

the magnetic effect in $\text{H}_3\text{KFe}_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$ probably is "swamped" by the nonmagnetic centers in the structure.

The entropy of $\text{H}_3\text{KFe}_3(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}(c)$ is 222.17 e.u. at 298.15° K. with an estimated uncertainty of 0.50 e.u. The calculated entropy at 298.15° K., using the "normal" heat capacity values below 36° K., is 220.96 e.u. The excess entropy contributed by the anomalous hump was calculated in two increments—0.18 e.u. (7° to 12.5° K.) and 1.03 e.u. (12.5° to 36° K.). The enthalpy, $H^\circ - H_0^\circ$, at 298.15° K. is 34,074 cal. per mole, of which 34,046 cal. per mole represents the enthalpy using the "normal" heat capacity values below 36° K., and 1.61 (7° to 12.5° K.) and 26.08 (12.5° to 36° K.) cal. per mole represent the excess enthalpy

under the hump. Curvature corrections to observed heat capacities were made as required (1).

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RECEIVED for review July 20, 1962. Accepted December 17, 1962.

Low Temperature Heat Capacity and Entropy of Basic Potassium Aluminum Phosphate

EDWARD P. EGAN, JR., ZACHARY T. WAKEFIELD, and BASIL B. LUFF
Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Ala.

The heat capacity of $\text{KAl}_2(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$ was measured over the range 10° to 300° K. At 298.16° K. the entropy is 70.43 e.u. and the enthalpy is 11,800 cal. per mole.

A BASIC potassium aluminum phosphate (3, 5) of the minyulite type, $\text{KAl}_2(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$, is of interest in soil-fertilizer relationships. As part of a continuing program of the determination of thermodynamic properties of compounds of interest in fertilizer technology, the low temperature heat capacities of basic potassium aluminum phosphate were measured over the temperature range 10° to 300° K., and the entropy and enthalpy at 298.16° K. were derived therefrom.

MATERIALS AND APPARATUS

The basic potassium aluminum phosphate was prepared by dissolving 18 grams of aluminum metal (supplied by Consolidated Aluminum Corp., Jackson, Tenn., who reported it iron-free and 99.994% pure) in a mixture of 300 grams of 85% phosphoric acid and 350 ml. of distilled water. The solution was filtered, diluted to 2 liters, and adjusted to pH 6.12 with 20% KOH solution. The pre-

cipitate was redispersed in 3 liters of hot water, and, after standing overnight at 75° C., the precipitate was again redispersed in 3 liters of water and digested at 95° C. until crystalline. The product was washed with hot water and dried over CaCl_2 in a vacuum at room temperature.

The crystals were 30 to 50 microns long; a few were not optically clear but showed "veiling." Chemical analysis gave 11.5% K, 16.06% Al, 18.32% P, and less than 0.005% Fe (stoichiometric values are: 11.64% K, 16.05% Al, 18.44% P).

The calorimeter (1, 2) contained 96.139 grams (vacuum) or 0.28609 mole of $\text{KAl}_2(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}(c)$. Temperatures were read to four decimal places and were so used in the calculation of small differences, but were rounded to two places in the tables. The calculations were made on an IBM 704 computer (2). One defined calorie was taken as 4.1840 absolute joules—the ice point as 273.16° K. This work was completed before adoption in this laboratory of the change of the ice point to 273.15° K. (4).

Table I. Observed Molal Heat Capacity of $KAl_2(PO_4)_2 \cdot OH \cdot 2H_2O(c)$, Cal. Deg.⁻¹

