Low Temperature Heat Capacity and Entropy of Variscite, AlPO$_4$·2H$_2$O, 10° to 310°K.

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The low temperature heat capacity of synthetic crystalline variscite, AlPO$_4$·2H$_2$O, was measured over the temperature range 10° to 310° K. The calculated entropy at 298.15° K. is 32.14 gibbs per mole and the enthalpy is 5708 cal. per mole.

VARISCITE is the aluminum end-member of the mineral series variscite-barrandite-strengite; its structure has been established as that of the hydrate AlPO$_4$·2H$_2$O (*1*) rather than that of the hydroxy acid phosphate AlH$_2$PO$_4$(OH)$_2$. Variscite is of interest in fertilizer technology because of the role of aluminum in the reactions of soil minerals with fertilizer phosphates. As part of a continuing program of determination of thermodynamic properties of compounds involved in fertilizer technology, the low temperature heat capacity of variscite was measured over the range 10° to 310° K. and its entropy and enthalpy at 298.15° K. were calculated from the results.

MATERIALS AND APPARATUS

The heat capacity measurements were made on two samples of variscite that were prepared by hydrothermal treatment of amorphous aluminum phosphate. The first sample (A) was prepared by the method of Deming and Cate (*2*). The second sample was prepared in two batches (B and C) by a simpler method in which about 200 grams of amorphous aluminum phosphate was precipitated by addition of an ammonium acetate solution to an acidic aluminum phosphate solution. The precipitate was suspended in 3 liters of near-boiling water for one hour, after which the mixture was filtered on a fritted-glass disk and the solid was sucked dry. The washing was repeated twice, and the 175 grams of wet solids was mixed with 50 grams of 10% H$_3$PO$_4$ solution and sealed in a glass tube which then was enclosed in a heavy metal jacket and heated at 110° C. for 3 weeks. The mixture was filtered and the solid product was washed with acetone and air dried. The product, which weighed 40 grams, was composed of uniform (15-micron) single crystals of variscite that had a few spots of low-index material on the edges of the crystals and a small amount of ammonium minyulite, (NH$_4$)$_2$Al$_4$(PO$_4$)$_4$(OH)$_2$·5H$_2$O, as a discrete second phase. The contaminating phases were removed by digestion of the product in 5% H$_3$PO$_4$ at 90° C. for one hour. The compositions of the variscite preparations are shown in Table I.

Sample A was used as calorimeter sample I. Samples B and C were combined to make calorimeter sample II. The weight of sample II charged to the calorimeter was 54.8677 grams (in vacuo) or 0.34730 mole (G.F.W. =

157.9836). The charged calorimeter was evacuated and filled with helium to an absolute pressure of 80 mm. of Hg. On the assumption that the sample contained 50% voids, the same mass of helium would have a pressure of 80 mm. of Hg in the charged calorimeter and 50 mm. of Hg in the empty calorimeter; calibration of the empty calorimeter with this amount of helium eliminated a correction for the heat capacity of the helium. As explained later, the results obtained with sample A are not reported.

The low temperature calorimeter has been described (*3, 4*). Temperatures were measured to 0.0001° K. for calculation of temperature differences but are rounded to two decimal places in the table. The defined calorie = 4.1840 abs. joules, the ice point = 273.15° K. The density of variscite, for buoyancy correction, was calculated from x-ray data to be 2.57 grams per cc.

The heat capacities were corrected for curvature (*4*) where significant.

OBSERVATIONS

The measured heat capacities of sample I followed a normal curve with no anomalous effects, but those of sample II showed a very small anomaly near the ice point; the energy contribution of this anomaly, however, was insignificant. The heat capacities of sample II showed some thermal hysteresis above the ice point—the low-energy curve could be reproduced by equilibration of the sample at the ice point, and the high energy curve by equilibration at 195° K. (solid CO$_2$), but the separation was only 0.075 gibbs per mole.

The calculated entropy for sample I was 0.75 gibbs per mole higher than that for sample II. In an attempt to explain this discrepancy, which is significantly larger than the experimental error, both samples were examined petrographically and by slow-scan x-ray diffraction, infrared spectroscopy, and differential thermal analysis. Petrographic examination showed sample II to be composed of some aggregates but mostly single crystals with average diameters between 10 and 25 microns; most of the particles in sample I ranged from less than 1 to 4 microns in diameter, and the mass of the sample was large aggregates of these particles. Electron micrographs (22,500x) showed that sample I contained a significant amount of particles smaller than 1 micron in diameter. Variscite dehydrates under vacuum at room temperature, so that its surface area cannot be measured by gas adsorption, but measurements by acetic acid absorption (*5*) gave 5.5 m.^{2} per gram for sample I and 0.02 m.^{2} per gram for sample II.

The x-ray diffraction pattern of sample II agreed with that of ASTM 8-157 for variscite; extraneous peaks at *d* spacings of 9.20 and 7.17 A. that appeared in the pattern of sample I did not appear in the pattern of sample II. The infrared spectrum of sample I contained an absorption band at 3300 cm.$^{-1}$ that did not appear in the spectrum of sample II. Differential thermal analysis showed that sample I lost water at a lower temperature and less sharply than sample II.

