[CONTRIBUTION FROM THE DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY[1]]

Thermodynamic Properties of Calcium Pyrophosphate, 10 to 1700°K.

BY EDWARD P. EGAN, JR., AND ZACHARY T. WAKEFIELD

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The heat capacity of β-calcium pyrophosphate crystals was measured over the range 10 to 305°K. The derived entropy at 298.16°K. is 45.25 ± 0.03 cal. deg.$^{-1}$ mole^{-1} and the heat content at 298.16°K. is 7430 cal. mole^{-1}. The heat content above 298.16°K. was measured between 400 and 1700°K. on the α, β, γ and liquid forms of calcium pyrophosphate. The heat of transition $\beta \rightarrow \alpha$ at 1413.16°K. is 1622 cal. mole^{-1} and the heat of fusion of the α-form at 1626.16°K. is 24,104 cal. mole^{-1}. Equations are presented for the heat content, entropy and heat capacity above 298.16°K.

A study of the thermodynamic properties of the calcium phosphates and related compounds in the technology of phosphate fertilizers has been under way for several years.[2] As part of this study, measurements were made on calcium pyrophosphate at low and high temperatures.

Materials and Apparatus.—Crystalline β-calcium pyrophosphate was prepared by heating recrystallized anhydrous dicalcium phosphate to constant weight at 600° and then at 1000°. No extraneous phases could be found in microscopic and X-ray examinations. The chemical composition was 44.33% CaO and 55.80% P_2O_5, as compared with a theoretical composition of 44.14% CaO and 55.86% P_2O_5 for $Ca_2P_2O_7$ (formula weight, 254.11).

When the study was near completion, a small sample of γ-calcium pyrophosphate was contributed by Hill,[3] who noted its formation in a study of the system $P_2O_5 \cdot 2CaO \cdot P_2O_5$. More of the γ-form, with matching optical and X-ray properties, was prepared by heating recrystallized anhydrous dicalcium phosphate at 550° for 4 days.

The calorimeters have been described.[2] One defined calorie was taken as 4.1840 abs. j., and 0° was taken to be 273.16°K. Temperatures were read to four decimal places and were so used in the calculations, since small differences were involved; the last two places were dropped in final tabulation of the results.

TABLE I

OBSERVED HEAT CAPACITY OF β-CALCIUM PYROPHOSPHATE, CAL. DEG.$^{-1}$ MOLE^{-1}

Point[a]	T, °K.	ΔT	C_p	Point[a]	T, °K.	ΔT	C_p	Point[a]	T, °K.	ΔT	C_p
87	9.97	2.18	0.076	54	96.10	6.51	17.74	8	200.38	6.00	35.04
88	14.45	6.09	.174	23	100.18	7.04	18.65	40	203.51	5.34	35.40
97	15.50	5.23	.224	55	102.80	6.88	19.17	9	206.92	7.08	35.84
89	20.45	5.72	.585	24	107.01	6.23	20.09	41	209.69	7.03	36.16
98	20.96	5.42	.625	56	109.84	7.20	20.64	10	213.93	6.96	36.66
90	25.45	4.14	1.158	25	113.47	6.30	21.40	42	216.67	6.92	36.95
99	26.14	4.85	1.257	57	116.52	6.17	21.98	11	220.84	6.85	37.44
100	29.98	2.72	1.877	26	119.64	6.03	22.61	43	223.54	6.82	37.70
91	30.21	5.33	1.918	58	122.56	5.92	23.15	12	227.64	6.75	38.17
101	33.48	4.22	2.540	27	125.87	6.43	23.80	44	230.31	6.72	38.42
92	35.58	5.40	2.956	59	128.69	6.33	24.30	13	234.35	6.66	38.86
102	37.97	4.70	3.480	28	132.18	6.20	24.95	45	236.99	6.63	39.10
93	41.92	7.29	4.368	60	134.92	6.12	25.43	14	240.97	6.58	39.54
103	43.40	6.14	4.715	29	138.57	6.59	26.08	46	243.58	6.55	39.77
94	49.06	6.98	6.143	61	141.23	6.51	26.52	15	247.51	6.49	40.21
104	49.62	6.30	6.281	30	145.05	6.38	27.18	47	250.09	6.47	40.44
81	54.82	3.38	7.584	62	147.65	6.32	27.59	16	253,97	6.42	40.84
95	54.85	4.60	7.622	31	151.35	6.20	28.22	48	256.53	6.40	41.06
76	55.18	4.55	7.683	63	154.22	6.83	28.66	17	260.35	6.35	41.45
82	58.46	3.45	8.512	32	157.74	6.59	29.23	49	262.90	6.34	41.67
77	60.40	5.90	9.025	70	159.13	3.27	29.41	18	266.64	6.27	42.05
83	62.96	5.53	9.708	64	160.90	6.53	29.70	50	269.20	6.28	42.27
78	66.22	5.73	10.56	71	163.99	6.44	30.17	19	272.89	6.21	42.64
84	68.46	5.47	11.12	65	167.35	6.37	30.65	51	275.44	6.21	42.85
79	71.91	5.65	11.98	72	170.35	6.29	31.10	2	277.84	6.98	43.09
85	73.92	5.45	12.46	66	173.91	6.76	31.60	34	279.61	6.90	43.20
80	77.53	5.60	13.37	73	176.83	6.67	32.00	3	284.78	6.89	43.72
86	79.14	5.00	13.78	67	180.61	6.64	32.53	36	288.24	6.87	43.99
20	82.18	4.81	14.55	74	183.43	6.53	32.92	4	291.64	6.84	44.32
52	82.48	6.68	14.61	68	187.43	6.99	33.44	37	295.08	6.80	44.57
21	87.71	6.24	14.90	75	190.15	6.90	33.81	5	298.44	6.76	44.92
53	89.34	7.02	16.25	69	194.38	6.91	34.33	38	301.84	6.73	45.17
22	93.74	5.83	17.24	7	195.86	3.04	34.42	6	304.61	5.56	45.45
				39	197.82	6.05	34.71				

