Low-Temperature Heat Capacity and Entropy of Phosphoryl Triamide

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The low-temperature heat capacity of phosphoryl triamide, $PO(NH_2)_3$, was measured over the range 10–320°K by adiabatic calorimetry. The heat capacity, C_p, entropy, $S°$, and Gibbs function, $(G° - H_o°)T$, at 298.15°K were calculated to be 31.32, 30.22, and −14.13 cal mol^{-1} deg^{-1}. The heat capacity showed only normal sigmate behavior.

In the continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of phosphoryl triamide, $PO(NH_2)_3$, was measured over the temperature range 10–320°K by adiabatic calorimetry.

Phosphoryl triamide is of interest as an experimental fertilizer material because it has good physical properties and has a high plant-nutrient content—it contains, by weight, 44.21% N and 32.59% P or 74.68% P_2O_5 equivalent. Greenhouse tests (*6*) have shown it to be as effective per unit of phosphorus and nitrogen as standard fertilizer materials.

MATERIALS AND APPARATUS

The phosphoryl triamide was prepared by the reaction

$$POCl_3 + 6NH_3 = PO(NH_2)_3 + 3NH_4Cl \qquad (1)$$

A 2-liter three-necked flask equipped with a power stirrer, Dry Ice–acetone-cooled reflux condenser, addition funnel, and a gas inlet tube was submerged in a Dry Ice–acetone bath and charged with 1000 ml of liquid ammonia. A solution of 155 ml (1.69 mole) of $POCl_3$ in 200 ml of chloroform was added dropwise over 4 hr. The bath was then removed and the mixture was allowed to reflux for 2.5 hr, after which excess ammonia was allowed to escape overnight. The residue was refluxed three times with a mixture of 250 ml of diethylamine and 750 ml of chloroform to convert the ammonium chloride into a compound soluble in chloroform by the reaction

$$NH_4Cl + (C_2H_5)_2NH = (C_2H_5)_2NH_2Cl + NH_3 \qquad (2)$$

The poorly crystallized phosphoryl triamide, insoluble in chloroform, was purified by dissolving 146 grams of the crude product in 150 ml of distilled water at 45°C and immediately filtering the solution into a flask submerged in an ice bath. The mixture was stirred for 30 min and then filtered, and the crystals were washed quickly with 50 ml of ice water, 250 ml of cold methanol, and finally with 200 ml of diethyl ether.

The recrystallized material was dried in a stream of nitrogen. Its X-ray diffraction pattern showed it to be well-crystallized $PO(NH_2)_3$ with properties in agreement with published values (*1*); no other phases were detected. Microscopic examination showed the material to be homogeneous, well-crystallized $PO(NH_2)_3$ with optical properties in agreement with earlier preparations whose identity had been established by X-ray. The average crystal size was 200 × 300 μm with no evidence of surface alteration. Paper chromatograms, made in both Ebel's basic (*2*) and Quimby's neutral (*4*) solvents, showed that, within the limits of detection of the method, no second phase was present. Results of chemical analysis were 32.4% P, 44.0% N, and no more than 0.1% H_2O (stoichiometric, 32.59% P, 44.21% N).

Preliminary tests showed the phosphoryl triamide to be stable at a pressure of 10^{-8} torr. The calorimeter then was charged with 59.6795 grams or 0.627933 mole of $PO(NH_2)_3$; the weight was corrected for buoyancy in air on the basis of a density of 1.581 grams/cc (*1*), and the gram formula weight was taken as 95.0411. 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 calorimeter and adiabatic shield (*3, 7*) are similar to those of Scott et al. (*5*). The copper calorimeter was about 5 cm in diameter and 5 cm deep. Vertical heat-distributing vanes were soldered between the outside wall and the thermometer well. A Leeds & Northrup capsule-type platinum resistance thermometer was soldered in a small copper spool, between the end flanges of which a thin-walled Monel jacket was silver soldered. A 50-Ω Constantan heater was wound on the Monel tube, and the heater-thermometer assembly was immersed in Woods metal in the well. Three chromel-Constantan differential thermocouples were located between the top, side, and bottom, respectively, of the calorimeter and corresponding positions on the adiabatic shield. The bottom differential couple had three junctions. The potential leads to the heater were divided between the calorimeter bottom and the shield bottom to minimize loss of measured energy, as recommended by Scott et al. (*5*).

The calorimeter was filled through a 1-cm opening in the cap. A $^1/_8$-in. copper tube was attached to the opening by means of solder and an annular copper adapter. After evacuating the calorimeter and adding a small amount of helium to improve the heat transfer, the copper tube was pinched closed, cut, and soldered close to the calorimeter cap. The calorimeter was suspended in the adiabatic shield by nylon thread. Additions of electrical energy to the calorimeter provided temperature increments of about 10% of the absolute temperature but not more than 10°K.

