Low Temperature Heat Capacity and Entropy of Anhydrous Dicalcium Phosphate, 10° to 310° K.

EDWARD P. EGAN, Jr., and ZACHARY T. WAKEFIELD
Tennessee Valley Authority, Wilson Dam, Ala.

An anomalous, unexplained broad hump with a maximum between 270° and 290° K. was observed in the heat capacity curve of $CaHPO_4(c)$. The calculated entropy at 298.15° K. for $CaHPO_4(c)$ was 26.62 e.u., and the enthalpy 4455 cal. per mole.

ANHYDROUS DICALCIUM PHOSPHATE, $CaHPO_4$, is a primary solid phase in the system $CaO–P_2O_5–H_2O$ (*5*). As part of a continuing program of collection of thermodynamic data on compounds of interest in fertilizer technology and in soil-fertilizer reactions, the low temperature heat capacity of anhydrous dicalcium phosphate was measured over the temperature range 10° to 310° K. The entropy and enthalpy at 298.15° K. were derived from the measurements.

In initial measurements on anhydrous dicalcium phosphate in 1951, a broad hump with a maximum at 285° K. was observed in the heat capacity curve. At about the time the measurements were completed, a definitive study of the analysis of $CaHPO_4$ showed that the calorimeter sample was significantly less pure than had previously been indicated. It was assumed that the heat capacity anomaly reflected the impurity content, but the present measurements with a better sample show the same anomaly.

Thermodynamic data on dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$, are reported in a companion paper (*3*).

MATERIALS AND APPARATUS

The 1951 sample (A) of anhydrous dicalcium phosphate was prepared from a solution of reagent grades of $CaHPO_4$ and H_3PO_4 that contained CaO 5%, P_2O_5 21%, and H_2O 74% (*5*). The solution was held at 100° C. for two hours to crystallize $CaHPO_4$, and the crystals were washed successively with hot distilled water and anhydrous acetone and dried at 105° C.

A new sample (B), which was used for the present measurements, was prepared batchwise by slowly raising the pH of a hot mother liquor through the hydrolysis of urea. A solution of 500 grams of the invariant-point solution in the system $CaO–P_2O_5–H_2O$ at 25° C. (*5*) in 900 grams of 10% H_3PO_4 was heated to 85° C. and seeded with crystalline $CaHPO_4$, and 200 ml. of a 10% urea solution was dripped slowly into the hot, vigorously stirred phosphate solution over a period of 175 hours. The reaction vessel was fitted with a condenser to prevent loss of water. The final pH of the solution was 2.0 to 2.4, so that basic calcium phosphates should not have formed.

About 25 grams of $CaHPO_4$ crystals was prepared in each batch. The crystals were washed successively with hot distilled water and acetone, air dried 1 hour, and dried at 105° C. The calorimeter sample was a composite of five preparations. Spectrographic examination of the sample showed traces of Na, Mg, Sr, and Fe, and petrographic examination showed that the crystals were aggregates with some veiling and bubble inclusions.

A third sample (C) of $CaHPO_4$ was prepared from $2m$ $CaCl_2$ solution and $2m$ $(NH_4)_2HPO_4$ solution. One liter of each solution was poured rapidly and simultaneously into a third vessel with vigorous stirring, and the thick gel was thinned by addition of 200 ml. of distilled water. The resultant slurry was added over 30 minutes to 200 ml. of calcium phosphate solution saturated at 95° C. (*5*). The temperature was maintained at 90° to 95° C. during the addition and for an additional 30 minutes of stirring. The slurry contained a fine-grained precipitate of $CaHPO_4 \cdot 2H_2O$ that dissolved and recrystallized as $CaHPO_4$ at 90° to 95° C. The final pH at room temperature was 4.1. The crystals were washed and dried as was sample B. Compositions of the three samples are shown in Table I.

The low temperature calorimeter has been described (*2, 4*). Temperatures were measured to 0.0001°, and were so used in calculation of small temperature differences; they were rounded to two decimals in the preparation of tables. The defined calorie is taken as 4.1840 absolute joules–the ice point as 273.15° K. The density of $CaHPO_4$, to be used in vacuum corrections, is 2.89 grams per cc. (*6*).

