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

Thermodynamic Properties of Fluorapatite, 15 to 1600°K.[1]

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

The heat capacity of crystalline fluorapatite, $Ca_{10}(PO_4)_6F_2$, from 15 to 300°K. was determined. At 298.16°K. the entropy is 185.5 ± 0.2 cal. per mole per degree, and the heat content, $H° - H_0°$ is 30,340 cal. per mole. The heat contents above 25° were measured to 1600°K. The equations expressing the heat content, heat capacity and entropy of fluorapatite are

$$H_T - H_{298.16} = 226.04T + 14.44 \times 10^{-3}T^2 + 48.82 \times 10^5T^{-1} - 85{,}050, \text{ cal./mole } (298.16° - 1580°\text{K.}; \pm 0.4\%)$$

$$C_p = 226.04 + 28.88 \times 10^{-3}T - 48.82 \times 10^5T^{-2}, \text{ cal./mole/deg.}$$

$$S_T - S_{298.16} = 520.48 \log T + 28.88 \times 10^{-3}T + 24.41 \times 10^5T^{-2} - 1324, \text{ cal./mole/deg.}$$

Fluorapatite, $Ca_{10}(PO_4)_6F_2$, is a major component of phosphate rock, the chief source of phosphatic fertilizers. This paper presents results of measurements of the low-temperature heat capacity, the entropy and heat content at 298.16°K. and the high-temperature heat contents of fluorapatite. The heat capacity and heat contents were used to derive a table of thermodynamic properties for the range 298.16 to 1600°K.

Preparation of Fluorapatite.—Crystalline fluorapatite was prepared by heating tricalcium phosphate and calcium fluoride. In the preparation, monocalcium phosphate, recrystallized from hot phosphoric acid solution, was heated slowly to 500° to form β-calcium metaphosphate. Calcium carbonate was precipitated by addition of ammonium carbonate to a hot solution of recrystallized calcium nitrate. Tricalcium phosphate was prepared by heating a stoichiometric mixture of calcium metaphosphate and calcium carbonate at 1150° for 5 hours. Calcium fluoride was prepared from calcium carbonate and hydrofluoric acid. A stoichiometric mixture of tricalcium phosphate and calcium fluoride was heated for 30 minutes at 1370° in a current of dry nitrogen; a platinum boat containing calcium fluoride was placed upstream from the apatite mixture to maintain an atmosphere of calcium fluoride over the mixture and thus prevent loss of fluorine from the apatite. The analysis of the fluorapatite is given in Table I.

TABLE I

QUALITY OF FLUORAPATITE

Constituent	Found, wt. %	Stoichiometric for $Ca_{10}(PO_4)_6F_2$, wt. %
CaO	55.6	55.60
P_2O_5	42.2	42.22
F	3.75	3.77
MgO	0.02	
SiO_2	.03	
SrO	.12	
Na_2O	< .02	
Al_2O_3	< .02	
CuO	< .01	
Fe_2O_3	< .03	

The value for fluorine in Table I is the average of six determinations; the maximum deviation was 0.05%. Microscopic examination showed that the fluorapatite was essentially a single phase but that a small amount of unreacted calcium fluoride, estimated to be less than 0.1%, was present. The refractive index was 1.622 as compared to a published value[2] of 1.631. The preparation gave a strong apatite pattern[3] by X-ray diffraction; no other crystalline phases were detected by X-ray examination.

(1) For table of observed heat capacities and the corresponding temperature intervals order Document 3310 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) L. Mitchell, G. T. Faust, S. B. Hendricks and D. S. Reynolds, *Am. Mineral.*, **28**, 356 (1943).

(3) St. Náray-Szabo, *Z. Krist.*, **75**, 387 (1930).

Apparatus.—The low-temperature and high-temperature calorimeters have been described.[4,5] In the present work, the mirror-to-scale distance of the galvanometers was increased from 1 to 2 meters, and a group of six saturated standard cells, certified by the National Bureau of Standards and maintained at 25°, replaced the three unsaturated standard cells as the laboratory reference of potential. The temperature of the water-bath used with the high-temperature calorimeter was maintained at 25°.

Low-Temperature Heat Capacity.—The observed heat capacities, $\Delta Q/\Delta T$, for the empty calorimeter and for the calorimeter filled with 85.7 g. (0.085 mole) of fluorapatite were plotted, and arbitrary smooth curves were drawn through the experimental points. Values read at 5° intervals from the smooth curves were used in the calculation of curvature corrections from second differences.[6] Equations were fitted to the corrected heat capacities, a deviation plot was made, and the values calculated from the equations were corrected from the deviation plot. A tabular presentation of the observed heat capacities on a mole basis is available.[1] The heat capacities at 5° intervals are given in Table II.

TABLE II

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

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15	0.98	115	90.32	215	149.7
20	2.47	120	94.33	220	151.8
25	4.81	125	98.18	225	153.8
30	7.87	130	101.9	230	155.8
35	11.67	135	105.5	235	157.8
40	15.86	140	109.0	240	159.8
45	20.51	145	112.3	245	161.7
50	25.62	150	115.6	250	163.6
55	31.01	155	118.7	255	165.4
60	36.58	160	121.8	260	167.2
65	42.08	165	124.7	265	168.9
70	47.47	170	127.6	270	170.6
75	52.73	175	130.3	275	172.2
80	58.03	180	132.9	280	173.9
85	63.22	185	135.5	285	175.6
90	68.15	190	138.0	290	177.2
95	72.87	195	140.5	295	178.8
100	77.42	200	142.9	298.16	179.73
105	81.85	205	145.3		
110	86.16	210	147.5		

The entropy at 298.16°K. is 185.5 ± 0.2 cal. per mole per degree, which is the sum of 0.2 e.u., ob-

(4) E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **73**, 5579 (1951).

