Table VI. *(Continued)*

P_2O_5, wt %	Temperature, °C 110	120	130	140	150	160	170	180	190	200
40	0.65									
45	0.61									
50	0.58				Boiling region					
55	0.54	0.55								
60	0.51	0.51	0.52	0.52						
65	0.47	0.48	0.48	0.49	0.49	0.50				
70	0.432	0.436	0.440	0.444	0.448	0.452	0.456	0.460	0.464	0.469
75	0.415	0.420	0.424	0.428	0.433	0.437	0.441	0.446	0.450	0.454
80	0.383	0.388	0.392	0.397	0.402	0.406	0.411	0.416	0.420	0.425
85	0.336	0.341	0.346	0.351	0.356	0.361	0.366	0.370	0.375	0.380
90	0.31	0.31	0.32	0.32	0.33	0.33	0.34	0.34	0.35	0.35
95	0.27	0.28	0.29	0.29	0.30	0.30	0.31	0.31	0.32	0.32
100	0.24	0.25	0.25	0.26	0.26	0.27	0.27	0.28	0.28	0.29

140 points; 8 points for crystalline P_2O_5 from 0–56.85°C (*1*), 10 points for liquid H_3PO_4 from 26–58°C, 8 points for liquid $2H_3PO_4 \cdot H_2O$ from 24–40°C (*9*), 64 points for acid concentrations in the range 32–68% P_2O_5 at temperatures from 15–80°C, and 50 points from this report for acid strengths in the range 70–86% P_2O_5 over the temperature range 25–200°C. The 9 points given for water in Table VI are taken from Osborne et al. (*6*).

The equation was of the form

$$C_p = B_0 + B_1T + B_2n + B_3T^2 + B_4n^2 + B_5Tn \qquad (5)$$

where

C_p = heat capacity, cal-g^{-1} °C^{-1}
T = temperature, °C
n = concentration, expressed as % P_2O_5
$B_0 = 8.90487 \times 10^{-1}$
$B_1 = 5.33763 \times 10^{-4}$
$B_2 = -7.77818 \times 10^{-3}$
$B_3 = -7.42939 \times 10^{-7}$
$B_4 = 5.64683 \times 10^{-6}$
$B_5 = 2.12033 \times 10^{-6}$

Addition of more terms did not improve the fit significantly. The standard deviation was 0.009 cal-g^{-1} °C^{-1}. A corresponding equation in units of $P_2O_5 \cdot nH_2O$ and cal (mole P_2O_5)$^{-1}$ gave similar results. The results of interpolations and extrapolations through use of Equation 5 are shown in Table VI as values shown to two decimal places.

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Enthalpy of Formation of Phosphoryl Triamide

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The enthalpy of formation of crystalline phosphoryl triamide, $PO(NH_2)_3$, from the elements in their standard states at 25°C is −143.2 kcal mol^{-1}. It was determined from its enthalpy of solution in 4*m* HCl at 25°C and from published values for the enthalpies of formation of H_3PO_4, $NH_4H_2PO_4$, and H_2O and for the enthalpy of dilution of H_3PO_4.

In a continuing study of the thermal properties of compounds with potential application in fertilizer technology, measurements were made to determine the standard enthalpy of formation of phosphoryl triamide, $PO(NH_2)_3$. This compound has a high plant nutrient content and good physical properties and was an excellent source of both nitrogen and phosphorus in greenhouse tests (*7*).

MATERIALS AND APPARATUS

Phosphoryl Triamide. The $PO(NH_2)_3$ samples were taken from the material removed from the low-temperature

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calorimeter after the measurement of its heat capacity (*8*). It had been prepared according to the reactions

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

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

A 2-liter three-necked flask equipped with a power stirrer, Dry Ice–acetone-cooled reflux condenser, addition funnel, and gas-inlet tube was submerged in a Dry Ice–acetone bath and charged with 1000 ml liquid ammonia. A solution of 155 ml (1.69 moles) $POCl_3$ in 200 ml chloroform was added dropwise over a 4-hr period. The bath was removed and the mixture 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 diethylamine and 750 ml chloroform to remove the ammonium chloride. Microscopic examination of the white residue detected no ammonium chloride or diethylamine hydrochloride and showed the product to be poorly crystallized phosphoryl triamide. The yield was 151 grams (95%).

The sample 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, then filtered, and the crystals were washed quickly with 50 ml ice water, 250 ml cold methanol, and finally with 200 ml diethyl ether. The crystals were dried in a stream of nitrogen and weighed 69.7 grams, a recovery of 48%. The X-ray diffraction pattern showed the product to be well crystallized $PO(NH_2)_3$ with properties in agreement with published values (*3*); no other phases were detected. Microscopic examination showed the recrystallized material to be phosphoryl triamide, homogeneous and well crystallized, with optical properties in agreement with those of earlier preparations (*4*) whose identities had been established by X-ray. There was no surface alteration, and the average particle size was 200 × 300 μm. The crystals contained 44.0% N and 32.4% P (stoichiometric: 44.21% N, 32.59% P). Nitrogen was determined by the Raney catalyst powder method (*1*), and phosphorus by the gravimetric quimociac method (*2*).