Table I. Anhydrous Dicalcium Phosphate Samples

	Composition, %								
	Analysis					Calculated composition			
		P_2O_5							
Sample	CaO	Total	Nonortho[a]	Ign. loss (1000° C.)	N	$CaHPO_4$	$Ca_2P_2O_7$	$Ca(H_2PO_4)_2 \cdot H_2O$	Trapped mother liquor
A	40.66	51.92	0.12	7.64	...	97.70	0.22	1.05	1.04
B	41.10	52.05	0.13	6.80	0.00	99.40	0.23	...	0.37
C	40.90	51.87	0.05	7.21	0.01	99.00	0.13	...	0.87
Stoichiometric	41.22	52.16	0.00	6.62	0.00	100.00	0.00	0.00	0.00

[a] Determined by difference by method of Gee and Deitz (*7*).

The heat capacities were corrected for curvature where it was significant. The calculations were made on an IBM 704 computer (*2*).

OBSERVATIONS

The calorimeter was filled with 122.6085 grams (vacuum) $CaHPO_4(c)$ or 0.901124 mole. The measured heat capacities showed a broad hump beginning at 223° K. with a maximum at 273° K. Although sample B contained least impurities, it gave the highest peak. Sample C was measured only through the temperature range 260° to 300° K. (not reported). Part of the observed peak for sample B is shown on an expanded scale in Figure 1 in which the peaks for all three samples are included.

The calculated "normal" heat capacity is indicated by the dashed line in Figure 1. The magnitudes of the observed peaks are unrelated to the calculated compositions of the corresponding samples. The only significant difference among the temperatures of preparation of the three samples was that sample B was held at 85° C. during crystallization for several days, whereas the other two samples were heated for not more than two hours. The measured heat capacities for sample A (not reported), which contained more impurities, were as much as 0.4 cal. per mole higher at the same temperatures than those of the other samples. There was no similar peak in the heat capacity curve of the hydrated salt (*3*).

Heat capacities of sample B that were measured when the calorimeter was cooled only to 273° K. followed a lower energy curve that is listed in Table II, but not shown in Figure 1. When the calorimeter was cooled below 223° K. and held there more than 12 hours, the data followed the high-energy curve shown in Figure 1. Cooling the calorimeter to temperatures between 223° K. and 273° K. gave values intermediate between the two curves whose magnitude depended upon the thermal history (not shown in Figure 1.)

The slope of the heat capacity curve above the hump was not a smooth continuation of the curve below 223° K. The selected "normal" heat capacities (dashed line in Figure 1) in the region of the hump were calculated from a fourth-degree polynomial fitted by least squares to 8 observed points between 200° and 223° K. and 1 point at 293.75° K. (the lowest point above the peak). The location of the "normal" curve in this manner was arbitrary.

