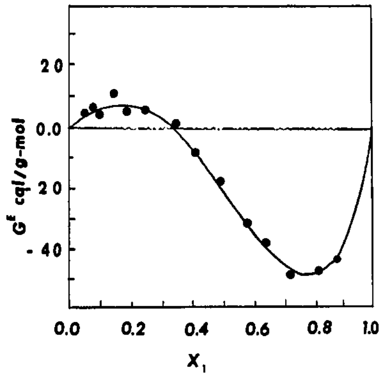


Figure 4. Excess Gibbs energy of system isobutyl alcohol–DMSO at 80°C

Table III. Constants of Redlich-Kister Equations for Isobutyl Alcohol–DMSO System

| °C | *B* | *C* | *D* |
|---|---|---|---|
| 80.0 | −0.427 | −0.352 | −0.085 |
| 92.5 | −0.343 | −0.265 | −0.029 |
| 105.0 | −0.273 | −0.184 | +0.021 |

and are plotted as a function of the mole fraction of isobutyl alcohol in the liquid phase for 80°C in Figure 4.

The data were correlated with the three-constant Redlich-Kister equation (*7*),

$$\log \frac{\gamma_1}{\gamma_2} = B(1 - 2x_1) + C[6x_1(1 - x_1) - 1] + D(1 - 2x_1)[1 - 8x_1(1 - x_1)] \quad (3)$$

The values of the Redlich-Kister constants at the three temperatures are given in Table III.

The standard errors in mole percent when 2-constant Redlich-Kister equations were used were 2.35, 1.23, and 2.35 at 80.0°, 92.5°, and 105.0°C, respectively, while for the 3-constant equations, the standard errors were 0.55, 0.45, and 0.43. The *t*-test shows that there is a 99% confidence level for the three-constant equation, the variance $\sigma^2$ being 0.00003, 0.00002, and 0.000019 at 80.0°, 92.5°, and 105.0°C, respectively.

## NOMENCLATURE

$B, C, D$ = constants of Redlich-Kister equation
$P^\circ$ = vapor pressure of pure component
$x$ = mole fraction of component in liquid phase
$y$ = mole fraction of component in vapor phase
$\gamma$ = activity coefficient
$\pi$ = total pressure
$\sigma^2$ = variance of fit
$g^E$ = excess free energy

SUBSCRIPTS

1 = isobutyl alcohol component
2 = DMSO component

## LITERATURE CITED

(1) Chandok, S. S., McMillan, A. F., *J. Chem. Eng. Data*, **14**, 286 (1969).
(2) Douglas, T. B., *J. Amer. Chem. Soc.*, **68**, 1072 (1946).
(3) Hipkin, H., Myers, H. S., *Ind. Eng. Chem.*, **46**, 2524 (1954).
(4) Perry, J. H., "Chemical Engineer's Handbook", pp 3–48, 4th ed., McGraw-Hill, New York, NY, 1963.
(5) Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," p 73, Prentice-Hall, Englewood Cliffs, NJ, 1967.
(6) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(7) Wohl, K., *Trans. Am. Inst. Chem. Eng.*, **42**, 215 (1946).

RECEIVED for review August 20, 1971. Accepted April 17, 1972. Work supported by the National Research Council of Canada.

---

# Solubility and Hydrolysis in System $NH_3$–$H_6P_4O_{13}$–$H_2O$

**THAD D. FARR, JOSEPH W. WILLIARD, and JOHN D. HATFIELD**
**Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, AL 35660**

**The 0°C solubility isotherm of the system $NH_3$–$H_6P_4O_{13}$–$H_2O$ comprises three branches in the pH range 2.2–6.3; the saturating solids are $(NH_4)_4H_2P_4O_{13}$, $(NH_4)_5HP_4O_{13}\cdot H_2O$, and $(NH_4)_6P_4O_{13}\cdot 2H_2O$. The invariant solution in equilibrium with the tetra- and pentaammonium salts contains 10.8% N and 48.6% $P_2O_5$ and has a pH of 4. In dilute solutions at 25°C ammonium tetrapolyphosphate hydrolyzes in a series of consecutive first-order reactions that produce tripoly-, pyro-, and orthophosphate; the several rate constants were determined as functions of pH.**

In the continuing study of the properties of ammonium polyphosphates (*3–5*), phase relationships in the system ammonia–tetrapolyphosphoric acid–water at 0°C were determined over the pH range 2.2 to 6.3, and the rates of hydrolysis of 0.2*M* solutions of ammonium tetrapolyphosphate at 25°C were determined as functions of pH.

