

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

## Specific Heats at Low Temperatures of $\text{Al}_2(\text{SO}_4)_3$ , $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , $\text{KAl}(\text{SO}_4)_2$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ <sup>1</sup>

BY C. HOWARD SHOMATE<sup>2</sup>

A determination of the thermodynamic properties of compounds encountered in certain methods of extracting alumina from clays and alunite has been undertaken at the Pacific Experiment Station of the Bureau of Mines. Low-temperature specific heat and entropy data are lacking in most instances; accordingly, this paper presents such data for anhydrous aluminum sulfate, aluminum sulfate hexahydrate, anhydrous potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate. Previous papers have presented data for the heats of formation<sup>3</sup> and high-temperature heat contents<sup>4</sup> of these and related substances.

### Materials

Recrystallized reagent grade aluminum sulfate octodecahydrate was used to prepare anhydrous aluminum sulfate. The water of crystallization was removed by heating gradually to 450°. The latter part of the heating was done in a stream of dry air at about 1 cm. pressure. Analysis gave 29.89%  $\text{Al}_2\text{O}_3$  (theoretical 29.80%) and 0.32%  $\text{H}_2\text{O}$ . The specific heat measurements were made on a 124.22-g. sample.

Aluminum sulfate hexahydrate was prepared from the octodecahydrate by heating the latter in air at 140° for eighteen hours. Analysis showed that too much water had been expelled, so the requisite amount of water was added, and the sample was pulverized and heated *in vacuo* at 80° for two days. Analysis gave 22.57%  $\text{Al}_2\text{O}_3$  (theoretical 22.64%). A 132.63-g. sample was used in the measurements.

Reagent grade potassium aluminum sulfate octodecahydrate was used to prepare the anhydrous salt. Dehydration was accomplished by heating, at gradually increasing temperatures up to 240°, for eight days. During the last thirty hours of heating at the highest temperature the sample was under vacuum. Analysis showed 19.65%  $\text{Al}_2\text{O}_3$  (theoretical 19.74%), and 0.4%  $\text{H}_2\text{O}$ . The measurements were made on a 146.04-g. sample.

The potassium aluminum sulfate dodecahydrate used in the measurements was reagent grade material purported to contain less than 0.02% impurities. Analysis gave 10.74%  $\text{Al}_2\text{O}_3$  (theoretical 10.74%). The sample used in the measurements weighed 116.16 g.

### Specific Heats

The method and apparatus used in the low temperature specific heat measurements have been described previously.<sup>5,6</sup> The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),<sup>7</sup> are listed in Table I and shown graphically in Fig. 1. The values of the specific heats at 298.16°K., obtained by extrapolation of a smooth curve through the experimental points, are also included in Table I. The molecu-

lar weights are in accordance with the 1941 International Atomic Weights. Corrections were made in the results of anhydrous aluminum sulfate for 0.32%  $\text{H}_2\text{O}$  and 0.26%  $\text{Al}_2\text{O}_3$  impurities. The anhydrous potassium aluminum sulfate data were corrected for 0.4%  $\text{H}_2\text{O}$  impurity. All weights were corrected to vacuum, using the following densities: anhydrous aluminum sulfate, 2.67; aluminum sulfate hexahydrate, 2.14; anhydrous potassium aluminum sulfate, 2.55; and potassium sulfate dodecahydrate, 1.75. Density determinations were made in this Laboratory by Albert E. Salo.<sup>8</sup>