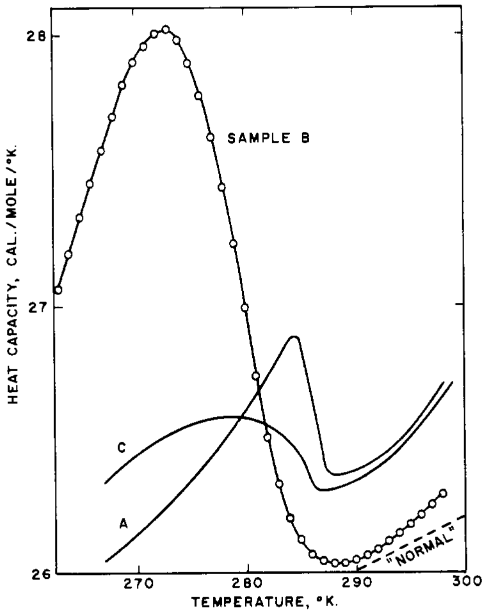

Figure 1. Hump in heat capcity curve of $CaHPO_4(c)$

Table II. Observed Molal Heat Capacity of $CaHPO_4(c)$

T, ° K.	C_p, Cal./° K.	T, ° K.	C_p, Cal./° K.
8.61	0.0041	205.91	21.25
8.82	0.0063	209.49	21.55
9.94	0.0124	213.39	21.88
10.60	0.0218	215.69	22.08
11.27	0.0241	217.42	22.20
12.02	0.0356	220.45	22.46
12.50	0.0401	220.70	22.51
13.37	0.0652	223.47	22.72
13.89	0.0692	226.47	22.99^a
16.12	0.1169	227.86	23.14^a
17.22	0.1464	229.46	23.28^a
20.84	0.2540	232.45	23.55^a
23.34	0.4085	234.86	23.79^a
26.17	0.6207	235.43	23.83^a
29.77	0.9015	238.40	24.14^a
31.63	1.084	241.72	24.47^a
34.38	1.389	244.45	24.76^a
38.30	1.879	248.15	25.18^a
39.38	2.016	250.71	25.49^a
44.39	2.691	254.43	25.92^a
45.57	2.862	257.90	26.39^a
48.56	3.290	260.84	26.78^a
50.53	3.583	261.84	26.68
52.61	3.911	262.96	27.01^a
54.52	4.181	264.96	27.31^a
56.74	4.522	265.03	27.12
59.93	5.026	266.95	27.56^a
62.60	5.469	267.09	27.58^a
65.04	5.867	268.18	27.52
67.77	6.290	268.96	27.81^a
70.07	6.633	271.00	27.96^a
72.56	6.994	271.30	27.80
75.15	7.374	273.06	28.02^a
77.22	7.679	273.24	27.94
79.59	8.032	274.24	27.85
81.19	8.282	274.25	26.90
84.13	8.701	274.40	27.80
87.67	9.200	274.65	27.86^a
91.04	9.640	275.13	27.88
94.33	10.06	275.60	26.80
97.75	10.49	276.26	27.55
100.86	10.89	276.39	26.76
104.03	11.27	276.72	27.64^a
107.30	11.67	277.21	27.57^a
110.23	12.01	278.53	26.55
113.70	12.42	278.80	27.27^a
116.69	12.76	279.31	27.18^a
120.05	13.14	280.34	26.32
123.11	13.48	280.69	26.27
126.16	13.82	280.90	26.73^a
129.52	14.18	281.44	26.64^a
132.79	14.53	282.86	26.03
136.17	14.87	283.03	26.32^a
139.16	15.18	283.58	26.27^a
142.81	15.55	285.04	25.93
145.54	15.82	285.18	26.11^a
149.22	16.18	285.57	25.95
152.17	16.46	285.74	26.08^a
155.65	16.79	287.22	25.92
158.83	17.09	287.33	26.03^a
162.13	17.39	289.40	25.95
165.31	17.68	289.48	26.04^a
168.41	17.98	291.02	26.06^a
171.57	18.27	291.58	26.01
174.56	18.53	291.63	26.08^a
177.79	18.82	291.78	26.05
180.82	19.08	293.75	26.08
184.03	19.36	293.96	26.17
187.18	19.63	294.94	26.18^a
190.14	19.89	296.88	26.24^a
192.93	20.12	298.10	26.31
195.63	20.36	298.78	26.36
198.83	20.64	301.24	26.44
203.20	21.01	303.12	26.53
		304.36	26.58
		307.47	26.74
		309.52	26.82
		309.99	26.85

[a] Points on high-energy curve in region of peak.

The heat capacities below 10° K. were obtained from a plot of C_p/T *vs.* T^2 that extrapolated smoothly to 0° K. The observed heat capacities are listed in Table II. Smoothed heat capacities and the corresponding entropy and enthalpy values are listed in Table III.

The calculated entropy at 298.15° K. for $CaHPO_4(c)$ was 26.62 e.u. and the enthalpy 4455 cal. per mole. The entropy increment under the peak (223° to 298.15° K.) was 0.25 e.u. and the enthalpy increment 66 cal. per mole; these increments were included in the calculated values. The estimated uncertainty is 0.5%; the estimate is liberal because of the uncertain nature of the peak. The calculated entropy of 26.62 e.u. may be compared with the estimated value of 28.0 (*6*) and the value of 21 e.u. selected by the National Bureau of Standards (*11*).

The fact that the curve above the peak is not a smooth continuation of the curve below the peak should rule out an effect of a small amount of impurity (*9*). However, a small amount of trapped "mother liquor" could cause a fusion-solution process that might account for the peak, since the fusion-solution process would be one or two orders of magnitude larger than the heat capacity. Crystalline $CaHPO_4$ consists of corrugated sheets of Ca-O-P bonded by Ca-O-P and PO_4-H-PO_4 bridges (*10*). Blinc and Hadži (*1*) interpret the absorption bands near 2800 and 2360 $cm.^{-1}$ in the infrared spectra of both anhydrous and hydrated calcium phosphates as indicative of a possible proton magnetic resonance transition that may be frozen-in at low temperature. Smith and Jones (*8*), however, found no support for this assumption in their x-ray data on dicalcium phosphate (both anhydrous and dihydrated) over the temperature range 77° to 300° K. Measurement of the heat capacity of a substance is a sensitive tool for location of its transitions, but the peak in the heat capacity curve was observed only with anhydrous dicalcium phosphate—not with its dihydrate (*3*). Further evidence, such as the effect of temperature on proton magnetic resonance and neutron diffraction, would be needed to relate the observed peak to hydrogen-bond shifts.