Point ^a	T, °K.	C _p	Point ^a	T, °K.	C _p
73	10.22	0.064	26	143.35	40.34
74	12.06	0.158	51	147.35	41.52
85	14.09	0.319	27	151.60	42.71
75	14.35	0.289	52	155.51	43.86
86	16.65	0.532	28	159.97	45.11
76	17.98	0.710	53	164.01	46.23
87	19.94	0.965	29	168.02	47.31
77	21.90	1.289	54	171.60	48.30
88	23.86	1.635	30	174.79	49.13
92	26.41	2.280	55	178.04	50.00
78	26.48	2.147	31	181.56	50.90
89	28.60	2.831	56	184.96	51.82
93	32.14	3.813	32	188.37	52.66
90	34.91	4.647	57	191.92	53.58
94	37.62	5.436	33	194.82	54.28
91	41.04	6.556	7	197.98	55.05
95	43.04	7.189	58	200.90	55.87
96	47.24	8.604	8	204.56	56.71
97	48.75	9.068	9	212.44	58.58
98	51.96	10.25	60	216.22	59.51
34	54.52	11.36	10	220.60	60.49
39	57.22	12.36	61	224.56	61.43
35	59.92	13.30	11	228.99	62.41
40	62.89	14.37	62	233.31	63.40
36	65.65	15.36	12	237.20	64.22
41	68.57	16.35	63	242.01	65.37
37	71.66	17.39	13	244.84	65.90
42	74.76	18.45	64	248.27	66.73
38	77.92	19.58	14	251.96	67.40
18	81.17	20.65	65	255.55	68.22
43	83.79	21.59	15	258.97	68.86
19	88.62	23.20	66	263.10	69.74
44	91.77	24.24	67	270.16	71.17
173	96.24	25.64	17	273.40	71.79
45	99.74	26.82	1	275.94	72.19
174	103.91	28.09	68	278.80	72.83
46	107.76	29.38	2	281.87	73.41
175	111.65	30.55	69	285.45	74.13
47	115.56	31.86	3	288.61	74.71
176	119.48	33.07	70	292.18	75.43
48	123.18	34.25	4	295.61	76.08
24	127.21	35.42	71	299.01	76.71
49	131.19	36.69	5	302.52	77.23
25	135.22	37.90	72	306.09	77.95
50	139.34	39.19	6	309.36	78.60

^a Numbered in chronological order.

RESULTS

The observed molal heat capacities are shown in Table I. Smoothed heat capacities and the corresponding entropies and enthalpies are shown in Table II. The average deviation of the observed from the smoothed heat capacities was 0.1%

Table II. Molal Thermodynamic Properties of $KAl_2(PO_4)_2 \cdot OH \cdot 2H_2O(c)$, Cal. Deg.⁻¹

T, °K.	C _p	S°	H° - H ₂₉₈
10	0.082	0.022	0.173
15	0.376	0.102	1.198
20	0.970	0.283	4.423
25	1.921	0.595	11.51
30	3.170	1.052	24.12
35	4.642	1.649	43.59
40	6.206	2.370	70.69
45	7.833	3.194	105.8
50	9.582	4.109	149.2
60	13.36	6.189	263.9
70	16.83	8.512	415.1
80	20.28	10.98	600.6
90	23.64	13.57	820.3
100	26.87	16.23	1,073
110	30.06	18.94	1,358
120	33.22	21.69	1,674
130	36.37	24.47	2,022
140	39.28	27.28	2,400
150	42.29	30.09	2,809
160	45.10	32.91	3,246
170	47.86	35.73	3,710
180	50.54	38.54	4,202
190	53.08	41.34	4,720
200	55.59	44.13	5,264
210	58.02	46.90	5,832
220	60.36	49.65	6,424
230	62.64	52.38	7,039
240	64.88	55.10	7,677
250	67.03	57.79	8,336
260	69.10	60.46	9,017
270	71.11	63.11	9,718
280	73.05	65.73	10,440
290	76.87	70.90	11,938
273.16	71.72	63.94	9,944
298.16	76.53	70.43	11,800

except at temperatures below 30° K. where the small magnitude impaired the accuracy.

The entropy of crystalline basic potassium aluminum phosphate at 298.16° K. is 70.43 ± 0.10 e.u. On the assumption that the solid represents the ideal state, the enthalpy, $H^\circ - H_{298}$, at 298.16° K. is 11,800 cal. per mole. Curvature corrections were made as required (2).

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