studied, protein and lysine contents were remarkably constant, as indicated by nonsignificant location and variety × location effects. Grain production showed strong interaction of varieties with locations and this was carried through to protein and lysine yields per acre.

It is desirable to identify genotypes that show a minimum interaction with environments. The variety × location interaction sums of squares in the analyses of variance (Table I) were subdivided using Wricke's (1962) method to determine the contribution of each variety (Table V). Since there were six varieties in the experiment, each is expected to contribute 16.7% to the total interaction. Positive deviations from this value indicate varietal instability and negative deviations indicate stability. Table V shows that, for grain, protein, and lysine yields, T-1324 triticale and INIA 66 wheat were unstable over environments. Rosner showed instability for lysine yield and Siete Cerros 66 was moderately unstable for grain and protein yields. Oviachic 65 was remarkably stable and 6TA-204 showed good stability. There was no qualitative difference in stability of triticale and wheat varieties and these results support the data of Kaltsikes (1971) in a study of Rosner triticale and four wheat varieties in Canada. Over all locations INIA 66 was the highest-yielding wheat variety and 6TA-204 was the highest-yielding triticale. It is somewhat surprising that these two varieties differ so greatly in stability. This difference is related to differences in growth characteristics of the varieties, but the particular factors have not yet been determined.

ACKNOWLEDGMENT

We gratefully acknowledge the assistance of B. L. Brannaman in lysine determinations and J. P. Gustafson, W. L. Lehman, and J. D. Prato in collecting the field data.

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Received for review December 18, 1972. Accepted March 5, 1973.

The System NH_3-K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 25°

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Study of the system NH_3-K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 25° disclosed the presence of three new ammonium potassium pyrophosphates—$(NH_4,K)_3HP_2O_7 \cdot H_2O$, $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$, and $(NH_4,K)_2H_2P_2O_{7-8}$ in each of which the ratio N:K ranged continuously within definite limits. These mixed salts, whose optical properties, X-ray powder diffraction patterns, and infrared spectra are reported, are not members of isomorphous series with the pure ammonium or potassium end members. Results of measurements of solubility in the system show that the total plant-nutrient content (N + P_2O_5 + K_2O) of the saturated solution can be raised from 51.9 to 56.1% by adding potassium phosphate to an ammonium phosphate solution, and from 63.6 to 65.2% by adding ammonium phosphate to a potassium phosphate solution.

Commercial liquid polyphosphate fertilizers that contain all three major plant nutrients (N, P_2O_5, and K_2O) have relatively low concentrations, such as 7-21-7, 14-8-8, and 4-11-11. In these solutions the potassium is usually added as the chloride, a salt that is slightly more soluble than the nitrate and more than twice as soluble as the sulfate, but only half as soluble as the phosphate when the pH is between 5.5 and 7.0, the range in which most liquid fertilizers fall.

In the continuing search for stable, high-analysis liquid fertilizers, measurements have been made of solubilities in the systems NH_3-$H_4P_2O_7$-H_2O at 0° and 25° (Farr and Fleming, 1965), NH_3-H_3PO_4-$H_4P_2O_7$-H_2O at 0° (Farr and Williard, 1971), and K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 25° (Frazier *et al.*, 1972). Each of these systems, however, contained only two of the three major plant nutrients, and the system NH_3-K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 25° was investigated to determine the concentrations of the three nutrient elements that could be obtained in a single solution. From previous studies it was concluded that this five-component system would contain no mixed orthopy-

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Table I. Ammonium Potassium Pyrophosphates