Salts and Acids. Ammonium dihydrogen phosphate was prepared by recrystallizing the reagent salt from distilled water and drying it at 110°C; it contained 14.8% NH_3 and 61.6% P_2O_5 (stoichiometric, 14.80% NH_3, 61.70% P_2O_5). Recrystallized reagent phosphoric acid was diluted with distilled water to a solution of 84.56% H_3PO_4 (61.24% P_2O_5 by chemical analysis). A 497.142-gram aliquot of the solution was diluted with 39.185 grams of water to form $H_3PO_4 \cdot 1.5H_2O$ (78.38% H_3PO_4). The calorimetric solvent was prepared by diluting reagent hydrochloric acid with distilled water to 4.01*m* HCl as determined by alkalimetric titration.

CALORIMETER AND PROCEDURE

The solution calorimeter was similar to that used by Southard (*6*). A 900-ml Dewar flask was supported in a constant temperature water bath by cork rings clamped between stainless steel plates. A flanged stainless steel collar, fitted closely around the neck of the Dewar flask, was silver soldered to the top plate. The space between the collar and the neck of the flask was filled with Apiezon W wax. A stainless steel plate, provided with three small stuffing boxes for the thermometer and heater supports and with a stainless steel ball bearing guide 4 in. long for the stirrer, was clamped to the flanged collar with six spring clamps. A neoprene gasket sealed the cover plate to the collar. A 4-lead helical constantan heater was mounted in a 5-mm glass tube that had been shaped into a helix. The head of a platinum resistance thermometer was sealed with Apiezon W wax to a flared 5-mm glass support tube. The heater and the thermometer were suspended from the calorimeter cover by anchoring three sections of $^1/_8$-in. Inconel tubing in the stuffing boxes and sealing the glass tubes to the Inconel tubes with Apiezon W wax. The heater and thermometer leads passed through these tubes. An inert plastic draft tube was fastened inside the glass helix with platinum wire, and the thermometer was located just inside the draft tube. A glass stirrer was sealed to a $^1/_4$-in. stainless steel tube just below the calorimeter cover with Apiezon W wax so that the impeller blades were only a few millimeters below the tip of the thermometer capsule.

In each measurement 850 ml of solvent were used and each sample of solute was suspended in a thin-walled glass bulb from a glass rod passing through the hollow stirrer shaft. The bulb was crushed against the bottom of the Dewar flask to start the solution period.

The calorimeter system was calibrated electrically immediately before and after each measurement. The platinum resistance thermometer was calibrated by the National Bureau of Standards. The Wenner potentiometer, Ayrton shunt, and standard resistors used in the energy measurements were calibrated against standard resistors and a potentiometer calibrated by the Redstone Arsenal, Huntsville, Ala., and traceable to the National Bureau of Standards. The defined calorie was taken as 4.1840 abs J.

Conventional "normal" and "reverse" readings of the resistance of the platinum resistance thermometer on a Leeds & Northrup G-2 Mueller bridge were made during rating periods to establish heat-leak corrections. Only normal readings were taken during the solution period, and to these were applied both the usual bridge corrections and an adjustment to compensate for the absence of reverse measurements. The observed temperature rise was the difference between the temperatures at the end and at the beginning of the solution period as calculated from linear equations for the rating periods. The correction to

Table I. Enthalpy of Solution of $H_3PO_4 \cdot 1.5H_2O$ in 850.0 Ml of 4.01*m* HCl at 25°C

Wt sample, g	Corr temp rise, °C	$-\Delta H_1$, cal/mol	Δ
3.30127	0.03908	1131	−17
3.40942	0.04097	1147	−1
3.45921	0.04138	1146	−2
3.47262	0.04162	1142	−6
3.47710	0.04180	1155	+7
3.48673	0.04209	1154	+6
3.51137	0.04219	1150	+2
3.69446	0.04462	1159	+11
Av, double standard deviation		1148	±6

Table II. Enthalpy of Solution of $PO(NH_2)_3$ in 850.0 Ml of 4.01*m* HCl and Stoichiometric $H_3PO_4 \cdot 1.5H_2O$ at 25°C

Wt sample, g	Corr temp rise, °C	$-\Delta H_2$, cal/mol	Δ
1.27770	0.96967	57376	+82
1.30443	0.98907	57318	+24
1.30819	0.99249	57362	+68
1.30982	0.99050	57201	−93
1.36084	1.03070	57212	−82
Av, double standard deviation		57294	±74

Table III. Enthalpy of Solution of $NH_4H_2PO_4$ in 850.0 Ml of 4.01*m* HCl at 25°C

Wt sample, g	−Corr temp rise, °C	ΔH_3, cal/mol	Δ
4.52507	0.29269	5948	−2
4.64954	0.30084	5950	0
4.77082	0.30836	5948	−2
4.86012	0.31409	5947	−3
4.99913	0.32334	5955	+5
5.06038	0.32696	5950	0
Av, double standard deviation		5950	±2

the observed temperature for heat leak was calculated by integration by the trapezoidal rule of the heat leak as a function of time from measurements taken at half-minute intervals. The calculation was simplified by the linear relationship of heat leak to temperature over the temperature range of the measurements.

