NOMENCLATURE

D = diameter of cylindrical heating element, cm
g = local acceleration due to gravity, cm/sec^2
M = molecular weight of gas, g/g mole
T = temperature, °K
q = wall heat flux density, cal/cm^2 sec
N_{Gr} = Grashof number, $gD^3(\rho_\infty/\rho_w - 1)/\nu_f^2$, dimensionless
N_{Nu} = Nusselt number, $qD/\lambda(T_w - T_\infty)$, dimensionless
λ = thermal conductivity, cal/cm sec °K
$\bar{\lambda}$ = integrated temperature average of thermal conductivity

$$= \frac{\int_{T_\infty}^{T_w} \lambda dt}{T_w - T_\infty}, \text{ cal/cm sec °K}$$

ν_f = kinematic viscosity at linear average temperature, $\frac{1}{2}(T_w + T_\infty)$, cm^2/sec
ρ = density, g/cm^3

Subscripts

∞ = state of bulk gas
w = state of cylinder wall surface

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Enthalpy of Formation of Ammonium Hydrogen Monoamidophosphate, $NH_4HPO_3NH_2$

ZACHARY T. WAKEFIELD[1], BASIL B. LUFF, and ROBERT B. REED
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 (monoclinic) ammonium hydrogen monoamidophosphate, $NH_4HPO_3NH_2$, is –292.42 ± 0.22 kcal per mole. It was determined from its enthalpy of solution in 4m HCl and from published values for the enthalpies of formation of H_3PO_4, $NH_4H_2PO_4$, and H_2O.

In a continuing study of the thermal properties of compounds with potential application in fertilizer technology, measurements were made of the enthalpy of formation of ammonium hydrogen monoamidophosphate, $NH_4HPO_3NH_2$. 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.

MATERIALS AND APPARATUS

Ammonium Hydrogen Monoamidophosphate. $NH_4HPO_3NH_2$ was prepared by adding 27.5 grams of phosphoryl trichloride (0.2 mole) slowly to 250 ml of a stirred, ice-cold 10% aqueous ammonia solution (1.5 moles of NH_3). There was some fuming and evolution of heat, and the reaction was complete within several minutes to form a clear solution.

Paper chromatography with a neutral solvent showed that the phosphate in the solution was distributed as 63.4% monoamidophosphate, 33.1% diamidophosphate, and 3.5% phosphoryl triamide. On dilution of the solution with 1 liter of acetone, two liquid phases were formed; the lower phase contained all the monoamidophosphate and the upper contained all the other species. The bottom layer was separated, neutralized with acetic acid, and cooled to induce crystallization. Additional product was obtained by dilution of the filtrate with an equal volume of ethanol.

The product was identified as $NH_4HPO_3NH_2$ by x-ray diffraction; the four strongest lines and their relative intensities were 5.77 (100), 4.22 (57), 4.30 (50), and 4.26 (51), corresponding, respectively, to 5.77 (100), 4.22 (46), 4.30 (35), and 4.26 (35) reported by Herzog (*3*). Similar agreement was found for the weaker reflections.

The calorimeter sample was a composite of four batches of about equal weight that were mixed thoroughly. Petrographic examination showed that all the individual batches had the same optical properties (monoclinic, $N_\alpha = 1.495$, $N_\beta = 1.522$, $N_\gamma = 1.541$)(*4*) as reference preparations whose identification was established by x-ray and chemical analysis. The composition of the composite was 24.6% total N, 12.4% ammoniacal N, and 27.15% P (stoichiometric: 24.56% total N, 12.28% ammoniacal N,

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[1] To whom correspondence should be sent.

27.16% P). The product was homogeneous and well crystallized; it melted sharply at 233° to 234° C.

Salt and Acids. Reagent ammonium dihydrogen phosphate was recrystallized from distilled water and dried by vacuum desiccation over P_2O_5. Its composition was 14.8% NH_3 and 61.7% P_2O_5 (stoichiometric: 14.81% NH_3, 61.70% P_2O_5). The acids used were reagent phosphoric acid containing 62.00% P_2O_5 by gravimetric analysis and reagent hydrochloric acid diluted with water to 4.030*m* as determined by alkalimetric titration.

