

**Table IV. Hydrolytic Degradation of Tetrapolyphosphates**

Temp, °C	pH	$k_4$ , min <sup>-1</sup> , × 10 <sup>6</sup>	Half-life, hr <sup>a</sup>	Ref.
65.5	2.55	1800	6.42	(1)
	5.35	830	13.9	(1)
	5	664	17.3	(14)
60	3	470	24.5	(16)
	4	460	25.2	(9)
	4.5	240	48.2	(16)
	7	200	57.8	(9)
	8	107	108	(16)
30	4	7.5	1540	(9)
	7	4.6	2520	(9)
25 <sup>b</sup>	2.55	5.93 <sup>b</sup>	1950	...
	3.00	5.65	2050	...
	4.00	5.06	2280	...
	4.50	4.79	2410	...
	5.00	4.53	2550	...
	5.35	4.36	2650	...
	7.00	1.93	5980	...
	8.00	1.105	10450	...

<sup>a</sup> Half-life, hr = 1.1553 × 10<sup>-2</sup>/k<sub>4</sub>, when k<sub>4</sub> is in min<sup>-1</sup>. <sup>b</sup> All data at 25°C from present work; values of k<sub>4</sub> calculated from equations in Table III.

tetrapolyphosphate in an ammonium polyphosphate solution (such as fertilizer grade 11-37-0) with pH 6 will be hydrolyzed in about 5 months.

The half-life periods calculated from the rate constants obtained in the present study and from those reported in the literature are compared in Table IV. If we assume the values are equally reliable, at pH 7, tetrapolyphosphate disappears 104 times as fast at 60°C as at 25°C; at pH 4, it disappears 91 times as fast at 60°C as at 25°C. These data indicate that the activation energy for the degradation process

is about 26 kcal/mol at pH 7 and 25 kcal/mol at pH 4. Our data for 25° and 50°C (6) indicate that the activation energy is 27.20 kcal/mol at pH 7 and 26.76 kcal/mol at pH 4.

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RECEIVED for review September 3, 1971. Accepted January 7, 1972. Complete data for Table II will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order \$3.00 for photocopy or \$2.00 for microfiche.

## Solubility in System NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>-H<sub>2</sub>O at 0°C

THAD D. FARR<sup>1</sup> and JOSEPH W. WILLIARD

Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, AL 35660

**In the pH range 5.6-7.1 at 0°C, solubility, expressed as % (N + P<sub>2</sub>O<sub>5</sub>), in the system NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>-H<sub>2</sub>O is higher than that in the system NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>2</sub>O or in any simpler system of the condensed ammonium phosphates. In the pH range studied, one invariant-point solution was determined and one more was estimated by interpolation of measured compositions and pH.**

Mixtures of the ammonium salts of ortho-, pyro-, tripoly-, tetrapoly-, and more highly condensed phosphoric acids are being used increasingly to prepare liquid fertilizers that will not salt out at low temperatures (8, 9). In the continuing study of the properties of ammonium polyphosphates (2-6), measurements were made of the compositions of solutions in the system ammonia-orthophosphoric acid-pyrophosphoric acid-tripolyphosphoric acid-tetrapolyphosphoric acid-water at 0°C with which solid phases of the four phosphate species are in equilibrium over the pH range 5.6-7.1.

The equilibration mixtures were prepared from reagent mono- and diammonium orthophosphates, ammonium pyro-,

and tripolyphosphates crystallized from liquid fertilizers produced by ammoniation of electric furnace superphosphoric acid, 80% P<sub>2</sub>O<sub>5</sub> (14), and hexaammonium tetrapolyphosphate that was prepared by a modification (6) of published procedures (7, 12). The composition and phosphate distribution of the ammonium polyphosphates are given in Table I. Although the ammonium tripoly- and tetrapolyphosphates contained small amounts of less highly condensed species, none of the products contained phosphates more highly condensed than tetrapolyphosphate, and thus were suitable for preparing the equilibration mixtures of this complex system.

Stock solutions of the ammonium orthophosphates were prepared by saturating conductivity water at 5°C with the respective salts. Portions of these cold orthophosphate solu-

<sup>1</sup> To whom correspondence should be addressed.