Enthalpies of Solution. The standard enthalpy of formation of $PO(NH_2)_3$ at 25°C was determined from the published enthalpies of formation of H_3PO_4, $NH_4H_2PO_4$, and H_2O, the enthalpy of dilution of H_3PO_4; and the enthalpy at 25°C of the reaction

$$2(H_3PO_4 \cdot 1.5H_2O) + PO(NH_2)_3 = 3NH_4H_2PO_4 \qquad (3)$$

Temperature changes during dissolution were arbitrarily limited to 1°C, which determined the size of the sample of phosphoryl triamide and thus the amounts of the other materials in Equation 3.

In a preliminary test, in which 0.44 gram of $PO(NH_2)_3$ was dissolved in 84 ml 4*m* HCl at 25°C, hydrolysis to orthophosphate was complete in 5 min.

The enthalpy of reaction of Equation 3 was determined by the scheme

$$\begin{array}{rl}
\text{ampul } H_3PO_4 \cdot 1.5H_2O + \text{solvent} = \text{solution A} & \Delta H_1 \\
\text{ampul } PO(NH_2)_3 + \text{solution A} = \text{solution B} & \Delta H_2 \\
\text{ampul } NH_4H_2PO_4 + \text{solvent} = \text{solution B} & \Delta H_3
\end{array}$$

Results of determinations of ΔH_1, ΔH_2, ΔH_3 and their average values and double standard deviations are shown in Tables I–III. The sum of $2\ \Delta H_1 + \Delta H_2 - 3\ \Delta H_3$ is $-77{,}440 \pm 74$ cal (double standard deviation) for the enthalpy of reaction of Equation 3.

From the standard enthalpies of formation at 25°C (*5*) of H_3PO_4(l), −302.8 kcal; and $H_3PO_4 \cdot 1.5H_2O$ (soln), −305.26 kcal (*5*); the enthalpy at 25°C of the reaction

$$H_3PO_4(l) + 1.5H_2O(l) = H_3PO_4 \cdot 1.5H_2O(soln) \qquad (4)$$

was calculated to be −2.46 kcal. Addition of twice this value to the enthalpy of reaction of Equation 3 shows the enthalpy at 25°C of the reaction

$$PO(NH_2)_3(c) + 2H_3PO_4(l) + 3H_2O(l) = 3NH_4H_2PO_4(c) \qquad (5)$$

to be −82.36 kcal. Substitution of the standard enthalpies of formation from the elements at 25°C (*5*) of $NH_4H_2PO_4$(c), −345.38 kcal/mol; and H_2O(l), −68.315 kcal/mol; and the standard enthalpy of formation at 25°C of H_3PO_4(l); and the enthalpy of reaction of Equation 5 in the equation

$$\Delta H_f°PO(NH_2)_3(c) = 3[\Delta H_f°NH_4H_2PO_4(c)] - 2[\Delta H_f°H_3PO_4(l)] - 3[\Delta H_f°H_2O(l)] - \Delta H_R \qquad (6)$$

gave −143.2 kcal/mol for the standard enthalpy of formation of $PO(NH_2)_3$(c) at 25°C. An estimate of the uncertainty is not given because it is largely dependent upon the uncertainty of the auxiliary enthalpies of formation taken from ref. *5*.

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Densities, Viscosities, and Vapor Pressures of Copper(II) Chloride Solutions in Hydrochloric Acid

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Densities and viscosities of 1.5*M* copper(II) chloride solutions in 4.0, 5.0, 6.0, and 7.0*M* hydrochloric acid as well as 0.5 and 1.0*M* copper(II) chloride solutions in 5.0*M* hydrochloric acid have been determined for a temperature range from 30–90°C. Equations for calculating densities and viscosities as a function of copper(II) chloride and hydrochloric acid concentration, as well as temperature derived by multiple regression analysis, are supplied. Vapor pressures of water and hydrogen chloride of the mentioned solutions are reported for a temperature range from 60–90°C.

Considerable data on the physical properties of hydrochloric acid are available, but no such data on copper(II) chloride solutions in hydrochloric acid have been published. Some properties of such solutions were determined and are reported.

EXPERIMENTAL

All temperature measurements were made by means of Princo thermometers graduated from −1.0–101.0°C in steps of 0.1°C. They were calibrated by immersing the thermometers into a silicone oil bath together with a standard platinum resistance thermometer (L&N 1119552) previously calibrated by the National Bureau of Standards.

Density measurements at different temperatures were made by measuring the volume expansion of a known amount of solution. A glass bulb was sealed to a precision buret so that 100 ml at room temperature would extend into the lower part of the buret. A stopcock at the upper end of the buret allowed us to keep the apparatus closed while bringing the system to temperature. Distilled water was employed to calibrate the graduation on the buret and to establish its linearity. Mea-

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