Low-Temperature Heat Capacity and Entropy of Pentaammonium Tripolyphosphate Monohydrate

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The low-temperature heat capacity of pentaammonium tripolyphosphate monohydrate, $(NH_4)_5P_3O_{10}\cdot H_2O$, was measured over the range 8–307 K by adiabatic calorimetry. The heat capacity, C_P; entropy, $S°$; and Planck function, $(G° - H_0°)/T$, at 298.15 K were calculated to be 119.0, 119.0, and −55.53 cal mol^{-1} deg^{-1}, respectively. The heat capacity showed only normal sigmate behavior.

In a continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of pentaamonium tripolyphosphate monohydrate, $(NH_4)_5P_3O_{10}\cdot H_2O$, was measured by adiabatic calorimetry over the temperature range 8–307 K. Related thermodynamic properties were derived.

Materials and Apparatus

Sodium tripolyphosphate that had been recrystallized three times was the starting material for preparation of the pentaammonium tripolyphosphate monohydrate. A solution of 50 g of the sodium salt dissolved in 350 ml of water then was passed through a column (2.5 × 80 cm) containing 300 g (dry weight) of the H^+ form of Amberlite IR-120 ion-exchange resin. The column was jacketed, and chilled water at 10 °C was passed through the jacket to prevent any hydrolysis. The effluent and washings (about 1 l.) were passed into 100 ml of 1:3 NH_4OH maintained at 10 °C by a chill plate. The ammonium tripolyphosphate was precipitated from the cold solution by the addition of methyl alcohol. The precipitate was filtered from the solution and washed with methyl alcohol twice. This precipitate then was dissolved in a minimum of water, and the pH of the solution was adjusted to 7.34 with aqueous ammonia. The salt was reprecipitated as before, and the mixture was stored at 4 °C for 3 h. The product then was filtered from the solution, washed with acetone three times, and spread to dry overnight at room conditions. Chemical anslysis of the product is compared with the theoretical composition in the tabulation.

	N	P_2O_5	Na	Free H_2O	Total H_2O
Analysis	19.26	59.10	0.01	0.3	5.00
Theoretical	19.36	58.96			4.99

Chromatograms of the product showed all the phosphorus in a single band with the correct R_f value for tripolyphosphate.

The bulk density of the material was very low so that only 23.1091 g or 0.063 992 mol could be placed in the calorimeter. The weight was corrected for buoyancy in air on the basis of a

Table I. Observed Heat Capacity (cal K^{-1} mol^{-1}) of Pentaammonium Tripolyphosphate Monohydrate

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
8.29	0.2172	51.76	21.71	140.98	64.08	234.15	98.70
8.83	0.3380	55.04	23.80	143.81	65.28	237.00	99.58
9.96	0.4819	55.78	24.28	147.34	66.74	239.98	100.79
10.22	0.4774	57.90	25.31	150.10	67.86	243.00	101.70
11.39	0.6558	60.07	26.42	153.53	69.18	245.94	102.66
11.50	0.6479	62.15	27.45	156.25	70.44	249.14	103.59
12.65	0.9082	64.83	28.83	159.61	71.65	252.05	104.63
12.83	1.077	67.54	30.10	162.26	72.79	255.22	105.57
13.82	1.343	70.14	31.25	165.56	74.01	258.09	106.52
14.31	1.529	73.08	32.49	168.40	75.10	261.23	107.40
15.30	1.784	75.74	33.80	171.64	76.35	264.08	108.35
16.03	2.100	79.50	35.79	174.68	77.60	267.39	109.18
17.17	2.501	81.54	36.89	177.86	78.80	270.20	110.06
18.09	2.890	84.92	38.61	180.82	79.99	271.34	110.41
19.33	3.401	88.65	40.47	183.97	80.97	272.91	110.89
20.40	3.873	91.39	41.69	186.88	82.11	274.74	111.33
21.87	4.526	94.52	43.12	190.22	83.27	276.26	111.96
23.19	5.199	97.46	44.50	193.08	84.46	279.22	112.95
24.83	5.993	100.42	45.94	196.06	85.45	282.09	113.76
26.32	6.841	103.57	47.41	197.65	86.06	285.21	114.81
28.06	7.734	106.72	48.86	200.78	87.27	288.05	115.61
29.67	8.595	109.72	50.24	203.92	88.50	291.35	116.65
31.64	9.657	113.05	51.80	207.00	89.58	294.16	117.63
33.46	10.70	115.94	53.07	210.10	90.64	297.42	118.89
35.57	11.92	119.14	54.50	213.14	91.52	301.02	119.81
37.56	13.00	122.22	55.89	216.20	92.78	304.82	120.76
39.79	14.26	125.31	57.31	219.21	93.67	307.02	121.07
41.98	15.45	128.57	58.77	222.31	94.75		
44.36	16.93	131.57	60.03	225.21	95.66		
46.76	18.36	134.73	61.42	228.26	96.96		
49.27	20.06	137.64	62.68	231.13	97.73		