Hexammonium tetrapolyphosphate of purity suitable for use in the solubility and hydrolysis studies was prepared by a modification of two published procedures (*8, 12*). Lead orthophosphate was heated for 32 hr at 570°C to produce lead tetrapolyphosphate which was dissolved and converted to the ammonium salt with ammonium sulfide; the last traces of lead were precipitated with hydrogen sulfide. The lead-free filtrate was treated with methyl alcohol, and the precipitated crystals were filtered off, dissolved in a minimum of water, and reprecipitated with alcohol. On air drying, the triclinic crystals contained 17.6% N and 25.7% P [calcd for $(NH_4)_6P_4O_{13}\cdot 2H_2O$, 17.65% N, 26.02% P] distributed as ortho- 0.5, pyro- 1.7, and tetrapolyphosphate 97.8%. This salt then was used to prepare $(NH_4)_5HP_4O_{13}\cdot H_2O$ and $(NH_4)_4H_2P_4O_{13}$ for use in solubility and hydrolysis studies and crystallographic examinations.

In the preparation of $(NH_4)_5HP_4O_{13}\cdot H_2O$, chilled (10°C) conductivity water was saturated with $(NH_4)_6P_4O_{13}$, and the solution was treated with the hydrogen form of Amberlite IR-120 resin to lower the pH to 4.9. The resin was filtered off, the solution was evaporated under vacuum at about 10°C to incipient crystallization, and the slurry was stored at 2°C for 16 hr. The crystals of $(NH_4)_5HP_4O_{13}\cdot H_2O$ were filtered off and air dried. The well-formed triclinic crystals contained 15.7% N and 28.1% P [calcd for $(NH_4)_5HP_4O_{13}\cdot H_2O$, 15.88% N, 28.09% P].

In the preparation of $(NH_4)_4H_2P_4O_{13}$, an aqueous solution of acetic acid (about 77% $CH_3COOH$) was saturated with $(NH_4)_6P_4O_{13}\cdot 2H_2O$, and the gently stirred solution was treated with methyl alcohol at about 25°C. The crystals were filtered off, washed with methyl alcohol, dissolved in a minimum of water, and reprecipitated with methyl alcohol. The air-dried, well-formed orthorhombic crystals contained 13.8% N and 30.4% P [calcd for $(NH_4)_4H_2P_4O_{13}$, 13.80% N, 30.51% P].

## EXPERIMENTAL

**Solubility at 0°C.** A stock solution was prepared by saturating cold conductivity water with $(NH_4)_6P_4O_{13}\cdot 2H_2O$. Portions of this solution were adjusted with anhydrous ammonia or with the hydrogen form of Amberlite IR-120 resin to selected pH values in the range 2–8, and each portion was evaporated under vacuum at about 10°C to incipient crystallization. Each slurry then was equilibrated in a glass-stoppered tube with occasional manual agitation in a cold room at 0.0° ± 0.5°C. The temperature of the cold room was controlled by a thermostat and checked occasionally with a standard thermometer. The approach to equilibrium was followed by periodic petrographic examination of the solid phases and by determination of the composition and pH of the liquid phases. The solid phases at equilibrium were determined by both petrographic and X-ray examinations.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*13*), and nitrogen was determined by distillation of ammonia with sodium hydroxide. The pH of each solution phase, after warming to 25°C, was measured with a conventional meter and a glass electrode. Hydrolysis of the tetrapolyphosphate during equilibration was checked by paper chromatography (*10*).