**Table I. Ammonium Polyphosphates Used in Preparation of Equilibration Mixtures**

Salt	Compn, %		Distribution of phosphate, % of total P <sub>2</sub> O <sub>5</sub>			
	N	P <sub>2</sub> O <sub>5</sub>	Ortho	Pyro	Tri- poly	
					Tetra- poly	
(NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	17.0	57.3	0.4	99.6	...	...
(NH <sub>4</sub> ) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	22.1	56.9	0.5	99.5	...	...
(NH <sub>4</sub> ) <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ·2H <sub>2</sub> O	18.4	56.0	1.7	2.3	96.0	...
(NH <sub>4</sub> ) <sub>6</sub> P <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O	17.2	58.4	0.4	1.2	1.4	97.0

tions were then saturated with the ammonium pyrophosphate expected to be the stable phase at each desired pH, and these solutions then were saturated with pentaammonium tripolyphosphate and finally with hexaammonium tetrapolyphosphate. The amounts of each phosphate used to saturate the solutions were estimated from the solubility data of the respective ternary systems at 0°C (2, 3, 6, 11). The pH of each mixture was adjusted to the desired value with either anhydrous ammonia or the hydrogen form of Amberlite IR-120 resin.

No attempt was made to approach equilibrium from undersaturation. The mixtures, in plastic bottles, were equilibrated at 0.0 ± 0.5°C in a cold room with manual agitation. The temperature of the cold room was controlled by a commercial thermostat and checked periodically with a standard thermometer. Cold water or solid salt was added to the mixtures when needed to maintain the ratio of liquid to solid at about three.

The approach to equilibrium was followed by periodic petrographic examination of the wet solids. When one or more of the phosphate species was absent from the mixtures of excess solids, a few grams of the missing species were added, and equilibration was continued. When successive examinations indicated that all four phosphate species were present, samples of the liquid phase were taken for determinations of pH, composition, and distribution of the phosphate species.

Nitrogen was determined by distillation of ammonia with

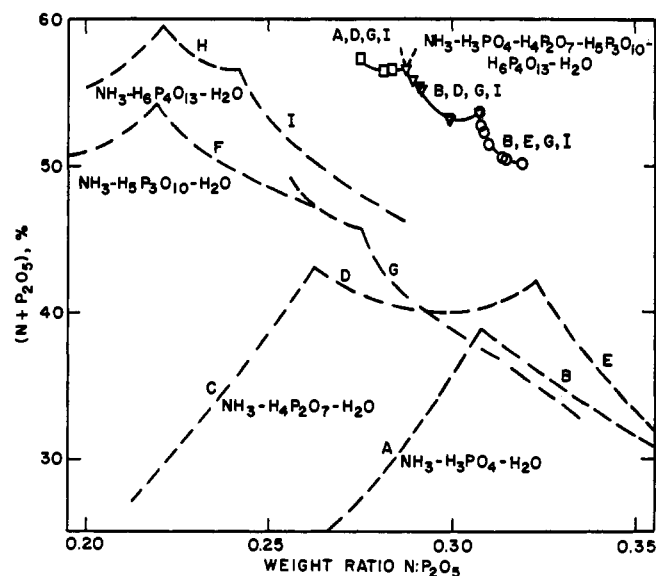
**Table II. System NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>-H<sub>2</sub>O at 0°C**

pH	Liquid phase		Distribution of phosphate, % of total P <sub>2</sub> O <sub>5</sub>				Solid phase <sup>a</sup>
	Compn, %		Ortho	Pyro	Tri- poly		
	N	P <sub>2</sub> O <sub>5</sub>			Tetra- poly		
7.05	12.12	38.05	20	20	18	42	B, E, G, I
6.72	12.05	38.28	20	23	16	41	B, E, G, I
6.69	12.06	38.41	21	27	16	36	B, E, G, I
6.45	12.14	39.22	21	33	15	31	B, E, G, I
6.38	12.34	40.03	22	37	14	27	B, E, G, I
6.36	12.36	40.15	21	35	14	30	B, E, G, I
6.40	12.39	40.26	21	31	14	34	B, E, G, I
6.36	12.56	40.92	22	34	13	31	B, D, E, G, I
6.39	12.61	41.04	21	35	14	30	B, D, E, G, I
6.15	12.21	40.80	25	32	15	28	B, D, G, I
6.14	12.22	40.90	25	32	14	29	B, D, G, I
5.98	12.45	42.76	28	28	16	28	B, D, G, I
5.96	12.49	43.02	...	...	...	...	B, D, G, I
5.90	12.49	43.23	29	29	15	27	B, D, G, I
5.90	12.62	43.99	30	26	17	27	B, D, G, I
...	12.43	44.01	27	29	18	26	A, D, G, I
5.74	12.35	43.93	25	25	19	31	A, D, G, I
5.61	12.38	45.07	23	23	21	32	A, D, G, I

<sup>a</sup> Identified by microscopic examination: A = NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, B = (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, D = (NH<sub>4</sub>)<sub>3</sub>HP<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O, E = (NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O, G = (NH<sub>4</sub>)<sub>5</sub>P<sub>3</sub>O<sub>10</sub>·2H<sub>2</sub>O, I = (NH<sub>4</sub>)<sub>6</sub>P<sub>4</sub>O<sub>13</sub>·2H<sub>2</sub>O.

