Enthalpy of Formation of Ammonium Tetrametaphosphate, $(NH_4PO_3)_4$

BASIL B. LUFF, ROBERT B. REED, and ZACHARY T. WAKEFIELD[1]
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

The enthalpy of formation from the elements in their standard states at 25°C of crystalline ammonium tetrametaphosphate, $(NH_4PO_3)_4$, is -1069.7 ± 0.4 kcal/mol. It was determined from its enthalpy of solution in 10*m* HCl at 40°C and from published values for the enthalpies of formation of $NH_4H_2PO_4$ and H_2O.

In the continuing study of the thermal properties of compounds with potential application in fertilizer technology, measurements were made of the enthalpy of formation of ammonium tetrametaphosphate, $(NH_4PO_3)_4$. This compound has good physical properties and was an excellent source of both nitrogen and phosphorus for corn in greenhouse tests (*11*).

MATERIALS AND APPARATUS

Salts and Acid. Ammonium tetrametaphosphate was prepared by metathesis of copper tetrametaphosphate and ammonium sulfide (*12*). The copper metaphosphate was prepared by the method of Thilo and Rätz (*10*) in which a mixture of cupric oxide and about 90% of the stoichiometric amount of 85% reagent phosphoric acid was heated at 400°C in a silica dish for 8 hr. The copper metaphosphate was crushed, washed with water, and added slowly to a solution of ammonium sulfide (*13*); the precipitated copper sulfide was filtered off, and ammonium tetrametaphosphate was precipitated by adding alcohol to the filtrate. The crude salt was recrystallized at 0°C by dissolving it in water, adjusting the pH to 7.0 with ammonium hydroxide, and adding an equal volume of methanol slowly to the solution. 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 product contained more than 99% ammonium tetrametaphosphate as shown by paper chromatography with Ebel acidic and basic solvents (*3*), and the optical (*4*), X-ray powder diffraction (*2*), and infrared (*8*) properties agreed with those established for ammonium tetrametaphosphate. The crystals contained 14.4% N and 32.0% P (stoichiometric: 14.45% N, 31.93% P). Nitrogen was determined by distillation of the ammonia from a caustic solution, and phosphorus was determined by the gravimetric quinolinium molybdophosphate method (*1*).

Reagent ammonium dihydrogen phosphate recrystallized from distilled water and dried by vacuum desiccation over P_2O_5 contained 12.2% N and 26.9% P (stoichiometric: 12.18% N, 26.93% P). The calorimetric solvent was prepared by diluting reagent hydrochloric acid with distilled water to 9.93*m* HCl as determined by alkalimetric titration.

Calorimeter and Procedure. The solution calorimeter was similar to that used by Southard (*7*). A 900-ml Dewar flask was supported in a constant-temperature water bath by cork rings that were 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 3 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. 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 was 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.

Conventional "normal" and "reverse" readings of the resistance of the platinum resistance thermometer on a Leeds & Northrup K-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 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.

The defined calorie was taken as 4.1840 abs J.

ENTHALPIES OF SOLUTION

The enthalpy of formation of ammonium tetrametaphosphate at 25°C was determined from published enthalpies of formation of H_2O and $NH_4H_2PO_4$ and the enthalpy of reaction at 25°C

$$(NH_4PO_3)_4(c) + 4H_2O(l) = 4NH_4H_2PO_4(c) \qquad (1)$$

---

[1] To whom correspondence should be addressed.

Examinations by paper chromatography showed that 10 grams of $(NH_4PO_3)_4$ was 99.8% hydrolyzed, and 4.25 grams was completely hydrolyzed in 1 hr at 40°C in 850 ml of 10*m* HCl. Actual calorimetric experiments indicated that the hydrolysis of 7 to 8 grams of $(NH_4PO_3)_4$ in 850.0 ml of 9.93*m* HCl was complete in 55 min at 40°C.

The enthalpy of reaction of Equation 1 at 40°C was determined by the scheme

$$\text{Ampul } H_2O + \text{solvent} = \text{solution A} \qquad \Delta H_1$$

$$\text{Ampul } (NH_4PO_3)_4 + \text{solution A} = \text{solution B} \qquad \Delta H_2$$

$$\text{Ampul } NH_4H_2PO_4 + \text{solvent} = \text{solution B} \qquad \Delta H_3$$

$$\Delta H_R(40°C) = 4\Delta H_1 + \Delta H_2 - 4\Delta H_3 \qquad (2)$$

The enthalpy of solution of ampuls of water in the calorimetric solvent is listed in Table I. The observed enthalpy of solution of H_2O in the solvent as a function of sample size is represented by the equation

$$-\Delta H = 460.3 - 0.467\ w \qquad (3)$$

where ΔH = enthalpy of solution, cal/mol, and w = weight, grams, of H_2O. Equation 3 was used to determine ΔH_1 (−460 cal/mol) by solving for the stoichiometric amount of water (1.4069 grams) corresponding to the average weight of ammonium tetrametaphosphate (7.5761) grams shown in Table II. The value of ΔH_2 (−15,306 cal/mol) was determined from the average enthalpies of solution of ampuls of ammonium tetrametaphosphate in the solvent to which the stoichiometric amounts of water had been added. The results are shown in Table II. An average value for ΔH_3 (5518 cal/mol) was determined from the enthalpies of solution of ampuls of ammonium dihydrogen phosphate in the solvent, and the results are shown in Table III. The sample weights of the ammonium dihydrogen phosphate were selected to cover the range of stoichiometry for the ammonium tetrametaphosphate sample weights, but, because no change in the enthalpy of solution with sample size was observed, the average enthalpy of solution was used for ΔH_3.

