extended. Melting points of hydrated aluminum sulfate in various stages of hydration indicated transition temperatures at ~111° and ~128°. Previous boiling point elevation values have been improved upon and extended to higher concentrations.

The phase relations in the system aluminum sulfate–water are, surprisingly, not well established considering the widespread use of the hydrates. There is, for instance, no complete agreement as to the identity of the highest hydrate[2] although the existence of (1) a hydrate or hydrates with 18, 17 or 16 moles, and (2) a hydrate with 10 or 9 moles of water of hydration is generally conceded. Smith and others[3] showed the highest hydrate at 25° to be the 17 but Bassett and others[4–6] still regard it as the 16 (see Discussion). The second highest hydrate would appear to be the 10 from the work of Gee[7] but 9 from that of Henry and King.[2] If, as Gee claims, the highest hydrate is the 10 (or 9) at 80° but the 16 at 30° there should be a break in the aqueous solubility curve between these two temperatures. This is not evident in the measurements of Taylor and Bassett.[6] Furthermore, the only published boiling point elevation data[8] were obtained by the crudest of methods, the authors themselves suggesting that their measurements be repeated.

Dissociation Pressures

To resolve the problem of the identity of hydrates it would appear that isothermal measurements of the equilibrium pressure of the system as water is gradually withdrawn would provide the best means, by noting the compositions of solid at which marked changes in pressure are observed. Such dissociation pressure measurements at 20° are described by Kremann and Hüttinger[9] using equilibration over sulfuric acid solutions, and the hydrates 18, 16, 12 and 2 were claimed. Their results are open to alternative interpretations, however, and their pressures do not agree with those reported below. Taylor and Bassett[6] give a brief reference to dissociation pressure measurements at 25° using a static manometric method. Equilibrium was approached from the direction opposite[10] to that used by us and their results differ from, and are less complete than, ours.

Experimental

In the present work pressures were measured by a method patterned after that of Logan.[11] The sample (A, Fig. 1) was contained in a thermostated 50-ml. glass bulb B leading directly to one arm of a mercury manometer C. The other arm led to a Hyvac pump and McLeod gage, and to a means of introducing or removing measured quantities of water. Air-free water was introduced by drawing water into E (previously evacuated) through F, boiling out the air through

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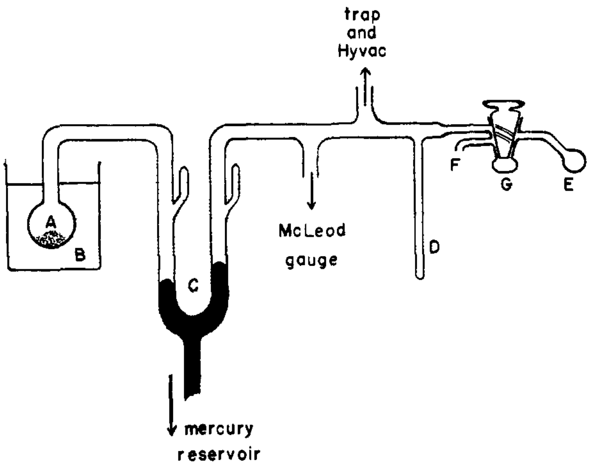

Fig. 1.—Apparatus.

F and then distilling into the calibrated tube D where the depth gave a measure of the quantity. It was then distilled into A. Tube D was used similarly to measure amounts of water withdrawn from A. By maintaining a negligible pressure on the right arm of the manometer, as shown by the McLeod gage, the differences in level, measured with a Gaertner cathetometer to 0.01 mm., gave the pressure of the system directly.

The aluminum sulfate was prepared from pure aluminum and sulfuric acid and recrystallized.[4] To remove free acid it was heated to intumescence, ground and heated *in vacuo* at 170°. Analysis of this product gave the following results: 96.86% $Al_2(SO_4)_3$ by aluminum[12] and 96.80% $Al_2(SO_4)_3$ by sulfate[13] analysis. No basic salt was present, therefore. This material was dissolved in water, sealed into the apparatus at A, excess water removed with suction and the resulting hydrate pumped off. It was then heated for two days at 170° under vacuum to degas. Higher temperatures decompose the sulfate to the oxide. This technique utilized the intumescent character of the substance to produce a porous degassed sample without loss of sulfur; when so prepared it showed no tendency to fill the apparatus with dust when heated.

