

Fig. 1.— x - y and x -temperature diagram for the system pyridine-acetic anhydride, at atmospheric pressure: —, Raoult's law; O, experimental points with anhydrous reagents; ●, experimental points with water added to pyridine.

used for three vapor-liquid equilibrium determinations, was evaporated on a steam-plate over a period of seventy-two hours and found to leave a

residue of 0.2% by weight. Thus, the weight per cent. of such tar present during the experiments, in which the liquid was boiled for a much shorter time, must have been quite small, and if the molecular weight of the tar was large its mole fraction and effect on the equilibrium could be expected to be negligible.

In an effort to avoid tar formation, water was added in several experiments to the pyridine to the extent of 0.5% as recommended by Wilson and Hughes. Tar formation was thus prevented when the pyridine content of the mixture was high, and greatly decreased when it was low. The content of acetic anhydride in the vapor was considerably reduced by the use of wet pyridine when the pyridine content was high, as would be expected from the formation of relatively non-volatile pyridinium acetate from the acetic acid formed on hydrolysis. Through most of the range of composition, the effect of 0.5% of water on the equilibrium is within the experimental error.

The data fit Raoult's law quite closely over most of the range of composition. It is evident that the vapors contain substantial amounts of acetic anhydride at all concentrations and that any vapor loss from this system would have a serious effect on analytical results.

Summary

The equilibrium vapor-liquid compositions over the whole range at atmospheric pressure have been obtained for the system pyridine-acetic anhydride. The system was found to obey Raoult's law quite closely.

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High-Temperature Heat Content of Hydroxyapatite

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Thermodynamic data for only a few compounds of interest in phosphatic fertilizer technology appear in the literature. Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, plays an important part in the physical chemistry of the calcium phosphates. In a review of the basic calcium phosphates, Eisenberger, Lehrman and Turner¹ concluded, "...it is only a fortuitous occurrence when the composition of any apatite may be expressed by small whole number ratios of atomic species suggesting a definite chemical compound." The preparations described in the present paper are believed, however, to represent as close an approach to the composition, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ as reasonably could be expected.

This paper is expected to be the first of a series

(1) S. Eisenberger, A. Lehrman and W. D. Turner, *Chem. Rev.*, **26**, 257-296 (1940).

on the thermal properties of calcium phosphates; hence, significant details of the construction of the calorimeter are presented. The calorimeter was calibrated primarily with electrical energy. Alumina and silica glass were used to test the calorimeter system, and the observed heat contents for these substances are included and compared with values from the literature.

Apparatus

The basic design of the high-temperature calorimeter was patterned after that of Southard.² Ready access to the receiving well in the gold-plated copper block was obtained by mounting the furnace on a hydraulic lift that permitted the furnace to be swung through an arc of 90° in the raised position.

The furnace temperature was controlled by means of a four-junction platinum-platinum + 10% rhodium ther-

(2) J. C. Southard, *This Journal*, **63**, 3142-3146 (1941).

mocouple adjacent to the furnace winding. The output of the thermocouple was fed into a Leeds & Northrup model NC controller. The controller, in conjunction with a Lindberg percentage timer that shunted a reactance in the furnace circuit, maintained the temperature of the furnace constant with a precision of $\pm 0.05^\circ$.

The temperature of the capsule was measured² with a Wenner thermocouple potentiometer. The measuring thermocouple was calibrated in place against a Bureau of Standards certified couple over the entire range of experimental temperatures. During measurements of heat contents, additional checks were made at every 200° interval.

Initially, the triggered plunger-and-tube dropping mechanism of Southard² was used, but it was abandoned in favor of an electrical dropping mechanism that eliminated mechanical difficulties. A four-hole ceramic tube, mounted in a zircon plug at the furnace top, extended to the isothermal zone. The tube was a common insulator for the measuring couple, with its hot junction close to the top of the suspended capsule, and for two heavy-gage platinum-rhodium wires that were bent into hooks at the lower end. A 40-gage platinum alloy fuse link, 1 cm. long, was looped over the hooks, and the capsule was suspended from the fuse link. A small silica washer was inserted between the bail of the capsule and the fuse to prevent welding of the two wires. The washer was used at all temperatures, although it was necessary only at temperatures above 1000° . A potential of 24 v., a. c., blew the fuse without sputtering metal onto the capsule.

