mium sulfate or a double salt of cadmium sulfate. These cells were measured at different temperatures.

The temperature coefficient of the cell containing lithium sulfate was such that if made with cadmium–bismuth amalgam it would have a temperature coefficient less than that of the sodium sulfate cell previously reported.

A number of the lithium sulfate cells with ternary amalgams were not as constant or reproducible as the sodium sulfate cell.

Further observations on the constancy and reproducibility of the sodium sulfate cell are reported.

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The System Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°

BY HAROLD A. HORAN AND JOHN A. SKARULIS

Systematic studies of the ternary system Li_2SO_4–$Al_2(SO_4)_3$–H_2O have been carried out at 30°[1] and at 0°[2] and in both cases it was concluded that the only solid phases in equilibrium were $Li_2SO_4·H_2O$ and $Al_2(SO_4)_3·18H_2O$. In the study at 0°, the solubility of pure lithium sulfate was found to be 25.43%, while for aluminum sulfate the value found was 27.02%. The former value differs considerably from that found by Friend,[3] namely, 26.51%, which was determined using carefully prepared and purified lithium sulfate and employing an analytical method which was direct and not subject to appreciable error. The aluminum sulfate value given above is considerably higher than the values found by Poggiale[4] and by Kremann and Hüttinger[5] and definitely lower than a recently found value[6] of 27.97%. The large differences in the values for both salts undoubtedly are due to differences in the purity of materials used, methods of obtaining equilibrium and the analytical methods employed.

Rather recently the existence and properties of a lithium alum have been reported.[7] The alum is supposedly formed at temperatures in the neighborhood of 0° although no definite temperature is mentioned.

In view of these claims as well as the disagreements in solubilities mentioned above, it was thought advisable to reinvestigate the ternary system at 0°, taking special care as to the materials used, methods of obtaining equilibrium and methods of analysis.

Purification of Materials

Lithium Sulfate.—Reagent grade (Merck) lithium carbonate was recrystallized from hot water according to the method of Kraus and Burgess.[8] After drying, this salt was used to neutralize 6 N sulfuric acid. This solution was heated to boiling and slowly evaporated. The lithium sulfate which crystallized out was separated from the solution, drained and washed with 95% alcohol and then dried at 130°. It was then heated in platinum to expel traces of sulfuric acid.

Aluminum Sulfate.—The problem of obtaining hydrated aluminum sulfate of known composition for use in making up complexes offered some difficulties. Hill and Kaplan[9] attempted to prepare the octadecahydrate by allowing the recrystallized salt to come to constant composition in desiccators over some partially dehydrated aluminum sulfate, which consisted of a mixture with the next lower hydrate, the supposed $16H_2O$. This procedure was not wholly successful in that the salt thus produced usually contained more than the required amount of water (as revealed by aluminum determinations on the material). This also has been the experience of Smith.[10] It is questionable whether occluded water is removed by this method of drying. It is believed that the slow crystallization of aluminum sulfate is favorable to the occlusion of considerable amounts of water.

The material used in this investigation was prepared in the following manner. Reagent grade (Merck) aluminum sulfate was dissolved in water at 60° to make a solution of sp. gr. 1.33. The filtered solution was cooled slowly to room temperature. The crystals were filtered off and sucked as dry as possible. After washing with 95% alcohol, the crystals were again sucked as dry as possible. In order to free the crystals of occluded water, they were effloresced in vacuum desiccators over sulfuric acid. The desiccators were evacuated repeatedly to remove the alcohol. The salt, in a finely divided condition, was placed in small amounts (5–10 g.) on petri dishes in desiccators over a saturated solution of sodium bromide dihydrate. Analysis of the salt for aluminum by the quinolate method[11]

(1) Schreinemakers and de Waal, *Chem. Weekblad*, **3**, 539 (1906).

(2) Sanders and Dobbins, *J. Phys. Chem.*, **35**, 3086 (1931).

(3) Friend, *J. Chem. Soc.*, **128**, 2330 (1929).

(4) Poggiale, *Ann. chim. phys.*, [3] **8**, 463 (1843).

(5) Kremann and Hüttinger, *Jahrb. K. K. geol. Reichsanst.*, **58**, 645 (1908).

(6) Dobbins and Addelston, *J. Phys. Chem.*, **39**, 637 (1935).

(7) Spencer, *Nature*, **138**, 169 (1936).

(8) Kraus and Burgess, THIS JOURNAL, **49**, 1227 (1927).

(9) Hill and Kaplan, *ibid.*, **60**, 551 (1938).

(10) Private communication from Mr. Norman Smith at New York University.