X-ray examinations in this laboratory at temperatures between 200° and 300° K. showed no changes in the x-ray pattern, and the x-ray patterns of the three preparations of $CaHPO_4$ were indistinguishable.

Differential thermal analyses and infrared absorption spectra of the three preparations were made in further attempts to explain their differences. The differential thermal analysis patterns, Figure 2, show that samples A and C were essentially the same, but that B, the purest sample, lost its water of constitution differently. The infrared absorption spectra are shown in Figure 3. The water-absorption peaks at 2.9 and 6.3 microns for sample B are less pronounced than those for samples A and C. The

Table III. Molal Thermodynamic Properties of $CaHPO_4(c)$

T, ° K.	C_p, Cal./° K.	$S°$ Cal./° K.	$H° - H°_0$, Cal.
10	0.0174	0.0046	0.0352
15	0.0877	0.0224	0.2595
20	0.2431	0.0663	1.047
25	0.5229	0.1482	2.906
30	0.9301	0.2775	6.484
35	1.466	0.4596	12.42
40	2.097	0.6957	21.30
45	2.782	0.9818	33.48
50	3.503	1.312	49.18
60	5.049	2.086	91.84
70	6.619	2.983	150.3
80	8.096	3.964	223.9
90	9.508	5.000	312.0
100	10.78	6.068	413.5
110	11.98	7.152	527.3
120	13.14	8.244	653.0
130	14.23	9.340	789.9
140	15.27	10.43	937.4
150	16.24	11.52	1095
160	17.20	12.50	1262
170	18.12	13.67	1439
180	19.01	14.73	1625
190	19.88	15.78	1819
200	20.74	16.82	2022
210	21.59	17.86	2234
220	22.44	18.88	2454
230	23.33	19.89	2682
240	24.29	20.90	2921
250	25.39	21.92	3169
260	26.62	22.94	3429
270	27.90	23.97	3702
280	26.99	24.97	3979
290	26.05	25.90	4242
300	26.37	26.78	4504
273.15	28.02	24.29	3786
298.15	26.30	26.62	4455

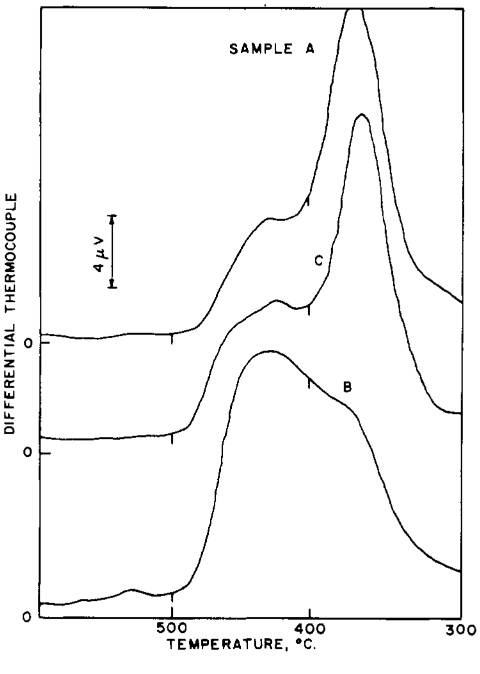

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Figure 2. Differential thermal analysis tracings of $CaHPO_4(c)$. Heating rate, 10° C. per minute

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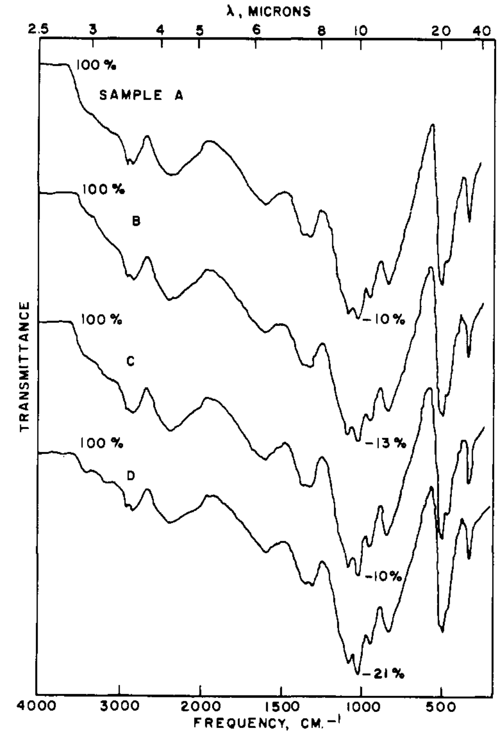
Figure 3. Infrared spectra of $CaHPO_4(c)$



fourth spectrum, sample D, is that of euhedral crystalline $CaHPO_4$ that was prepared by very slow diffusion; only a small amount of this preparation was available. The results of the several examinations confirm the differences observed in the heat capacity measurements but do not explain them.