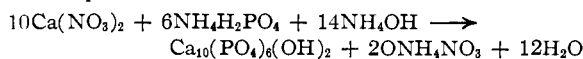
The calorimeter proper, a gold-plated cylindrical copper block 15.2 cm. in diameter by 16.5 cm. in height and weighing 26 kg., rested on three bakelite cones in a can that was immersed in a water-bath at $29.78 \pm 0.01^\circ$. The calorimeter thermometer was a copper-manganin bridge arrangement^{2,3} covering about 80% of the cylindrical surface of the block. The thermometer was calibrated in terms of the electrical energy, in defined calories (1 cal. = 4.1833 international joules), required to raise the e. m. f. of the thermometer by 1 μ v. Thermometer current, 0.002 ampere, and potential were measured on a shielded 100,000- μ v. White double potentiometer. Standard cells were compared with a group of three unsaturated cells, certified by the Bureau of Standards and reserved as reference cells.

Time was measured in integral seconds with a Standard Electric Time Co. master clock and a "second accumulator" that automatically turned the heating current on and off at the beginning and end of a preselected heating period. The average deviation for a set of ten determinations of the thermometer e. m. f.-calibration energy relationship was 0.05%.

The observed heat contents of the platinum-rhodium capsule plus the silica washer above 29.8° were subtracted from the measured heat contents of sample plus capsule plus washer. Corrections for small deviations of the silica washers from their nominal weight of 50 mg. were based on the heat contents for silica reported by Southard.² Although the error for the washer was thrown onto the empty capsule, the observed heat contents for the empty capsule agreed with the values reported by Kelley⁴ for platinum and rhodium.

Materials

Hydroxyapatite.—Hydroxyapatite was prepared by the acidimetric precipitation method of Rathje,⁵ which is based upon the reaction



About 3 liters each of 0.20 *M* calcium nitrate and 0.12 *M* monoammonium phosphate solutions were added at a rate of 100 ml. per hour to 35 liters of distilled water at 95° . The substrate was stirred continuously and maintained

just alkaline to brom phenol blue by addition of ammonium hydroxide. The precipitate was allowed to settle, washed with distilled water, dried at 110° and soaked for seventy-two hours at 950° in an atmosphere containing 20% water vapor to promote crystallization. The sample so prepared was designated HY-43.

The chemical analysis of the thermally aged product is given in Table I. The only significant contaminant shown by spectrographic analysis was 0.3% alumina. A trace of glassy phase was observed by crystallographic analysis. X-Ray patterns showed a sharp crystalline pattern with the lines attributed to hydroxyapatite in the ASTM classification⁶ but with two weak lines corresponding to the two strongest lines of chlorapatite, although chlorine could not be detected by chemical analysis.

TABLE I
ANALYSIS OF HYDROXYAPATITE

Sample	Per cent.			CaO/ P ₂ O ₅ wt. ratio	Refrac. index
	CaO	P ₂ O ₅	Impurity		
HY-43	55.68	42.38	0.3 Al ₂ O ₃	1.315	1.637
	55.71	42.33			
XP-12	55.64	42.27	.18 Cl	1.317	1.640
	55.78	42.37			
Stoichiometric	55.80	42.39	1.316	1.6367

A second sample of hydroxyapatite, designated XP-12, was prepared in a manner similar to that used for HY-43 with the exceptions that 0.12 *M* monopotassium phosphate was substituted for the ammonium phosphate and that 1.0 *M* ammonium chloride was added to the substrate to promote crystal growth. The chemical analysis of sample XP-12 is given in Table I. The only significant contaminant was 0.18% chlorine. A trace of crystalline phase was identified as potassium nitrate by crystallographic analysis. X-Ray analysis was the same as for HY-43.