Calorimeter and Procedure. The solution calorimeter (*1*, *2*) was modified in a few details. The heater was replaced with a 4-lead constantan heater mounted in a glass tube that was shaped into a helix and suspended from the calorimeter cover by two 5-mm glass tubes through which the current and potential leads were passed. A draft tube of inert plastic was fastened with platinum wire inside the glass helix. Temperatures were measured with a precision of 0.1 millidegree by conventional "normal" and "reverse" readings of the resistance of a platinum resistance thermometer on a Leeds & Northrup K-2 Mueller bridge.

The calorimeter system was calibrated electrically immediately before and after each solution period, and the mean calibration value for each run was used to compute the corresponding enthalpy value. One defined calorie was taken as 4.1840 absolute joules. Electrical power was determined by measuring with a Wenner standardizing potentiometer the potential drop across a standard resistor in series with the calorimeter heater and across a portion of an Arytron shunt in parallel with the calorimeter heater. A double-pole double-throw switch simultaneously started a second-timer and switched the heating current from a dummy heater to the calorimeter heater.

The solution periods for all calorimeter runs were short; the temperature change became linear after 2 or 3 minutes, and the temperature rise was determined by extrapolating the fore and after rating periods to the time of bulb breakage. The corrected temperature rise for the 600-second electrical calibrations was determined by extrapolating the fore and after rating periods to the mean time of the calibration.

ENTHALPIES OF SOLUTION

In the equation

$$NH_4HPO_3NH_2(c) + H_3PO_4\cdot 0.9151\ H_2O(liq) + 0.0849\ H_2O(liq) = 2\ NH_4H_2PO_4(c) \quad (1)$$

the amidophosphate was the only compound for which the enthalpy of formation was not known. The enthalpy of reaction of Equation 1 was determined as the difference between the sum of the enthalpies of solution of the products and the sum of the enthalpies of solution of the reactants in 4*m* HCl at 25° C under such conditions that the ionic concentrations of the solutions of reactants and products were the same. The reactions are shown in the equations

$$\{0.0849\ H_2O\}(liq) + \{3.1674\ (HCl\cdot 13.7767\ H_2O)\}(soln) = \{3.1674\ (HCl\cdot 13.8035\ H_2O)\}(soln) \quad (2)$$

$$[3.1674\ (HCl\cdot 13.8035\ H_2O)](soln) + \{H_3PO_4\cdot 0.9151\ H_2O\}(soln) = \{H_3PO_4 + 3.1674\ (HCl\cdot 14.0924\ H_2O)\}(soln) \quad (3)$$

$$\{H_3PO_4 + 3.1674\ (HCl\cdot 14.0924\ H_2O)\}(soln) + \{NH_4HPO_3NH_2\}(c) = \{2\ NH_4H_2PO_4 + 3.1674\ (HCl\cdot 13.7767\ H_2O)\}(soln) \quad (4)$$

$$\{2\ NH_4H_2PO_4\}(c) + \{3.1674\ (HCl\cdot 13.7767\ H_2O)\}(soln) = \{2\ NH_4H_2PO_4 + 3.1674\ (HCl\cdot 13.7767\ H_2O)\}(soln) \quad (5)$$

Equation 1 then is the difference between Equation 5 and the sum of Equations 2, 3, and 4.

All enthalpy-of-solution measurements were made in 4.030*m* HCl. Sample weights were corrected for buoyancy.

The enthalpies of solution of $H_3PO_4\cdot 0.9151\ H_2O$ in 4.030*m* HCl to which the stoichiometric amount of H_2O had been added are listed in Table I. The observed enthalpy of solution of $H_3PO_4\cdot 0.9151\ H_2O$ is represented by the equation

$$-\Delta H = 1921.02 - 7.185w \quad (6)$$

where ΔH = enthalpy of solution, calories per mole and w = weight, grams, of $H_3PO_4\cdot 0.9151\ H_2O$.