TABLE I

SPECIFIC HEATS					
$T$ , °K.	$C_p$ , cal./mole	$T$ , °K.	$C_p$ , cal./mole	$T$ , °K.	$C_p$ , cal./mole
$\text{Al}_2(\text{SO}_4)_3$ (mol. wt. = 342.12)		$\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ (mol. wt. = 450.22)		$\text{KAl}(\text{SO}_4)_2$ (mol. wt. = 258.19)	
54.7	8.668	54.5	19.47	54.6	9.361
58.4	9.712	58.4	21.41	58.4	10.35
62.4	10.86	62.6	23.49	62.8	11.42
66.9	12.20	66.9	25.65	67.3	12.52
71.7	13.63	71.2	27.81	71.9	13.61
75.9	14.90	75.7	30.03	76.4	14.62
80.2	16.15	80.4	32.30	80.6	15.54
84.5	17.43	84.3	34.09	85.1	16.45
94.4	20.30	94.7	39.09	95.0	18.49
104.4	23.10	104.3	43.55	104.6	20.38
114.9	25.94	114.9	48.44	115.0	22.36
123.9	28.29	124.2	52.64	124.2	24.08
134.8	31.13	135.1	57.53	134.9	25.91
145.5	33.72	145.6	62.08	145.7	27.65
155.2	35.99	155.6	66.35	155.6	29.22
165.6	38.41	165.4	70.44	165.7	30.75
175.6	40.68	175.6	74.64	175.6	32.23
185.4	42.70	185.6	78.58	186.5	33.71
196.0	44.83	195.9	82.63	196.3	34.99
205.8	46.78	206.0	86.46	206.2	36.37
216.7	48.86	216.6	90.31	216.5	37.55
226.0	50.42	226.3	93.74	226.0	38.59
235.5	52.05	235.7	97.01	237.9	39.93
246.2	53.87	245.9	100.6	246.9	40.95
256.0	55.60	256.2	104.3	256.3	42.05
265.9	57.14	265.9	107.6	266.3	43.09
276.4	58.56	276.0	110.8	276.1	44.08
286.0	60.24	286.1	114.0	286.3	45.01
296.2	61.73	296.1	117.5	296.5	45.99
(298.16)	(62.00)	(298.16)	(117.8)	(298.16)	(46.12)
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (mol. wt. = 474.38)					
52.7	33.21	79.4	51.38	196.0	110.7
52.9	33.35	83.9	53.96	205.8	115.2
55.3	35.53 <sup>a</sup>	94.6	60.00	216.4	120.4
56.7	37.57 <sup>a</sup>	104.6	65.46	226.0	124.5
57.5	38.21 <sup>a</sup>	115.0	70.90	235.6	128.6
59.1	40.19 <sup>a</sup>	124.2	75.70	246.1	133.3
60.6	41.25 <sup>a</sup>	135.0	81.24	256.0	138.1
60.9	48.86 <sup>a</sup>	145.6	86.44	265.9	142.3
62.3	40.53	155.5	91.21	276.1	146.6
65.4	42.43	165.4	95.98	286.0	150.3
70.0	45.46	175.6	101.1	296.1	154.7
75.0	48.66	185.5	105.7	(298.16)	(155.6)

<sup>a</sup> Specific heat values affected by the transition.

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Chemist, Pacific Experiment Station.

(3) Young, THIS JOURNAL, 67, 257 (1945).

(4) Shomate and Naylor, *ibid.*, 67, 72 (1945).(5) Kelley, *ibid.*, 63, 1137 (1941).(6) Shomate and Kelley, *ibid.*, 66, 1490 (1944).(7) Mueller and Rossini, *Am. J. Physics*, 12, 1 (1944).

(8) Metallurgist, Pacific Experiment Station.