Table II. Molal Thermodynamic Properties of Pentammonium Tripolyphosphate Monohydrate

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$-(G° - H_0°)/T$, cal K^{-1}
5	0.0485	0.0158	0.0604	0.0037
10	0.4480	0.1381	1.049	0.0332
15	1.691	0.5210	5.978	0.1225
20	3.690	1.271	19.25	0.3082
25	6.119	2.349	43.63	0.6035
30	8.800	3.700	80.82	1.006
35	11.53	5.261	131.7	1.498
40	14.36	6.984	196.4	2.075
45	17.38	8.848	275.6	2.722
50	20.55	10.84	370.4	3.434
60	26.46	15.13	606.5	5.022
70	31.15	19.57	894.9	6.782
80	36.03	24.04	1231	8.659
90	41.06	28.58	1616	10.62
100	45.72	33.15	2050	12.64
110	50.40	37.72	2531	14.72
120	54.90	42.30	3057	16.82
130	59.38	46.87	3629	18.96
140	63.67	51.43	4244	21.12
150	67.82	55.97	4902	23.29
160	71.86	60.47	5600	25.47
170	75.73	64.95	6388	27.37
180	79.62	69.39	7115	29.86
190	83.22	73.79	7929	32.05
200	86.99	78.15	8780	34.25
210	90.59	82.49	9669	36.44
220	93.95	86.78	10590	38.63
230	97.36	91.03	11550	40.82
240	100.7	95.24	12540	43.00
250	103.9	99.42	13560	45.17
260	107.1	103.6	14620	47.34
270	110.0	107.7	15700	49.50
280	113.1	111.7	16820	51.65
290	116.2	115.7	17960	53.79
300	119.6	119.7	19140	55.92
310	121.2	123.7	20350	58.04
273.15	111.0	108.9	16050	50.18
298.15	119.0	119.0	18920	55.53

density of 1.61 g cm^{-3} (*1*), and the gram formula weight was taken as 361.1236. The heat capacity of the sample ranged from 19% of the total at 10 K to 41% at 300 K. Air in the calorimeter was removed and replaced with the same mass of helium used in measurements on the empty calorimeter; the helium facilitated heat transfer and thermal equilibrium.

The adiabatic calorimeter and the method of operation have been described previously (*4*), and the overall accuracy of our technique has been reported (*2*). The defined calorie was taken as 4.1840 absolute J, and the ice point as 273.15 K. The measured heat capacities were corrected for curvature (*3*) and for a small difference in the amount of eutectic solder relative to the empty calorimeter. Because small temperature differences were important, temperatures were measured to four decimal places, but these were rounded to two decimal places in the final tabulation. The heat capacities below 10 K were read from a large scale plot of C_p/T against T^2 that extrapolated smoothly to 0 K. Observed molal heat capacities are shown in Table I. Smoothed heat capacities and derived functions at round values of temperature are shown in Table II.

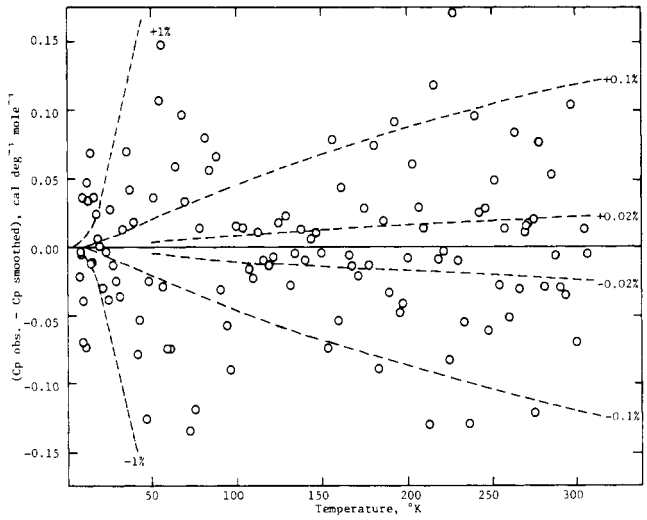

Figure 1. Deviations of observed heat capacities from smoothed values of pentaammonium tripolyphosphate monohydrate.

The heat capacity curve had the normal sigmate shape and showed no thermal anomalies except in the temperature range 270–273 K where a slight peak indicated the presence of "free" water. If the energy in the peak is due only to the enthalpy of fusion of water, it indicates the presence of less than 0.01% free water. This, however, ignores the enthalpy of solution of the salt in the water. The deviations of the observed heat capacity values from the smoothed curve are shown in Figure 1.

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Received for review March 8, 1976. Accepted May 27, 1976.