Equilibrium was established in 15–48 days without significant hydrolysis of the tetrapolyphosphate. The results are summarized in Table I and Figure 1. In the pH range 2.2 to 6.3, the 0°C isotherm comprises three branches representing solutions saturated with $(NH_4)_4H_2P_4O_{13}$, $(NH_4)_5HP_4O_{13}\cdot H_2O$, and $(NH_4)_6P_4O_{13}\cdot 2H_2O$, respectively. The invariant solution saturated with the tetra- and pentaammonium tetrapolyphosphates contained 10.77% N and 48.64% $P_2O_5$, and had a pH of 4.02. The other invariant solution saturated with the penta- and hexammonium tetrapolyphosphates was not observed; it was estimated to contain 11.0% N and 45.5% $P_2O_5$ and to have a pH of 4.84.

Table I. System $NH_3$–$H_6P_4O_{13}$–$H_2O$ at 0°C

| Liquid phase |  |  |  |
|---|---|---|---|
| Composition, % |  |  |  |
| N | $P_2O_5$ | pH | Solid phase |
| 8.94 | 46.00 | 2.25 | $(NH_4)_4H_2P_4O_{13}$ |
| 9.24 | 46.06 | 2.81 | $(NH_4)_4H_2P_4O_{13}$ |
| 9.65 | 46.67 | 3.56 | $(NH_4)_4H_2P_4O_{13}$ |
| 9.81 | 46.77 | 3.66 | $(NH_4)_4H_2P_4O_{13}$ |
| 10.56 | 48.32 | 4.07 | $(NH_4)_4H_2P_4O_{13}$ |
| 10.77 | 48.64 | 4.02 | $(NH_4)_4H_2P_4O_{13}$ + $(NH_4)_5H_2PO_{13}\cdot H_2O$ |
| 10.72 | 47.76 | 4.25 | $(NH_4)_5HP_4O_{13}\cdot H_2O$ |
| 10.83 | 45.83 | 4.74 | $(NH_4)_5HP_4O_{13}\cdot H_2O$ |
| 10.95 | 45.52 | 4.83 | $(NH_4)_5HP_4O_{13}\cdot H_2O$ |
| 11.03 | 45.58 | 4.85 | $(NH_4)_6P_4O_{13}\cdot 2H_2O$ |
| 10.70 | 43.15 | 5.47 | $(NH_4)_6P_4O_{13}\cdot 2H_2O$ |
| 10.37 | 38.84 | 5.76 | $(NH_4)_6P_4O_{13}\cdot 2H_2O$ |
| 10.38 | 38.64 | 5.76 | $(NH_4)_6P_4O_{13}\cdot 2H_2O$ |
| 10.31 | 36.07 | 6.28 | $(NH_4)_6P_4O_{13}\cdot 2H_2O$ |

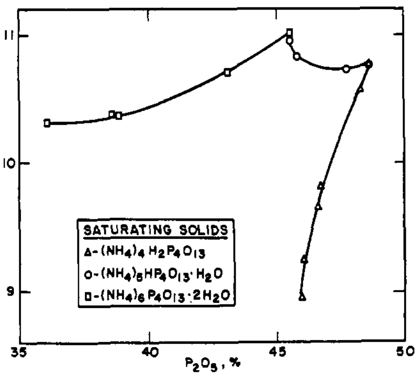


Figure 1. Solubility in the system $NH_3$–$H_6P_4O_{13}$–$H_2O$ at 0°C

Compositions of the saturated liquid phases of the ammonium tetrapolyphosphate system are compared in Figure 2 with those of the systems $NH_3$–$H_3PO_4$–$H_2O$ (*11*), $NH_3$–$H_4P_2O_7$–$H_2O$ (*3*), $NH_3$–$H_5P_3O_{10}$–$H_2O$ (*4*), and $NH_3$–$H_3PO_4$–$H_4P_2O_7$–$H_5P_3O_{10}$–$H_2O$ (*5*). The total nutrient contents (N + $P_2O_5$) of the solutions saturated with ammonium tetrapolyphosphate are significantly higher than those of solutions with the same ratio N:$P_2O_5$ that are saturated with ammonium tripoly- or pyrophosphate. In the range of overlap, weight ratio N:$P_2O_5$ 0.27 to 0.29, the saturated ammonium tetrapolyphosphate solutions are less concentrated than those in the system $NH_3$–$H_3PO_4$–$H_4P_2O_7$–$H_5P_3O_{10}$–$H_2O$, although the addition of tetrapolyphosphate to the five-component system probably would increase the total nutrient contents of the saturated solutions.