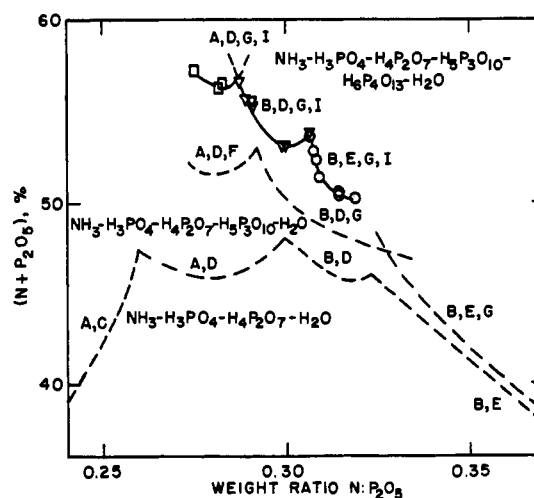
sodium hydroxide, and phosphorus was determined gravimetrically as quinolinium molybdophosphate (13); the pH of each liquid phase after warming to room temperature (about 25°C) was measured with a commercial meter and a glass electrode. The distribution of phosphate species was determined by one-dimensional paper chromatography (1, 10).

Equilibrium was established in a minimum of nine days. The results are summarized in Table II and plotted in Figures 1 and 2. Portions of the 0°C isotherms of the systems NH<sub>3</sub>-H<sub>2</sub>PO<sub>4</sub>-H<sub>2</sub>O (11), NH<sub>3</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O (2), NH<sub>3</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>2</sub>O (3), and NH<sub>3</sub>-H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>-H<sub>2</sub>O (6) are included in Figure 1; the 0°C isotherms of the multiphosphate systems NH<sub>3</sub>-H<sub>2</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O (5) and NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>-H<sub>2</sub>O (4) are included in Figure 2. The coordinates of the figures were



**Figure 1. Solubility in ammonium phosphate systems at 0°C**

- |   |  |
|---|--|
| A. NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>                                   | F. (NH <sub>4</sub> ) <sub>5</sub> P <sub>3</sub> O <sub>10</sub>                    |
| B. (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>                                 | G. (NH <sub>4</sub> ) <sub>6</sub> P <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O |
| C. (NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub>                   | H. (NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O  |
| D. (NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O | I. (NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O   |
| E. (NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O  |  |



**Figure 2. Solubility in multicomponent ammonium phosphate systems at 0°C**

- |   |  |
|---|--|
| A. NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>                                   | E. (NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O   |
| B. (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>                                 | F. (NH <sub>4</sub> ) <sub>5</sub> P <sub>3</sub> O <sub>10</sub>                    |
| C. (NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub>                   | G. (NH <sub>4</sub> ) <sub>6</sub> P <sub>4</sub> O <sub>13</sub> ·2H <sub>2</sub> O |
| D. (NH <sub>4</sub> ) <sub>3</sub> HP <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O | I. (NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O   |

selected to facilitate comparison of the total fertilizer nutrient contents,  $N + P_2O_5$ , of the saturated solutions in the several systems.

