

Enthalpy of Formation of Pentaammonium Triphosphate Monohydrate, $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$

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The standard enthalpy of formation of pentaammonium triphosphate monohydrate, $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, is $-1008.5 \text{ kcal mol}^{-1}$. It was determined from the enthalpies of solution of $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $\text{H}_3\text{PO}_4\cdot 16.26\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and H_2O in 10 *m* HCl at 40 °C and from published values for the heat capacities of these compounds and the enthalpies of formation of $\text{H}_3\text{PO}_4\cdot 100\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and H_2O .

A continuing study of the thermal properties of compounds of interest in fertilizer technology included a determination of the enthalpy of formation at 25 °C of pentaammonium triphosphate monohydrate, $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, a component in ammonium polyphosphate fertilizers.

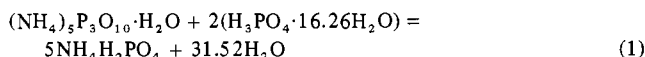
Materials and Apparatus

The preparation of pentaammonium triphosphate monohydrate (gram formula weight = 361.1236) has been described (6). Reagent-grade ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$ (gram formula weight = 115.0259), was recrystallized from distilled water and dried by vacuum desiccation over P_2O_5 . Chemical analysis showed its composition to be 12.2% N and 26.9% P (stoichiometric: 12.18% N, 26.83% P). Recrystallized reagent phosphoric acid was diluted to yield $\text{H}_3\text{PO}_4\cdot 16.26\text{H}_2\text{O}$ (18.16% P_2O_5 by chemical analysis, gram formula weight = 390.82). The calorimetric solvent was prepared by diluting reagent hydrochloric acid to 9.93 *m* HCl as determined by alkalimetric titration.

The solution calorimeter and the method of measurement have been described (5), with the exception that the Wenner potentiometer and Aryton shunt were replaced by a Hewlett-Packard Model 3490A multimeter that measured the voltage drop directly across the calorimeter heater as well as across a standard resistor in series with the heater. The correction to the observed temperature rise for heat leak was calculated by integration by the trapezoidal rule of the heat leak as a function of time from measurements taken at 0.5-min intervals. The calculation was simplified by the linear relationship of heat leak to temperature over the temperature range of the measurements. Corrections were made for the vaporization of the solvent into the vapor space above the liquid in the calorimeter and for the energy of bulb breaking. The defined calorie was taken as 4.1840 absolute J.

Enthalpies of Solution

The enthalpy of formation of pentaammonium triphosphate monohydrate at 25 °C was determined from published enthalpies of formation of H_3PO_4 in 100 mol of H_2O , $\text{NH}_4\text{H}_2\text{PO}_4$, and H_2O , the enthalpies of dilution of phosphoric acid solutions, and the enthalpy of reaction at 25 °C represented by the equation



Bulb volume limited the sample size of the pentaammonium triphosphate monohydrate and thus, by stoichiometry, the amounts of the other compounds in eq 1. The concentration

Table I. Enthalpy of Solution of $\text{H}_3\text{PO}_4\cdot 16.26\text{H}_2\text{O}$ in 9.93 *m* HCl at 40 °C

Sample wt, g	Cor temp rise, °C	-Enthalpy of soln, cal/sample	$-\Delta H_2^a$, cal/mol
17.294 13	0.2412	173.3	3916
17.983 95	0.2517	181.1	3937
18.706 96	0.2607	187.8	3924
19.229 77	0.2675	193.0	3922
19.931 55	0.2769	199.7	3916

$$^a \Delta H_2 = -3966 + 2.32w, w = 18.101 14, \text{ std dev} = 8, \Delta H_2 = -3924.$$

Table II. Enthalpy of Solution of $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ in 9.93 *m* HCl + Stoichiometric $\text{H}_3\text{PO}_4\cdot 16.26\text{H}_2\text{O}$ at 40 °C

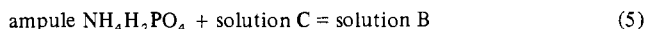
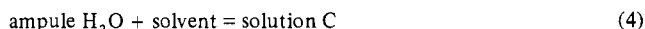
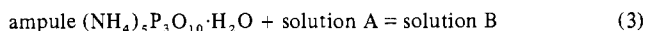
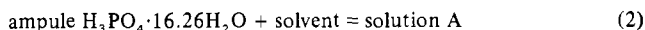
Sample wt, g	Cor temp rise, °C	-Enthalpy of soln, cal/sample	$-\Delta H_3^a$, cal/mol
7.916 64	0.3102	224.9	10 261
7.975 01	0.3117	225.7	10 218
8.203 96	0.3220	233.8	10 258
8.773 83	0.3404	246.7	10 156
8.939 42	0.3491	254.0	10 259

$$^a \Delta H_3 = -10 494 + 31.49w, w = 8.361 17, \text{ std dev} = 43, \Delta H_3 = -10 230.$$

of the acid selected for the second term of eq 1 was that to give the maximum temperature change for the enthalpy-of-solution measurements, considering the space limitations on the bulb volume and the mass of H_3PO_4 required for stoichiometry. This concentration was based on earlier determinations of the enthalpies of solution of phosphoric acid (3) and of water (4) in 10 *m* HCl at 40 °C and the relative apparent molal heat content of phosphoric acid solutions (1).

Preliminary runs, in which samples of the solution taken at 10-min intervals were analyzed for total and orthophosphate, showed that 8 g of $(\text{NH}_4)_5\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ was completely hydrolyzed in 40 min at 40 °C in 850 mL of the calorimetric solvent. Calorimetric measurements indicated, however, that hydrolysis was complete in 30 min.