The enthalpies of solution of $NH_4H_2PO_4$ in 4.030*m* HCl and of $NH_4HPO_3NH_2$ in 4.030*m* HCl to which the stoichiometric amounts of H_2O and H_3PO_4 had been added are listed in Tables II and III.

The average weights of $NH_4HPO_3NH_2$ and of 4.030*m* HCl in Table III were used to calculate the stoichiometric amount of $H_3PO_4\cdot 0.9151\ H_2O$ (9.46379 grams) and of H_2O (0.12644 gram) in the reaction and the change in concentration of HCl brought about by the addition of this amount

Table II. Enthalpy of Solution of $NH_4H_2PO_4$ in 4.030*m* HCl at 25° C

Sample Wt., Grams	Corr. Temp. Rise, ° C	Enthalpy of Soln., Cal/Sample	ΔH, Cal/Mole	Δ
15.96803	−1.0215	821.56	5918.1	16.8
16.06429	−1.0266	824.62	5904.6	3.3
16.54634	−1.0498	848.28	5897.1	−4.2
16.98911	−1.0781	871.18	5898.4	−2.9
17.11727	−1.0942	879.10	5907.5	6.2
17.50016	−1.1097	896.52	5892.7	−8.6
17.92120	−1.1370	918.94	5898.2	−3.1
18.49076	−1.1717	947.38	5893.4	−7.9
18.65654	−1.1900	957.19	5901.5	0.3
		Av.	5901.3	±2.6

Table I. Enthalpy of Solution of $H_3PO_4\cdot 0.9151\ H_2O$ in 4.030*m* HCl + Stoichiometric H_2O at 25° C

Sample Wt., Grams	Corr. Temp. Rise, ° C	Enthalpy of Soln., −Cal/Sample	$-\Delta H$, Obsd., Cal/Mole	$-\Delta H$, Calcd., Cal/Mole	ΔH, Calcd., $-\Delta H$, Obsd.
7.47417	0.1521	122.01	1868.8	1867.2	−1.6
8.54875	0.1729	139.20	1864.1	1859.4	−4.7
8.97148	0.1810	145.19	1852.7	1856.4	3.7
9.78233	0.1956	157.46	1842.7	1850.6	7.9
10.06219	0.2026	162.59	1849.8	1848.6	−1.3
10.83134	0.2170	174.90	1848.6	1843.0	−5.6
11.05900	0.2209	177.79	1840.5	1841.4	0.9
12.82044	0.2546	204.85	1829.2	1828.7	0.6
				Standard deviation	±1.6

Table III. Enthalpy of Solution of $NH_4HPO_3NH_2$ in 4.030*m* HCl + Stoichiometric H_2O + Stoichiometric H_3PO_4 at 25° C

Sample Wt., Grams	Solvent Wt., Grams	Corr. Temp. Rise, ° C	Enthalpy of Soln., –Cal/Sample	$-\Delta H$, Cal/Mole	Δ
9.03748	902.0304	1.1574	933.92	11784.8	–5.3
9.38211	901.3658	1.2009	969.16	11780.3	0.8
9.42745	901.3487	1.2089	974.55	11788.8	9.3
9.43190	901.4408	1.2051	973.33	11768.5	–11.0
9.46471	901.7051	1.2087	977.39	11776.7	–2.8
9.51416	901.5680	1.2157	982.39	11775.4	–4.1
9.51861	901.3247	1.2167	983.34	11781.2	1.7
9.53206	901.9604	1.2172	983.69	11768.8	–10.7
9.53890	901.6901	1.2224	986.24	11790.9	11.4
9.42749	901.6038		Av.	11779.5	± 2.7

of water. The enthalpy of solution of 0.12644 gram (0.00702 mole) of H_2O in 3.1674 moles of 4.030*m* HCl,

