NOMENCLATURE

$\bar{P}$ = the net pressure drop across the magnesium-salt interface and was assumed equal to the total pressure applied to the magnesium phase (sum of the gas pressure and hydrostatic pressure due to the magnesium head) minus the hydrostatic pressure of the salt phase at the bore tip, grams/cm^2
R = radius of the bore, cm
g = gravity, cm/sec^2
h = $\bar{P}/(\rho_s - \rho_{Mg})$, cm

Greek Letters

γ = the magnesium-salt interfacial tension, dyn/cm
ρ_s = density of the salt phase, grams/cm^3
ρ_{Mg} = density of the molten magnesium, grams per cm^3

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Low-Temperature Heat Capacity and Entropy of Ammonium Tetrametaphosphate

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The low-temperature heat capacity of ammonium tetrametaphosphate, $(NH_4PO_3)_4$, was measured over the temperature range 10–300° K. The heat capacity, C_p; entropy, $S°$; and Gibbs function, $(G° - H°_0)/T$, at 298.15° K are 110.23, 111.14, and −51.97 cal deg^{-1} mole^{-1}, respectively. The small upward shift in heat capacity over the range 200–300° K that occurred during the course of the measurements is thought to be the result of an unidentified monotropic transition of the material.

In a continuing program of measurement of thermodynamic and thermochemical properties of materials of interest in fertilizer technology, the heat capacity of ammonium tetrametaphosphate $(NH_4PO_3)_4$, was measured over the temperature range 10-300° K by adiabatic calorimetry.

Ammonium tetrametaphosphate is of interest in fertilizer technology because it has a moderately higher nutrient content than ammonium polyphosphates. In greenhouse tests, granular ammonium tetrametaphosphate produced significantly higher yields of maize forage than an equivalent amount of concentrated superphosphate. The degradation of tetrametaphosphate to orthophosphate in soils has not been described, but the results of the greenhouse test indicate that the cyclic form and its intermediate degradation products may be more effective sources of phosphorus than the usual orthophosphates.

MATERIALS AND APPARATUS

The calorimeter charge of ammonium tetrametaphosphate was prepared by metathesis of copper tetrametaphosphate and ammonium sulfide. The copper tetrametaphosphate was prepared by the method of Thilo and Rätz (*7*).

$$2CuO + 4H_3PO_4 = Cu_2(PO_3)_4 + 6H_2O \qquad (1)$$

Copper oxide (160 grams) was mixed with reagent phosphoric acid (246 ml, 85% H_3PO_4) to form a blue paste. The mixture was heated in a silica dish at 400° C for 8 hr to produce a light green solid, $Cu_2(PO_3)_4$.

The copper tetrametaphosphate was converted to ammonium tetrametaphosphate by the method of Warschauer (*10*). The copper salt (360 grams) was crushed, washed with water, and added in small portions to 810 ml of a stirred, cooled 20% $(NH_4)_2S$ solution to effect the metathesis

$$Cu_2(PO_3)_4 + 2(NH_4)_2S = (NH_4PO_3)_4 + 2CuS \qquad (2)$$

The precipitated copper sulfide was filtered off and the ammonium tetrametaphosphate (182 grams) was crystallized by addition of alcohol to the solution.

Recrystallization of the crude (95%) ammonium tetrametaphosphate at room temperature by adding methanol to its aqueous solution increased its purity only slightly; of its phosphate, 1% was present as ortho-, 1% as pyro-, and 2% as tripolyphosphate. Chromatographic analysis of the mother liquor showed that there had been considerable hydrolysis of the tetrametaphosphate; the phosphate was distributed as tetrameta- 73%, ortho- 2%, pyro- 5%, tripoly- 16%, tetrapoly- 3%, and more highly condensed phosphates 2%.

The recrystallization was repeated at 0° C to minimize hydrolysis. The crude $(NH_4PO_3)_4$ (152 grams) was dissolved in 220 ml of water at 0° C, the pH was adjusted to 7.0

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Table I. Observed Heat Capacity of Ammonium Tetrametaphosphate $(NH_4PO_3)_4$, Cal Deg^{-1} Mol^{-1}