[a] Numbered in chronological order.

Low Temperature Heat Capacity.—The observed heat capacities, $\Delta Q/\Delta T$, for the empty calorimeter and for the calorimeter charged with 98.9232 g. (vacuum) or 0.389293 mole of β-calcium pyrophos-

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[1] Article not copyrighted.

[2] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **72**, 2418 (1950); **73**, 5579, 5581 (1951); **78**, 1811 (1956).

[3] W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 542 (1944).

phate were plotted on a large scale, 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.[4] Equations were fitted to the corrected heat capacities, a deviation plot was made and values calculated from the equations were corrected from the deviation plot. The observed molal heat capacities are listed in Table I. The heat capacities at integral temperatures are shown in Table II.

The precision of the measurements was ±0.05% between 30 and 300°K.; the deviation increased as the temperature was lowered below 30°K. and was ±10% at 10°K.

The entropy of β-calcium pyrophosphate at 298.16°K. is 45.25 ±0.03 e.u., of which 0.03 e.u. represents a Debye extrapolation ($\theta = 284$) between 0 and 9.968°K., and 45.22 e.u. represents graphical integration between 9.968 and 298.16°K. The graphical integration was checked by tabular integration[5] at 5° intervals. On the assumption that the measured solid represents the ideal state, the heat content ($H° - H°_0$) at 298.16°K. is 7430 cal. mole^{-1}.

TABLE II

HEAT CAPACITY OF β-CALCIUM PYROPHOSPHATE AT INTEGRAL TEMPERATURES, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
10	0.070	110	20.68	210	36.19
15	.194	115	21.69	215	36.77
20	.540	120	22.67	220	37.33
25	1.102	125	23.62	225	37.87
30	1.884	130	24.55	230	38.40
35	2.843	135	25.45	235	38.92
40	3.925	140	26.32	240	39.43
45	5.120	145	27.17	245	39.94
50	6.379	150	27.99	250	40.44
55	7.642	155	28.78	255	40.93
60	8.924	160	29.56	260	41.41
65	10.24	165	30.31	265	41.88
70	11.51	170	31.04	270	42.36
75	12.74	175	31.76	275	42.83
80	14.01	180	32.45	280	43.28
85	15.21	185	33.12	285	43.72
90	16.39	190	33.77	290	44.16
95	17.51	195	34.39	295	44.60
100	18.59	200	35.01	300	45.03
105	19.65	205	35.60	273.16	42.655
				298.16	44.873

High Temperature Heat Content.—The heat contents above 298.16°K. of two samples of β-calcium pyrophosphate were measured alternately. About 7 g. (0.028 mole) of calcium pyrophosphate filled each covered platinum–rhodium crucible. The measurements were made at 100° intervals, and the heat contents of a sample of synthetic sapphire were measured at 200° intervals as a check on the reliability of the measurements. The observed heat contents of the crucible plus pyrophosphate less the observed heat contents of the empty crucible were converted to calories per mole. The observed heat contents, uncorrected for heats of fusion or transition, are shown in Table III.