	Composition, %				Mole/mole P_2O_5				
Compound	$(NH_4)_2O$	K_2O	P_2O_5	H_2O (diff)[a]	$(NH_4)_2O$	K_2O	K_2O + $(NH_4)_2O$	H_2O	Mole ratio N:K
$(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$	8.2	23.9	56.9	11.0	0.39	0.63	1.02	1.52	0.62[b]
Mole ratio N:K, 0.61 to 0.74	8.3	23.4	56.9	11.4	0.40	0.62	1.02	1.58	0.64
	8.6	22.7	57.6	11.1	0.41	0.60	1.01	1.52	0.70
	9.0	22.3	57.4	11.3	0.44	0.59	1.03	1.55	0.74[c]
$(NH_4,K)_2H_2P_2O_7$	15.3	14.3	61.9	8.5	0.68	0.35	1.03	1.08	1.93[b]
Mole ratio N:K, 1.9 to 3.0	15.9	13.5	62.3	8.3	0.70	0.33	1.03	1.05	2.11
	17.0	12.8	61.3	8.9	0.76	0.32	1.08	1.14	2.40
	17.8	10.8	62.9	8.5	0.77	0.26	1.03	1.06	2.98[c]
$(NH_4,K)_3HP_2O_7 \cdot H_2O$	13.9	24.6	51.0	10.5	0.74	0.73	1.47	1.62	1.02[b]
Mole ratio N:K, 1.0 to 2.8	18.0	19.4	52.2	10.4	0.94	0.56	1.50	1.57	1.68
	19.5	16.8	53.0	10.7	1.00	0.48	1.48	1.59	2.08
	21.5	13.7	53.4	11.4	1.11	0.39	1.50	1.68	2.84[c]

[a] $H_2O = 100 - [(NH_4)_2O + K_2O + P_2O_5]$. [b] Sample prepared at potassium edge of its field of stability. [c] Sample prepared at ammonium edge of its field of stability.

Table II. Optical Properties of Ammonium Potassium Pyrophosphates

Compound	Crystal system, class, habit	Refractive indices	Optical properties[a]
$(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$ Mole ratio N:K, 0.61 to 0.74	Orthorhombic, *mmm*. Rods elongated along *c* with prominent {110} and smaller (010) and terminated by {011}	$n_\alpha = 1.494$ $n_\beta = 1.495$ $n_\gamma = 1.525$	Biaxial (+). 2*V* = 10° (21°), OAP = (010), *a* = X. *d* = 2.25
$(NH_4, K)_2H_2P_2O_7$ Mole ratio N:K, 1.93 to 2.98	Triclinic, 1. Highly modified prisms and rods; contact twinning frequent	$n_\alpha = 1.511$ $n_\beta = 1.525$ $n_\gamma = 1.542$	Biaxial (+). 2*V* = 85° (85°). *d* = 2.07
$(NH_4,K)_3HP_2O_7 \cdot H_2O$ Mole ratio N:K, 1.02 to 2.84	Monoclinic, 2/*m*. Plates elongated along *b* and tabular on (001), modified by {101} and {111}	$n_\alpha = 1.476$[b] $n_\beta = 1.488$[c] $n_\gamma = 1.497$[b]	Biaxial (−). 2*V* = 80° (80°), OAP = (010), $Z\angle a = 22°$ in acute β, $\angle\beta = 108°$. *d* = 1.87

[a] Values for 2*V* in parentheses are calcd. All values for densities calculated by Gladstone–Dale equation (Larsen and Berman, 1934). [b] ±0.002. [c] ±0.003.

rophosphates, but that new ammonium potassium pyrophosphates were to be expected as stable solid phases.

MATERIALS AND METHODS

The equilibration mixtures were prepared from reagent KH_2PO_4, $NH_4H_2PO_4$, KOH, and NH_4OH, and recrystallized $K_2H_2P_2O_7$ and $(NH_4)_3HP_2O_7 \cdot H_2O$. The pH of the liquid phase of each mixture was adjusted to a selected value in the range 2.0 to 10.2; the most acidic solutions were prepared by use of the H-form of a cation-exchange resin. The mixtures were allowed to stand at room temperature with occasional manual agitation, and the solid phases were examined microscopically at suitable intervals to ensure that the desired salts were present as stable solid phases. The mixtures then were equilibrated in a 25.0 ± 0.1° water bath for periods as long as 4 weeks, after which the liquid phases were sampled for chemical analysis and determination of pH, and the solid phases were identified petrographically. Mixtures with the pH below 2.5 were placed in the bath and stirred vigorously for 5 hr, by which time it was thought that a satisfactory compromise had been reached between attainment of equilibrium and hydrolysis of pyro- to orthophosphate.