Table I. Enthalpy of Solution of H_2O in 850.0 Ml of 9.93*m* HCl at 40°C

Sample wt., grams	Corr. temp. rise, °C	$-\Delta H_1$, obsd., cal/mol	$-\Delta H_1$, calcd., cal/mol
5.12032	0.18492	456.2	457.9
7.17786	0.25771	458.2	457.0
10.00820	0.35638	456.8	455.6
12.07271	0.42809	456.3	454.7
14.08492	0.49370	452.6	453.7
16.09300	0.55941	450.9	452.8
18.02653	0.62695	452.2	451.9
20.20552	0.70017	451.5	450.9
		Std dev	±1.5

Table II. Enthalpy of Solution of $(NH_4PO_3)_4$ in 850.0 Ml of 9.93*m* HCl + Stoichiometric H_2O at 40°C

Sample wt., grams	Corr. temp. rise, °C	$-\Delta H_2$, cal/mol
7.00694	0.38912	15243
7.21177	0.40310	15376
7.39512	0.41041	15240
7.62522	0.42497	15329
7.79788	0.43310	15292
7.99146	0.44667	15353
8.00408	0.44556	15306
7.57607[a]		15306[a]
	Std dev	±20

[a] Average.

Table III. Enthalpy of Solution of $NH_4H_2PO_4$ in 850.0 Ml of 9.93*m* HCl at 40°C

Sample wt., grams	Corr. temp. rise, °C	ΔH_3, cal/mol
8.17314	−0.55233	5524
8.51080	−0.57436	5519
8.78559	−0.59293	5520
9.05196	−0.60995	5512
9.31314	−0.62830	5517
9.54463	−0.64433	5519
	Av	5518
	Std dev	±2

Substitution of the enthalpies of solution, ΔH_1, ΔH_2, and ΔH_3, in Equation 2 gives −39,218 ± 22 cal for the enthalpy of reaction for Equation 1 at 40°C. The enthalpy of reaction at 40°C was adjusted to the enthalpy of reaction at 25°C by the equation

$$\Delta H_R(25°C) = \Delta H_R(40°C) + \int_{40}^{25} \Delta C_p dT \qquad (4)$$

The equation for ΔC_p, the difference between the heat capacities of the product and of the reactants, was derived from equations for heat capacity as a function of temperature from the data of Osborne et al. (*6*) for water, the data of Stephenson and Zettlemoyer (*9*) for $NH_4H_2PO_4$, and the data of Wakefield et al. (*12*) for $(NH_4PO_3)_4$.

$$\int_{40}^{25} \Delta C_p dT = \int_{40}^{25} (-48.1 + 0.08\ T - 0.2 \times 10^{-3}\ T^2 - 0.14 \times 10^{-5}\ T^3)dT = 685 \text{ cal} \qquad (5)$$

Addition of 685 cal to the enthalpy of reaction at 40°C gives −38,533 cal for the enthalpy of reaction of Equation 1 at 25°C. The standard enthalpies of formation from the elements at 25°C (*5*) are: $H_2O(l)$, −68.315 ± 0.01; and $NH_4H_2PO_4(c)$, −345.38 ± 0.1 kcal/mol. Substitution of these values, along with the enthalpy of reaction of Equation 1 at 25°C in the equation

$$\Delta H_f°(NH_4PO_3)_4(c) = 4[\Delta H_f°NH_4H_2PO_4(c)] - 4[\Delta H_f°H_2O(l)] - \Delta H_R(25°C) \qquad (6)$$

gives −1069.7 ± 0.4 kcal/mol for the standard enthalpy of formation of $(NH_4PO_3)_4$ at 25°C.

LITERATURE CITED

(1) Association of Official Analytical Chemists, "Official Methods of Analysis," 11th ed., Method **2.025**, 1970.
(2) Coates, R. V., Woodard, G. D., *J. Chem. Soc.*, **1964**, p 1780.
(3) Ebel, J. P., *Mikrochim. Acta*, **1954**, p 679.
(4) Lehr, J. R., Brown, E. H., Frazier, A. W., Smith, J. P., Thrasher, R. D., *Tenn. Valley Author., Chem. Eng. Bull.*, **6**, Muscle Shoals, Ala., May 1967.
(5) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Tech. Note **270-3** (1968).
(6) Osborne, N. S., Stimson, H. F., Ginnings, D. C., *J. Res. Nat. Bur. Stand.*, **23**, 238 (1939).
(7) Southard, J. C., *Ind. Eng. Chem.*, **32**, 442 (1940).
(8) Steger, E., *Z. Anorg. Allgem. Chem.*, **294**, 146 (1958).
(9) Stephenson, C. C., Zettlemoyer, A. C., *J. Amer. Chem. Soc.*, **66**, 1402 (1944).
(10) Thilo, E., Rätz, R., *Z. Anorg. Allgem. Chem.*, **260**, 255 (1949).
(11) Wakefield, Z. T., Allen, S. E., McCullough, J. F., Sheridan, R. C., Kohler, J. J., *J. Agr. Food Chem.*, **19**, 99 (1971).
(12) Wakefield, Z. T., Luff, B. B., Sheridan, R. C., *J. Chem. Eng. Data*, **16**, 195 (1971).
(13) Warschauer, F., *Z. Anorg. Allgem. Chem.*, **36**, 137 (1903).

RECEIVED for review May 27, 1971. Accepted October 7, 1971.