**Hydrolysis at 25°C.** In the production of solid ammonium polyphosphates and their solutions, it is important to know not only the solubility relationships of the multicomponent

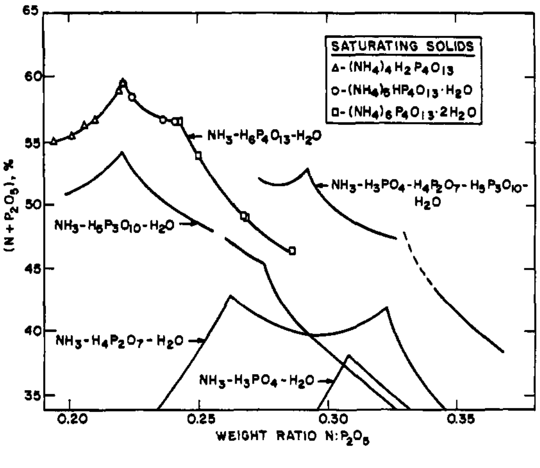


Figure 2. Solubility of ammonium phosphates at 0°C

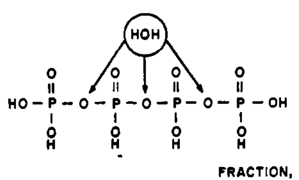
systems but also the rate and extent of hydrolysis of the different phosphate species as affected by pH and temperature. Measurements were made of the rates of hydrolysis of 0.2*M* solutions of the ammonium tetrapolyphosphates at 25°C. The probable mechanisms by which tetrapolyphosphate hydrolyzes are shown in Figure 3. If only one end oxygen bridge of a tetrapolyphosphate molecule is attacked by a water molecule, tripoly- and orthophosphate molecules are formed and, of the phosphate initially hydrolyzed, 75% will be tripolyphosphate and 25% will be orthophosphate. If the middle oxygen bridge is attacked, pyrophosphate is the only initial product.

Griffith and Buxton (*9*) studied the hydrolytic degradation of sodium tetrapolyphosphate at 30° and 60°C. The dilute solutions (concentrations are not reported) were prepared from polyphosphoric acid by a combination of amine stripping and cation exchange techniques. The first-order rate constants for the disappearance of tetrapolyphosphate in these solutions at pH 4, 5, and 11 are reported to be 7.5, 4.6, and 2.0 $\times 10^{-6}$ min$^{-1}$ at 30°C and 4.6, 2.0, and 0.9 $\times 10^{-4}$ min$^{-1}$ at 60°C. Other values reported in the literature (*1, 7, 14, 16*) were obtained in studies at 60° or 65.5°C of tetrapolyphosphate solutions that contained more highly condensed phosphates, and these rate constants are considered less reliable than those of Griffith and Buxton (*9*).

In the present study, $(NH_4)_6P_4O_{13}\cdot 2H_2O$ that was free of more highly condensed species was dissolved in cold conductivity water to form a 0.2*M* stock solution. Portions of this stock solution were treated with the hydrogen form of Amberlite IR-120 resin or with anhydrous ammonia to adjust the pH to selected values in the range 3 to 8. The solutions in screw-capped glass vials were placed in a water bath at 25.00° ± 0.02°C and sampled periodically for determinations of pH, composition, and distribution of phosphate species. The distribution of phosphate species was determined by one- and two-dimensional paper chromatography (*2*). The amount of trimetaphosphate produced at 25°C corresponded to less than 1% of the total phosphorus. In our current study at 50°C (*6*), as much as 5% of the phosphorus initially present in the ammonium tetrapolyphosphate solutions (0.2*M*) degraded to the cyclic trimetaphosphate. Wieker (*16*) found in his study of guanidinium tetrapolyphosphate solutions at 60°C that as much as 20% of the phosphorus initially in his 0.014*M* solutions of guanidinium tetrapolyphosphate had altered to the trimetaphosphate. The formation of trimetaphosphate from tetrapolyphosphate thus is highly temperature dependent.