(5) E. P. Egan, Jr., Z. T. Wakefield and Kelly L. Elmore, *ibid.*, **72**, 2418 (1950).

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

tained by Debye extrapolation ($\theta = 112$) between 0 and 13.32°K., and 185.3 e.u., obtained by graphical integration between 13.32 and 298.16°K. The graphical integration was checked by tabular integration[7] 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 30,340 cal. per mole. No correction was made for impurities. The assumption was made that the derived entropy and heat content represented the ideal state for the solid.

The heat capacity of fluorapatite parallels that of hydroxyapatite,[4] as might be expected from the similar constitution of the two large molecules. The heat capacity of fluorapatite is slightly higher than that of hydroxyapatite at temperatures below 70°K., but is lower at temperatures above 70°K. The entropy of hydroxyapatite[4] at 298.16°K. is 186.6 e.u.

The precision of the measurements was 0.05% at temperatures above 30°K.; at lower temperatures the deviations progressively increased, reaching 1.0% at 13°K. As with hydroxyapatite,[4] it was necessary to apply a correction for a slight heat leak into the system below 30°K. The absolute accuracy was not estimated. The unit of thermal energy used in the measurements was the defined calorie: 1 cal. = 4.1833 international joules.

High-Temperature Heat Content.—The heat contents above 25° of two samples of the fluorapatite were measured alternately. About 9 g. (0.009 mole) of fluorapatite filled each covered platinum–rhodium crucible. The heat contents were measured at 100° intervals, and the heat contents of a sample of synthetic sapphire were measured at 200° intervals as a check upon the reliability of the measurements.

TABLE III

HEAT CONTENT OF FLUORAPATITE, CALORIES PER MOLE, AT TEMPERATURES ABOVE 25°

T, °K.	$H_T - H_{298.16}$ (obsd.)	Obsd. − smoothed	Deviation, %
474.6	36,130	− 10	0.03
575.9	58,440	−193	.33
576.1	58,890	205	.35
676.0	80,600	−446	.55
676.4	80,880	−265	.33
775.7	104,820	12	.01
776.5	104,190	−820	.78
873.0	129,350	299	.23
873.5	128,960	−197	.15
974.1	153,120	−140	.09
974.3	153,220	−100	.07
1074.1	178,970	−126	.07
1075.3	179,690	278	.15
1167.3	202,510	−224	.11
1172.9	204,370	178	.09
1281.5	231,610	−822	.35
1376.3	256,940	−599	.23
1376.4	258,820	1256	.49
1472.9	283,150	91	.03
1479.9	284,810	84	.03
1581.5	310,370	278	.09
1581.7	309,470	−670	.22
		Average	0.22

(7) Works Progress Administration, Mathematical Tables Project, "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1944.

The observed heat contents for fluorapatite, in calories per gram, were converted to calories per mole on the basis of a gram-formula weight of 1008.68 for $Ca_{10}(PO_4)_6F_2$. With the value for the heat capacity at 298.16°K. of 179.73 cal. per mole per degree, an equation was fitted to the observed heat contents by the Shomate method,[8] a deviation plot was made, and a smooth curve was drawn through the deviations from the derived equation. Heat contents at even intervals of temperature and smoothed values at the observed temperatures were taken from the deviation curve. The observed heat contents are compared with the smoothed values in Table III.

The heat contents and entropies of fluorapatite above 25° at round values of absolute temperature are given in Table IV. The values of $(H° - H°_0)_{298.16}$, and $S_{298.16}$, taken from the low-temperature data, are included in the table to facilitate calculation of $(H° - H°_0)°_T$ and $S°_T$ at the listed temperatures. The entropies were computed, through the method given by Kelley,[8] from the entropy equation and the heat content deviations.

TABLE IV

THERMODYNAMIC PROPERTIES OF FLUORAPATITE, CALORIES PER MOLE, AT TEMPERATURES ABOVE 25°

T, °K.	$H_T - H_{298.16}$	$(H_T - H_{298.16})/T$	$S_T - S_{298.16}$
298.16	0	0.0	0.0
400	20,100	50.2	57.5
500	41,700	83.4	104.9
600	64,060	106.8	145.9
700	86,490	123.6	181.3
800	110,790	138.5	214.2
900	135,650	150.7	242.7
1000	159,710	159.7	268.6
1100	185,720	168.8	293.0
1200	211,140	176.0	315.0
1300	237,310	182.5	335.9
1400	263,810	188.4	355.3
1500	290,130	193.4	373.4
1600	315,000	196.9	389.6
	$H° - H°_0$		$S°$
298.16	30,340		185.5

The Shomate equation[8] for the heat content, and the heat capacity and entropy equations are

$$H_T - H_{298.16} = 226.04T + 14.44 \times 10^{-3}T^2 + 48.82 \times 10^5T^{-1} - 85{,}050, \text{ cal./mole} \quad (298.16° - 1580°\text{K.}; \pm 0.4\%)$$

$$C_p = 226.04 + 28.88 \times 10^{-3}T - 48.82 \times 10^5T^{-2}, \text{ cal./mole/deg.}$$

$$S_T - S_{298.16} = 520.48 \log T + 28.88 \times 10^{-3}T + 24.41 \times 10^5T^{-2} - 1324, \text{ cal./mole/deg.}$$

The samples of fluorapatite were examined microscopically and with X-rays at the completion of the runs. The material appeared to be unchanged, and it is concluded that no significant decomposition of the fluorapatite had occurred.

WILSON DAM, ALABAMA RECEIVED APRIL 21, 1951

(8) K. K. Kelley, Bur. Mines Bull. No. 476 (1949).