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

TABLE I

ISOTHERM AT $0°$ FOR $Li_2SO_4-Al_2(SO_4)_3-H_2O$

Line no.	Solution		Original complex		Wet residue		Solid phase
	Wt. % $Al_2(SO_4)_3$	Wt. % Li_2SO_4	Wt. % $Al_2(SO_4)_3$	Wt. % Li_2SO_4	Wt. % $Al_2(SO_4)_3$	Wt. % Li_2SO_4	
1	0.0	26.50	...	...	...	...	$Li_2SO_4 \cdot 1H_2O$
2	1.90	25.08	...	...	...	...	$Li_2SO_4 \cdot 1H_2O$
3	7.27	21.21	5.75	34.39	...	...	$Li_2SO_4 \cdot 1H_2O$
4	10.48	18.91	...	...	5.18	52.85	$Li_2SO_4 \cdot 1H_2O$
5	15.17	15.55	13.11	25.03	...	...	$Li_2SO_4 \cdot 1H_2O$
6	16.83	14.45	16.22	16.99	...	...	$Li_2SO_4 \cdot 1H_2O$ + $Al_2(SO_4)_3 \cdot nH_2O^a$
7	16.82	14.46	25.74	11.81	...	...	$Li_2SO_4 \cdot 1H_2O$ + $Al_2(SO_4)_3 \cdot nH_2O^a$
8	17.76	13.07	20.42	12.19	...	...	$Al_2(SO_4)_3 \cdot nH_2O^a$
9	18.17	12.92	...	...	35.04	6.58	$Al_2(SO_4)_3 \cdot nH_2O^a$
10	21.56	7.86	...	...	33.82	4.95	$Al_2(SO_4)_3 \cdot nH_2O^a$
11	23.78	4.64	26.01	4.35	...	...	$Al_2(SO_4)_3 \cdot nH_2O^a$
12	25.74	2.30	...	...	...	...	$Al_2(SO_4)_3 \cdot nH_2O^a$
13	27.50	0.0	...	...	...	...	$Al_2(SO_4)_3 \cdot nH_2O^a$

^{a} n is not definitely decided in this study. It may be between 15 and 18 H_2O.

revealed progressive hydration. After a month's time, during which the salt was stirred thoroughly each day, aluminum determinations revealed little if any further change in composition. At this time the aluminum value was 8.34%, considerably higher than that required at $Al_2(SO_4)_3 \cdot 18H_2O$, i. e., 8.09%. In the belief that the vapor pressure within the desiccators was insufficient fully to hydrate the salt, it was transferred to desiccators over a saturated solution of sodium chloride.[12] Little change was observed in three weeks time. Aluminum determinations at this time were 8.30%. The salt was definitely homogeneous and there was no evidence of further change. This aluminum value corresponds closely to that required by $Al_2(SO_4)_3 \cdot 17H_2O$, namely, 8.32%. The salt was kept in the desiccators until needed for making up complexes. In making these the salt was weighed, by difference, from a glass-stoppered container into the solubility tubes. The percentage anhydrous aluminum sulfate in the complexes was calculated from the aluminum (quinolate) value obtained on a representative sample taken while the former were being made up.

Experimental

In several cases complexes containing accurately known amounts of anhydrous lithium sulfate, hydrated aluminum sulfate and water were prepared. In other cases the compositions of the original complexes were not known accurately. The mixtures, contained in 60-ml. glass-stoppered tubes, were rotated for two weeks in a well insulated bath maintained at $0 \pm 0.05°$. Samples were removed at the end of ten days and again at the end of two weeks and aluminum determinations on both showed that equilibrium had been reached. These samples were removed with a previously cooled pipet fitted with a filter. In the cases where the compositions of the original complexes were not known accurately, samples of the residues were collected on a filter kept near the temperature of the bath, and the excess mother liquid quickly removed. These wet residues were transferred as quickly as possible to weighing bottles.

(12) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 123.

For analysis, aluminum was determined as the quinolate.[11] The combined filtrate and washings from this precipitation were evaporated to approximately 25 ml. At this point a mixture of concentrated hydrochloric acid and nitric acid (10 ml. to 5 ml.) was introduced along with sufficient sulfuric acid to convert the lithium to sulfate. The solution was then evaporated to fumes of sulfur trioxide. The residue was washed into a large platinum crucible. After the introduction of a drop or so of sulfuric acid, the solution was evaporated to incipient dryness in a radiator. The excess of sulfuric acid was expelled and the residue gently ignited. The lithium was then weighed as the sulfate. Several blank determinations on solutions containing no lithium revealed a constant blank of 1.5 mg. In the analyses this amount was deducted from the weight of the residues. The amounts of lithium sulfate weighed in most cases were greater than 0.15 g. The entire procedure was tested successfully many times on solutions containing known amounts of lithium sulfate and aluminum sulfate, the ratio of the two being varied considerably.