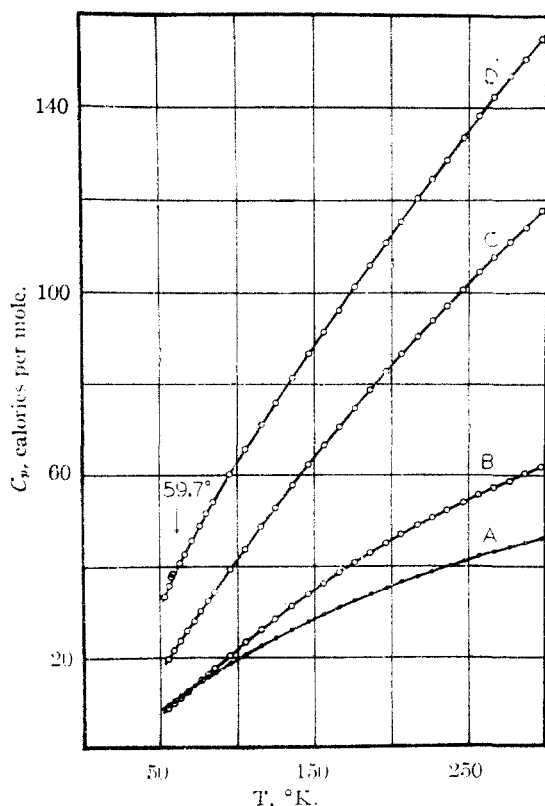


Fig. 1.—Specific heats: A,  $\text{KAl}(\text{SO}_4)_2$ ; B,  $\text{Al}_2(\text{SO}_4)_3$ ; C,  $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ; D,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

With the exception of a sharp transition occurring in potassium aluminum sulfate dodecahydrate at  $59.7^\circ\text{K}$ ., the substances exhibited normal behavior in the temperature range studied.

### Entropies

The evaluation of the entropy at  $298.16^\circ\text{K}$ . is obtained by graphical integration of a plot of  $C_p$  against  $\log T$ . This necessitates the extrapolation of the specific heat curve from the temperature of the lowest measurement down to the absolute zero of temperature. It was found that the following function sums adequately represent the specific heat data (within 1%) throughout the measured temperature range

$$\begin{aligned} \text{Al}_2(\text{SO}_4)_3: & D\left(\frac{155.7}{T}\right) + 3E\left(\frac{238}{T}\right) + 6E\left(\frac{528}{T}\right) + 6E\left(\frac{1194}{T}\right) \\ \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}: & D\left(\frac{78.9}{T}\right) + 3E\left(\frac{142.5}{T}\right) + 8E\left(\frac{340}{T}\right) + 16E\left(\frac{872}{T}\right) \\ \text{KAl}(\text{SO}_4)_2: & D\left(\frac{124.3}{T}\right) + 2E\left(\frac{200.6}{T}\right) + 3E\left(\frac{409}{T}\right) + 4E\left(\frac{878}{T}\right) + 4E\left(\frac{2060}{T}\right) \end{aligned}$$

The symbols  $D$  and  $E$  denote, respectively, Debye and Einstein functions. The above functions

were used for extrapolating the specific heat curves to  $0^\circ\text{K}$ .

The transition at  $59.7^\circ\text{K}$ . in potassium aluminum sulfate dodecahydrate makes extrapolation of the specific heat curve difficult by any method. It is noted in Fig. 1 that the specific heat determinations immediately below the transition temperature are abnormally high because of pre-transition effect. Several reasonable extrapolation methods were employed yielding values for the extrapolated portion of the entropy agreeing within 10%. The extrapolated value adopted here is obtained by the method of Kelley, Parks, and Huffman,<sup>9</sup> using for the "standard substance" in their method the sum of the specific heats of ice<sup>10</sup> and anhydrous potassium aluminum sulfate, and assuming that the constant "B" in their method is zero. Effectively, this extrapolation may be summed as follows:  $C_{p\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}} = 1.0045 (C_{p\text{KAl}(\text{SO}_4)_2} + 12C_{p\text{H}_2\text{O}})$  for the range 0 to  $53^\circ\text{K}$ .

The total heat absorption in the region of the transition was determined by a separate run to be 276.97 cal./mole between  $57.00$  and  $63.00^\circ\text{K}$ . This checks the value of 276.78 cal./mole obtained by summing the energies of four successive specific heat determinations over this same temperature range in the manner described by Shomate.<sup>11</sup> Subtracting the energy associated with the "normal" curves below and above the transition temperature leaves 46.9 cal./mole for the heat of transition, or 0.785 E. U./mole for the entropy of transition.