More than enough water to hydrate the material fully was now admitted and the pressure measured after withdrawal of small measured amounts of water. At the conclusion of the run the residue in B was analyzed and the composition for each observed pressure calculated. In contrast to the findings of Taylor and Bassett[10] equilibrium appeared to be readily obtainable only on dehydration and not on hydration, and, even then, only for higher water content of solid. Measurements were conducted with varying sample weights at 25°, 14° and 0° ± 0.03. Figure 2 gives the resulting pressures, corrected to 0°, for the corresponding total compositions of solid phase. Points marked with a vertical arrow are not reliable, as the pressure was still rising very slowly.

Discussion of Results

At all three temperatures the data indicate approximate initial constancy of pressure as water is withdrawn followed by a *gradual* drop in pressure to a new approximately constant value. This constancy was much better in some runs than in others. In all but run 3 the drop in pressure began at a solid composition of about 52.8% and ended at about 54.0% $Al_2(SO_4)_3$. Inasmuch as the calculated compositions of the $17H_2O$ and $16H_2O$ are 52.76% and 54.27% $Al_2(SO_4)_3$, respectively, the existence of both of these compounds is indicated. The higher constant value refers, then, to the system vapor–liquid–$17H_2O$ and the lower to the system vapor–$16H_2O$–xH_2O where "xH_2O" is the next lower hydrate which was not identified in this study because attainment of equilibrium required a prohibitive time for lower water contents. The gradual drop in vapor pressure shows that the $17H_2O$ is capable of losing up to one mole of water present as solid solution. It may be argued that the $16H_2O$ is a true compound, but that the fact that the upper limit of solid solution corresponds to the stoichiometric composition of $17H_2O$ is merely a coincidence; it should be observed, however, that the correspondence was found at all three temperatures. Within the range of conditions studied, then, the $17H_2O$ has the phase behavior of a compound. As essentially the same results were obtained with different sample weights at 25° the possibility of accounting for the additional mole of water in terms of adsorption[4,6] seems to be ruled out. In run 3 the drop in pressure occurred between 51.0% and 53.0% $Al_2(SO_4)_3$ caused by what is believed to be a non-uniform sample. The latter was unusually large and portions of it may well have been protected from dehydration. In spite of this, the pressure values, if not the compositions, are believed to be dependable. It may be noted that this larger sample gave a better lower constant pressure, as would be expected.

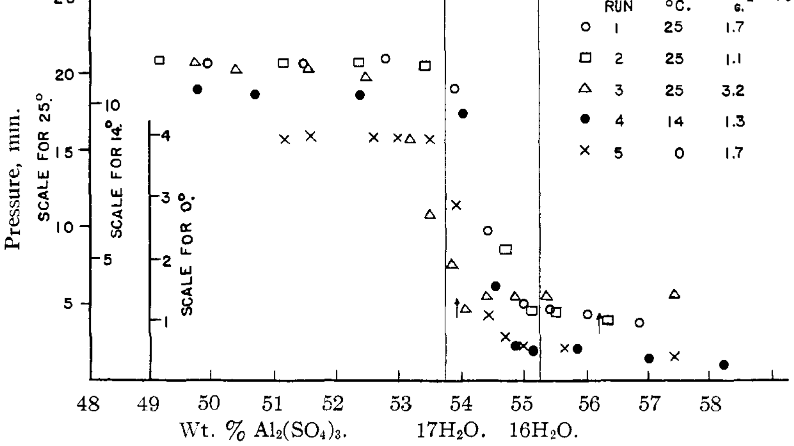

Fig. 2.—Variation of pressure of water vapor with over-all composition of solid.