Silica.—Fused quartz was prepared by grinding and screening Vitreosil tubing. The impurities did not exceed 0.01%.

Alumina.—Alumina was obtained from Linde Air Products as synthetic sapphire of 99.99% purity.

Results

One sample, about 8 g., of each preparation of hydroxyapatite, HY-43 and XP-12, was used in the measurements. About twice as many measurements were made with sample HY-43 as with XP-12. The heat contents above 29.78° were measured at 100° intervals. The heat content of the alumina was measured at 200° intervals as a check, the assumption being that if acceptable values were obtained for it, the values for hydroxyapatite would be reliable.

The observed heat contents for hydroxyapatite, in calories per gram, were converted to calories per mole on the basis of a gram-formula weight of 1004.70 for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. An arbitrary curve was drawn through a plot of the observed heat contents, and values of the heat content were read therefrom at even intervals of temperature and smoothed. A small extrapolation ($H_{302.94} - H_{298.16}$) was added to bring the data to a base temperature of 25° . Table II compares the observed heat contents, in calories per mole, at temperatures above 25° with the smoothed values.

(6) ASTM card file of X-ray data.

(7) W. F. Bale, J. F. Bonner, H. C. Hodge, H. Adler, A. R. Wreath and R. Bell, *Ind. Eng. Chem., Anal. Ed.*, **17**, 491-495 (1945).

(3) C. G. Maier, *J. Phys. Chem.*, **34**, 2860-2868 (1930).

(4) K. K. Kelley, *Bur. Mines Bull.* No. 371 (1934).

(5) W. Rathje, *Bodenkunde u. Pflanzenernähr.*, **12**, 121-128 (1939).

TABLE II

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

T, °K.	Sample	$H_T - H_{298.16}$ (obsd.)	Obsd.- smoothed	Devi- ation, %
298.16		0	0	0.00
473.4	XP-12	36,360	30	.08
474.3	HY-43	36,830	180	.49
572.2	HY-43	59,620	70	.12
572.6	HY-43	59,690	60	.10
673.8	HY-43	83,570	-610	.73
674.2	HY-43	83,860	-360	.43
674.4	XP-12	84,330	-10	.01
772.8	HY-43	108,420	90	.08
774.0	HY-43	108,250	-380	.35
774.2	XP-12	108,280	-360	.33
872.2	HY-43	133,290	120	.09
873.2	HY-43	132,980	-410	.31
874.2	XP-12	133,640	0	.00
973.3	HY-43	160,020	570	.36
973.5	XP-12	159,530	10	.01
973.6	HY-43	159,370	-180	.11
1073.6	HY-43	186,140	500	.27
1073.9	HY-43	185,610	-280	.15
1073.9	XP-12	185,440	-450	.24
1172.2	HY-43	213,390	810	.38
1173.2	HY-43	213,390	-530	.25
1173.3	XP-12	213,450	-590	.28
1271.4	HY-43	239,850	170	.07
1271.5	HY-43	239,140	-540	.23
1371.3	XP-12	268,500	400	.15
1371.8	HY-43	267,730	-470	.18
1472.1	HY-43	296,300	830	.28
1472.5	XP-12	297,310	50	.02

Average 0.22

Table III gives the thermodynamic properties of hydroxyapatite at round values of absolute temperature. The heat contents are smoothed values. The heat capacities were calculated from the heat contents by the differentiation coefficients of Salzer⁸ and the entropies by 5-point Lagrangian integration coefficients.⁹

