Table III. Viscosities at 35° C.

X_A	X_B	$\nu \times 10^2$ Exptl.	$\nu \times 10^2$ Calcd. (*1*)	$\nu \times 10^2$ Calcd. (2)
Methyl Ethyl Ketone (A)-1-Butanol (B)				
$w_{\text{visc.}}$ = 422.485 cal. per gram mole; ν_{AB} = 0.6907; ν_{BA} = 1.1640				
0.0996	0.9004	1.9960	1.9782	...
0.2002	0.7998	1.5570	1.5946	1.6210
0.2999	0.7001	1.3245	1.2999	1.3450
0.4004	0.5996	1.0619	1.0686	1.1110
0.5002	0.4998	0.9029	...	0.9385
0.5998	0.4002	0.8002	0.7689	0.8072
0.6998	0.3002	0.6796	0.6635	0.6996
0.7997	0.2003	0.5966	0.5805	0.6039
0.8998	0.1002	0.5366	0.5149	...
Methyl Ethyl Ketone (A)-Isoamyl Alcohol (B)				
$w_{\text{visc.}}$ = 719.715 cal. per gram mole; ν_{AB} = 0.7087; ν_{BA} = 0.9217				
0.0996	0.9004	2.4753	2.5884	...
0.2003	0.7997	1.9362	1.9394	1.8880
0.3000	0.7000	1.4906	1.4924	1.4820
0.4004	0.5996	1.1825	1.1739	1.0910
0.5000	0.5000	0.9474	...	0.9051
0.5997	0.4003	0.8074	0.7831	0.7721
0.6998	0.3002	0.6975	0.6658	0.6704
0.8002	0.1998	0.6050	0.5737	0.6010
0.9001	0.0999	0.5268	0.5092	...
1-Butanol (A)-Isoamyl Alcohol (B)				
$w_{\text{visc.}}$ = 14.492 cal. per gram mole; ν_{AB} = 2.8180; ν_{BA} = 3.1490				
0.1001	0.8999	3.3992	3.3888	...
0.2004	0.7996	3.2627	3.2527	3.2880
0.3004	0.6996	3.1809	3.1303	3.1790
0.4001	0.5999	3.0992	3.0158	3.0730
0.4998	0.5002	2.9117	...	2.9690
0.5998	0.4002	2.8764	2.8145	2.8690
0.6998	0.3002	2.7629	2.7228	2.7710
0.8003	0.1997	2.6638	2.6390	2.6760
0.9002	0.0988	2.5826	2.5576	...

column 3 of Table III. In column 4, the viscosity values calculated by the method suggested by Katti and Chaudhri (*1*) are given. The equation can be written as

$$\ln \nu M = X_A \ln \nu_A M_A + X_B \ln \nu_B M_B + X_A X_B \frac{w_{\text{viscous}}}{RT}$$

The values of w_{viscous} for the systems are also given. The values calculated by using the McAllister formula (*2*) are given in column 5. The binary constants for each system are also shown in Table III. The experimental values agree with the calculated values (*1, 2*) within about 3% error.

NOMENCLATURE

X = mole fraction
ν = kinematic viscosity, cm.^{2} per second
w_{viscous} = interaction energy for activation of flow, cal. per gram mole
ν_{AB}, ν_{BA} = binary constants
M = molecular weight

LITERATURE CITED

(1) Katti, P.A., Chaudhri, M.M., J. Chem. Eng. Data **9**, 442 (1964).
(2) McAllister, R.A., *A.I.Ch.E. J.* **6**, 427 (1960).
(3) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E.E., "Organic Solvents," 2nd ed., pp. 94, 101, 138, Interscience, New York, 1955

Received for review August 26, 1969. Accepted December 16, 1969.