The highest hydrate in equilibrium with saturated solution is, then, the $17H_2O$, in agreement with previous workers. (This is substantiated further by a fourth run at 25° (not shown) using 1.6 g. of $Al_2(SO_4)_3$ in which the sample was removed and analyzed directly when the pressure of the system just began to fall below that of the higher level. Its composition was 52.6% $Al_2(SO_4)_3$.) Over the range of conditions studied both the 16- and $17H_2O$ appear to be chemical individuals and form a com-

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(12) I. M. Kolthoff and E. B. Sandell, THIS JOURNAL, **50**, 1900 (1928).

(13) Reference 4, p. 2242.

plete series of solid solutions in each other. It is seen, further, that the composition of the hydrated material is especially sensitive to prevailing humidity conditions and this probably accounts for the lack of agreement among the various investigators as to its composition.

Bassett and co-workers,[4,6] on the other hand, assign to the saturating phase at 25° the formula $Al_2(SO_4)_3 \cdot 16H_2O$ while admitting that its composition can vary between that of the $16H_2O$ and the $17H_2O$. The claim for the $16H_2O$ is made by Bassett and Goodwin from a study of the system Al_2O_3–SO_3–H_2O at 25° for the following reasons: (a) In the appropriate isothermally univariant region "all the tie-lines come very close to the point" for that composition, (b) all the solid phases so obtained have the same appearance and X-ray pattern, and (c) the solid obtained at higher acid concentrations showed no change when kept over more dilute acid solutions. Referring to (a) the quotation above is true if one considers only those tie-lines where the acid concentration in the saturated solution is high enough to give results of significance, but the tie-lines in Taylor and Bassett's paper,[6] for what is essentially the same situation (but extended to nearly 50% H_2SO_4), actually run (on the average) closer to the point for $17H_2O$ than for $16H_2O$. Concerning (b) it is entirely possible that the extra zeolitic water would not make a detectable alteration in the appearance or the X-ray pattern. Observation (c) is in harmony with our experience that, except for the lowest hydrates, hydration proceeds with great difficulty in the absence of direct contact with a liquid phase.

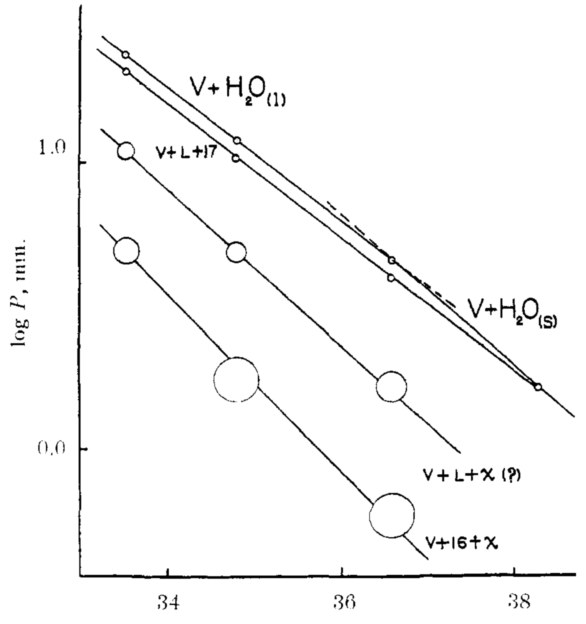

Fig. 3.—Variation of dissociation pressure with temperature.

In order to obtain the isothermally invariant pressures represented by each horizontal in Fig. 2 all the values which seemed to refer to the given horizontal were averaged, yielding the results shown in Table I. The numerals in parentheses refer to the number of readings averaged.

TABLE I

INVARIANT PRESSURES (MM.)

	Upper horizontal	Lower horizontal
25°	20.6 ± 0.1(9)	5.0 ± 0.5(10)
14°	10.4 ± 0.1(3)	1.73 ± 0.34(4)
0°	3.95 ± 0.02(5)	0.58 ± 0.10(4)

In runs 1, 4 and 5 it was possible to obtain a few data from the direction of hydration rather than dehydration by distilling into the system a small quantity of water immediately after the last point for the dehydration had been obtained. The resulting pressures were constant for only an hour or two, but seemed to be significant. They are recorded in Table II.