In the pH range studied, the disappearance of tetrapolyphosphate follows a first-order reaction, as shown in Figure 4. The amounts of tripoly-, pyro-, and orthophosphates produced support the following sequence of reactions:

$$P_4O_{13} \rightarrow P_3O_{10} + PO_4,\ k_4$$
$$P_3O_{10} \rightarrow P_2O_7 + PO_4,\ k_3$$
$$P_2O_7 \rightarrow PO_4 + PO_4,\ k_2$$



| BRIDGE ATTACK | IONIC PRODUCTS | | FRACTION, %, OF P INITIALLY HYDROLYZED TO | | |
|---|---|---|---|---|---|
| | | | TRIPOLY | PYRO | ORTHO |
| END | $P_3O_{10} + PO_4$ | + 2H | 75 | 0 | 25 |
| BOTH ENDS | $P_2O_7 + 2PO_4$ | + 4H | 0 | 50 | 50 |
| MIDDLE | $P_2O_7 + P_2O_7$ | + 2H | 0 | 100 | 0 |
| ALL | $P_3O_{10} + P_2O_7 + PO_4$ | + 3H | 50 | 33 | 17 |

**Figure 3. Mechanism of the hydrolysis of tetrapolyphosphates**

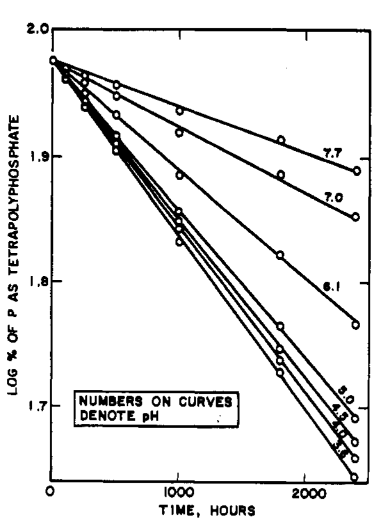


**Figure 4. Rate of hydrolysis of ammonium tetrapolyphosphate at 25°C**

In the first 100 hr at 25°C, 67-73% of the phosphate that was hydrolyzed formed tripolyphosphate; the rest formed orthophosphate. The principal initial reaction, therefore, was the splitting off of an end $PO_4$ group. The tripolyphosphate that was produced hydrolyzed to pyro- and orthophosphates, and the pyrophosphate in turn hydrolyzed to orthophosphate.

The differential equations for these consecutive and simultaneous first-order hydrolysis reactions are (*15*)

$$-dP_4O_{13}/dt = k_4\cdot P_4O_{13} \tag{1}$$

$$dP_3O_{10}/dt = (3/4)k_4\cdot P_4O_{13} - k_3\cdot P_3O_{10} \tag{2}$$

$$dP_2O_7/dt = (2/3)k_3\cdot P_3O_{10} - k_2\cdot P_2O_7 \tag{3}$$

$$dPO_4/dt = (1/4)k_4\cdot P_4O_{13} + (1/3)k_3\cdot P_3O_{10} + k_2P_2O_7 \tag{4}$$

in which the chemical formulas represent fractions of the total phosphorus present as the corresponding species.