In the course of this study, three new potassium ammonium pyrophosphates were identified and characterized: $(NH_4,K)_3HP_2O_7 \cdot H_2O$, $(NH_4,K)_2H_2P_2O_7$, and $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$. The compositions of representative preparations of the new salts are shown in Table I, their optical properties are shown in Table II, their infrared spectra are in Table III, and their X-ray powder diffraction patterns are in Table IV. Their optical and crystallographic properties show that none of these new salts are members of isomorphous series with any known ammonium or potassium pyrophosphates (Frazier *et al.*, 1965, 1972; Lehr *et al.*, 1967).

The compositions of preparations of the new salts showed that in each salt the ratio of ammonia to potassium was continuously variable within the limits of possible substitution. In the preparations these limits were approached by preparing each salt under the conditions expected to exist near the boundaries of their regions of existence. Thus, the high-potassium member of the series $(NH_4,K)_3HP_2O_7 \cdot H_2O$ was prepared by adding successive small portions of $(NH_4)_3HP_2O_7 \cdot H_2O$ to a stirred slurry of $K_3HP_2O_7 \cdot 3H_2O$ in its saturated aqueous solution. The ammonium salt dissolved rapidly, the mixed salt formed, and the potassium salt disappeared. When the last trace of $K_3HP_2O_7 \cdot 3H_2O$ disappeared, as shown by microscopic examination, the euhedral crystals of $(NH_4,K)_3HP_2O_7 \cdot H_2O$ were filtered off, soaked in a mixture of 4 parts ethanol and 1 part water to remove the mother liquor, again filtered off, and air dried. The high-ammonium member was prepared similarly from $K_3HP_2O_7 \cdot 3H_2O$ and a slurry of $(NH_4)_3HP_2O_7 \cdot H_2O$ in its saturated aqueous so-

Table III. Infrared Absorption Bands

cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a	cm^{-1}	I^a
$(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$				$(NH_4,K)_2H_2P_2O_7$				$(NH_4,K)_3HP_2O_7 \cdot H_2O$						$K_2H_2P_2O_7$				$K_4P_2O_7 \cdot 3H_2O$	
High K		High N		High K		High N		High K		High N		$K_2H_2P_2O_7 \cdot 0.5H_2O$				$K_3HP_2O_7 \cdot 3H_2O$			
3400	M,b			3220	S,b	3225	S,b	3350	S,b	3320	S,b	3473	M	2730	W	3420	sh	3300	S
3230	M,b	3190	S,b	3080	S,b	3080	S,b	3200	S,b	3180	S,b	2730	W	2350	W	3380	S	1620	W
3090	M,b	3060	S,b	2870	S,b	2870	S	3030	S,b	3030	S,b	2350	W	1650	W	3298	S	1144	S
2877	M,b	2860	S,b	2380	W,b	2380	W,b	2780	S,b	2780	S,b	1650	W	1310	M	3190	S	1115	S
2350	W,b	2350	W,b	1670	W,b	1670	W,b	2500	W,b	2500	W,b	1305	M	1200	S	2363	W	1065	S
1690	W,b	1670	W,b	1475	W	1478	W	2415	W,b	2380	W,b	1222	S	1121	M	2250	W	1009	M
1461	M	1448	M	1430	M	1435	S	2200	W,b	2180	W,b	1197	S	1042	S	1690	W	962	M
1434	M	1420	M	1398	sh	1398	sh	1920	W,b			1124	M	954	S	1233	M	875	S
1399	W	1390	W	1329	W,b	1330	W,b	1660	W,b			1104	M	907	S	1185	sh	695	M
1300	W,b	1285	W,b	1200	S	1200	S	1485	sh			1073	S	698	M	1176	S	582	W
1182	S	1172	S	1150	sh	1150	S	1432	M	1422	M	1044	S	577	W	1169	sh	538	S
1136	S	1135	S	1072	S	1072	S	1395	sh			964	S	542	S	1100	S	503	W
1088	S	1088	S	960	S	960	S	1272	M	1265	M	909	S	521	S	1045	S	454	W
988	S	985	S	894	S	900	S	1168	S	1160	S	703	W	500	S	1007	S	410	W
966	S	966	S	711	M	711	M	1099	S	1095	S	571	W	437	M	997	S		
907	S	905	S	589	W	589	W	1052	S	1050	S	520	S	401	W	957	S		
702	W	702	M	560	sh	560	sh	990	sh	990	sh	490	S			923	S		
689	W	689	M	537	S	537	S	948	S	950	sh	458	W			866	S		
563	M	563	M	510	S	510	S	917	S	921	S	410	W			721	M		
532	S	525	S	500	S	497	S	701	M	701	M					640	M		
529	S	510	S	460	W	460	W	541	S	533	S					572	sh		
477	S	472	M	389	M	389	M	489	M	481	M					526	S		
								460	sh							490	M		
								407	W	402	W					481	M		
																441	M		
																409	W		