TABLE II

METASTABLE DISSOCIATION PRESSURES

	P, mm.	Wt. % $Al_2(SO_4)_3$
Run 1 (25°)	10.9 ± 0.7[a]	54.72
Run 4 (14°)	4.85 ± 0.40	55.60
Run 5 (0°)	1.65 ± 0.20	54.79

[a] Three earlier exploratory runs had yielded the values 10.3, 10.9, 10.6 mm.

In view of the method whereby they were obtained they are believed to represent metastable equilibria for the system vapor–liquid–xH_2O. They refer probably to the same equilibria which Taylor and Bassett[6] describe as the system vapor–$14H_2O$–$16H_2O$. The probable error in the above pressure values is unknown, but estimated to be that shown.

Dissociation pressures of the following isothermally invariant systems were thus obtained: vapor–liquid–$17H_2O$, vapor–$16H_2O$–xH_2O and vapor–liquid–xH_2O (?). A plot of log P vs. $1/T$ (Fig. 3) gives straight lines, the slopes of which lead to the following mean values of ΔH (per mole of water vapor formed)

$$\text{Liquid} \rightleftarrows Al_2(SO_4)_3 \cdot 17H_2O(s) + \text{vapor}; \quad \Delta H \doteq 10{,}700 \text{ cal.} \pm 50$$

$$\text{Liquid} \rightleftarrows Al_2(SO_4)_3 \cdot xH_2O(s) + \text{vapor}; \quad \Delta H = 12{,}400 \text{ cal.} \pm 2000$$

$$Al_2(SO_4)_3 \cdot 16H_2O(s) \rightleftarrows Al_2(SO_4)_3 \cdot xH_2O(s) + \text{vapor}; \quad \Delta H = 14{,}300 \text{ cal.} \pm 2000$$

The slope for the first of these three systems is indistinguishable from that for the system $H_2O(l) \rightleftarrows H_2O(v)$, also included in the figure along with the sublimation curve of ice.

Solid–Liquid Equilibria.—The only published measurements of the freezing points of aqueous aluminum sulfate solutions are those of Kremann and Hüttinger[9] and it seemed desirable to repeat them. Mallinckrodt hydrated material (Analytical Reagent) was dissolved, cooled to 0°, stirred with ice in a Dewar flask and the final temperature recorded to ±0.1°. Samples of the liquid were withdrawn for analysis giving the following results which are included in Fig. 4

Wt. % $Al_2(SO_4)_3$	0	6.37	16.20	23.9	27.2
Freezing point (°C.)	0	−0.8	−3.3	−9.6	−12.0 (eutectic)

These freezing points are lower than those found by Kremann and Hüttinger especially for the higher concentrations. (Their value for the eutectic was 23.4% and −4.0°.) The solid phases are ice and $Al_2(SO_4)_3 \cdot 17H_2O$. There is, therefore, a quadruple point (ice + $17H_2O$ + liq. + vap.) at −12° and 1.63 mm.

The smoothed solubility curve for the hydrated salt is also shown in Fig. 4. It is drawn through the recent values of Taylor and Bassett[6] and those of Horan and Skarulis[3] and the authors. The latter obtained their data by rotating sealed glass-stoppered tubes containing excess salt and water in a thermostat and removing samples for aluminum analysis by a pipet. Our figure for 25° agrees well with that of Taylor and Bassett (not shown). Some data of Henry and King[2] are also shown for comparison. We believe our solubility figure for 80.6° (37.4% $Al_2(SO_4)_3$) may be too high because of possible loss by evaporation during sampling, but our purpose was chiefly to decide whether the stable solid phase at this temperature is highly hydrated or not. The solid was separated by decanting off the liquid phase and rapidly blotting to near dryness. Analysis of it showed 48.0% $Al_2(SO_4)_3$ so that it could hardly be the $10H_2O$ (65.5% $Al_2(SO_4)_3$) at 80° as claimed by Gee.[7] Apart from this no other solid phase analyses were conducted for: (a) the solid phase at 25, 14 and 0° had already been established in the dehydration experiments described above, (b) the smoothness of the solubility curve in Fig. 4 from the eutectic to 110° made a change of solid phase unlikely, (c) the $17H_2O$ was found to undergo no melting below about 110°. The solid phase for the entire temperature range is, therefore, the $17H_2O$. The very small temperature coefficient of solubility from −12° to above room temperature is noteworthy.