Low-Temperature Heat Capacity and Entropy of Phosphonitrilic Hexaamide Monohydrate

ZACHARY T. WAKEFIELD, BASIL B. LUFF, and JOHN J. KOHLER
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

PHOSPHONITRILIC hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, is of interest as a potential ultrahigh-analysis phosphorus nitrogen fertilizer compound. It is water-soluble, and preliminary greenhouse tests indicate that the phosphorus and nitrogen contents are readily available to plants. In a continuing program of collection of thermodynamic data on materials involved in fertilizer technology, the low-temperature heat capacity of the compound was measured over the temperature range 10° to 320° K.

MATERIALS AND APPARATUS

The low-temperature calorimeter has been described (*2*). 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, 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 defined calorie was taken as 4.1840 absolute joules, the ice point as 273.15° K. The heat capacities were corrected for curvature (*3*). Since small differences were important, temperatures were read to four decimal places, but they were rounded to two decimal places in the final tabulation.

The phosphonitrilic hexaamide monohydrate was prepared by placing in a 2-liter Parr bomb 236 grams (0.68 mole) of distilled and recrystallized phosphonitrilic chloride

Heat capacities of phosphonitrilic hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, were measured by adiabatic calorimetry over the temperature range 10° to 320° K. The calculated entropy at 298.15° K. is 70.98 ± 0.03 cal. deg.$^{-1}$ mole^{-1} and the enthalpy is 11,768 ± 6 cal. mole^{-1}. The accuracy of the heat capacity and of the derived thermal properties at 298.15° K. is decreased moderately by anomalous effects above 250° K. A small anomalous peak (about 12 cal. per mole), observed from about 262° to 275° K., was assigned to a fusion of free water. A reversible transition peak (583 cal. per mole) was observed between 277° and 315° K., with a maximum at 292° K. After several sets of measurements in and above the transition region, an exothermic decomposition process occurred spontaneously, after which significant changes were observed in the heat capacity of the sample. All heat capacity measurements reported were taken before the reaction occurred.

trimer, 200 ml. of anhydrous diethyl ether, and 600 ml. of liquid ammonia at −70° C.; the bomb was sealed and allowed to warm to room temperature. After standing overnight, the pressure was released, and the excess ammonia and ether were allowed to evaporate. The residue was refluxed with 1 liter of chloroform and 300 ml. of anhydrous diethylamine until the evolution of ammonia ceased. The remaining solids were washed with chloroform and dried. Several batches prepared by this method—all of which were at least twice crystallized from water—were combined and dissolved in 200 ml. of distilled water at 60° C. The solution was filtered immediately into a flask submerged in an ice bath, whereupon a white solid began to separate. The mixture was stirred for 30 minutes and filtered, and the product was washed with 50 ml. of ice water, 200 ml. of absolute ethanol, and 200 ml. of anhydrous diethyl ether. It was then air-dried until the odor of ether was no longer detectable, and stored in a refrigerator at 7° C.

Microscopic examination showed the product to be homogeneous well-formed crystals of phosphonitrilic hexaamide monohydrate with average size of 80 by 350 microns; the largest crystals were about 350 by 550 microns, but fragments from mechanical breakage were present also. Chemical analysis showed 51.1% N and 37.4% P (stoichiometric 50.61% N, 37.30% P). The calorimeter charge was 60.2950 grams (vacuum) (sp. gr. 1.68) or 0.242058 mole, based on a gram formula weight of 249.0927.

Observed molal heat capacities are shown in Table I. The heat capacities below 10° K. were read from a large-scale plot of C_p/T *vs.* T^2 over the range 10° to 30° K. that extrapolated smoothly to 0° K. The unusually large number of measurements above 190° K. resulted from study of two peaks that were observed at about 270° and 290° K. and subsequent check points at lower temperatures for evidence of change in the sample—points separated by less than 1° K. are not reported.

The smoothed heat capacities and the corresponding derived properties are shown in Table II. Contributions from the transition that was observed between 277° and 315° K. are not included. A small correction to the heat capacity was made for differences in the amounts of helium gas and eutectic solder between the empty calorimeter and the calorimeter with the sample.