The 0°C isotherm of the multiphosphate system over the pH range studied comprises three branches representing solutions saturated, respectively, with  $(NH_4)_2HPO_4$ ,  $(NH_4)_4P_2O_7 \cdot H_2O$ ,  $(NH_4)_5P_3O_{10} \cdot 2H_2O$ , and  $(NH_4)_6P_4O_{13} \cdot 2H_2O$ ;  $(NH_4)_2HPO_4$ ,  $(NH_4)_3HP_2O_7 \cdot H_2O$ ,  $(NH_4)_5P_3O_{10} \cdot 2H_2O$ , and  $(NH_4)_6P_4O_{13} \cdot 2H_2O$ ; and  $NH_4H_2PO_4$ ,  $(NH_4)_3HP_2O_7 \cdot H_2O$ ,  $(NH_4)_5P_3O_{10} \cdot 2H_2O$ , and  $(NH_4)_6P_4O_{13} \cdot 2H_2O$ . Only one invariant solution was determined. It was saturated with  $(NH_4)_2HPO_4$ ,  $(NH_4)_3HPO_7 \cdot H_2O$ ,  $(NH_4)_4P_2O_7 \cdot H_2O$ ,  $(NH_4)_5P_3O_{10} \cdot 2H_2O$ , and  $(NH_4)_6P_4O_{13} \cdot 2H_2O$ , and contained 12.61% N and 41.04%  $P_2O_5$  distributed as ortho- 21, pyro- 35, tripoly- 14, and tetrapolyphosphate 29%. It had a pH of 6.39, a value near that (6.50) of the invariant solution of the ternary system  $NH_3-H_4P_2O_7-H_2O$  saturated with tri- and tetraammonium pyrophosphate and near that (6.44) of the invariant solution of the quaternary system  $NH_3-H_3PO_4-H_4P_2O_7-H_2O$  saturated with tri- and tetraammonium pyrophosphates and diammonium orthophosphate. A second invariant point, representing a solution saturated with  $NH_4H_2PO_4$ ,  $(NH_4)_2HPO_4$ ,  $(NH_4)_3HP_2O_7 \cdot H_2O$ ,  $(NH_4)_5P_3O_{10} \cdot H_2O$ , and  $(NH_4)_6P_4O_{13} \cdot 2H_2O$ , was estimated from plots of pH vs. N or  $P_2O_5$  to contain 12.6% N and 44.2%  $P_2O_5$  and to have a pH of 5.9.

As shown in Figure 1, the total fertilizer nutrient contents of the solutions saturated with ammonium ortho-, pyro-, tripoly-, and tetrapolyphosphates are significantly higher than those of solutions with the same ratio N: $P_2O_5$  that are saturated with only a single phosphate species. As shown in Figure 2, at each ratio N: $P_2O_5$ , a solution of the six-component system saturated with ammonium ortho-, pyro-, tripoly-, and tetrapolyphosphates has a nutrient content ( $N + P_2O_5$ ) 5–10% higher than that of a solution of the five-component system

saturated with only ammonium ortho-, pyro-, and tripolyphosphates, and 10–25% higher than that of a solution of the four-component system saturated with only ammonium ortho- and pyrophosphates.

The isotherms in Figure 2 will be useful in the preparation of ammonium polyphosphate solutions in the most desirable pH range with maximum fertilizer nutrient contents that will not salt out at 0°C.

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## Measured Enthalpies for Mixtures of Benzene with *n*-Pentane

JOHN M. LENOIR<sup>1</sup>

University of Southern California, Los Angeles, CA 90007

HOWARD G. HIPKIN

C. F. Braun & Co., Alhambra, CA 91802

**A flow calorimeter was used to measure four compositions of benzene with *n*-pentane between 260° and 700°F, with pressures ranging up to 1400 psia.**

This experimental study reports the calorimetric measurements of four mixtures of benzene with *n*-pentane, a paraffin of lower boiling point and molecular weight than benzene. This present work complements an earlier study of benzene and *n*-octane mixtures (7). The measurements were made with a flow calorimeter that operates isobarically and measures the enthalpy difference relative to 75°F and the pressure of measurements. The details of the calorimeter and its operation have been discussed (8).

Prior to this present study the accuracy of the calorimeter was determined by making measurements with pure pentane and liquid water, and comparing with published literature values (2, 3, 6, 9). These reported results showed an average

deviation of 1.2 Btu/lb for pentane and 0.98 Btu/lb with water, and it was concluded that the enthalpy measurements have an uncertainty of about 1.5 Btu/lb. For the period of measurements on the pentane–benzene mixtures, 144 additional measurements were made with pure pentane showing an average deviation from the literature values of 0.93 Btu/lb. An additional 66 measurements were performed with water, with average deviation of 0.69 Btu/lb. During the time period of approximately four years' operation of the calorimeter, the measurement accuracy has not declined, and an expectation of an accuracy of 1.5 Btu/lb is considered justified.

Enthalpy values have already been presented for the pure components, benzene and pentane, as discussed (7, 8). At the outset of this present study, it was believed that no previous enthalpy measurements had been made on the benzene–

<sup>1</sup> To whom correspondence should be addressed.