Table I. Preparation of Variscite

Sample	Composition, %			Moles/Mole P$_2$O$_5$	
	Al$_2$O$_3$	P$_2$O$_5$	H$_2$O diff.	Al$_2$O$_3$	H$_2$O diff.
A	31.99	44.43	23.58	1.002	4.18
B	31.74	45.09	23.17	0.980	4.05
C	31.65	45.06	23.29	0.978	4.07
Stoichiometric	32.27	44.92	22.81	1.000	4.00

Table II. Observed Molal Heat Capacity of Variscite

Point[a]	T, °K.	C_p, cal./°K.	Point[a]	T, °K.	C_p, cal./°K.	Point[a]	T, °K.	C_p, cal./°K.
105	8.66	0.0292	54	74.76	6.825	70	204.33	28.32
94	9.05	0.0385	49	77.58	7.360	6	204.54	28.30
106	10.57	0.0434	8	80.93	7.935	22	207.37	28.71
95	10.80	0.0392	55	84.05	8.500	71	210.92	29.22
107	12.46	0.0524	9	87.34	9.095	7	211.19	29.21
56	12.76	0.0566	56	90.52	9.656	23	214.52	29.68
108	14.95	0.1023	10	93.58	10.18	72	218.28	30.20
97	15.58	0.1114	57	96.87	10.77	24	222.05	30.66
109	18.28	0.1782	11	100.05	11.33	73	226.26	31.23
98	19.48	0.2164	58	103.73	11.99	25	229.94	31.68
110	22.20	0.3166	32	107.77	12.70	74	234.33	32.25
99	23.73	0.3940	59	110.79	13.25	26	237.91	32.70
111	26.67	0.5775	33	114.05	13.83	75	242.24	33.25
100	28.73	0.7045	60	117.70	14.49	27	246.19	33.79
112	32.09	0.9625	34	121.07	15.08	76	249.76	34.18
101	34.52	1.185	61	124.53	15.71	28	253.39	34.65
113	37.41	1.476	35	128.67	16.43	77	256.90	35.03
102	40.41	1.789	62	131.56	16.93	29	260.48	35.45
114	43.00	2.075	36	136.92	17.85	78	263.94	35.86
103	46.59	2.524	63	140.02	18.38	30[b]	267.24	36.24
115	49.41	2.862	37	145.44	19.28	80[b]	275.06	37.11
104	52.67	3.343	64	149.07	19.89	16	275.87	37.20
12	52.83	3.365	38	153.92	20.68	81	279.13	37.58
44	53.35	3.438	65	158.04	21.34	17	280.57	37.75
50	53.67	3.480	39	162.36	22.03	82	283.40	38.07
13	56.30	3.866	66	166.64	22.70	18	285.89	38.35
45	57.20	3.986	40	170.81	23.34	83	288.29	38.61
51	58.62	4.201	67	174.94	23.97	19	292.68	39.08
14	60.58	4.510	41	179.25	24.63	84	294.23	39.24
46	61.39	4.641	68	183.24	25.24	20	299.17	39.79
52	63.37	4.968	42	186.77	25.77	85	300.33	39.91
15	65.09	5.253	69	190.76	26.37	86	305.07	40.40
47	66.13	5.422	43	194.45	26.92	87	309.76	40.87
53	68.47	5.790	5	198.79	27.49			
48	71.59	6.262	21	201.71	27.92			

[a] Points numbered in chronological order. [b] Points at short intervals between 270° and 274° K. are omitted.

Table III. Molal Thermodynamic Properties of Variscite

T, °K.	C_p, cal./°K.	$S°$, cal./°K.	$H° - H_0°$, cal.
10	0.028	0.010	0.074
15	0.099	0.033	0.373
20	0.234	0.078	1.174
25	0.458	0.153	2.864
30	0.799	0.273	6.046
35	1.233	0.433	11.09
40	1.743	0.625	18.50
45	2.320	0.863	28.63
50	2.962	1.140	41.80
60	4.429	1.807	78.59
70	6.034	2.608	130.8
80	7.773	3.526	199.7
90	9.560	4.545	286.4
100	11.32	5.644	390.8
110	13.11	6.806	512.9
120	14.90	8.023	653.0
130	16.66	9.286	810.8
140	18.37	10.58	986.0
150	20.04	11.91	1178
160	21.65	13.25	1387
170	23.22	14.61	1611
180	24.75	15.98	1851
190	26.25	17.36	2106
200	27.69	18.75	2376
210	29.07	20.13	2659
220	30.41	21.51	2957
230	31.70	22.89	3268
240	32.98	24.27	3591
250	34.22	25.64	3927
260	35.40	27.01	4275
270	36.55	28.36	4635
280	37.68	29.71	5006
290	38.80	31.06	5388
300	39.87	32.39	5782
273.15	36.90	28.79	4750
298.15	39.67	32.14	5708

The results of these examinations indicated that sample I was contaminated with a small amount of a second phase, but that most of the difference between the entropies of the two samples could be attributed to a surface energy effect of the large fraction of very small particles in sample I. Sample II was considered the better specimen of variscite, and the measured and calculated values for sample I are not reported.

From the measurements on sample II, the entropy of variscite at 298.15° K. is 32.14 gibbs per mole. On the assumption that the measured solid represents the ideal state, the enthalpy at 298.15° K., $H° - H_0°$, is 5708 cal. per mole. The heat capacities at one-degree intervals below 10° K. were read from a large-scale plot of the observed values of C_p/T vs. T^2 between 10° and 30° K. that extrapolated smoothly to 0° K.

The observed molal heat capacities are listed in Table II and the molal heat capacities at even temperatures in Table III. The estimated uncertainty is 0.1% for the measured sample II, but this does not necessarily represent euhedral crystalline variscite with the stoichiometric composition of $AlPO_4 \cdot 2H_2O$.

LITERATURE CITED

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