An automatic shield-control system was used for all measurements. Energy was supplied to the calorimeter by a constant-current device (Princeton Applied Research, Model TC-100.2AR) and the voltage was measured by a digital voltmeter (Hewlett-Packard Dymec, Model 2401C). Energy measurements with this system were compared with those made with the previously used battery supply and Hi-Wenner potentiometer. The potentiometer, voltbox, and standard resistors were calibrated by the Redstone Arsenal, Huntsville, Ala., and are traceable to the National Bureau of Standards; measurements by the two systems agreed within 0.02%. The platinum resistance thermometer was calibrated by the National Bureau of Standards, its R_o value was periodically redetermined by measurement of its resistance at the triple point

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Table I. Observed Heat Capacity of Phosphoryl Triamide, Cal Deg^{-1} Mol^{-1}

T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p
8.25	0.0856	63.24	7.319	158.28	17.43	257.71	27.47
8.37	0.0693	65.68	7.624	161.70	17.80	260.60	27.74
9.98	0.1159	68.08	7.897	164.25	18.06	263.63	28.04
10.12	0.1237	70.68	8.180	167.41	18.41	266.61	28.31
11.90	0.1910	73.24	8.460	170.25	18.69	268.09	28.46
12.27	0.2086	76.14	8.788	173.50	19.05	270.11	28.65
13.95	0.3195	78.97	9.116	176.28	19.33	271.11	28.79
14.87	0.3922	79.91	9.229	179.45	19.68	272.11	28.88
16.14	0.4980	82.11	9.465	182.17	19.95	272.66	28.91
17.19	0.6012	84.92	9.781	185.27	20.28	273.11	29.00
18.36	0.7268	87.56	10.06	188.10	20.56	273.64	28.96
19.50	0.8535	90.48	10.37	191.13	20.90	274.11	29.05
20.92	1.023	93.25	10.63	194.06	21.16	274.52	29.04
22.26	1.204	96.28	10.95	196.29	21.37	274.64	29.08
23.94	1.443	99.17	11.24	198.56	21.62	275.64	29.18
25.44	1.665	102.05	11.55	200.88	21.84	276.13	29.21
27.28	1.948	105.06	11.84	203.87	22.17	276.75	29.30
28.90	2.201	108.05	12.16	206.90	22.47	278.73	29.48
30.84	2.518	110.93	12.45	209.84	22.77	280.32	29.68
32.55	2.801	114.02	12.78	212.81	23.07	282.17	29.82
34.58	3.141	117.02	13.08	215.84	23.37	284.61	30.04
36.57	3.476	119.98	13.41	218.77	23.66	286.30	30.26
39.05	3.877	123.08	13.72	221.88	23.97	288.24	30.39
41.06	4.199	125.94	14.04	224.76	24.24	290.54	30.61
43.99	4.652	128.94	14.33	227.82	24.55	292.31	30.81
45.86	4.948	131.89	14.67	230.80	24.83	294.24	30.94
48.60	5.364	134.80	14.95	233.80	25.15	296.51	31.15
50.82	5.692	138.05	15.32	236.87	25.42	298.25	31.37
53.22	6.013	140.87	15.59	239.82	25.75	300.16	31.51
53.96	6.122	144.21	15.97	242.84	26.02	301.66	31.62
55.02	6.248	146.95	16.24	245.74	26.33	302.40	31.71
56.34	6.419	150.20	16.60	248.72	26.59	307.26	32.15
58.77	6.736	152.86	16.86	251.71	26.90	312.79	32.66
60.81	7.001	156.02	17.20	254.64	27.17	318.25	33.16

of water and adjustment of the results to the ice point, 273.15°K. The defined calorie was taken as 4.1840 abs J.

The measured heat capacities were corrected for curvature (*5*) and for a small difference between the mass of eutectic solder on the full calorimeter and that on the empty calorimeter. Because small temperature differences were important, temperatures were measured to four decimal places, but 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. Heat capacity and derived functions at round values of temperature are shown in Table II. The heat capacity curve had the normal sigmate shape and showed no thermal anomaly. The average deviation of the observed heat capacity values from the smoothed curve was ± 0.004 cal deg^{-1} mol^{-1} below 20°K and ± 0.010 cal deg^{-1} mol^{-1} from 20–320°K. The uncertainty in the heat capacity is estimated to be 0.1%. At 10°K the heat capacity of the sample was 38% of that of the loaded calorimeter, and at 320°K it was 65%.

Table II. Molal Thermodynamic Properties of Phosphoryl Triamide

T, °K	C_p, cal deg^{-1}	$S°$, cal deg^{-1}	$H° - H_o°$, cal	$-\left(\frac{G° - H_o°}{T}\right)$
5	0.015	0.005	0.019	0.001
10	0.119	0.040	0.297	0.010
15	0.400	0.134	1.504	0.033
20	0.912	0.314	4.707	0.079
25	1.595	0.588	10.90	0.152
30	2.384	0.948	20.83	0.254
35	3.206	1.377	34.80	0.383
40	4.028	1.859	52.89	0.537
45	4.817	2.379	75.02	0.712
50	5.563	2.926	101.0	0.906
60	6.902	4.061	163.5	1.337
70	8.109	5.217	238.6	1.808
80	9.229	6.373	325.3	2.306
90	10.31	7.524	423.1	2.823
100	11.33	8.663	531.3	3.350
110	12.35	9.790	649.7	3.884
120	13.40	10.91	778.4	4.423
130	14.46	12.02	917.7	4.965
140	15.51	13.13	1068	5.509
150	16.57	14.24	1228	6.054
160	17.61	15.34	1399	6.600
170	18.67	16.44	1580	7.147
180	19.73	17.54	1772	7.694
190	20.76	18.64	1975	8.241
200	21.76	19.73	2187	8.788
210	22.79	20.81	2410	9.335
220	23.78	21.90	2643	9.881
230	24.76	22.97	2886	10.43
240	25.75	24.05	3138	10.97
250	26.73	25.12	3401	11.52
260	27.69	26.19	3673	12.06
270	28.65	27.25	3955	12.60
280	29.61	28.31	4246	13.15
290	30.57	29.36	4547	13.69
300	31.49	30.42	4857	14.23
310	32.38	31.46	5177	14.77
320	33.33	32.51	5505	15.30
273.15	28.95	27.58	4045	12.77
298.15	31.32	30.22	4799	14.13

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