Low-Temperature Heat Capacity and Entropy of Diammonium Orthophosphate

Basil B. Luff,* Robert B. Reed, and Robert H. Nash
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Alabama 35660

The low-temperature heat capacity of diammonium orthophosphate, $(NH_4)_2HPO_4$, was measured over the temperature range 8–316 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 42.82, 42.30, and −19.53 cal mol^{-1} deg^{-1}, respectively. The accuracy of the measurements was established by comparing measured values of the heat capacity of pure benzoic acid with those reported by the National Bureau of Standards.

In the continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of diammonium orthophosphate, $(NH_4)_2HPO_4$, was measured by adiabatic calorimetry over the temperature range 8–316 K. Related thermodynamic properties were derived.

Materials and Apparatus

Reagent-grade diammonium phosphate was dissolved in distilled water to make a 71% solution and the solution was filtered. The stirred filtrate was treated dropwise with methanol (25 parts of methanol per 100 parts of solution) to precipitate diammonium phosphate. The precipitate then was recrystallized by the same procedure to give a material that had the correct composition but contained large voids in the crystals.

The purified diammonium phosphate was used to prepare a 21% solution with distilled water and the pH was adjusted to 8.05 (*2*), the ambient temperature was maintained by cooling, methanol was dropped into the solution to the point of cloudiness, and the solution was placed in a refrigerator at about 0 °C for crystallization. The crystals were filtered off and the procedure was repeated with the filtrate to obtain a second crop of crystals. The crystals were washed on the filter with acetone and air-dried. The first crop of crystals contained voids, but the second crop was relatively free of voids.

Chemical analysis showed the material to contain 21.2% N, 53.8% P_2O_5, and 0.05% H_2O (stoichiometric: 21.21% N, 53.74% P_2O_5). Petrographic examination showed it to be homogeneous as moderately large, well-developed crystals. Inclusions, which appeared to be both air and mother liquor, made up about 0.5% of the total volume of the material. Preliminary tests showed that the material lost weight slowly over P_2O_5 at 10^{-3} mmHg; the calorimeter was filled and dried under this pressure for 5 h.

The calorimeter charge was 59.9555 g or 0.454 014 mol of $(NH_4)_2HPO_4$; the weight was corrected for bouyancy in air on the basis of a density of 1.61 g cm^{-3} (*4*), and the gram formula weight was taken as 132.0565. Its heat capacity ranged from 32% of the total at 10 K to 64% at 300 K. The 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 (*5*). 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 capacity and derived functions at round values of temper-

Table I. Observed Heat Capacity (cal K^{-1} mol^{-1}) of Diammonium Orthophosphate

T, K	C_p	T, K	C_p	T, K	C_p
8.70	0.1479	89.96	14.66	220.58	33.85
8.73	0.0915	92.61	15.12	225.07	34.40
9.85	0.1308	95.76	15.65	226.81	34.60
10.10	0.1352	98.74	16.15	231.23	35.15
11.25	0.1893	101.72	16.66	232.95	35.37
11.68	0.2018	105.01	17.21	237.30	35.89
12.97	0.3038	107.84	17.69	239.12	36.12
13.66	0.3624	111.19	18.24	243.41	36.61
14.96	0.4936	113.90	18.69	245.33	36.85
15.80	0.5828	117.31	19.25	248.34	37.20
17.10	0.7377	119.91	19.67	249.56	37.34
18.04	0.8597	123.39	20.23	251.46	37.55
19.48	1.058	125.90	20.62	254.43	37.90
20.63	1.227	129.43	21.20	255.62	38.02
22.17	1.474	131.86	21.60	257.50	38.25
24.02	1.797	135.64	22.17	260.44	38.58
25.06	1.970	137.99	22.55	261.61	38.77
27.69	2.443	141.84	23.17	263.60	38.94
28.20	2.535	144.29	23.55	266.50	39.29
31.25	3.122	148.02	24.14	267.64	39.42
31.66	3.204	150.58	24.49	269.73	39.64
35.00	3.851	154.20	25.01	270.54	39.76
35.35	3.920	156.87	25.39	272.48	39.98
38.93	4.640	160.38	25.91	273.72	40.13
39.22	4.696	163.16	26.30	274.42	40.16
43.17	5.486	166.58	26.79	275.07	40.21
43.42	5.538	169.45	27.20	275.79	40.32
47.76	6.457	172.79	27.67	276.25	40.37
47.98	6.508	175.76	28.08	277.25	40.45
52.55	7.511	179.02	28.52	279.87	40.83
52.73	7.549	181.93	28.91	282.23	41.07
55.78	8.283	185.12	29.36	283.22	41.12
57.02	8.570	188.13	29.75	285.93	41.43
59.17	9.045	191.24	30.16	288.26	41.74
61.59	9.517	194.35	30.57	289.24	41.80
63.91	9.985	196.06	30.79	292.04	42.16
66.48	10.43	196.23	30.81	294.33	42.40
68.94	10.85	197.40	30.95	295.31	42.47
71.64	11.30	200.86	31.41	298.08	42.84
74.37	11.80	202.13	31.57	299.16	42.90
77.32	12.34	206.85	32.16	300.83	43.10
80.12	12.87	208.24	32.34	303.96	43.47
80.78	13.00	212.88	32.91	306.99	43.76
84.34	13.66	214.39	33.10	310.09	44.09
86.63	14.08	218.96	33.65	313.07	44.38
				316.14	44.68