A temperature of 1413°K. for the β→α transition and a melting point of 1626 ± 3°K. for α-calcium pyrophosphate have been reported.[6] In the present measurements the β-form persisted to 1473°K. and was converted to the α-form at 1523°K. The α-form prepared at 1573°K. reverted to 75% β-form when reheated at 1273°K. and to α-form plus a trace of β-form when reheated at 1433°K.

Because of the sluggishness of the transition in bulk samples, the transition temperature was not confirmed, nor was the heat of transition at the transition temperature observed directly. The poorly formed β-crystals improved in form as the transition temperature was approached; above 1473°K. three to five β-crystals were converted into one euhedral α-crystal.

TABLE III

OBSERVED HEAT CONTENT ABOVE 298.16°K. OF CALCIUM PYROPHOSPHATE, CAL. MOLE^{-1}

T °K.[a]	Crystal form	$H_T - H_{298.16}$	T, °K.[a]	Crystal form	$H_T - H_{298.16}$
473.34	β	8,964	1473.02	β	74,075
473.24	β	8,948	1522.78	α, 95%	77,815
573.17	β	14,621	1522.80	α	77,898
573.20	β	14,603	1572.82	α	80,651
673.20	β	20,484	1473.45	α, 98%	74,462
673.19	β	20,559	1433.38	α, tr. β	71,443
773.35	β	26,547	1433.20	β, 50–75%	71,618
773.34	β	26,612	1572.87	α	81,621
873.20	β	32,989	1599.93	α	84,149
873.17	β	33,029	1599.79	α	86,510
971.72	β	39,403	1613.67	α, tr. β	84,719
971.74	β	39,462	1597.08	α, tr. β	83,492
1073.08	β	46,285	1635.72	α	110,889
1073.18	β	46,191	1634.32	α	110,145
1173.30	β	53,035	1634.68	β	113,000
1173.36	β	53,014	1634.92	α	110,760
1273.22	β	60,060	1634.84	α	110,640
1273.33	β	60,176	1634.71	α	110,055
1322.87	β	63,766	1634.84	α	110,454
1322.87	β	63,778	1653.42	α	112,650
1373.19	β	67,456	1653.46	β	114,810
1373.34	β	67,479	1653.48	α	112,210
1373.29	β	67,153	1653.25	α	112,380
1373.49	β	67,368	1673.32	α	114.421
1398.57	β	69,109	1643.50	α	111,690
1398.39	β	69,238	1643.27	α	111,220
1407.96	β	69,776	1673.50	α	114,390
1408.22	β	69,931	672.27	γ	20,520
1423.38	β	70,781	672.31	γ	20,444
1423.38	β	70,954	773.96	γ	26,620
1473.38	α, 90%	73,987	870.54	γ	33,040
1473.25	β	74,743	870.55	γ	32,940

[a] Listed in chronological order.

The melting point reported by Hill[6] was accepted without redetermination. Similar prepara-

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

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

[6] W. L. Hill, G. T Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 457 (1944).

tions of calcium pyrophosphate in another study[7] had a melting point of 1624°K.

At 1614°K. the product was the α-form plus a trace of β-form with no glass present. At 1634°K. and above two of the liquid samples quenched to all β-form and the others quenched to all α-form with no glass phase remaining; thus, the heat of fusion was included in the measured heat contents. Apparently the kinetic conditions during quenching govern the crystallization of the glass as α- or β-form and, at temperatures below 1625°K., account for the appearance of a trace of β-form in the α-form, but the conditions are not reproducible at will. Hill[6] noted the readiness with which calcium pyrophosphate crystallizes from the melt.

The heat contents for the liquid → α crystallization and for all α-form below m.p. 1626°K. fell within 0.1% of straight lines. Upon extrapolation of the two lines to 1626°K., the indicated difference in heat contents corresponded to a heat of fusion of 24,104 cal. mole^{-1}.

The heat of transition at 1413°K. was determined indirectly. The two heat contents above m.p. 1626°K. for liquid crystallizing to the β-form included the heat capacity effect for the liquid, the heat of fusion, the difference in heat capacities of the α- and β-forms and the heat of transition. A straight line through the two heat contents for liquid → β fixed the heat content of the glass above 298.16°K. This line was extrapolated to the melting point, and the heat of fusion was subtracted; this fixed the heat content above 298.16°K. for the α-form at 1626°K., and from this point a line parallel to the line for the α-form fixed the heat contents above 298.16°K. for the α-form including the heat of transition. The line for the α-form was then extrapolated to the transition point, 1413°K., and the difference between this value and the heat content of the β-form at 1413°K. gave 1622 cal. mole^{-1} for the heat of the β→α transition.