Table II summarizes the entropy calculations of the four substances.

TABLE II  
ENTROPIES AT  $298.16^\circ\text{K}$ . (E. U./mole)

	$\text{Al}_2(\text{SO}_4)_3$	$\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	$\text{KAl}(\text{SO}_4)_2$
0–53.09°K.	3.76	11.23	4.97
53.09–298.16°K.	53.43	100.88	43.91
$S_{298.16}^0$	$57.2 \pm 0.3$	$112.1 \pm 0.7$	$48.9 \pm 0.3$
		$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	
0–53.09°K.		20.94	
53.09–59.7°K.		4.22	
59.7° (Transition)		0.78	
59.7–298.16°K.		138.33	
$S_{298.16}^0$		$164.3 \pm 2.0$	

### Free Energies

The heats, entropies and free energies of formation from the elements are listed in Table III, together with the thermal data for other pertinent reactions. The heats of reaction are those recently determined by Young.<sup>8</sup> The entropies of reaction combine the values in Table II with the entropies of the elements,<sup>12</sup> liquid water,<sup>10</sup> and potassium sulfate.<sup>13</sup> Free energies of reaction

(9) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(10) Gianque and Stout, *THIS JOURNAL*, **58**, 1144 (1936).

(11) Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

(12) Kelley, Bureau of Mines Bulletin 434, 1941.

(13) Moore and Kelley, *THIS JOURNAL*, **64**, 2949 (1942).

TABLE III  
THERMAL DATA AT 298.16°K.

	$\Delta H_{298.16}^0$ , cal./mole	$\Delta S_{298.16}^0$ , E. U./mole	$\Delta F_{298.16}^0$ , cal./mole
(1) $2Al + 3S(rh.) + 6O_2 \longrightarrow Al_2(SO_4)_3$	$-820,990 \pm 430$	$-273.3 \pm 0.4$	$-739,500 \pm 450$
(2) $2Al + 3S(rh.) + 6H_2 + 9O_2 \longrightarrow Al_2(SO_4)_3 \cdot 6H_2O$	$-1,268,150 \pm 360$	$-552.9 \pm 0.8$	$-1,103,300 \pm 430$
(3) $K + Al + 2S(rh.) + 4O_2 \longrightarrow KAl(SO_4)_2$	$-589,170 \pm 310$	$-184.4 \pm 0.4$	$-534,190 \pm 330$
(4) $K + Al + 2S(rh.) + 12H_2 + 10O_2 \longrightarrow KAl(SO_4)_2 \cdot 12H_2O$	$-1,447,700 \pm 260$	$-738.0 \pm 2.0$	$-1,227,660 \pm 650$
(5) $Al_2(SO_4)_3 + 6H_2O(liq.) \longrightarrow Al_2(SO_4)_3 \cdot 6H_2O$	$-37,250 \pm 220$	$-45.6 \pm 0.8$	$-23,650 \pm 320$
(6) $KAl(SO_4)_2 + 12H_2O(liq.) \longrightarrow KAl(SO_4)_2 \cdot 12H_2O$	$-38,720 \pm 210$	$-85.6 \pm 2.1$	$-13,200 \pm 660$
(7) $\frac{1}{2}K_2SO_4 + \frac{1}{2}Al_2(SO_4)_3 \longrightarrow KAl(SO_4)_2$	$-7,340 \pm 230$	$-0.7 \pm 0.4$	$-7,130 \pm 260$
(8) $\frac{1}{2}K_2SO_4 + \frac{1}{2}Al_2(SO_4)_3 + 12H_2O(liq.) \longrightarrow$ $KAl(SO_4)_2 \cdot 12H_2O$	$-46,060 \pm 130$	$-86.3 \pm 2.1$	$-20,330 \pm 640$

are computed from the relationship  $\Delta F_{298.16}^0 = \Delta H_{298.16}^0 - 298.16 \Delta S_{298.16}^0$ .

