Table III. Comparison of Our Results with Literature Values

Compound	Lit values[a]	Our values[a]
Cycloheptane	0.8109^{20} (*10*)	0.8108^{20}
n-Nonanol	0.8273^{20} (*10*); 0.8280^{20}, 0.8247^{25}, 0.8215^{30} (*8*)	0.8281^{20}, 0.8249^{25}, 0.8215^{30}
2-Methylcyclohexanol	0.9194^{26} (*10*)	0.9184^{26}
Benzaldehyde	1.0415^{25} (*10*)	1.0418^{25}
Chlorobenzene	1.1065^{20}, 1.1013^{25} (*6*); 1.10112^{25} (*2*)	$1.1065_8{}^{20}$, $1.1009_8{}^{25}$, $1.0954_6{}^{30}$
	1.10654^{20}, 1.10118^{25}, 1.09574^{30}, 1.08484^{40} (*7*)	$1.0900_0{}^{35}$, 1.08460^{40}, $1.0761^{47.9}$
	1.0901^{35}, 1.0690^{55}, $1.0415^{80.4}$, $1.0235^{96.1}$ (*5*)	1.0685^{55}, $1.0561^{66.4}$, $1.0464^{75.1}$
	$1.0955^{30.1}$, $1.0763^{47.9}$, $1.0562^{66.4}$, $1.0470^{75.1}$	$1.0408^{80.4}$, $1.0228^{94.8}$, $1.0212^{96.1}$
	$1.0251^{94.8}$ (*9*)	
Bromobenzene	1.49500^{20}, 1.48824^{25}, 1.48150^{30} (*3*)	1.4944^{20}, $1.4880_5{}^{25}$, $1.4816_3{}^{30}$
	$1.4841^{28.3}$, $1.4553^{49.5}$, $1.4392^{61.4}$, $1.4257^{71.2}$ (*5*)	$1.4838^{28.3}$, $1.4559^{49.5}$
		$1.4397^{61.4}$, $1.4260^{71.2}$

[a] Superscript denotes temperature, °C.

in Table II along with the average and maximum deviations. The regression analysis was carried out with an IBM 7044 computer. The accuracy in the experimental values was estimated to be within ±0.0005 g cm^{-3} (*1*).

Discussion

Comparison of our results with the literature values is reported in Table III. The agreement for cycloheptane, methylcyclohexanol, and benzaldehyde with the limited literature values is satisfactory. For *n*-nonanol our values agree very well with the Thermodynamics Research Center selected values (*8*). For chlorobenzene the agreement with the measurements of Nyvlt and Erdos (*7*) from 20° to 40°C is within our assigned uncertainty. However, at higher temperatures our values are lower than those reported by Meyer and Mylius in 1920 (*5*) and Velasco in 1927 (*9*). For bromobenzene our values agree very well with those of Dreisbach and Martin (*3*) and Meyer and Mylius (*5*).

Acknowledgment

The authors thank the IIT-Kanpur Computer Center for providing the computer facilities.

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Received for review January 29, 1973. Accepted June 27, 1973.

Enthalpy of Formation of Triammonium Hydrogen Pyrophosphate Monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$

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The enthalpy of formation from the elements in their standard states at 25°C of crystalline (triclinic) triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, is −712.7 kcal mol^{-1}. It was determined from the enthalpies of solution of $(NH_4)_3HP_2O_7 \cdot H_2O$, $H_3PO_4 \cdot 16.24H_2O$, $NH_4H_2PO_4$, and H_2O in 10*m* HCl at 40°C and from published values for the heat capacities of these compounds and enthalpies of formation of H_3PO_4 and $NH_4H_2PO_4$.

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 triammonium hydrogen pyrophosphate monohydrate, $(NH_4)_3HP_2O_7 \cdot H_2O$, a major component of ammonium polyphosphate fertilizers.

