This value differs by about 0.3% from the value of -399.04 ± 0.24 kcal./mole obtained by Snyder and Seltz[10] and by 0.6% from the value of -402.9 ± 0.4 kcal./mole obtained by Roth, Wolf and Fritz.[11]

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[10] P. E. Snyder and H. Seltz, THIS JOURNAL, **67**, 683 (1945).

[11] W. A. Roth, U. Wolf and O. Fritz, *Z. Elektrochem.*, **46**, 42 (1940).

CONTRIBUTION FROM THE RESEARCH SECTION, DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Low-Temperature Heat Capacity and Entropy of Hydroxyapatite[1]

BY EDWARD P. EGAN, JR., ZACHARY T. WAKEFIELD AND KELLY L. ELMORE

Heat capacities of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, are reported for temperatures from 13.18 to 298.16°K. Derived values for the entropy, 186.6 cal. per mole per degree, and the heat content, 30,710 cal. per mole, at 298.16°K. are combined with previously reported high-temperature heat contents to yield the thermodynamic properties of hydroxyapatite at temperatures from 298.16 to 1500°K.

The development of a clear understanding of the chemistry involved in the production and use of phosphatic fertilizers has been retarded by a meagerness of thermodynamic data on the calcium phosphates and certain related compounds. The Tennessee Valley Authority is determining the thermodynamic properties of some of these compounds.

The heat contents and heat capacities of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, at temperatures above 25° have been reported.[2] The present paper extends the study of heat capacities to low temperatures. The derived heat content and entropy at 25° are combined with previously reported values[2] to obtain the thermodynamic properties of hydroxyapatite.

The heat capacities were measured at temperatures down to 11°K. through use of a Collins[3] helium cryostat manufactured by Arthur D. Little, Incorporated. Since this paper is expected to be the first of a series on low-temperature heat capacities, significant details of the apparatus are presented.

Quality of Hydroxyapatite.—Hydroxyapatite was precipitated by a method that has been described[2] and was thermally aged for 72 hours at 950° in a nitrogen–steam atmosphere. A chemical analysis of the product showed that the CaO and P_2O_5 contents were within a few hundredths of a per cent. of the stoichiometric values, 55.80 and 42.39%, respectively, and that 0.03% Cl was present. The only significant contaminant found in a spectrographic analysis was 0.05% SiO_2. An optical analysis indicated the presence of < 0.3% β-$Ca_3(PO_4)_2$. The refractive index was 1.639 as compared to 1.636 reported by Bale[4] for ignited hydroxyapatite.

Apparatus.—The calorimeter and adiabatic vacuum shield were patterned after those of Scott.[5] The copper calorimeter was about 5 cm. in diameter by 5 cm. deep; it held about 62 g. of hydroxyapatite or 0.06 mole on the basis of a gram-formula weight of 1004.70. Vertical heat-distributing vanes were soldered between the outside wall and the thermometer well. The capsule-type resistance thermometer was soldered in a small copper spool, between the end flanges of which a thin-walled Monel jacket was silver-soldered. A 50-ohm constantan heater was wound on the Monel tube, and the heater-thermometer assembly was immersed in Woods metal in the well. Three chromel–constantan differential thermocouples were located between the top, side and bottom, respectively, of the calorimeter and corresponding positions on the adiabatic shield. The bottom differential couple had three junctions. The potential leads to the heater were divided between the calorimeter bottom and the shield bottom to minimize loss of measured energy, as recommended by Scott.[5]

Temperatures were measured with a Leeds & Northrup capsule-type platinum resistance thermometer that had been calibrated down to 11°K. by the National Bureau of Standards. The thermometer resistance was measured in international ohms by means of a Mueller bridge that had been calibrated by NBS and was recalibrated during use against an NBS-certified standard resistance.

Energy measurements were made by means of a Wenner standardizing potentiometer.[5] The energy was measured in international joules and was converted to defined calories by the relation: 1 cal. = 4.1833 international joules. The potential of the standard cell was checked periodically against three NBS-certified unsaturated cells that were reserved for reference. Time was measured in integral seconds with a Standard Electric Time Company master clock and a "second accumulator" that turned the heating current on and off automatically at the beginning and end of a preselected heating period. The accuracy of timing was ±0.01 second.

The calorimeter was filled in a dry-box under dry nitrogen through a 1-cm. opening in the cap. A $^1/_8$-inch copper tube was attached to the opening by means of solder and an annular copper adapter. The calorimeter was evacuated, and $^1/_3$ atm. of helium was admitted. The copper tube was then pinched closed, cut and soldered close to the calorimeter cap. The calorimeter was hung in the adiabatic shield from the projecting copper tube end with nylon thread.

