Low-Temperature Heat Capacity and Entropy of Triammonium Hydrogen Pyrophosphate Monohydrate

ZACHARY T. WAKEFIELD[1] and BASIL B. LUFF
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

The low-temperature heat capacity of triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, was measured over the temperature range 10–300K by adiabatic calorimetry. The heat capacity, C_p; entropy, $S°$; and Gibbs function, $(G° - H_0°)/T$ at 298.15K are 80.69, 82.14, and −38.22 cal K^{-1} mol^{-1}, respectively, and the enthalpy, $H° - H_0°$, is 13,094 cal mol^{-1}. These values include contributions from an enantiotropic transition that started at about 200K, reached a maximum at 255K, and ended at 260K.

In the continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, a major component of ammonium polyphosphate fertilizers, was measured over the temperature range 10–300K by adiabatic calorimetry. Related thermodynamic properties of the compound were derived from the results of the measurements.

MATERIALS AND APPARATUS

Triammonium hydrogen pyrophosphate monohydrate was prepared from a granular ammonium polyphosphate from a TVA pilot plant. A saturated solution of the polyphosphate had a pH of about 4.6, and 83% of the phosphorus was present as pyrophosphate. In the first step of purification, $(NH_4)_3HP_2O_7 \cdot H_2O$ about 93% pure was obtained by simultaneously adding concentrated NH_4OH and solid ammonium polyphosphate to the saturated solution of the ammonium polyphosphate in the proportions to maintain the pH at 5.5. The crystalline product was filtered off and redissolved to saturation in distilled water at 25°C, and the solution was stored at 0°C to effect slow crystallization. The low-temperature recrystallization was repeated three times. The largest single crystals (several centimeters long) were removed, blotted free of mother liquor with absorbent paper, and stored in a sealed glass bottle.

For use in the calorimeter, the crystals were crushed, with a minimum of grinding, to pass a 50-mesh screen. Paper chromatographic analysis showed that 99.7% of the phosphorus in the material was present as pyrophosphate. The 0.3% present as orthophosphate was assumed to be within the limits of sensitivity of the chromatographic method, and no correction was made for impurity. The recrystallized material contained 17.0% N, 25.1% P, and 7.2% H_2O (stoichiometric: 17.01% N, 25.07% P, 7.29% H_2O) and was shown by petrographic and X-ray examination to be well-crystallized homogeneous $(NH_4)_3HP_2O_7 \cdot H_2O$ (*2*).

In preliminary examinations before loading the calorimeter, the salt lost water of hydration slowly at a pressure of 10^{-3} torr at room temperature but was stable for short periods at 100 torr. A sample was evacuated to a pressure of 100 torr in a glass vessel with about the same dimensions as the calorimeter, then relieved to atmospheric pressure with air dried by passage through P_2O_5. This cycle was repeated three times. There was no significant change in weight, and petrographic examination of the sample showed no significant alteration.

The calorimeter was charged by the same procedure except that the vacuum was relieved with helium in each of three cycles and then the residual helium was adjusted to the same mass used in the measurements on the empty calorimeter. The evacuation tube was pinched shut, cut off, and sealed with eutectic solder. The calorimeter charge was 58.8838 grams in vacuo or 0.238316 mole [sp. gr., 1.66 (*3*); gram formula weight, 247.0824]. Its heat capacity ranged from 40% of the total at 10K to 64% at 300K.

The previously described (*1*) low-temperature calorimeter was used with automatic shield control. Calibration and standardization of all devices used for the measurements of temperature, potential, and resistance, and their traceability to values maintained by the National Bureau of Standards have been described (*4*). The defined calorie was taken as 4.1840 abs J, and the ice point as 273.15K. The measured heat capacities were corrected for curvature and for a small difference in the amount of eutectic solder relative to the empty calorimeter. Since small temperature differences were important, temperatures were read to four decimal places, but they were rounded to two decimal places in the final tabulation. The average deviation between the observed and the calculated values for heat capacity was 0.015 cal K^{-1} mol^{-1} for measurements below 20K and 0.019 cal K^{-1} mol^{-1} for measurements above 20K. This corresponds to an average deviation of 0.06% for all values above 20K. Graphical integration of the deviations of observed heat capacity values from the smoothed curve indicates the uncertainty in the enthalpy value at 298.15K to be ±4 cal. The overall accuracy is estimated to be 0.1%. The heat capacities below 10K were read from a large-scale plot of C_p/T vs. T^2 that extrapolated smoothly to 0K. Observed molal heat capacities are shown in Table I.