T, °K	C_p	T, °K	C_p	T, °K	C_p
9.08	0.705	92.82	38.74	216.4	86.91
9.98	0.726	95.96	40.23	218.7	87.63
10.46	0.881	99.04	41.62	222.6	88.80
11.26	1.015	102.1	43.09	224.9	89.52
11.87	1.241	105.2	44.46	228.9	90.67
12.92	1.510	108.2	45.87	231.2	91.37
13.65	1.739	111.3	47.21	235.0	92.53
15.32	2.339	114.4	48.68	237.3	93.22
16.39	2.830	117.6	49.99	241.1	94.37
18.14	3.459	120.7	51.47	243.5	95.06
20.39	4.367	123.8	52.83	247.3	96.20
21.46	4.832	126.9	54.21	249.8	96.90
25.11	6.442	130.0	55.49	253.5	98.00
26.75	7.181	133.1	56.87	255.9	98.60
30.58	8.925	136.2	58.12	259.7	99.73
33.06	10.09	139.3	59.47	262.0	100.32
36.00	11.48	142.4	60.70	265.8	101.38
38.89	12.86	145.5	61.99	268.2	102.03
41.24	13.93	148.6	63.20	272.1	103.20
44.34	15.42	151.7	64.46	274.2	103.68
46.77	16.60	154.8	65.64	274.7	103.83
49.83	18.07	157.9	66.89	276.2	104.29
52.30	19.26	161.1	68.04	276.3	104.35
53.86	19.97	164.2	69.24	278.2	104.83
54.89	20.43	167.3	70.38	279.4	105.18
56.62	21.23	170.4	71.58	281.4	105.77
58.51	22.14	173.6	72.68	282.4	106.00
60.40	23.06	176.7	73.83	284.3	106.56
62.69	24.22	179.8	74.87	285.5	106.83
65.06	25.43	182.9	75.98	287.5	107.40
67.42	26.56	186.0	77.03	288.5	107.62
70.34	27.89	189.1	78.14	290.4	108.17
72.72	28.99	192.3	79.16	291.6	108.43
75.63	30.41	195.6	80.23	293.5	108.96
78.05	31.63	197.6	80.87	294.5	109.23
79.16	32.18	199.9	81.66	296.4	109.80
80.59	32.90	204.0	82.93	297.6	110.06
83.73	34.47	206.2	83.73	299.5	110.57
86.78	35.95	210.2	84.97	300.4	110.83
89.83	37.38	212.5	85.72		

Table II. Molal Thermodynamic Properties of Ammonium Tetrametaphosphate

T, °K	C_p, cal/°K	$S°$, cal/°K	$H° - H°_0$, cal	$-\left(\frac{G° - H°_0}{T}\right)$
5	0.1110	0.0381	0.1423	0.0096
10	0.7680	0.2769	2.048	0.0722
15	2.223	0.8320	9.136	0.2230
20	4.198	1.739	25.13	0.4824
25	6.380	2.907	51.51	0.8468
30	8.681	4.273	89.14	1.302
35	11.00	5.785	138.3	1.833
40	13.36	7.407	199.2	2.427
45	15.75	9.118	272.0	3.075
50	18.14	10.90	356.7	3.768
60	22.89	14.63	561.8	5.265
70	27.74	18.52	814.9	6.879
80	32.60	22.54	1117	8.584
90	37.46	26.66	1467	10.36
100	42.08	30.85	1865	12.20
110	46.65	35.08	2309	14.09
120	51.15	39.33	2798	16.01
130	55.52	43.60	3331	17.97
140	59.74	47.87	3908	19.95
150	63.78	52.13	4525	21.96
160	67.66	56.37	5183	23.98
170	71.39	60.58	5878	26.00
180	74.96	64.76	6610	28.04
190	78.41	68.91	7377	30.08
200	81.67	73.01	8177	32.13
210	84.92	77.08	9010	34.17
220	88.03	81.10	9875	36.21
230	91.02	85.08	10,770	38.25
240	94.03	89.02	11,696	40.29
250	96.96	92.92	12,651	42.31
260	99.77	96.77	13,635	44.33
270	102.54	100.59	14,646	46.35
280	105.35	104.37	15,686	48.35
290	108.04	108.12	16,753	50.35
300	110.73	111.82	17,846	52.34
273.15	103.43	101.79	14,970	46.98
298.15	110.23	111.14	17,642	51.97

with ammonium hydroxide, and the solution was stirred at 0° C while an equal volume of methanol was dripped into it. The precipitate was filtered off and washed successively with 50% methanol, anhydrous methanol, and diethyl ether, and the solvent was removed by aeration with dry nitrogen. The crystals (136 grams) were well developed and homogeneous.

The product was examined chromatographically by spotting 50 μl of its solution (500 μg) on Whatman No. 31 extra-heavy paper, and developing the chromatograms for 24 hr at 0° C with both the acid and the basic solvents of Ebel (*2*). Each chromatogram showed only a single band, that corresponding to $(NH_4PO_3)_4$, and analysis of the chromatograms showed that 99.7–100.0% of the total phosphorus was present as tetrametaphosphate.

The optical (*5*), X-ray powder diffraction (*1*), and infrared (*6*) properties of the product agreed with those established for ammonium tetrametaphosphate. Results of chemical analysis were 31.97% P and 14.43% N (stoichiometric: 31.93% P, 14.45% N). The calorimeter charge was 59.9297 grams *in vacuo* or 0.154441 mole (sp gr, 1.811; gram formula wt, 388.0423).

The low-temperature calorimeter has been described (*3*, *9*). The 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, volt-box, 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_0 value was periodically redetermined in a triple-point-of-water cell.