The solutions of the four equations are

$$P_4O_{13} = (P_4O_{13})_0 \exp(-k_4t) \tag{5}$$

$$P_3O_{10} = C_1 \exp(-k_4t) + [(P_3O_{10})_0 - C_1] \exp(-k_3t) \tag{6}$$

$$P_2O_7 = C_2 \exp(-k_4t) + C_3 \exp(-k_3t) + [(P_2O_7)_0 - C_2 - C_3] \exp(-k_2t) \tag{7}$$

where

$$C_1 = (3/4)k_4(P_4O_{13})_0/(k_3 - k_4)$$
$$C_2 = (2/3)k_3C_1/(k_2 - k_4)$$
$$C_3 = (2/3)k_3[(P_3O_{10})_0 - C_1/(k_2 - k_3)]$$
$$PO_4 = 1 - (P_4O_{13} + P_3O_{10} + P_2O_7) \tag{8}$$

The parameters of these equations that gave the best fit to the experimental results were determined by nonlinear least-squared regression. (The computer program is available on request.) The measured and calculated concentrations of the tetrapoly-, tripoly-, pyro-, and orthophosphates at four sampling times and four pH levels are given in Table II; complete tables have been deposited with the ACS Microfilm Depository Service. There is excellent agreement between the measured and calculated results, even in the values for orthophosphate which include, through Equation 8, all the errors in the values for the other three species. The standard deviations are 0.316 for $P_4O_{13}{}^{6-}$, 0.234 for $P_3O_{10}{}^{5-}$, 0.286 for $P_2O_7{}^{4-}$, and 0.487 for $PO_4{}^{3-}$.

The effect of pH on the simultaneous hydrolysis of tetra-, poly-, tripoly-, and pyrophosphates is shown in Figure 5. The effect of pH on the hydrolysis of tetra- and tripolyphosphate is obvious, and both species hydrolyze much more

Table II. Hydrolysis of Ammonium Tetrapolyphosphate at 25°C

| Time, hr | | Distribution, %, of phosphate<br>Tetra-poly | Tri-poly | Pyro | Ortho |
|---|---|---|---|---|---|
| | | Results at pH 3.61 | | | |
| 0 | obs | 94.62 | 2.28 | 1.94 | 1.15 |
| | calc | 94.28 | 2.31 | 2.26 | 1.15 |
| 500 | obs | 80.37 | 11.51 | 2.74 | 5.39 |
| | calc | 80.50 | 11.39 | 2.91 | 5.20 |
| 1000 | obs | 68.25 | 17.00 | 5.74 | 9.00 |
| | calc | 68.73 | 17.61 | 4.37 | 9.29 |
| 2400 | obs | 44.28 | 25.16 | 10.13 | 19.28 |
| | calc | 44.14 | 24.99 | 10.21 | 20.66 |
| | | Results at pH 5.02 | | | |
| 0 | obs | 94.66 | 2.39 | 1.88 | 1.07 |
| | calc | 94.57 | 2.23 | 2.01 | 1.19 |
| 500 | obs | 82.65 | 10.51 | 2.29 | 4.55 |
| | calc | 82.62 | 10.51 | 2.31 | 4.56 |
| 1000 | obs | 72.23 | 16.72 | 3.37 | 7.68 |
| | calc | 72.18 | 16.91 | 3.07 | 7.84 |
| 2400 | obs | 49.26 | 27.53 | 6.51 | 15.43 |
| | calc | 49.45 | 27.32 | 6.51 | 16.72 |
| | | Results at pH 6.97 | | | |
| 0 | obs | 94.54 | 2.38 | 1.91 | 1.17 |
| | calc | 94.20 | 2.41 | 2.03 | 1.36 |
| 500 | obs | 89.03 | 6.27 | 2.04 | 2.67 |
| | calc | 88.97 | 6.27 | 2.04 | 2.72 |
| 1000 | obs | 83.38 | 10.13 | 2.28 | 4.21 |
| | calc | 84.03 | 9.84 | 2.08 | 4.04 |
| 2400 | obs | 71.51 | 18.70 | 2.36 | 7.32 |
| | calc | 71.61 | 18.52 | 2.40 | 7.48 |
| | | Results at pH 7.72 | | | |
| 0 | obs | 94.64 | 2.22 | 1.86 | 1.29 |
| | calc | 94.30 | 2.34 | 2.02 | 1.34 |
| 500 | obs | 90.67 | 5.05 | 1.96 | 2.32 |
| | calc | 90.66 | 5.03 | 1.98 | 2.32 |
| 1000 | obs | 86.84 | 7.61 | 2.16 | 3.39 |
| | calc | 87.16 | 7.60 | 1.96 | 3.28 |
| 2400 | obs | 78.00 | 14.31 | 1.94 | 5.75 |
| | calc | 78.07 | 14.12 | 1.99 | 5.82 |