RESULTS AND DISCUSSION

An enantiotropic transition peak, shown in Figure 1, began at about 200K, reached a maximum at about 255K, and then dropped sharply and ended at 260K with return to normal heat capacity values. Heat capacity values in the region of the peak were readily reproducible and temperature equilibrium was reached in the usual time of 9 min, except for two points which required an additional 2 min. After completion of the measurements an X-ray diffraction pattern of the calorimeter sample maintained at 80K was indistinguishable from the 25°C pattern.

The enthalpy of the peak was determined by two methods that differed by 0.38 cal per sample (1.6 cal mol^{-1}). From the measured total energy input of nine consecutive points through which the material passed from the stable state below the peak to the stable state above the peak was subtracted the

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[1] To whom correspondence should be addressed.

Table I. Observed Heat Capacity of Triammonium Hydrogen Pyrophosphate Monohydrate, Cal K^{-1} Mol^{-1}

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
8.75	0.2214	74.47	22.88	185.12	56.72	251.63	74.09
9.35	0.2590	76.96	23.80	188.22	57.55	252.29	74.30
10.29	0.3603	79.16	24.63	191.25	58.31	252.94	74.58
10.81	0.4150	80.39	25.08	194.29	59.12	253.59	75.05
11.88	0.5538	83.25	26.11	196.92	59.75	254.24	75.41
12.26	0.6079	86.14	27.15	197.26	59.85	254.89	75.97
12.87	0.7026	89.07	28.17	198.07	60.05	256.16	74.24
13.80	0.8666	91.79	29.04	199.58	60.46	256.18	74.24
14.85	1.081	95.06	30.12	201.06	60.79	256.84	73.15
16.74	1.550	97.86	31.03	203.96	61.55	257.50	72.97
19.75	2.387	101.20	32.14	205.44	61.94	258.16	72.91
20.10	2.490	104.11	33.07	206.90	62.29	258.82	72.99
22.19	3.160	107.50	34.17	209.90	63.02	259.48	73.13
22.74	3.343	110.21	35.02	211.36	63.40	260.14	73.22
24.89	4.089	113.73	36.16	212.79	63.74	260.27	73.19
27.61	5.063	116.48	37.01	216.02	64.53	260.80	73.31
28.02	5.221	119.89	38.11	217.45	64.88	261.83	73.46
31.49	6.514	122.75	38.98	218.86	65.22	264.49	73.92
33.47	7.286	126.02	40.01	222.18	66.03	265.24	74.04
35.20	7.953	128.97	40.92	223.73	66.41	270.84	75.18
38.93	9.413	132.12	41.88	225.25	66.80	271.58	75.32
39.69	9.692	135.17	42.79	228.38	67.54	274.48	75.74
44.05	11.39	138.22	43.71	230.05	67.96	275.64	75.94
44.67	11.65	141.35	44.67	231.67	68.44	275.87	76.17
49.23	13.44	144.30	45.55	234.62	69.09	277.08	76.36
49.34	13.49	147.53	46.48	236.25	69.53	278.72	76.68
53.99	15.28	150.57	47.35	237.84	70.02	281.13	77.21
54.32	15.39	153.70	48.21	240.75	70.69	283.29	77.63
54.92	15.60	157.01	49.16	242.49	71.19	284.78	77.91
56.48	16.19	160.06	49.99	243.92	71.64	287.02	78.44
58.27	16.88	163.45	50.95	246.02	72.26	289.42	78.88
60.24	17.63	166.42	51.73	247.06	72.51	290.89	79.16
62.16	18.40	169.73	52.66	248.10	72.79	292.98	79.67
64.60	19.35	172.64	53.42	249.14	73.17	295.48	80.13
66.58	20.10	175.86	54.33	249.84	73.51	296.94	80.39
69.29	21.04	178.86	55.07	250.32	73.52	299.00	80.88
71.55	21.84	182.02	55.92	250.98	73.74	301.47	81.39