The defined calorie was taken as 4.1840 abs J, the ice point as 273.15° K. The measured heat capacities were corrected for curvature and for a small difference in the amount of 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 smoothed (*4*) values for heat capacity was 0.029 cal deg^{-1} mol^{-1} below 20° K and 0.023 cal deg^{-1} mol^{-1} above 20° K. This corresponds to an average deviation of 0.055% for all values above 20° K. The uncertainty in the heat capacity is estimated to be 0.1%.

DISCUSSION

The small upward shift in the measured heat capacity values over the range 200–300° K is believed to be caused by an unidentified monotropic transition of the calorimeter charge. Initially measured heat capacities in the range 195–

300° K were lower than final reproducible values by an amount that increased progressively from 0 at about 190° K to 0.046 cal deg^{-1} $sample^{-1}$ (0.299 cal deg^{-1} mol^{-1}) at 300° K. A low-energy transition was suspected, but after 5 days of equilibration at 300° K, measurements from 273–300° K reproduced the higher curve. Additional measurements from 195–273° K and again from 273–300° K also reproduced the higher curve. After further equilibration for 14 days at 300° K, the higher curve was again reproduced from 273–300° K.

Auxiliary tests were made on a sample taken from the unused portion of the material that formed the calorimeter charge. After petrographic, X-ray, and infrared examination showed it to be the same as it was before charging the calorimeter, the sample was equilibrated at 77° K for 10 days. No change in its properties could be detected. The material in the calorimeter was removed and its petrographic, X-ray, and infrared properties were found to be the same as they were originally. Because there was no direct evidence of the presence of more than one form of the tetrametaphosphate in the calorimeter sample, it can only be assumed that the sample contained a small amount of a second form that underwent a monotropic transition.

The discussion by Van Wazer (*8*) of the boat and chair forms of ammonium tetrametaphosphate supports this possibility. A second form of $(NH_4PO_3)_4$ was prepared by slow neutralization of a cold aqueous solution of tetrametaphosphoric acid with a mixture of ammonium hydroxide and ethanol. Addition of acetone precipitated a mixture of triammonium hydrogen tetrametaphosphate and an unidentified gummy material. Addition of alcoholic ammonium hydroxide to the filtrate precipitated a crystalline material with a composition between that of $(NH_4PO_3)_4$ and $(NH_4)_3H(PO_3)_4 \cdot H_2O$. This form had optical and X-ray properties different from those of the usual form, but on recrystallization from water it appeared as the usual form. The new form is presumed to be the boat form described by Van Wazer (*8*). Complete neutralization of the filtrate and addition of more ethanol produced the usual form of $(NH_4PO_3)_4$.

Earlier measurements showed very similar thermal properties for an ammonium tetrametaphosphate sample found by paper chromatography to contain 1% orthophosphate, 1% pyrophosphate, and 2% tripolyphosphate. It also originally showed a low-heat capacity curve and, after the same temperature cycles, a reproducible higher curve. Cubic equations were fitted to the high and low curves of each sample. The differences between the high and low curve were integrated from 195–300° K, and the calculated enthalpy changes were nearly the same for the two samples—17 cal mol^{-1} for the pure sample and 11 cal mol^{-1} for the impure sample. The increase in enthalpy between 190° and 300° K is 10,469 cal mol^{-1}. The difference between 17 and 11 cal is 0.06% of the enthalpy increase and may be assigned to experimental error. This similar behavior of two different samples supports the assumption that a change in form occurred during the measurements. Similarity of the two samples is shown also by their thermal properties at 298.15° K; values of C_p, S°, and $H^\circ - H_0^\circ$ are 110.2, 111.1, and 17,642 for the pure sample and 110.4, 111.0, and 17,637 for the impure sample.

Measurements on the impure sample are not reported. Observed molal heat capacities for the pure sample are shown in Table I. The heat capacities below 10° K were read at 1° K intervals from a large-scale plot of C_p/T vs. T^2 over the range 10–25° K that extrapolated smoothly to 0° K. A fourth-power analytical expression derived by the method of least squares gave essentially the same results. The smoothed heat capacities and the derived properties are given in Table II.

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Thermodynamic Study of Water and Propylene Oxide Solutions

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The excess enthalpies and volumes of mixing of water and propylene oxide have been measured at 5° and 25° C over the composition regions where the components are fully miscible. The mutual solubilities of the two components have also been restudied and the upper consulate has been temperature determined.

The present work forms part of a program concerned with the thermodynamic properties of aqueous solutions of some cyclic ethers (*5*). The system water and propylene oxide shows partial miscibility and the solid-liquid, liquid-liquid, and liquid-vapor equilibria have been previously studied (*9*). Freezing point measurements (*9*) indicate weak hydrate formation, which is confirmed by low frequency dielectric studies (*4*) corresponding to the formula propylene oxide–17 H_2O. The mutual solubilities of the two components have not previously been reported above the normal boiling point, 35° C, of propylene oxide, and the present measurements complete the miscibility curve. The regions of complete miscibility are sufficiently large to allow the excess enthalpies and volumes to be determined over a

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