Heat capacity measurements down to 52°K., attained with pumped solid nitrogen, were made in the conventional manner. For measurements below 52°K., the calorimeter was transferred to a second shield system that was located in the cold zone of the helium cryostat. The calorimeter was cooled to about 10°K., and the cryostat operating pressure of 200 p.s.i. then was reduced to about 100 p.s.i. to balance the refrigeration load as evidenced by lack of motion of the helium gas holder. The calorimeter could have been cooled to 4.2°K., but means of measuring temperatures below 11°K. had not been incorporated into the calorimeter. The present application of the Collins helium cryostat permits the attainment of a temperature of 10°K. without the hazards associated with liquid hydrogen.

Observations.—The observed heat capacities, $\Delta Q/\Delta T$, for the calorimeter plus hydroxyapatite

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[1] For table of observed heat capacities and the corresponding temperature intervals order Document 3309 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **72**, 2418 (1950).

[3] S. C. Collins, *Rev. Sci. Instruments*, **18**, 157 (1947).

[4] W. F. Bale, J. F. Bonner, H. C. Hodge, H. Adler, A. R. Wreath and R. Bell, *Ind. Eng. Chem., Anal. Ed.*, **17**, 491 (1945).

[5] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945).

and for the empty calorimeter were plotted on a large scale, and smooth curves were drawn through the observed points. Values read at 5° intervals from the smooth curves were used in the calculation of curvature corrections from second differences.[5] Analytical expressions were fitted to the observed heat capacities plus the calculated curvature corrections, a deviation plot was made and values calculated at 5° intervals from the analytical expressions were adjusted from the deviation plot. A tabular presentation of the observed heat capacities on a mole basis and the corresponding temperature intervals is available.[1] The heat capacities at 5° intervals are given in Table I. The entropy at 298.16°K. is 186.6 ± 0.2 cal. per mole per degree, which represents the sum of 0.3 e.u. from a Debye extrapolation ($\theta = 95$) between 0° and 13.18°K. and 186.3 e.u. from a graphical integration between 13.18° and 298.16°K. The graphical integration was checked by tabular integration[6] of C_p/T against T at 5° intervals. The heat content, $H° - H_0°$, at 298.16°K., as derived from the integration of C_p against T, is 30,710 cal. per mole.

TABLE I

HEAT CAPACITY OF HYDROXYAPATITE AT 5° INTERVALS, CALORIES PER MOLE PER DEGREE

T, °K.	C_p	T, °K.	C_p
15	1.10	160	122.7
20	2.32	165	125.8
25	4.76	170	128.8
30	7.76	175	131.6
35	11.36	180	134.4
40	15.35	185	137.1
45	19.57	190	139.8
50	23.94	195	142.5
55	28.76	200	145.0
60	34.75	205	147.6
65	41.22	210	150.0
70	47.22	215	152.3
75	52.75	220	154.5
80	57.88	225	156.7
85	63.01	230	158.7
90	68.17	235	160.8
95	73.14	240	162.9
100	77.83	245	164.9
105	82.30	250	167.0
110	86.49	255	168.9
115	90.57	260	170.8
120	94.54	265	172.7
125	98.39	270	174.5
130	102.2	275	176.3
135	105.9	280	177.9
140	109.4	285	179.7
145	112.9	290	181.4
150	116.2	295	183.1
155	119.5	298.16	184.07

Thermodynamic Properties.—The entropy and heat content at 298.16°K. are combined in Table II with previously reported[2] values for higher temperatures to give ($H° - H_0°$) and $S°$ at round temperatures up to 1500°K. The observed values for the heat content are assumed to correspond to the ideal state for the solid.

TABLE II

THERMODYNAMIC PROPERTIES OF HYDROXYAPATITE, CALORIES PER MOLE

T, °K.	$(H° - H_0°)$	$(H° - H_0°)/T$	$S°$	C_p
298.16	30,710	103.0	186.6	184.07
400	51,050	127.6	245.3	213.1
500	73,400	146.8	294.6	228.3
600	96,710	161.2	337.1	236.7
700	120,720	172.5	374.1	243.5
800	145,420	181.8	407.1	250.5
900	170,800	189.8	436.9	257.1
1000	196,840	196.8	464.4	263.5
1100	223,490	203.2	489.8	269.6
1200	250,760	209.0	513.5	275.6
1300	278,600	214.3	535.8	281.2
1400	306,990	219.3	556.8	286.5
1500	335,890	223.9	576.7	291.3

The precision of the measurements was 0.1% from 25 to 300°K. Because of heat leak into the system, the heat capacities were not measured adiabatically[7] at temperatures below 25°K. The drifts were evaluated in degrees per minute and the corrections for heat leak were made on this basis.[8] The deviation of the observed heat capacities increased from 0.1% at 25°K. to 2% at 12°K. No correction was made for impurities.

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[6] Works Progress Administration, Mathematical Tables Project, "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1944.

[7] J. G. Aston and G. J. Szasz, THIS JOURNAL, **69**, 3108 (1947).

[8] W. P. White, "The Modern Calorimeter," Chemical Catalog Company (Reinhold Publ. Corp.), New York, N. Y., 1928.