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



and

$$\Delta H_1 = 2(\Delta H_2) + \Delta H_3 - 31.52(\Delta H_4) - 5(\Delta H_5) \quad (6)$$

where ΔH_1 is the enthalpy of reaction 1 in calories and ΔH_2 , ΔH_3 , ΔH_4 , and ΔH_5 are the enthalpies of reactions 2, 3, 4, and 5, respectively, in cal/mol of the materials in the ampules.

Results and Discussion

Results of determinations of ΔH_2 , ΔH_3 , ΔH_4 , and ΔH_5 are listed in Tables I, II, III, and IV, respectively. Straight line

Table III. Enthalpy of Solution of H₂O in 9.93 m HCl at 40 °C

Sample wt, g	Cor temp rise, °C	-Enthalpy of soln, cal/sample	-ΔH ₄ ^a , cal/mol
10.020 05	0.3551	254.4	457
11.010 88	0.3873	277.8	455
12.054 48	0.4242	305.7	456
13.021 93	0.4572	329.0	455
15.028 65	0.5268	380.1	456

^a ΔH₄ = -458 + 0.20w, w = 13.144 93, std dev = 1, ΔH₄ = -455.

Table IV. Enthalpy of Solution of NH₄H₂PO₄ in 9.93 m HCl + Stoichiometric H₂O at 40 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH ₅ ^a , cal/mol
12.915 02	-0.8600	624.8	5565
13.310 58	-0.8879	646.3	5585
13.695 95	-0.9125	663.5	5572
14.119 04	-0.9392	684.3	5575
14.514 73	-0.9650	703.6	5576

^a ΔH₅ = 5534 + 2.95w, w = 13.316 08, std dev = 7, ΔH₅ = 5573.

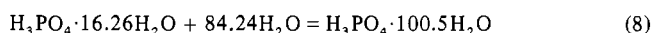
equations of the enthalpies of solution as a function of sample weight, *w*, were fitted to the observed values by the "least-squares" method. These equations were solved where *w* was the average weight of (NH₄)₅P₃O₁₀·H₂O or the stoichiometric amount of H₃PO₄·16.26H₂O, NH₄H₂PO₄, or H₂O corresponding to that weight. The equations along with the standard deviations and the values of ΔH₂, ΔH₃, ΔH₄, and ΔH₅ for the specified values of *w* also are listed in Tables I-IV. Substitution of these calculated values of the enthalpies of solution in eq 6 gives -31 592 ± 66 cal (standard deviation) for the enthalpy of reaction 1 at 40 °C. This value was adjusted by 242 cal to give -31 350 ± 66 cal for the enthalpy of reaction 1 at 25 °C according to the equation

$$\Delta H_1(25^\circ\text{C}) = \Delta H_1(40^\circ\text{C}) + \int_{40}^{25} \Delta C_p dT \quad (7)$$

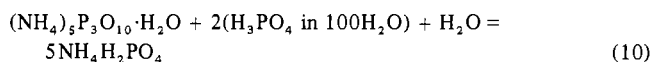
through use of polynomial equations for determining differences

between the heat capacities of the products and the reactants. The heat capacity equations were derived from the data of Osborne et al. for water (8), of Stephenson and Zettlemyer for NH₄H₂PO₄ (9), of Egan et al. for phosphoric acid solutions (2), and of Luff and Williard for (NH₄)₅P₃O₁₀·H₂O (6).

The data of Egan and Luff (1) were used to determine ΔH₈ and ΔH₉, the enthalpies of reactions 8 and 9 at 25 °C, as -436



and -1 cal, respectively. Subtracting twice the difference between ΔH₈ and ΔH₉ from ΔH₁ at 25 °C gives ΔH₁₀, the enthalpy of reaction 10 at 25 °C, as -30 480 cal.



The standard enthalpies of formation of NH₄H₂PO₄(c), H₂O(l), and H₃PO₄ in 100H₂O are -345.38, -68.315, and -308.176 kcal/mol, respectively (7). Substituting these enthalpies of formation and the enthalpy of reaction 10 in the equation

$$\Delta H_f^\circ((\text{NH}_4)_5\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}) = 5(\Delta H_f^\circ(\text{NH}_4\text{H}_2\text{PO}_4)) - 2(\Delta H_f^\circ(\text{H}_3\text{PO}_4 \text{ in } 100\text{H}_2\text{O})) - \Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_{10} \quad (11)$$

gives -1011.8 kcal/mol as the standard enthalpy of formation of (NH₄)₅P₃O₁₀·H₂O.

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Pressure-Volume-Temperature Relationships of Several Polar Liquids

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The specific volumes of liquid CCl₂F₂, CHClF₂, CH₃Cl, CH₃I, CH₃Br, C₂H₅Br, and CH₃COOCH₃ have been measured at several temperatures from -20 to +40 °C and at pressures from the saturated vapor pressures to near 1600 atm with an accuracy better than 0.13%. The data were fitted to the Tait equation of state at each temperature with a maximum deviation of 0.2%.

An accurate knowledge of the specific volumes of polar liquids under high pressures is important in the interpretation of the polarity effect on the compressibility in connection with the elucidation of the internal structure problems of polar liquids.

Most studies of *P-V-T* relationships have been made on nonpolar liquids, and very few measurements are available on polar liquids. The purpose of the present work is, therefore, to obtain the specific volumes of polar liquids. The measurements were made at temperatures from -20 to +40 °C, and at pressures up to near 1600 atm.

Experimental Section

Materials. The origin and purity of samples are recorded as follows: CCl₂F₂ and CHClF₂, Daikin Kogyo Co., Ltd., Japan, 99.9%; CH₃Cl, Matheson Gas Products, a Division of Will Ross, Inc., 99.5%; CH₃I, Kokusan Kagaku Co., Ltd., Japan, 98.2%;