OBSERVATIONS

In preliminary petrographic examinations before charging the calorimeter, the phosphonitrilic hexaamide monohydrate underwent alteration in which the well-formed crystals developed low-index sites which then spread throughout the crystals. The alteration accelerated with rise in temperature. An apparently identical alteration occurred at room temperature under reduced pressure. No alteration could be detected at a pressure of 0.1 mm. of Hg at −70° C.

Table I. Observed Heat Capacity of Phosphonitrilic Hexaamide Monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, Cal. Deg.$^{-1}$ Mole^{-1}

T, ° K.	C_p	T, ° K.	C_p	T, ° K.	C_p
9.91	0.3651	93.84	23.18	203.30	53.61
10.36	0.3962	96.49	23.80	204.22	53.84
11.70	0.6027	99.70	24.77	207.05	54.62
11.91	0.5561	102.21	25.44	210.12	55.54
13.11	0.7546	105.78	26.41	214.07	56.68
13.53	0.8384	108.42	27.13	217.23	57.64
14.20	0.9064	111.83	28.07	219.77	58.37
15.18	1.106	114.82	28.89	222.61	59.16
15.71	1.206	117.85	29.73	225.94	60.24
18.41	1.796	121.16	30.64	227.02	60.50
18.84	1.870	124.07	31.45	228.60	61.03
22.49	2.781	127.48	32.39	231.48	61.99
22.68	2.848	130.50	33.23	234.73	62.98
25.18	3.527	133.77	34.14	236.85	63.68
27.07	4.072	136.90	35.01	238.90	64.42
28.80	4.590	140.06	35.88	241.77	65.31
32.30	5.671	143.28	36.78	245.37	66.52
33.76	6.138	146.33	37.62	247.44	67.28
37.54	7.322	149.65	38.55	248.74	67.72
39.00	7.767	152.60	39.26	251.96	68.84
42.64	8.854	155.83	40.27	254.08	69.65
44.48	9.410	158.87	41.11	256.25	70.50
48.08	10.51	162.01	41.98	258.66	71.47
50.23	11.14	165.16	42.85	260.64	72.25
53.39	12.03	168.21	43.69	262.16	72.79
53.56	12.09	171.46	44.60	264.21	73.76
54.31	12.29	174.26	45.38	266.66	74.64
56.72	12.95	177.77	46.36	268.51	75.51
59.17	13.62	180.32	47.07	270.52	76.61
61.46	14.30	183.92	48.08	272.60	77.64
64.10	15.07	186.58	48.82	274.59	78.70
66.45	15.73	190.09	49.82	275.83	79.57
69.11	16.43	193.02	50.65	276.73	80.04
71.51	17.04	196.13	51.49	277.99	80.66
74.20	17.76	196.44	51.61	278.98	81.32
76.65	18.45	197.56	51.91	279.00	81.13
79.78	19.36	198.20	52.12	285.00[a]	83.9
81.60	19.86	199.02	52.32	290.00[a]	86.2
84.62	20.71	200.14	52.71	295.00[a]	88.4
87.93	21.63	200.76	52.83	300.00[a]	90.3
90.73	22.38	202.67	53.34		

[a] Calculated from equation for "normal" heat capacity.

A petrographic microscope equipped with a controllable hot stage was used to estimate the degree of alteration to be expected in the process of filling and soldering the calorimeter closure disk. Temperature, monitored during the actual soldering of the calorimeter by temporary connections to the platinum resistance thermometer, stayed within the time-temperature stability limits established with the hot-stage microscope.