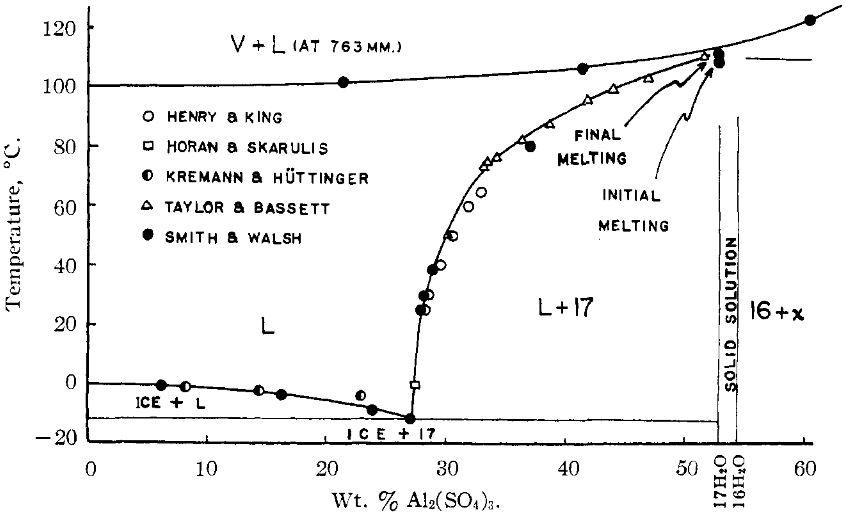

Fig. 4.—Temperature–concentration relations in the system $Al_2(SO_4)_3$–H_2O.

In an attempt to extend the measurements to higher temperatures where high viscosity becomes a problem, the melting point approach was used. Ground samples of recrystallized hydrate, brought to various stages of dehydration by heating at 90°, were analyzed and melted in sealed capillaries. The precise temperatures of initial and, particularly, of final melting were difficult to observe, but the results indicate transitions at ~111° and, possibly, ~128°. The exact phase relations of the liquid 17- and $16H_2O$ above 100° are not yet clear. Taylor and Bassett[6] are similarly in doubt. Nevertheless, the $17H_2O$ prepared carefully in the apparatus of Fig. 1 melted at 109.0–111.5°.[14] It is difficult to say whether this is congruent or incongruent melting. Mixtures richer than about 60% had not melted completely at 200°.

Liquid–Vapor Equilibria.—In order to improve on the previous boiling point values for aqueous aluminum sulfate solutions boiling points were redetermined at 763 mm. ±1 using Analytical Reagent grade material and a Cottrell apparatus. The solutions were analyzed subsequent to boiling. For the more concentrated solutions higher boiling points were obtained than found earlier.[8] A discolored, but clear and very viscous, solution heated under reflux without the Cottrell pump, boiled steadily at 123° in contact with a solid phase (not identifiable). The liquid composition was 60.4% $Al_2(SO_4)_3$. While the possibility of appreciable hydrolysis is not ruled out it seems unlikely at such high concentrations, for no loss of sulfuric acid occurs on heating the hydrate in air to several hundred degrees. The data obtained are given below and included in Fig. 4

Wt. % $Al_2(SO_4)_3$	0	21.1	41.4	60.4
B.p. at 763 mm., °C.	100.1	101.1	106.3	123

Many of the above results are collected in Fig. 4, including the temperature of initial and final melting of $Al_2(SO_4)_3 \cdot 17H_2O$. It is of interest to note that the latter substance (52.8% $Al_2(SO_4)_3$) finishes melting at a temperature just below that of the boiling point of a liquid of that composition. This unique juxtaposition of melting and boiling points combines with the viscous character of the melt to give the hydrate its property of intumescence.

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NEW YORK, NEW YORK

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(14) *Cf.* the value of ~114° for the mineral alunogen, $Al_2(SO_4)_3 \cdot xH_2O$, quoted by J. D. Dana, "The System of Mineralogy," 7th Ed., Vol. 2, John Wiley and Sons, Inc., New York, N. Y., p. 538.