$$3.1674\ (HCl \cdot 13.7767\ H_2O) + 0.0070\ H_2O = 3.1674\ (HCl \cdot 13.7789\ H_2O) \quad (7)$$

calculated from a cubic equation fitted to the enthalpy-of-dilution data for HCl (*5*), is –68.57 cal per mole, the difference between the enthalpies of formation of the two concentrations of HCl. The enthalpy of solution of the stoichiometric amount of $H_3PO_4 \cdot 0.9151\ H_2O$ in 4.030*m* HCl to which the stoichiometric amount of H_2O had been added was calculated from Equation 6 to be –1853.03 cal per mole of $H_3PO_4 \cdot 0.9151\ H_2O$.

Substitution in Equation 1 of the measured enthalpies of solution gives –25,441 ± 6 cal for the enthalpy of reaction. The standard enthalpies of formation from the elements at 25° C (*5*) are: H_2O(liq), –68.315 ± 0.01; $NH_4H_2PO_4$(c), –345.38 ± 0.1; and $H_3PO_4 \cdot 0.9151\ H_2O$(liq), –304.58 ± 0.1 kcal per mole. The published value for $H_3PO_4 \cdot H_2O$ (*5*) was adjusted to the concentration $H_3PO_4 \cdot 0.9151\ H_2O$ by the heat-of-dilution data of Egan and Luff (*1*). The uncertainty intervals are the standard deviation of measured values. The values taken from NBS 270-3 (*5*) are used with uncertainty intervals of 10 in the last figure given. Substitution of these values in Equation 1 gives –292.42 ± 0.22 kcal per mole for the standard enthalpy of formation of $NH_4HPO_3NH_2$ at 25° C.

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Apparent Molal Volumes of Aqueous Sodium Tetraphenylboron Solutions from 0° to 60° C

FRANK J. MILLERO
Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Fla. 33149

The concentration and temperature behavior of the apparent molal volumes, ϕ_V's, of electrolytes that contain nonpolar hydrocarbon groups is abnormal compared to the more common electrolytes (*2-6, 10-15, 18, 21, 25, 26-28, 31, 34-38*). For example, the ϕ_V's of the Bu_4N^+ halides have larger negative deviations from the limiting law, which become less negative at higher temperatures; at higher concentrations the ϕ_V's of the Bu_4N^+ halides go through a minimum and the ϕ_V's increase with increasing concentration. At infinite dilution, the partial molal volumes of the Bu_4N^+ halides do not appear to go through a maximum as a function of temperature—i.e., $\partial^2 \bar{V}_2^\circ / \partial T^2$ is positive. The anomalous concentration dependence of the ϕ_V's of the Bu_4N^+ halides has been attributed to ion-pairing (*18, 21, 37*), "hydrophobic bonding" (*10*), "iceberg" effects (*9, 31, 36*), micelle formation (*37*), "salting-in" effects (*3-5, 34*), and induced cation-cation interactions (*2, 11, 14, 15, 35, 36*). The abnormal temperature behavior of the $\bar{V}_2^\circ$'s of the Bu_4N^+ halides has been attributed to the ability of the nonpolar hydrocarbon portion of the Bu_4N^+ ion to increase or enforce the structure of water (*8, 9, 11*) and the release of the water with increasing temperature (*2, 13, 14, 15, 27, 31*).

The present work on the ϕ_V's of sodium tetraphenylboron ($NaBPh_4$) solutions was undertaken to obtain accurate ϕ_V data as a function of concentration and temperature for an electrolyte that contains a nonpolar hydrocarbon group on a large anion. By comparing the ϕ_V results for this large anion with the large cation, Bu_4N^+, we can hopefully obtain a better understanding of the ion-ion and ion-water interactions of electrolytes with nonpolar hydrocarbon groups. Recently (*33*), the partial molal heat capacities at infinite dilution were shown to behave abnormally between 40° and 80°; thus, the results of this study may possibly be useful in explaining this behavior [since there appears to be a parallism between the partial molal volumes and the partial molal heat capacities of electrolytes as a function of temperature (*19*)].