The heat capacity of a similar preparation of hydroxyapatite, as determined from unpublished low-temperature data, is 184.07 cal. per gram per degree at 298.16° K., and this value was combined with the observed heat contents in the derivation of an equation by the method of Shomate.¹⁰ The resultant equation was

$$(H_T - H_{298.16}) = 228.52T + 19.81 \times 10^{-3}T^2 + 50.00 \times 10^6T^{-1} - 86,670 \quad (1)$$

Two expressions were derived from equation 1

$$C_p = 228.52 + 39.62 \times 10^{-3}T - 50.00 \times 10^6T^{-2} \quad (2)$$

$$(S_T - S_{298.16}) = 526.19 \log T + 39.62 \times 10^{-3}T + 25.00 \times 10^6T^{-2} - 1342 \quad (3)$$

(8) H. E. Salzer, "Table of Coefficients for Obtaining the First Derivative Without Differences," Natl. Bur. Stds., Applied Math. Ser., 1948, 2.

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

(10) C. H. Shomate, THIS JOURNAL, 66, 928-929 (1944).

TABLE III

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

T, °K.	C_p	$(H_T - H_{298.16})$	$\frac{(H_T - H_{298.16})}{T}$	$\frac{(S_T - S_{298.16})}{T}$
298.16	184.07	0	0.0	0.0
400	213.1	20,340	50.9	58.7
500	228.3	42,690	85.4	108.0
600	236.7	66,000	110.0	150.5
700	243.5	90,010	128.6	187.5
800	250.5	114,710	143.4	220.5
900	257.1	140,090	155.7	250.3
1000	263.5	166,130	166.1	277.8
1100	269.6	192,780	175.3	303.2
1200	275.6	220,050	183.4	326.9
1300	281.2	247,890	190.7	349.2
1400	286.5	276,280	197.3	370.2
1500	291.3	305,180	203.5	390.1

The 0.3% alumina in hydroxyapatite HY-43 and the 0.18% chlorine in hydroxyapatite XP-12 were without detectable effect on the agreement of the observed values for the two preparations. After the runs at 1000° and 1200°, portions of each sample were submitted to X-ray and optical examination. The X-ray patterns were not changed from the initial patterns. The optical examination showed no change in sample HY-43, whereas sample XP-12, after the run at 1200°, showed 10 to 15% of a new phase, tentatively identified as calcium pyrophosphate. A rough estimate indicated that the heat content per gram of calcium pyrophosphate would be of the same magnitude as that of hydroxyapatite, and that the presence of 10 to 15% pyrophosphate therefore would have small effect on the observed heat content. The samples lost about 0.1% in weight between 1000 and 1100° and an additional 0.1% between 1100 and 1200°. Hydroxyapatite is known to decompose⁷ at 1400°. Presumably, a slow decomposition had begun above 1000°.

The derived equation fitted the observed heat contents of hydroxyapatite within an average deviation of 0.3%. The least accurate part of the measurements was the temperature of the capsule as it entered the well. Furnace temperatures were measured to 0.01° and are reported to 0.1°, but it is doubtful that the temperatures of the capsule are known closer than 1.0°. No correction for impurities was made, because the physical states of the impurities were not known.

The heat content data for silica glass, as summarized by Southard,² are compared with the observed heat contents per mole at temperatures above 25° in Table IV. A slight extrapolation was made in the observed results to correct them to a base temperature of 25°.

The heat content of alumina at temperatures above 25° has been reported by Shomate and Naylor¹¹ of the Bureau of Mines and at tempera-

(11) C. H. Shomate and B. F. Naylor, *ibid.*, 67, 72-75(1945).