Table III. Constants in Equations $pk_i = a + b\text{pH}$[a]

| | $a$ | $b \times 10^2$ | pH range | Standard error in $pk_i$ |
|---|---|---|---|---|
| $pk_4$ | 3.326 | 4.793 | 3.5–5.6 | 0.0022 |
| $pk_4$ | 2.237 | 24.27 | 5.6–8 | 0.0161 |
| $pk_3$ | 2.518 | 23.36 | 3.5–5 | 0.0174 |
| $pk_3$ | 1.726 | 39.07 | 5–8 | 0.0402 |

[a] $k_i$ in units of $hr^{-1}$.

rapidly at pH values below about 5 than at higher pH values. Plots of $pk$ vs. pH of the unpublished data from our current study of the same system at 50°C show similar breaks. The hydrolysis of pyrophosphate follows a similar pattern, but the effect of pH is obscured by the less precise determination of $k_2$. The constants of the linear relationships

$$pk_i = a + b\text{pH} \qquad (9)$$

where $k_i$ is in units of $hr^{-1}$, are shown in Table III.

The tripolyphosphate formed in the 0.2*M* solutions of the system $NH_3$–$H_6P_4O_{13}$–$H_2O$ hydrolyzed at about the same rate as that in concentrated solutions of the system $NH_3$–$H_5P_3O_{10}$–$H_2O$ (*4*), as shown in Figure 6. In the pH range 4.5 to 8 the hydrolysis constant for the dilute solutions is proportional to the 0.4 power of the pH whereas that for the concentrated solutions is proportional to the 0.5 power of the pH. Thus a change of 2 pH units changes the rate of hydrolysis of tripolyphosphate by a factor of 6.3 in the dilute solutions and by a factor of 10 in the concentrated solutions.

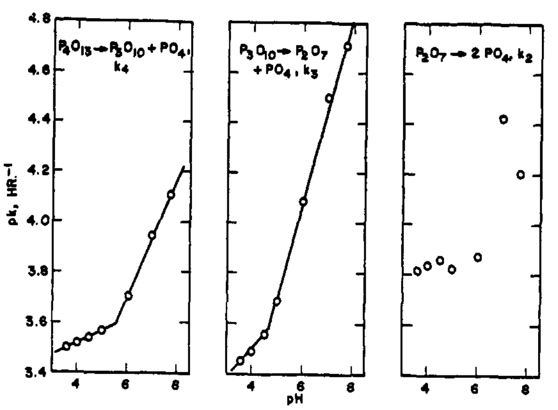


Figure 5. Effect of pH on the rate of hydrolysis of ammonium tetrapolyphosphate at 25°C