Table II. Molal Thermodynamic Properties of Diammonium Orthophosphate

T, K	C_p, cal K^{-1}	S, cal K^{-1}	$H^\circ - H_0^\circ$, cal	$-(G^\circ - H_0^\circ)/T$, cal K^{-1}
5	0.0152	0.0051	0.0191	0.0013
10	0.1308	0.0420	0.3166	0.0103
15	0.4972	0.1538	1.756	0.0367
20	1.128	0.3785	5.735	0.0918
25	1.952	0.7158	13.37	0.1811
30	2.883	1.153	25.43	0.3054
35	3.848	1.670	42.25	0.4626
40	4.846	2.248	63.98	0.6490
45	5.872	2.878	90.76	0.8614
50	6.950	3.552	122.8	1.096
60	9.205	5.021	203.7	1.626
70	11.03	6.581	305.1	2.222
80	12.85	8.172	424.5	2.866
90	14.67	9.792	562.2	3.545
100	16.37	11.43	717.4	4.252
110	18.04	13.06	889.5	4.978
120	19.68	14.71	1078	5.720
130	21.29	16.34	1283	6.475
140	22.87	17.98	1504	7.238
150	24.41	19.61	1740	8.009
160	25.85	21.23	1992	8.785
170	27.28	22.84	2257	9.564
180	28.66	24.44	2537	10.35
190	30.00	26.03	2830	11.13
200	31.29	27.60	3137	11.91
210	32.56	29.16	3456	12.70
220	33.78	30.70	3788	13.48
230	35.00	32.23	4132	14.26
240	36.22	33.74	4488	15.04
250	37.39	35.24	4856	15.82
260	38.55	36.73	5236	16.60
270	39.68	38.21	5627	17.37
280	40.79	39.67	6029	18.14
290	41.91	41.12	6443	18.91
300	43.02	42.56	6867	19.67
310	44.09	43.99	7303	20.43
273.15	40.03	38.67	5752	17.61
298.15	42.82	42.30	6788	19.53

ature are shown in Table II. The deviations of the observed heat capacity values from the smoothed curve are shown in Figure 1.

Heat Capacity of a Standard Sample of Benzoic Acid

In order to verify the overall accuracy of our technique, measurements were made on the heat capacity of pure benzoic acid made available by the National Bureau of Standards in conjunction with the program of the Calorimetry Conference. A sample of 60.6145 g (in vacuo) of benzoic acid was utilized. The results are compared with the values reported by Ginnings and Furukawa (*1*) in Table III.

Literature Cited

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Table III. Heat Capacity of Benzoic Acid

T, K	C_p, cal K^{-1} mol^{-1} NBS	C_p, cal K^{-1} mol^{-1} This laboratory
10	0.4596	0.5110
20	2.629	2.648
30	5.239	5.282
40	7.572	7.593
50	9.441	9.460
60	10.97	10.98
70	12.25	12.24
80	13.35	13.35
90	14.37	14.38
100	15.28	15.29
110	16.18	16.19
120	17.09	17.09
130	17.99	17.99
140	18.90	18.89
150	19.81	19.81
160	20.73	20.74
170	21.68	21.68
180	22.63	22.64
190	23.60	23.60
200	24.59	24.60
210	25.60	25.60
220	26.62	26.62
230	27.67	27.66
240	28.73	28.74
250	29.81	29.81
260	30.89	30.89
270	31.98	31.98
280	33.08	33.06
290	34.18	34.17
300	35.29	35.27
310	36.40	36.39

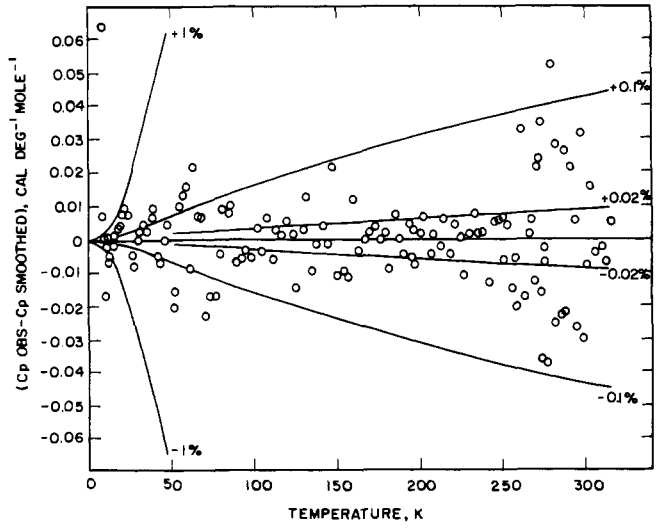

Figure 1. Deviations of observed heat capacities from smoothed values for diammonium orthophosphate.

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