Table II. Molal Thermodynamic Properties of Phosphonitrilic Hexaamide Monohydrate

T, ° K.	C_p, Cal./° K.	$S°$, Cal./° K.	$H° - H_0°$, Cal.	$-\left(\frac{G° - H_0°}{T}\right)$
5	0.0500	0.0167	0.063	0.004
10	0.3682	0.1283	0.956	0.033
15	1.0741	0.3968	4.385	0.104
20	2.150	0.8458	12.323	0.230
25	3.477	1.464	26.31	0.412
30	4.966	2.228	47.37	0.649
35	6.512	3.110	76.06	0.936
40	8.066	4.081	112.5	1.268
45	9.580	5.118	156.6	1.638
50	11.06	6.204	208.3	2.040
60	13.89	8.473	333.1	2.921
70	16.66	10.82	485.9	3.882
80	19.40	13.22	666.1	4.899
90	22.16	15.67	874.0	5.959
100	24.82	18.14	1109	7.054
110	27.57	20.64	1371	8.175
120	30.32	23.15	1660	9.319
130	33.09	25.69	1977	10.48
140	35.87	28.25	2322	11.66
150	38.61	30.81	2695	12.85
160	41.42	33.39	3095	14.05
170	44.19	35.99	3523	15.27
180	46.98	38.59	3979	16.49
190	49.79	41.21	4462	17.72
200	52.62	43.83	4974	18.96
210	55.51	46.47	5515	20.21
220	58.43	49.12	6085	21.46
230	61.47	51.78	6684	22.72
240	64.76	54.47	7315	23.99
250	68.15	57.18	7979	25.26
260	71.99	59.93	8680	26.54
270	76.32	62.72	9420	27.83
280	81.69	65.59	10211	29.13
290	86.22	68.54	11051	30.44
300	90.32	71.54	11934	31.76
273.15	77.99	63.62	9664	28.24
298.15	89.63	70.98	11768	31.51

The material was shown to be stable under vacuum at low temperature by cooling it in a glass vessel to −70° C., evacuating to a pressure of 100 mm. of Hg, and relieving to atmospheric pressure with air dried by passage through P_2O_5. After 3 such cycles and warming to room temperature, petrographic examination showed no significant alteration of the sample and no significant change in weight. The same procedure was used for charging the calorimeter, except that the vacuum was relieved with helium in each of three cycles and on the fourth cycle the calorimeter was filled to atmospheric pressure with helium to improve temperature equilibration. The evacuation tube was pinched shut, cut off, and immediately sealed with eutectic solder. The calorimeter was stored in a desiccator at 7° C. until the weighed amounts of copper and eutectic solder were added to match those used for heat capacity measurements on the empty calorimeter. The calorimeter then was installed in the adiabatic shield system, immediately cooled to 0° C., and kept at temperatures below the ice point until all measurements below 273° K. were completed. The heat capacity values were regular from 10° K. to near the ice point. The heat capacity curve showed a small peak near the ice point (2.94 cal. per sample, about 12 cal. per mole of hexaamide) which was interpreted as the heat of fusion of free water. No correction was made for the free water because it was assumed that it came from dehydration, and that the heat capacity of the free water and the corresponding amount of anhydrous hexaamide would be practically the same as that of the monohydrate.

The standard deviation between the observed and calculated values for the heat capacity was 0.0049 cal. mole^{-1} deg.$^{-1}$ from 10° to 25° K., 0.0029 from 25° to 250° K., and 0.0149 from 250° to 300° K. Above 250° K., the precision of the measurements was decreased by hysteresis of the sample and sluggishness in reaching equilibrium. The effect of the decreased precision on the enthalpy and entropy at 298.15° K. was estimated by calculation of the standard deviation for each 25° K. interval of temperature. The successive deviations were plotted as departures from the smooth heat capacity curve and integrated. The values obtained were 11,768 ± 6 cal. mole^{-1} for the enthalpy and 70.98 ± 0.03 cal. mole^{-1} deg.$^{-1}$ for the entropy at 298.15° K. These values are derived from the normal heat capacity and do not include contributions from the transition energy. The uncertainty intervals are twice the standard deviation.

A lambda-type transition peak began at about 280° K. and ended at about 315° K. (Figure 1). After each of five sets of measurements made at temperatures as high as 319° K., the sample was cooled to 195° K. and the original values for heat capacity were obtained, showing that the phenomenon causing the peak was reversible—i.e., that the sample was not permanently altered by being taken above the temperature range of the peak.