The data are given in Table I and the results are represented graphically in Fig. 1.

Discussion of Results

The solubility of pure aluminum sulfate at $0°$ has been found to be 27.50%.[13] This is considerably different from previously accepted values.[2,4,5,6] It is close to the values obtained for the same salt 25° by Hill and Kaplan[9] and Smith,[10] viz., 27.39 and 27.89%, respectively. In the light of this it is questioned whether the solid phase in equilibrium at 25° is the same as that at 0°.

The solubility found for pure lithium sulfate at 0° agrees well with that of Friend[3] and is definitely higher than that of Sanders and Dobbins.[2]

(13) The solubility of unrecrystallized Merck reagent grade aluminum sulfate, which according to the label had as main impurities alkali sulfates 0.15%, free acid 0.12%, was determined in the same manner and found to be 27.70%.

No lithium alum has been found at 0°. Its formation at lower temperatures is still a possibility. In this study only two solid phases were found to exist. One is definitely lithium sulfate monohydrate. On the aluminum sulfate side, in addition to being too few in number, the extrapolations are too scattered due to slight variations in the composition of the aluminum sulfate used in making up the complexes as well as accidental errors in the analyses to be significant in the designation of the formula of the hydrate in equilibrium with the saturated solutions. Similar scattering in the extrapolations was found by Hill and Kaplan[9] when working with aluminum sulfate.

In previous ternary investigations involving aluminum sulfate as one of the phases, the octadecahydrate has been assumed to be the solid phases over a considerable range of temperatures although in the few cases where the tie lines were extrapolated, large deviations from the theoretical values were evident.

Additional work is being carried out in this Laboratory in an attempt to decide the hydration of aluminum sulfate at 0° as well as at other temperatures. The results of this work will be reported later.

The isothermally invariant point for this system has been found to be 16.83% aluminum sulfate and 14.45% lithium sulfate. This is considerably different than the previously reported value[2] at this temperature.
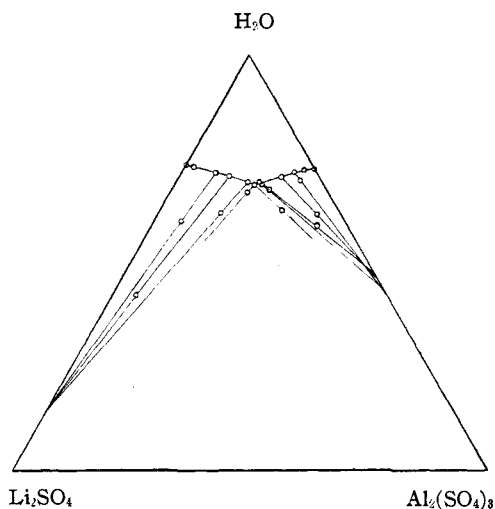

Fig. 1.—0° Isotherm: Li_2SO_4–$Al_2(SO_4)_3$–H_2O.

Summary

Solubility measurements are given for the system Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°. There is no evidence of double salt formation or solid solution.

A new value for the solubility of aluminum sulfate at 0° is given.

The degree of hydration of aluminum sulfate in contact with a saturated solution at 0° has not been determined with certainty. The previous assumptions of the existence of the octadecahydrate at this temperature have been questioned.

Binary Liquid Systems. I. Vapor–Liquid Equilibria in the System Carbon Tetrachloride–Ethyl Acetate

BY PHILIP W. SCHUTZ

In a survey of the behavior and properties of homogeneous binary liquid systems it became of interest to investigate the system carbon tetrachloride–ethyl acetate. A careful search of the literature showed that the only vapor–liquid equilibria data available, covering the complete range of composition for this system, were those due to Tyrer.[1] These data have been quoted in the "International Critical Tables" and other similar compilations. Unfortunately, a careful scrutiny of these data shows that they are most probably in error. When the vapor and liquid

compositions given are plotted against the boiling temperature (at 745 mm. in this case) as the concentration of carbon tetrachloride increases from zero mole per cent., both curves show the normal behavior for a system which exhibits a minimum boiling mixture. The behavior continues normal until the composition of the azeotropic mixture is reached (about 51 mole per cent.) at which point the vapor and liquid curves *cross* instead of becoming *tangent*. The vapor curve then continues to lie below the liquid curve through the rest of the concentration range. This behavior leads to the theoretically impossible situation of a system ex-

(1) Tyrer, *J. Chem. Soc.*, **101**, 81 (1912).