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Low Temperature Heat Capacity and Entropy of Dicalcium Phosphate Dihydrate, 10° to 310° K.

EDWARD P. EGAN, Jr., and ZACHARY T. WAKEFIELD
Tennessee Valley Authority, Wilson Dam, Ala.

The heat capacity of $CaHPO_4 \cdot 2H_2O$ was measured over the range 10° to 310° K. At 298.15° K. the entropy is 47.10 e.u. and the enthalpy is 7490 cal. per mole.

DICALCIUM phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$, is an important solid phase in the system $CaO-P_2O_5-H_2O$. Although this salt is metastable at room temperature, it is formed by the reaction of calcium phosphate fertilizers in soil solutions (*4, 5*) and it will often crystallize in preference to the more stable anhydrous dicalcium phosphate. The heat capacities of $CaHPO_4 \cdot 2H_2O(c)$ between 10° and 310° were measured, and the entropy and enthalpy were calculated from the results.

MATERIALS AND APPARATUS

It is not difficult to prepare crystals of $CaHPO_4 \cdot 2H_2O$ that appear microscopically clean, but it is difficult to obtain microscopic "cleanness" and stoichiometric composition in the same preparation. The method of preparation used is the result of numerous trials.

A saturated solution of monocalcium phosphate in water was prepared by adding an excess of $Ca(H_2PO_4)_2 \cdot H_2O$ to three liters of distilled water and allowing the mixture to stand for several days at room temperature. The composition of the liquid phase was then close to that of the metastable invariant point in the system $CaO-P_2O_5-H_2O$ at 25° C. (*4*). The mixture was filtered and ammonium hydroxide solution (14% NH_3) was added dropwise until the precipitate that formed redissolved only slowly.

The clear solution was placed in a one-gallon Dewar flask, cooled to 10° C. with a glass cooling coil, and stirred gently mechanically while a dilute gaseous mixture of ammonia in nitrogen was introduced slowly. About one part of the nitrogen was bubbled through dilute (5% NH_3) ammonium hydroxide and then combined with 19 parts of nitrogen that had been bubbled through an equal head of water. The gas stream was admitted to a solution through a 0.3-mm. glass tip close to the stirrer blades; the gas rate at the start of a preparation was 30 bubbles per minute, and this rate was increased gradually to 150 bubbles per minute near the end. The excess nitrogen provided a rapid gas flow to prevent clogging of the tip from local overammoniation while the ammonia was added slowly.

The solution was seeded with dicalcium phosphate dihydrate crystals—relatively crude crystals were used at first, and several short preparations were made until good quality seed crystals were obtained. The seed crystals began to grow when the pH of the solution was raised to 2.2, and growth continued nearly uniformly until the pH reached 2.5, whereupon the growth slowed abruptly. Each preparation yielded 10 to 25 grams of crystals per day and a total of 125 grams in seven days.

The crystals were washed with distilled water, then three times with acetone, and air dried for three hours. Dry nitrogen then was passed through the crystals, which were supported in a fritted glass funnel, for one hour to complete the drying.

The crystals were euhedral single-crystal rods. They were free of ammoniacal nitrogen and contained CaO 32.63%, P_2O_5 41.26%, and ignition loss at 1100° C. 26.14% (stoichiometric: CaO 32.59%, P_2O_5 41.24%, and H_2O 26.17%). The density was calculated from crystal-structure data (*1, 6*) to be 2.304 grams per cc.

The low temperature calorimeter (*2*) was used without modification. The defined calorie is taken as 4.1840 absolute joules—the ice point as 273.15° K. The heat capacities were corrected for curvature (*2*) as required. Because of the importance of small temperature differences, temperatures were read to four decimal places and rounded to two decimal places in the final tabulation.

The calorimeter contained 91.8225 grams (vacuum) or 0.533557 mole of $CaHPO_4 \cdot 2H_2O$.

RESULTS

The observed molal heat capacities are shown in Table I, and the smoothed heat capacities and the corresponding entropy and enthalpy increments are shown in Table II.

In the early measurements, there was an indication of a small peak near the ice point, and numerous extra points were measured to relate the peak to the thermal history of the sample. It was found, however, that the difficulty had arisen from a fault in the energy-measuring circuit, and only selected points in the region of 273° K. are listed in Table I. The average deviation of the observed from the