The existence of two crystalline forms of the monohydrate was confirmed by x-ray. A low-temperature pattern was obtained by passing air through liquid nitrogen to produce cold vapor to cool the sample. A different x-ray pattern was obtained after the sample was allowed to warm to room temperature. All samples used in the x-ray studies dehydrated at room temperature in 10 to 24 hours and then gave the known pattern for the anhydrous material. Stability of the sample material was indicated in the interval from 275° to 280° K. by rapid temperature equilibration

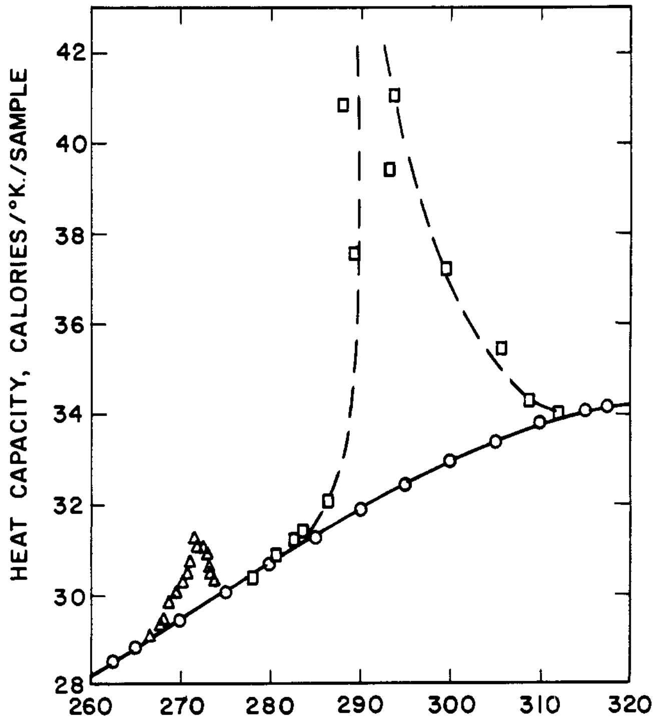

Figure 1. Heat capacity of $P_3N_3(NH_2)_6 \cdot H_2O$ in transition region

○ Normal heat capacity

☐ Transition

△ Fusion of water

after each heating period. In the regions of the peaks for both the fusion of water and the transition, temperature drifts were present after equilibration for as long as 24 hours.

Energy values for the fusion of ice and for the transition peak were determined by heating from a reproducible state below the peak to a reproducible state above the peak with appropriate integration of an equation for the "normal" heat capacity. A cubic equation for "normal" heat capacity was derived by the method of least squares from 80 points measured between 238° and 280° K. and 5 points above the transition peak between 312.5° and 318.9° K. The average deviation between the observed values and those calculated from the equation was 0.16%. The average of three measurements of the heat of fusion of ice (3.18, 2.79, 2.86) was 2.94 calories per sample. Only one measurement was made of the transition peak energy before the sample decomposed—141.2 calories per sample or 583 cal. $mole^{-1}$

In a final series of measurements of the heat capacity in the region above the transition peak, an exothermic reaction began spontaneously at 311.5° K. Two attempts to measure the heat capacity were unsuccessful, and the heating effect persisted and was greater at 318° K. Adiabatic conditions were maintained by automatic shield control and the self-heating rate was measured over 26 hours. The calorimeter was then cooled to 298° K. and the rate of heating was measured over 23 hours, then for 16 hours at 273° and at 251° K. The rate of heating was quite low at 273° and 251° K., but increased when the sample was warmed, indicating that, after initiation, the reaction could be slowed at low temperatures but would resume its original rate upon warming. From the known heat capacity of the calorimeter and the measured self-heating rates, values were calculated for the rate of heat generation as a function of temperature on the assumption that the rate of heat generation was proportional to the rate of reaction. With these values (cal. $min.^{-1}$) as specific rate constants, an Arrhenius plot indicated the energy of activation to be about 17 kcal. $mole^{-1}$.