TABLE IV

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

T, °K.	$H_T - H_{298.16}$ (obsd.)	Obsd.-calcd. ²	Deviation, %
298.16	0	0	0.00
763.2	6,567	-28	.42
764.5	6,656	-42	.64
865.3	8,219	3	.04
866.5	8,218	-23	.28
967.3	9,913	28	.28
967.6	9,865	-25	.25
1068.1	11,533	-28	.24
1068.4	11,589	23	.20
1171.3	13,390	82	.62
1172.5	13,396	67	.50
1273.4	15,069	3	.02
1274.4	15,113	30	.20
1374.6	16,714	-121	.72
1469.7	18,663	142	.77
Average			0.37

tures above 0° by Ginnings and Corruccini¹² of the Bureau of Standards. The following equation expresses the present measurements, in calories per gram, at temperatures above 0°

$$(H_T - H_{273.16}), \text{ cal./g.} = 0.2587T + 2.0 \times 10^{-5}T^2 + 7.2 \times 10^3T^{-1} - 98.51 \quad (4)$$

TABLE V

HEAT CONTENT OF ALUMINA, CALORIES PER GRAM, AT TEMPERATURES ABOVE 0°

Furnace temp., °C.	Observed	Deviation from equation 4, %
304.4	70.03	0.17
304.6	69.69	.73
401.2	95.55	.01
402.0	96.47	.74
506.9	125.19	.57
508.3	125.40	.43
600.8	151.20	.17
601.1	151.51	.31
699.6	178.91	.29
700.9	179.03	.42
799.9	208.32	.26
800.2	208.29	.31
896.3	237.44	.07
897.8	238.64	.25
997.4	268.89	.28
1093.1	296.80	.20
1093.2	297.55	.05
1194.6	328.83	.02
1195.1	328.83	.02
1299.4	361.94	.12
Average		0.23

(12) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, No. 6, 593-600 (1947).

The observed heat contents above 29.78° for alumina, corrected to a base temperature of 0°, are compared with values from equation 4 in Table V. The observed values from Table V, the Bureau of Mines data above 25°, and the Bureau of Standards data above 0° are compared, on a common base temperature of 0°, in Fig. 1. The sensitivity of the plot has been increased by plotting the observed heat contents as mean specific heats. The average deviation of the present measurements from the Bureau of Standards data was 0.55% and from the Bureau of Mines data, 0.3%.

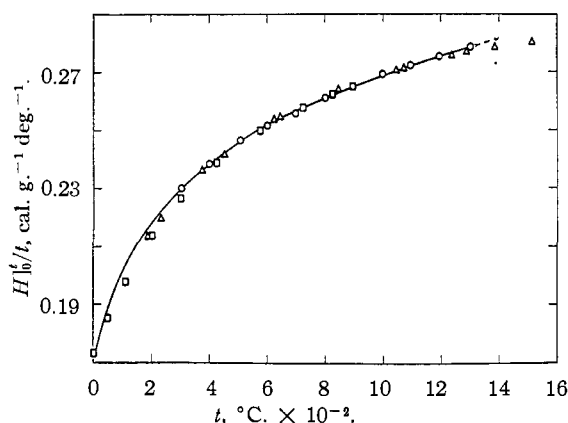


Fig. 1.—Mean specific heat of alumina: Δ , Shomate and Naylor¹¹; \square , Ginnings and Corruccini¹²; \circ , this work; —, equation 4.

Acknowledgment.—The spectrographic, X-ray and optical analyses were made by J. A. Brabson, J. P. Smith and J. R. Lehr.

Summary

The heat content of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, was measured at temperatures above 25° in a copper aneroid calorimeter. Equations expressing the heat content, heat capacity and entropy per mole of hydroxyapatite were derived from the observed heat contents

$$(H_T - H_{298.16}) = 228.52T + 19.81 \times 10^{-3}T^2 + 50.00 \times 10^6T^{-1} - 86,670$$

(298.16°-1475°K.; $\pm 0.3\%$)

$$C_p = 228.52 + 39.62 \times 10^{-3}T - 50.00 \times 10^6T^{-2}$$

$$(S_T - S_{298.16}) = 526.19 \log T + 39.62 \times 10^{-3}T + 25.00 \times 10^6T^{-2} - 1342$$

As a means of testing the calorimeter system, the heat contents of silica glass and alumina at temperatures above 25° were measured and compared with values reported in the literature.

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