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

Table I. Observed Molal Heat Capacity of Dicalcium Phosphate Dihydrate, $CaHPO_4 \cdot 2H_2O(c)$

Point[a]	T, ° K.	C_p, Cal./° K.	Point[a]	T, ° K.	C_p, Cal./° K.	Point[a]	T, ° K.	C_p, Cal./° K.
132	9.90	0.0395	59	95.07	17.23	78	208.96	36.23
144	10.25	0.0400	23	98.27	17.88	110	210.02	36.38
133	11.00	0.0647	60	101.56	18.55	7	212.31	36.66
145	11.56	0.0780	24	104.42	19.12	9	216.24	37.21
134	12.21	0.0940	61	107.90	19.81	80	219.67	37.74
146	13.09	0.1332	25	110.64	20.33	10	222.41	38.05
135	14.09	0.1809	62	113.92	20.97	81	225.61	38.52
147	15.50	0.2466	26	116.95	21.53	11	228.65	38.88
136	16.69	0.3152	63	120.04	22.12	82	231.63	39.30
148	18.73	0.4448	27	123.34	22.73	13	234.72	39.67
137	20.15	0.5764	64	126.42	23.30	83	237.91	40.08
149	22.33	0.7110	28	129.81	23.91	14	241.08	40.48
138	24.25	0.9690	65	133.06	24.49	84	244.88	40.95
150	27.03	1.408	29	136.36	25.06	15	248.61	41.38
139	29.15	1.714	66	139.78	25.66	85	251.74	41.78
151	32.34	2.301	31	142.84	26.17	16	254.78	42.12
140	35.32	2.926	67	146.27	26.75	86	258.35	42.59
152	38.00	3.524	32	149.26	27.25	17	261.50	42.92
141	41.25	4.270	68	152.55	27.79	87	264.86	43.33
153	43.47	4.798	33	155.79	28.32	103	267.74	43.64
142	46.19	5.462	69	158.97	28.83	18	268.13	43.71
154	48.16	5.957	34	162.42	29.38	99	271.62	44.10
46	52.41	7.021	70	165.48	29.86	19	274.52	44.46
52	55.43	7.798	35	169.01	30.40	131	277.18	44.71
41	58.85	8.671	71	172.09	30.88	92	281.52	45.21
53	62.31	9.59	36	175.43	31.38	3	284.35	45.55
49	66.53	10.70	72	178.80	31.93	158	288.74	46.06
43	69.48	11.42	37	181.84	32.35	166	291.41	46.34
50	71.92	11.99	73	185.09	32.83	159	293.88	46.65
55	73.29	12.32	38	188.24	33.30	167	296.72	46.93
51	76.82	13.16	74	191.49	33.77	160	299.48	47.24
45	79.05	13.69	39	194.50	34.20	168	302.14	47.52
57	83.34	14.71	75	196.01	34.41	161	304.52	47.76
21	86.19	15.36	106	199.91	34.95	169	307.16	48.04
58	89.31	16.04	108	202.81	35.30	162	309.68	48.32
22	92.20	16.64	109	206.44	35.84			

[a] Numbered in chronological order.

Table II. Molal Thermodynamic Properties of Dicalcium Phosphate Dihydrate, $CaHPO_4 \cdot 2H_2O(c)$

T, ° K.	C_p, Cal./° K.	$S°$, Cal./° K.	$H° - H°_0$, Cal.	T, ° K.	C_p, Cal./° K.	$S°$, Cal./° K.	$H° - H°_0$, Cal.
5	0.0054	0.0017	0.0063	140	25.69	18.17	1607
10	0.0550	0.0163	0.1242	150	27.37	20.00	1872
15	0.2170	0.0643	0.7435	160	28.99	21.82	2154
20	0.5427	0.1666	2.559	170	30.56	23.63	2452
25	1.092	0.3425	6.551	180	32.16	25.42	2765
30	1.863	0.6063	13.84	190	33.52	27.19	3094
35	2.852	0.9653	25.55	200	34.96	28.95	3426
40	3.982	1.419	42.59	210	36.37	30.69	3793
45	5.176	1.956	65.47	220	37.74	32.41	4164
50	6.409	2.565	94.42	230	39.06	34.12	4548
60	8.989	3.960	171.3	240	40.33	35.81	4945
70	11.54	5.540	274.1	250	41.55	37.48	5354
80	13.92	7.237	401.5	260	42.75	39.14	5776
90	16.20	9.009	552.2	270	43.91	40.77	6209
100	18.21	10.82	724.3	280	45.05	42.39	6654
110	20.22	12.65	916.6	290	46.19	43.99	7110
120	22.11	14.49	1128	300	47.30	45.57	7577
130	23.94	16.34	1359	273.15	44.26	41.28	6348
	23.94	16.34	1359	298.15	47.10	45.28	7490

smoothed heat capacities was less than 0.1 per cent, except at temperatures below 30° K. where the small magnitudes impaired the accuracy. The low end of the heat-capacity curve was located by plotting C_p/T against T^2 and extrapolating smoothly to 0° K.

The entropy of $CaHPO_4 \cdot 2H_2O(c)$ at 298.15° K. is 47.10 e.u. The enthalpy at 298.15° K., on the assumption that the measured solid represents the ideal state, is 7490 cal. per mole. The calculations were made on an IBM computer (*2*).

The heat capacity of $CaHPO_4(c)$ is reported in a companion paper (*3*). The anhydrous salt showed a broad hump between 220° and 294° K. that was not observed for the dihydrate.

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