Materials and Apparatus

Salts and acids. Samples of $(NH_4)_3HP_2O_7 \cdot H_2O$ (GFW = 247.0824) were taken from the charge in a low-temperature calorimeter after the heat capacity had been measured (*9*). The pyrophosphate was prepared originally from a granular ammonium polyphosphate produced in a TVA pilot plant. A saturated solution of the polyphosphate had a pH of about 4.6, and 83% of the phosphorus was present as pyrophosphate. In the first step of purification, $(NH_4)_3HP_2O_7 \cdot H_2O$ about 93% pure was obtained by simultaneously adding concentrated NH_4OH and solid ammonium polyphosphate to the saturated solution of the ammonium polyphosphate in the proportions to maintain the pH at 5.5. The crystalline product was filtered off and redissolved to saturation in distilled water at 25°C, and the solution was stored at 0°C to effect slow crystallization. The low-temperature recrystallization was repeated three times. The largest single crystals (several centimeters long) were removed, blotted free of mother liquor with absorbent paper, and stored in a sealed glass bottle.

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For measurement of the heat capacity, the crystals were crushed with a minimum of grinding to pass a 50-mesh screen. Paper-chromatographic analysis showed that 99.7% of the phosphorus in the material was present as pyrophosphate. The 0.3% present as orthophosphate was assumed to be within the limits of sensitivity of the chromatographic method, and no correction was made for impurity. The recrystallized material contained 17.0%, N, 25.1% P, and 7.2% H_2O (stoichiometric: 17.01% N, 25.07% P, 7.29% H_2O) and was shown by petrographic and X-ray examination to be well-crystallized homogeneous $(NH_4)_3HP_2O_7 \cdot H_2O$ (*3*).

Reagent ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (GFW = 115.0259), was recrystallized from distilled water and dried by vacuum desiccation over P_2O_5. It analyzed 12.2% N and 26.9% P (stoichiometric: 12.18% N, 26.83% P). Recrystallized reagent phosphoric acid was diluted to yield $H_3PO_4 \cdot 16.24H_2O$ (18.17% P_2O_5 by chemical analysis, GFW = 390.60). The calorimetric solvent was prepared by diluting reagent hydrochloric acid to 10.34*m* HCl as determined by alkalimetric titration.

Calorimeter. The solution calorimeter and the method of determining temperature have been described (*10*). The platinum resistance thermometer was calibrated by the National Bureau of Standards. The calorimeter system was calibrated electrically immediately before and after each solution period, and the mean calibration value for each run was used in computing the corresponding enthalpy value. The Wenner potentiometer, Ayrton shunt, and standard resistor for the electrical energy measurements were calibrated with standard resistors and a potentiometer calibrated by the Redstone Arsenal, Huntsville, Ala., and are traceable to the National Bureau of Standards. The defined thermochemical calorie (1 cal = 4.1840 abs J) was used to convert electrical energy to thermal energy.

The corrected temperature for the solution period was determined by a method described by Rossini (*7*).

Enthalpies of solution. The enthalpy of formation of triammonium hydrogen pyrophosphate at 25°C was determined from published enthalpies of formation of $H_3PO_4(l)$ and $NH_4H_2PO_4(c)$ and the enthalpy of reaction at 25°C as represented by the equation.

$$(NH_4)_3HP_2O_7 \cdot H_2O(c) + H_3PO_4 \cdot 16.24H_2O(l) = 3NH_4H_2PO_4(c) + 16.24H_2O(l) \quad (1)$$

Temperature changes during dissolution were arbitrarily limited to 1°C, which determined the sample size of monoammonium phosphate and thus, by stoichiometry, the amounts of other materials in Equation 1. The concentration of acid selected for the second term of Equation 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 (*4*) and of water in 10*m* HCl at 40°C, together with published values for 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 P_2O_5, showed that 14.7 grams of $(NH_4)_3HP_2O_7 \cdot H_2O$ was completely hydrolyzed in 1 hr at 40°C in 850 ml of 10*m* HCl. Calorimetric measurements indicated, however, that hydrolysis was complete in 40 min.