Heat contents above 1300°K., corrected for heats of transition and fusion, are shown in Fig. 1. The measurement of high temperature heat contents was discontinued at 1700°K., because at higher temperatures the combined effect of high surface tension and low viscosity caused the liquid to creep out around the cap of the container.

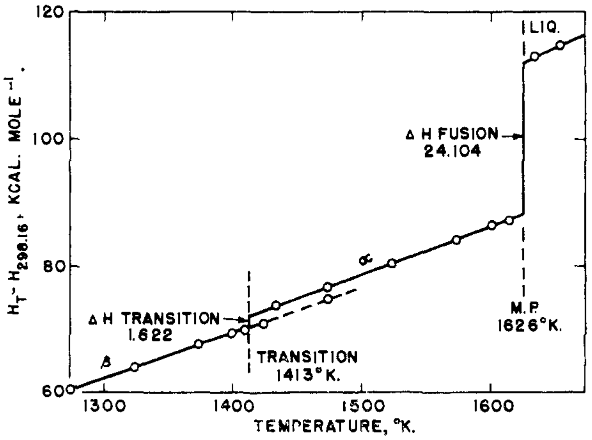

Fig. 1.—Heat content above 298.16°K. of calcium pyrophosphate.

The heat contents of the γ-form at 673, 773 and 873°K. proved to be the same as those for the β-form. The temperature at which the γ→β transition occurs is not known. In the absence of detailed information on the range of existence of the γ-form, the tables in the present paper are set up on the assumption that the relative heat content of the β-form at 298.16°K. is 0. The heat of transition of the γ-form to the β-form could not be measured; the β-crystals dissolved too slowly in acid of the concentration that could be used in the solution calorimeter at hand.

An equation was fitted to the observed heat contents by the method of Shomate,[8] the value for the heat capacity at 298.16°K. being taken from Table II. A deviation plot was made, and a smooth curve was drawn through the deviations from the derived equation. Heat contents at integral temperatures, calculated from the equation and corrected from the deviation curve, are shown in Table IV. A heat capacity equation and an entropy equation were derived from the heat content equation, and the calculated heat capacities and entropies as well as the heat content function, $(H_T - H_{298.16})/T$, are included in Table IV.

TABLE IV

HIGH TEMPERATURE THERMAL DATA FOR CALCIUM PYROPHOSPHATE, CAL. MOLE^{-1}

T, °K.	$H_T - H_{298.16}$	$(H_T - H_{298.16})/T$	$S_T - S_{298.16}$	C_p
		β-Form		
298.16	0	0.00	0.00	44.87
400	5,010	12.53	14.40	52.11
500	10,430	20.87	26.48	56.26
600	16,150	26.92	36.90	59.11
700	22,120	31.60	46.09	61.33
800	28,320	35.40	54.37	63.23
900	34,720	38.59	61.91	64.94
1000	41,320	41.32	68.86	66.53
1100	48,040	43.67	75.26	68.04
1200	54,930	45.77	81.26	69.50
1300	62,040	47.72	86.95	70.92
1400	69,290	49.49	92.32	72.32
1413.16	70,232	49.73	92.99	72.50
β → α	1,622		1.15	
		α-Form		
1413.16	71,854	50.85	94.14	76.11
1500	78,460	52.31	98.68	76.11
1600	86,080	53.80	103.59	76.11
1626.16	88,066	54.16	104.83	76.11
α → liq.	24,104		14.82	
		Liquid		
1626.16	112,170	68.98	119.65	96.85
1650	114,480	69.38	121.06	96.85
1700	119,320	70.19	123.95	96.85

The derived equations for the molal thermo-

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(7) P. E. Stone, E. P. Egan, Jr., and J. R. Lehr, *J. Am. Ceram. Soc.*, **39**, 89 (1956).

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

dynamic properties at high temperature are listed below.

$H_T - H_{298.16}$

β: $54.90T + 6.452 \times 10^{-3}T^2 + 12.73 \times 10^5T^{-1} - 21{,}210$ ($\pm 0.2\%$; 298.16 to 1413.16°K.)

α: $76.111\ T - 35{,}700$ ($\pm 0.1\%$; 1413.16 to 1626.16°K.)

Liq: $96.854T - 45{,}330$ ($\pm 0.1\%$; 1626.16 to 1700°K.)

$S_T - S_{298.16}$

β: $126.412 \log T + 12.904 \times 10^{-3}T + 6.365 \times 10^5T^{-2} - 323.808$ (298.16 to 1413.16°K.)

α: $175.25 \log T - 457.97$ (1413.16 to 1626.16°K.)

Liq: $223.02 \log T - 596.52$ (1626.16 to 1700°K.)