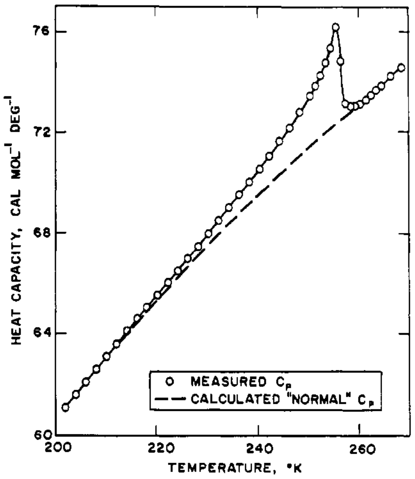

Figure 1. Enantiotropic transition peak

Table II. Molal Thermodynamic Properties of Triammonium Hydrogen Pyrophosphate Monohydrate

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$-\left(\frac{G° - H_0°}{T}\right)$, cal K^{-1}
5	0.0415	0.0136	0.0514	0.0033
10	0.3300	0.1100	0.8260	0.0274
15	1.113	0.3712	4.176	0.0928
20	2.456	0.8688	12.99	0.2195
25	4.113	1.589	29.29	0.4180
30	5.964	2.502	54.44	0.6869
35	7.868	3.564	89.01	1.020
40	9.817	4.741	133.2	1.411
45	11.78	6.011	187.2	1.851
50	13.73	7.353	251.0	2.333
60	17.57	10.20	407.5	3.404
70	21.30	13.19	602.0	4.587
80	24.93	16.27	833.2	5.854
90	28.46	19.41	1100	7.185
100	31.74	22.58	1401	8.566
110	34.96	25.76	1735	9.984
120	38.13	28.93	2100	11.43
130	41.23	32.11	2497	12.90
140	44.26	35.28	2925	14.38
150	47.18	38.43	3382	15.88
160	49.98	41.56	3868	17.39
170	52.73	44.68	4382	18.90
180	55.39	47.77	4922	20.42
190	57.99	50.83	5489	21.94
200	60.56	53.87	6082	23.46
210	63.09	56.89	6700	24.98
220	65.49	59.88	7343	26.50
230	67.98	62.84	8010	28.02
240	70.56	65.79	8703	29.53
250	73.44	68.73	9422	31.04
260	73.12	71.64	10164	32.54
270	74.96	74.43	10904	34.04
280	76.94	77.19	11664	35.54
290	79.01	79.93	12444	37.02
300	81.08	82.64	13244	38.50
273.15	75.56	75.30	11142	34.52
298.15	80.69	82.14	13094	38.22

energy calculated by integrating the cubic equation for the "normal" heat capacity over the same temperature range. The equation for "normal" heat capacity was derived by the method of least squares from 17 points between 170 and 210K and 24 points above 260K. The equation fitted the measured points with an average deviation of 0.04%. The second method was by determination of the area under the peak as drawn in Figure 1 by analytical integration from 200–246K and by graphical integration from 246–260K. The same cubic equation for "normal" heat capacity was used in both methods. Enthalpy of the peak was 56.2 cal mol^{-1} by the first method and 54.6 cal mol^{-1} by the second method. The value determined by the first method, which is a direct measurement, is preferred.

Heat capacity and derived values given in Table II include the contributions of the transition peak. Values in the region of the peak were determined by adding the peak contributions to "normal" values calculated by the equation for "normal" heat capacity described above. The accuracy of the enthalpy at 298.15K is estimated to be impaired by not more than 2 cal mol^{-1} which is within the estimated uncertainty. The accuracy of the heat capacity and of the entropy is not affected to the number of significant figures given in the table.

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