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

Ampoule $H_3PO_4 \cdot 16.24H_2O$ + Solvent = Solution A ΔH_1
Ampoule $(NH_4)_3HP_2O_7 \cdot H_2O$ + Solution A = Solution C ΔH_2
Ampoule H_2O + Solvent = Solution B ΔH_3
Ampoule $NH_4H_2PO_4$ + Solution B = Solution C ΔH_4

Results of determinations of ΔH_1, ΔH_2, ΔH_3, and ΔH_4 (endothermic) and their average values and standard deviations are shown in Tables I-IV. The operation $\Delta H_R = \Delta H_1 + \Delta H_2 - 16.24\Delta H_3 - 3\Delta H_4$ gives −14,123 ± 32

Table I. Enthalpy of Solution of $H_3PO_4 \cdot 16.24H_2O$ in 850.0 ml of 10.34*m* HCl at 40°C

Wt sample, g	Corr temp rise, °C	$-\Delta H_1$, cal/mol	Δ
16.86328	0.26925	4499	+12
16.89785	0.26855	4460	−27
16.90180	0.27003	4487	±0
16.93014	0.26988	4491	+4
16.99812	0.27101	4476	−11
17.01477	0.27181	4507	+20
17.05783	0.27256	4501	+14
17.06456	0.27215	4488	+1
17.06684	0.27197	4486	−1
17.08902	0.27254	4480	−7
17.25466	0.27520	4487	±0
	Av, double SD	4487	±8

Table II. Enthalpy of Solution of $(NH_4)_3HP_2O_7 \cdot H_2O$ in 850.0 ml of 10.34*m* HCl and Stoichiometric $H_3PO_4 \cdot 16.24H_2O$ at 40°C

Wt sample, g	Corr temp rise, °C	$-\Delta H_2$, cal/mol	Δ
10.69361	0.08346	1373	+51
10.71231	0.07863	1302	−20
10.72467	0.07640	1268	−54
10.74201	0.07558	1248	−74
10.74970	0.07925	1309	−13
10.74996	0.08278	1356	+34
10.76358	0.08184	1346	+24
10.76761	0.08058	1327	+5
10.78908	0.08277	1363	+41
10.80658	0.07830	1286	−36
10.89534	0.08418	1368	+46
	Av, double SD	1322	±26

Table III. Enthalpy of Solution of H_2O in 850.0 ml of 10.34*m* HCl at 40°C

Wt sample, g	Corr temp rise, °C	$-\Delta H_3$, cal/mol	Δ
12.53029	0.47905	495.5	+0.1
12.56580	0.48089	496.0	+0.6
12.56726	0.48109	496.4	+1.0
12.59423	0.48171	495.0	−0.4
12.66411	0.48404	495.0	−0.4
12.73172	0.48668	495.2	−0.2
12.73982	0.48504	494.8	−0.6
12.77636	0.48824	494.3	−1.1
12.81710	0.49233	497.3	+1.9
12.85980	0.49192	496.2	+0.8
12.90319	0.49480	493.8	+1.6
12.94108	0.49481	495.7	+0.3
	Av, double SD	495.4	±0.6

Table IV. Enthalpy of Solution of $NH_4H_2PO_4$ in 850.0 ml of 10.34*m* HCl and Stoichiometric H_2O at 40°C

Wt sample, g	—Corr temp rise, °C	ΔH_4, cal/mol	Δ
14.90333	0.97704	5457	+4
15.00510	0.98473	5453	±0
15.02232	0.98401	5448	−5
15.10264	0.98916	5451	−2
15.12050	0.99038	5447	−6
15.15361	0.99289	5466	+13
15.20558	0.99578	5452	−1
15.22108	0.99749	5451	−2
	Av, double SD	5453	±4

cal (double standard deviation) for Equation 1 at 40°C. This value was adjusted by −1552 ± 2 cal to give −15,675 ± 32 cal for the enthalpy of reaction at 25°C according to the equation

$$\Delta H_R(25°C) = \Delta H_R(40°C) + \int_{313.15}^{298.15} \Delta C_p \, dT \quad (2)$$

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 (*6*), of Stephenson and Zettlemoyer for $NH_4H_2PO_4$ (*8*), of Egan et al. for phosphoric acid solutions (*2*), and of Wakefield and Luff for $(NH_4)_3HP_2O_7 \cdot H_2O$ (*9*).

