y = mole fraction of component in vapor phase
β = second virial coefficient of pure component in vapor phase, cm.^{3} per gram mole
γ = liquid phase activity coefficient

Subscripts

1 = carbon tetrachloride
2 = hydrocarbon

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Solubility in the System NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C.

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Measurements were made of the compositions of solutions in the system NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C., in which solid phases of all three phosphate species are in equilibrium over the pH range 5.5 to 7.5. The most concentrated solution contained 12.00% N and 41.00% P_2O_5, and had pH 5.75.

IN THE CONTINUING study of the properties of ammonium polyphosphates (*1, 2*), measurements were made of the compositions of solutions in the system ammonia–orthophosphoric acid–pyrophosphoric acid–tripolyphosphoric acid–water at 0° C., in which solid phases of all three phosphate species are in equilibrium over the pH range 5.5 to 7.5.

The equilibration mixtures were prepared from reagent mono- and diammonium orthophosphates, and ammonium pyro- and tripolyphosphates that were crystallized from fluid fertilizers produced by ammoniation of electric furnace superphosphoric acid, 80% P_2O_5 (*7*). The composition and phosphate distribution of the ammonium phosphates are given in Table I. Conductivity water (30 ml.) at about 5° C. was saturated with salts of the three phosphate species, and the pH of each solution was adjusted to a predetermined value with anhydrous ammonia or reagent 86% H_3PO_4. Cold water or solid salt was added when necessary to adjust the ratio of solids to liquid. The complexes were equilibrated in 60-ml. plastic-capped bottles at 0.0° ± 0.5° C. with occasional manual agitation.

Table I. Ammonium Phosphates Used to Prepare Equilibration Mixtures

Salt	Composition, %		Distribution, %, of P_2O_5			
	N	P_2O_5	Ortho	Pyro	Tripoly	Other
$NH_4H_2PO_4$	12.1	61.6	100.0	...	...	...
$(NH_4)_2HPO_4$	21.2	53.5	100.0	...	...	...
$(NH_4)_3HP_2O_7 \cdot H_2O$	17.0	57.2	0.8	98.3	...	0.9
$(NH_4)_4HP_3O_{10}$	18.5	56.7	4.0	7.4	88.0	0.6

The approach to equilibrium was followed by periodic petrographic examinations of the solid phases (*4*) and by determinations of the composition and pH of the liquid phases. When examination of the wet solids indicated the absence of any of the three phosphate species, a few grams of the missing species was added and equilibration was continued.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*6*), and nitrogen was determined

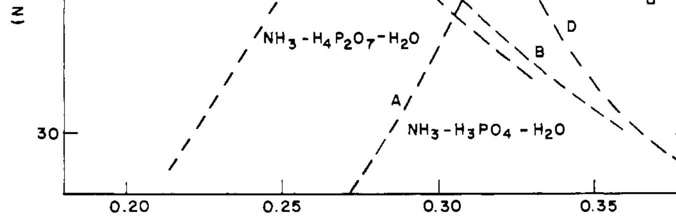

Figure 1. Solubility in the system NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C.
Saturating solids: A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_3HP_2O_7 \cdot H_2O$, D = $(NH_4)_4P_2O_7 \cdot H_2O$, E = $(NH_4)_4HP_3O_{10}$, F = $(NH_4)_5P_3O_{10} \cdot 2H_2O$

Table II. The System NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C.

No.	pH	Composition, % N	Composition, % P_2O_5	Distribution, %, of P_2O_5[a] Ortho	Pyro	Tripoly	Other	Compounds[b]
				Liquid phase				
1	7.53	10.40	28.26	34	39	26	1	
2	...	10.72	30.04	...	...	...	...	
3	7.25	10.85	30.76	34	37	29	0	
4	...	10.97	31.85	...	...	...	...	
5	7.04	11.11	32.55	31	37	32	0	
6	...	11.70	35.85	...	...	...	...	
7	...	11.61	35.89	...	...	...	...	
8	6.42	11.54	36.71	32	46	22	0	
9	6.26	11.53	37.35	34	43	23	0	
10	5.93	11.62	38.89	40	40	20	0	
11	5.78	11.86	40.42	41	39	20	0	
12	5.75	12.00	41.00	39	42	19	0	
13	5.67	11.67	40.44	37	40	23	0	
14	...	11.33	40.15	...	...	...	...	
15	5.53	11.22	40.30	25	41	34	0	
16	5.46	11.21	40.96	24	40	36	0	
				Solid phases[c]				
1	...	20.6	54.0	16	81	3	0	B, D, F
2	...	...	...	...	...	...	...	B, D, F
3	...	20.6	53.6	23	73	3	1	B, D, F
4	...	...	...	...	...	...	...	B, D, F
5	...	20.6	54.4	50	36	13	1	B, D, F
6	...	...	...	...	...	...	...	B, C, F
7	...	...	...	...	...	...	...	B, C, F
8	...	18.7	54.4	37	9	54	0	B, C, F
9	...	18.4	56.1	34	22	43	1	B, C, F
10	...	18.3	55.4	35	60	5	0	B, C, F
11	...	18.9	55.8	38	27	35	0	B, C, F
12	...	19.4	54.1	60	9	31	0	A, B, C, F
13	...	16.8	56.9	...	...	...	...	A, C, E
14	...	...	...	...	...	...	...	A, C, E
15	...	15.9	56.3	22	40	36	2	A, C, E
16	...	15.4	54.0	25	41	34	0	A, C, E

[a] Ortho = PO_4^{-3}, Pyro = $P_2O_7^{-4}$, Tripoly = $P_3O_{10}^{-5}$, Other = more highly condensed phosphates. [b] Identified by microscopic examination. A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_3HP_2O_7 \cdot H_2O$, D = $(NH_4)_4P_2O_7 \cdot H_2O$, E = $(NH_4)_4HP_3O_{10}$, F = $(NH_4)_5P_3O_{10} \cdot 2H_2O$. [c] Filtered on fritted glass at about 5° C. and air-dried.

by distillation of ammonia with sodium hydroxide; pH was determined with a glass electrode in a commercial meter. The different phosphate species—ortho-, pyro-, and tripolyphosphates— were determined by one-dimensional paper chromatography (*3*); occasional examinations of the liquid phases showed that no significant hydrolysis of the condensed phosphates occurred during the equilibration.

Equilibrium was established in 14 to 18 days. The results are summarized in Table II and plotted in Figure 1, which includes portions of the 0° C. isotherms of the ternary ammonium ortho-, pyro-, and tripolyphosphate systems (*1, 2, 5*).

The branches of the isotherm of the multicomponent system have slopes and contours that resemble those of the three ternary systems, but the total nutrient contents, N + P_2O_5, of the saturated solutions in the multicomponent system are significantly higher than those of solutions with weight ratios N to P_2O_5 between 0.27 and 0.36—those suitable for use as liquid fertilizers—that are saturated with only one of the three species.

Only one invariant solution was observed in the multicomponent system. It was saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and contained 12% N and 41% P_2O_5 distributed as ortho- 39, pyro- 42, and tripolyphosphate 19%. This invariant solution had a pH of 5.75, a value very near that, 5.82, of the invariant solution of the ternary system NH_3-H_3PO_4-H_2O saturated with mono- and diammonium orthophosphate. A second invariant point, representing a solution saturated with $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_4P_2O_7 \cdot H_2O$, and $(NH_4)_5P_3O_{10} \cdot 2H_2O$, was estimated from plots of pH *vs.* N or P_2O_5 contents to contain 11.7% N and 35.7% P_2O_5, and to have a pH of 6.8.

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