C_p

β: $54.90 + 12.904 \times 10^{-3}T - 12.73 \times 10^5T^{-2}$ (298.16 to 1413.16°K.)

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WILSON DAM, ALABAMA

[CONTRIBUTION NO. 61 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Ethanethiol and 2-Thiapropane: Heats of Formation and Isomerization; The Chemical Thermodynamic Properties from 0 to 1000°K.[1]

BY J. P. MCCULLOUGH, W. N. HUBBARD, F. R. FROW, I. A. HOSSENLOPP AND GUY WADDINGTON

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Experimental and computational investigations of ethanethiol and 2-thiapropane were made to supply previously lacking information needed for complete tables of chemical thermodynamic properties. Experimental results included values of heat of formation, $\Delta Hf°_{298.16}$ (liq.), for ethanethiol (-17.61 kcal. mole^{-1}) and 2-thiapropane (-15.64 kcal. mole^{-1}); heat of vaporization of 2-thiapropane, $\Delta Hv = 9087 - 4.1794\ T - 1.3860 \times 10^{-2}\ T^2$, cal. mole^{-1} (275 − 310°K.); vapor heat capacity of 2-thiapropane, $Cp° = 5.628 + 4.9990 \times 10^{-2}\ T - 1.5535 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (318–500°K.); and second virial coefficient of 2-thiapropane, $B = V(PV/RT - 1) = -264 - 21.70 \exp(1000/T)$, cc. mole^{-1} (275–500°K.). These results and previously published data provide experimental values of $\Delta Hf°$, $S°$ and $Cp°$ in the ideal gaseous state for both ethanethiol and 2-thiapropane. A revised vibrational assignment was made for 2-thiapropane, and thermodynamic properties of this compound were calculated from calorimetric, spectroscopic and molecular structure information. The height of the barrier to internal rotation in 2-thiapropane (2100 cal. mole^{-1}) was determined from the calorimetric value of $S°$; and empirical anharmonicity corrections were determined from the experimental values of $Cp°$. For consistency, previously published thermodynamic properties of ethanethiol were revised to include anharmonicity corrections. Values of the following thermodynamic functions of ethanethiol and 2-thiapropane were calculated at selected temperatures to 1000°K.: $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$, $Cp°$, $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$. Values of $\Delta Hi°$, $\Delta Fi°$ and $\log_{10} Ki$ for the isomerization of ethanethiol to 2-thiapropane also are reported.

Ethanethiol and 2-thiapropane are among the important sulfur-bearing constituents of the low-boiling fractions of petroleum.[2] The thermodynamic properties of these substances have been the subject of several calorimetric and computational investigations.[3-7] This paper reports additional calorimetric data that permit calculation of the chemical thermodynamic properties over a wide range of temperatures. The new experimental data presented include values of the heats of combustion and formation of ethanethiol and 2-thiapropane and values of the heat of vaporization and vapor heat capacity of 2-thiapropane. The calculated thermodynamic properties of ethanethiol given in an earlier paper from this Laboratory[7] were revised to include anharmonicity corrections and extended to include values of the heat, free energy and logarithm of the equilibrium constant of formation. The entropy datum of Osborne, Doescher and Yost[4] and the vapor heat capacity and heat of formation data from this investigation were used with spectroscopic and molecular structure information in new calculations of the thermodynamic properties of 2-thiapropane. Values of the following thermodynamic functions are reported at selected temperatures between 0 and 1000°K. for both ethanethiol and 2-thiapropane: $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$, $Cp°$, $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$.

Experimental

Physical Constants.—The 1951 International Atomic Weights[8] and, where practicable, the 1951 values of the fundamental physical constants[9] were used. The results are based on a molecular weight of 62.134 for the C_2H_6S isomers and the following relations: 0° = 273.16°K.; and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale.[10] Measurements of mass, energy and resistance were made in terms of standard devices calibrated at the National Bureau of Standards.

The Materials.—The samples of ethanethiol and 2-thiapropane used in the combustion calorimetric studies were portions of the Standard Samples of Sulfur Compounds, NBS serial no. 904 and API-USBM serial no. 13, respectively, which were prepared and purified at the Laramie,

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(1) This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) C. J. Thompson, H. J. Coleman, H. T. Rall and H. M. Smith, *Anal. Chem.*, **27**, 175 (1955).

(3) J. Thomsen, *Thermochemische Untersuchungen*, Vol. 4, Leipzig, 1886.

(4) D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942).

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(7) J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, Guy Waddington and H. M. Huffman, THIS JOURNAL, **74**, 2801 (1952).

(8) Edward Wichers, *ibid.*, **74**, 2447 (1952).

(9) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(10) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).