When the heating-rate measurements were completed, the calorimeter was cooled to 77° K. The heat capacity was then significantly different from that of the original sample. The exothermic reaction was assumed to be hydrolysis of the hexaamide by the hydration water to phosphoryl triamide and its degradation products, ammonium orthophosphates.

In an effort to define the exothermic reaction in which NH_3, and almost certainly water, would be released, the calorimeter was cooled to 150° K. to freeze any possible combination of NH_3 and H_2O (*4*). The heat capacity of the altered material, measured from 150° to 279° K., was lower below 193° K. than that of the original material, moderately higher above 193° K., and showed a large fusion peak (251 cal. per sample or 1037 cal. per mole) extending from about 250° to 281° K., with a maximum at 263° K. Taking the peak maximum of 263° K. as the fusion temperature of a mixture of H_2O and NH_3, the phase diagram (*4*) indicates the composition to be 90% water and 10% ammonia, corresponding to 2.84 grams of water and 0.32 gram of ammonia liberated by the exothermic reaction. The corresponding quantities, determined later by chemical analysis, were in reasonably good agreement, 2.47 grams of H_2O and 0.60 gram of NH_3.

When the calorimeter was opened the sample was moist, had a strong odor of NH_3, and was blue-green from reaction of the liberated NH_3 and H_2O with exposed surfaces of the copper calorimeter. A portion of the sample material was washed with anhydrous methanol to remove surface NH_3, H_2O, and Cu salts. The washed solids contained 39.1% P and 52.8% N, close to the composition of the anhydrous hexaamide.

Petrographic and x-ray examinations of the material before and after washing with anhydrous methanol showed that it was no longer the monohydrate, but the anhydrous material. Paper chromatography showed the presence of a significant amount of phosphoryl triamide, indicating that the reaction was hydrolysis of the hexaamide by the freed hydrate water, as reported by Dostal *et al.* (*1*). The reaction is of interest in the chemistry of the phosphonitrilic hexaamide, but does not affect the results obtained for thermal values of the monohydrate, because all heat capacity measurements reported were measured before the reaction occurred.

LITERATURE CITED

(1) Dostal, K., Kouril, M., Novak, J., *Z. Chem.* 4 (9), 353 (1964).
(2) Egan, E.P., Jr., Luff, B.B., Wakefield, Z.T., J. CHEM. ENG. DATA **13**, 543 (1968).
(3) Egan, E.P., Jr., Wakefield, Z.T., *J. Phys. Chem.* **64**, 1953 (1960).
(4) Mironov, K.E., *J. Gen. Chem. (USSR)* **25**, 1039 (1955).

RECEIVED for review September 10, 1969. Accepted December 8, 1969.

Solubility of C_9 and Two C_{10} Aromatic Hydrocarbons in Liquid CO_2

T. H. GOUW
Chevron Research Co., Richmond, Calif. 94802

Solubilities of all C_9 and two C_{10} aromatic hydrocarbons in liquid CO_2 have been measured at temperatures from –25° to –65° C. Most of the binary systems studied exhibit a region where two immiscible liquid phases are formed with an upper critical solution temperature.

THE SOLUBILITY of the C_6-C_8 aromatic hydrocarbons in liquid CO_2 has been described (*2*). The same apparatus and measurement technique are used. Measurements are carried out in a calibrated 7.5-inch-long, 1-inch-i.d. Lab Crest glass pressure reaction vessel (Fischer and Porter Co., Warminster, Pa.), connected to a manifold and immersed in an acetone bath. Mixing of the contents of the tube is facilitated by a magnetic stirring bar in the tube. The temperature of the solution is measured by a thermocouple immersed in the liquid mixture. CO_2 can be introduced into and vented out of the system by opening the appropriate valves. The data are, therefore, obtained with the solution in equilibrium with the vapor phase. Because of the very low partial pressure of the hydrocarbons