### Summary

Specific heats of anhydrous aluminum sulfate, aluminum sulfate hexahydrate, anhydrous potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate, were measured in the temperature range 52 to 298°K. Potassium aluminum sulfate dodecahydrate has a transition at 59.7°K., with a heat of transition of 46.9 cal./mole.

The following molal entropies at 298.16°K. were computed: anhydrous aluminum sulfate, 57.2  $\pm$  0.3; aluminum sulfate hexahydrate,

112.1  $\pm$  0.7; anhydrous potassium aluminum sulfate, 48.9  $\pm$  0.3; and potassium aluminum sulfate dodecahydrate, 164.3  $\pm$  2.0.

Combination of the above entropies with related thermal data yields the free energies of formation from the elements at 298.16°K.: anhydrous aluminum sulfate, -739,500  $\pm$  450; aluminum sulfate hexahydrate, -1,103,300  $\pm$  430; anhydrous potassium aluminum sulfate, -534,190  $\pm$  330; and potassium aluminum sulfate dodecahydrate, -1,227,660  $\pm$  650 cal./mole. Other pertinent thermal data have been calculated.

BERKELEY, CALIFORNIA RECEIVED JANUARY 27, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

## A Polarographic Study of Barium Ion Removal by Complex Phosphates<sup>1</sup>

By J. A. CAMPBELL<sup>2</sup> AND CHARLES SCHENKER<sup>3</sup>

The question of what compounds may be formed by the dehydration of orthophosphoric acid has been actively discussed since metaphosphoric acid was first prepared by Graham in 1833.<sup>4</sup> The existence of many alkali salts of complex phosphates has been claimed, but, in most cases, the supporting evidence is inconclusive, and a survey of the extensive literature seems to lead only to the conclusion that considerable confusion exists throughout the entire field. A review of the more important work has been given by Partridge, Hicks and Smith.<sup>5</sup>

Modern interest in these phosphates was increased by the happy discovery by Hall<sup>6</sup> that one of them, the so-called sodium hexametaphosphate, has the property of binding up alkaline earth ions in such a way as to render them inert to their usual precipitating agents.

Complex salts of pentavalent phosphorus may be divided into two classes: the polymers of

metaphosphates and the polyphosphates, which latter may be looked upon as salts formed from orthophosphoric acid by a degree of dehydration intermediate between that which yields metaphosphoric acid and that which results in pyrophosphoric acid. These substances can also be viewed as a series of compounds formed by molecular addition of pyrophosphates to metaphosphates.

It was the purpose of this work to study the effect of various phosphates on dilute solutions of barium ion. The substances investigated were stoichiometrically equivalent to sodium hexametaphosphate, tetrasodium pyrophosphate, sodium triphosphate, and sodium tetrphosphate, each prepared as hereinafter indicated.

Sodium hexametaphosphate ( $NaPO_3$ )<sub>6</sub> is the glass obtained by quenching a melt of primary sodium orthophosphate which has been heated above 650° for several hours.

The theory advanced for the binding up of the metallic ion is that the hexametaphosphate ionizes according to the equation



The anion can then react with the metallic ion



The barium is thus sequestered in a complex

(1) From a thesis submitted by Charles Schenker in partial fulfillment of the requirements for the degree of Master of Science. Original manuscript received April 20, 1943.

(2) Present address: University of Idaho, Moscow, Idaho.

(3) Present address: Ashland Oil and Refining Company, Ashland, Kentucky.

(4) Graham, *Phil. Trans. Royal Soc.*, **123**, 253 (1833).

(5) Partridge, Hicks and Smith, *This Journal*, **63**, 454 (1941).

(6) Hall, U. S. Patent 1,956,515 (1934), reissue 19,719 (1935).