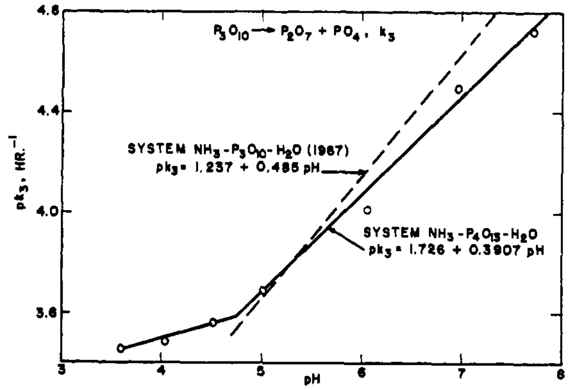


Figure 6. Rate of hydrolysis of ammonium tripolyphosphate at 25°C

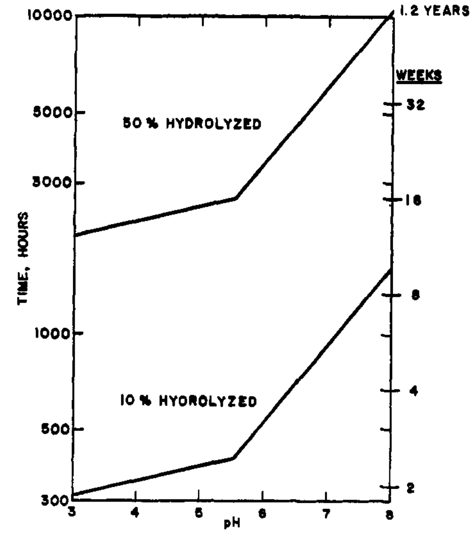


Figure 7. Hydrolysis of ammonium tetrapolyphosphate at 25°C

The time required to hydrolyze 10 and 50% of the tetrapolyphosphate in the pH range 3 to 8 is shown in Figure 7. For example, 10% of the tetrapolyphosphate will be hydrolyzed in about 69 days at pH 8 and 16 days at pH 5, or about a four-fold difference. This graph also indicates that 50% of the

Table IV. Hydrolytic Degradation of Tetrapolyphosphates

| Temp, °C | pH | $k_4$, min$^{-1}$, $\times 10^6$ | Half-life, hr$^a$ | 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$^b$ | 2.55 | 5.93$^b$ | 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 | ... |

$^a$ Half-life, hr = $1.1553 \times 10^{-2}/k_4$, when $k_4$ is in min$^{-1}$. $^b$ All data at 25°C from present work; values of $k_4$ 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.

## LITERATURE CITED

(1) Crowther, J., Westman, A. E. R., *Can. J. Chem.*, **34**, 969 (1956).

(2) Ebel, J. P., *Mikrochim. Acta*, **1954**, p 679.

(3) Farr, T. D., Fleming, J. D., *J. Chem. Eng. Data*, **10**, 20 (1965).

(4) Farr, T. D., Fleming, J. D., Hatfield, J. D., *ibid.*, **12**, 141 (1967).

(5) Farr, T. D., Williard, J. W., *ibid.*, **14**, 367 (1969).

(6) Farr, T. D., Williard, J. W., unpublished data, 1971.

(7) Gill, J. B., Riaz, S. A., *J. Chem. Soc.*, Part I (A), 183 (1969).

(8) Griffith, E. J., *J. Inorg. Nucl. Chem.*, **26**, 1381 (1964).

(9) Griffith, E. J., Buxton, R. L., *J. Amer. Chem. Soc.*, **89**, 2884 (1967).

(10) Karl-Kroupa, E., *Anal. Chem.*, **28**, 1091 (1956).

(11) Muromtsev, B. A., Nazarova, L. A., *Bull. Acad. Sci. U.R.S.S., Classe Sci. Math. Nat., Sér. Chim.*, 1938 (1), p 177.

(12) Osterheld, R. K., Langguth, R. P., *J. Phys. Chem.*, **59**, 76 (1955).

(13) Perrin, C. H., *J. Assoc. Offic. Agr. Chemists*, **41**, 758 (1958).

(14) Strauss, U. P., Day, J. W., *J. Polym. Sci. Part C*, **16**, 2161 (1967).

(15) Westman, A. E. R., DeLury, D. B., *Can. J. Chem.*, **34**, 1134 (1956).

(16) Wieker, W. V., *Z. Anorg. Allgem. Chem.*, **355**, 20 (1967).

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 $NH_3$–$H_3PO_4$–$H_4P_2O_7$–$H_5P_3O_{10}$–$H_6P_4O_{13}$–$H_2O$ at 0°C

**THAD D. FARR[1] 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 + $P_2O_5$), in the system $NH_3$–$H_3PO_4$–$H_4P_2O_7$–$H_5P_3O_{10}$–$H_6P_4O_{13}$–$H_2O$ is higher than that in the system $NH_3$–$H_3PO_4$–$H_4P_2O_7$–$H_5P_3O_{10}$–$H_2O$ 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% $P_2O_5$ (*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-

---

[1] To whom correspondence should be addressed.