# Enthalpy of Formation of Pentaammonium Triphosphate Monohydrate, $(NH_4)_5P_3O_{10}\cdot H_2O$

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**The standard enthalpy of formation of pentaammonium triphosphate monohydrate, $(NH_4)_5P_3O_{10}.H_2O$, is −1008.5 kcal mol$^{-1}$. It was determined from the enthalpies of solution of $(NH_4)_5P_3O_{10}\cdot H_2O$, $H_3PO_4\cdot 16.26H_2O$, $NH_4H_2PO_4$, 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 $H_3PO_4\cdot 100H_2O$, $NH_4H_2PO_4$, 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, $(NH_4)_5P_3O_{10}\cdot H_2O$, a component in ammonium polyphosphate fertilizers.

## Materials and Apparatus

The preparation of pentammonium triphosphate monohydrate (gram formula weight = 361.1236) has been described (*6*). Reagent-grade ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (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 $H_3PO_4\cdot 16.26H_2O$ (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 $H_2O$, $NH_4H_2PO_4$, and $H_2O$, the enthalpies of dilution of phosphoric acid solutions, and the enthalpy of reaction at 25 °C represented by the equation

$$(NH_4)_5P_3O_{10}\cdot H_2O + 2(H_3PO_4\cdot 16.26H_2O) = 5NH_4H_2PO_4 + 31.52H_2O \qquad (1)$$

Table I. Enthalpy of Solution of $H_3PO_4\cdot 16.26H_2O$ 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] $\Delta H_2 = -3966 + 2.32w$, $w = 18.101\ 14$, std dev = 8, $\Delta H_2 = -3924$.

Table II. Enthalpy of Solution of $(NH_4)_5P_3O_{10}\cdot H_2O$ in 9.93 *m* HCl + Stoichiometric $H_3PO_4\cdot 16.26H_2O$ 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] $\Delta H_3 = -10\ 494 + 31.49w$, $w = 8.361\ 17$, std dev = 43, $\Delta H_3 = -10\ 230$.

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 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 $(NH_4)_5P_3O_{10}\cdot H_2O$ 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

$$\text{ampule } H_3PO_4\cdot 16.26H_2O + \text{solvent} = \text{solution A} \qquad (2)$$

$$\text{ampule } (NH_4)_5P_3O_{10}\cdot H_2O + \text{solution A} = \text{solution B} \qquad (3)$$

$$\text{ampule } H_2O + \text{solvent} = \text{solution C} \qquad (4)$$

$$\text{ampule } NH_4H_2PO_4 + \text{solution C} = \text{solution B} \qquad (5)$$

and

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

where $\Delta H_1$ is the enthalpy of reaction 1 in calories and $\Delta H_2$, $\Delta H_3$, $\Delta H_4$, and $\Delta H_5$ 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 $\Delta H_2$, $\Delta H_3$, $\Delta H_4$, and $\Delta H_5$ are listed in Tables I, II, III, and IV, respectively. Straight line

Table III. Enthalpy of Solution of $H_2O$ in 9.93 *m* HCl at 40 °C

| Sample wt, g | Cor temp rise, °C | −Enthalpy of soln, cal/sample | $-\Delta H_4$,[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] $\Delta H_4 = -458 + 0.20w$, $w = 13.144\,93$, std dev = 1, $\Delta H_4 = -455$.

Table IV. Enthalpy of Solution of $NH_4H_2PO_4$ in 9.93 *m* HCl + Stoichiometric $H_2O$ at 40 °C

| Sample wt, g | Cor temp rise, °C | Enthalpy of soln, cal/sample | $\Delta H_5$,[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] $\Delta H_5 = 5534 + 2.95w$, $w = 13.316\,08$, std dev = 7, $\Delta H_5 = 5573$.

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 $(NH_4)_5P_3O_{10}\cdot H_2O$ or the stoichiometric amount of $H_3PO_4\cdot 16.26H_2O$, $NH_4H_2PO_4$, or $H_2O$ corresponding to that weight. The equations along with the standard deviations and the values of $\Delta H_2$, $\Delta H_3$, $\Delta H_4$, and $\Delta H_5$ 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

$$\Delta H_1(25\ ^\circ\mathrm{C}) = \Delta H_1(40\ ^\circ\mathrm{C}) + \int_{40\ ^\circ\mathrm{C}}^{25\ ^\circ\mathrm{C}} \Delta C_P \,\mathrm{d}T \qquad (7)$$

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 Zettlemoyer for $NH_4H_2PO_4$ (*9*), of Egan et al. for phosphoric acid solutions (*2*), and of Luff and Williard for $(NH_4)_5P_3O_{10}\cdot H_2O$ (*6*).

The data of Egan and Luff (*1*) were used to determine $\Delta H_8$ and $\Delta H_9$, the enthalpies of reactions 8 and 9 at 25 °C, as −436

$$H_3PO_4\cdot 16.26H_2O + 84.24H_2O = H_3PO_4\cdot 100.5H_2O \qquad (8)$$

$$H_3PO_4\cdot 100H_2O + 0.5H_2O = H_3PO_4\cdot 100.5H_2O \qquad (9)$$

and −1 cal, respectively. Subtracting twice the difference between $\Delta H_8$ and $\Delta H_9$ from $\Delta H_1$ at 25 °C gives $\Delta H_{10}$, the enthalpy of reaction 10 at 25 °C, as −30 480 cal.

$$(NH_4)_5P_3O_{10}\cdot H_2O + 2(H_3PO_4 \text{ in } 100H_2O) + H_2O = 5NH_4H_2PO_4 \qquad (10)$$

The standard enthalpies of formation of $NH_4H_2PO_4$(c), $H_2O$(l), and $H_3PO_4$ in $100H_2O$ 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

$$\Delta H_f^\circ((NH_4)_5P_3O_{10}\cdot H_2O) = 5(\Delta H_f^\circ(NH_4H_2PO_4)) - 2(\Delta H_f^\circ(H_3PO_4 \text{ in } 100H_2O)) - \Delta H_f^\circ(H_2O) - \Delta H_{10} \qquad (11)$$

gives −1011.8 kcal/mol as the standard enthalpy of formation of $(NH_4)_5P_3O_{10}\cdot H_2O$.

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# Pressure–Volume–Temperature Relationships of Several Polar Liquids

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**The specific volumes of liquid $CCl_2F_2$, $CHClF_2$, $CH_3Cl$, $CH_3I$, $CH_3Br$, $C_2H_5Br$, and $CH_3COOCH_3$ 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: $CCl_2F_2$ and $CHClF_2$, Daikin Kogyo Co., Ltd., Japan, 99.9%; $CH_3Cl$, Matheson Gas Products, a Division of Will Ross, Inc., 99.5%; $CH_3I$, Kokusan Kagaku Co., Ltd., Japan, 98.2%;

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