The standard enthalpies of formation of $H_3PO_4(l)$, −302.8 kcal, and $H_3PO_4 \cdot 15H_2O$ (soln), −307.715 kcal (*5*), were used to determine the enthalpy of the reaction

$$H_3PO_4(l) + 15H_2O = H_3PO_4 \cdot 15H_2O \quad (3)$$

at 25°C, −4.9 kcal. The enthalpy of the reaction

$$H_3PO_4 \cdot 15H_2O + 1.24H_2O = H_3PO_4 \cdot 16.24H_2O \quad (4)$$

at 25°C, −36.65 cal, was determined from the data of Egan and Luff (*1*). The summation of the enthalpies of reaction of Equations 1, 3, and 4 gives the enthalpy of the reaction

$$(NH_4)_3HP_2O_7 \cdot H_2O(c) + H_3PO_4(l) = 3NH_4H_2PO_4(c) \quad (5)$$

at 25°C, −20.61 ± 0.1 kcal.

The standard enthalpy of formation of $NH_4H_2PO_4(c)$ is −345.38 kcal/mol (*5*). Substituting the known enthalpies of formation and the enthalpy of reaction of Equation 5 in the equation

$$\Delta H_f°(NH_4)_3HP_2O_7 \cdot H_2O(c) = 3[\Delta H_f° NH_4H_2PO_4(c)] - \Delta H_f° H_3PO_4(l) - \Delta H_R(25°C) \quad (6)$$

gives −712.7 kcal/mol as the standard enthalpy of formation of $(NH_4)_3HP_2O_7 \cdot H_2O(c)$ 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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Received for review February 1, 1973. Accepted May 21, 1973.

High-Precision Vapor-Pressure Data for Eight Organic Compounds

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Vapor-pressure data are obtained via comparative ebulliometry for butyronitrile, cyclohexene, 1,3-cyclohexadiene, methylene cyclohexane, di-*n*-propyl ether, and cyclohexanone. In addition, corrected data are presented for capronitrile and lauronitrile. Constants for Antoine and Cox equations, with their statistical uncertainties, are included. The overall average differences between calculated and observed pressures for the new data, expressed as $\Delta p/p$, are 5.6×10^{-5} for the Antoine and 4.7×10^{-5} for the Cox equation.

During a study concerning thermodynamics of solution by use of gas-liquid chromatography, the need arose for enthalpy of vaporization data for several compounds. To estimate the enthalpy of vaporization from the Clapeyron equation, we measured the vapor pressures (from about 50°C to slightly above the normal boiling point) of five compounds for which such data are not presently available: cyclohexene, 1,3-cyclohexadiene, methylenecyclohexane, cyclohexanone, and di-*n*-propyl ether. In addition, we are including improved data for butyronitrile and corrected data for lauronitrile and capronitrile.

Experimental

A comparative ebulliometric technique was used with an apparatus similar to that described by Ambrose (*1*). Instead of four bubble caps, however, only one was used in the present ebulliometer, allowing the use of significantly smaller samples (3 ml) without sacrificing the high precision characteristic of the method.

Two platinum-resistance thermometers were used to measure the temperatures of the liquid-vapor equilibria of water and the liquid under investigation. That used for the latter was calibrated (at Leeds and Northrup) according to IPTS-48. The other was calibrated in this laboratory by use of the triple point of water and several temperatures up to 108°C. The latter was accomplished by using fresh samples of deionized, degassed water in both boilers of

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