[a] S = strong, M = medium, W = weak, b = broad, sh = shoulder.

lution, and well-crystallized preparations of the high-potassium and high-ammonium forms of the other two salts were obtained through use of similar procedures.

As shown in Table II, the refractive indices of the salts rose with increase in the ratio N:K; this change was significant for $(NH_4,K)_3HP_2O_7 \cdot H_2O$ but not for $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$ or $(NH_4,K)_2H_2P_2O_7$.

The ammonium ion absorbs strongly in the infrared, and the ratios of the intensity of the NH_4 absorption at 1430 cm^{-1} to that of the P–O absorption at 1160 cm^{-1}, both measured above background at 1800 cm^{-1}, may be used to calculate the ratio N:K in the potassium ammonium pyrophosphates. Substitution of potassium for ammonium causes a shift in the P–O frequencies, and this shift also may be used as a basis for calculation of the ratio N:K in $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$ or $(NH_4,K)_3HP_2O_7 \cdot H_2O$, but the shift in $(NH_4,K)_2H_2P_2O_7$ is too small for such calculations. In agreement with the optical data, the greatest shifts were observed in the infrared spectra of $(NH_4,K)_3HP_2O_7 \cdot H_2O$.

The infrared spectra of the isotypic potassium pyrophosphates, which have not been reported before, are included in Table III. The infrared spectra of the ammonium pyrophosphates were reported previously (Lehr *et al.*, 1967).

The X-ray powder diffraction patterns of the potassium ammonium pyrophosphates did not change significantly with change in the ratio N:K, and in Table IV only one pattern is shown for each mixed salt.

The System NH_3–K_2O–$H_4P_2O_7$–H_2O. The simpler four-component system was examined first to provide background information for study of the five-component system containing orthophosphate. Equilibration mixtures in the four-component system were selected to produce saturated solutions of invariant composition with which three solid phases were in equilibrium, or solutions of univariant composition with which two solid phases were in equilibrium.

Because of the complexity introduced by the potassium ammonium pyrophosphates, the equilibration mixtures were prepared to form solutions in equilibrium with the simple potassium or ammonium pyrophosphates and the corresponding mixed salt. Mixtures with pH below 2.5 were prepared in duplicate and, when the presence of the desired solid phases was established, these were equilibrated at 25° with vigorous agitation for 5 hr. Excellent agreement between duplicates was obtained, and in most mixtures no more than 4.5% of the P_2O_5 (1.8 out of 40.3%) was present as orthophosphate; mixtures containing a higher proportion of orthophosphate were discarded. The results are shown in Table V and summarized in Figure 1.

The System NH_3–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O. Equilibration mixtures in the five-component system were prepared in the same manner as those in the four-component system, except that four stable solid phases were required for equilibrium with saturated solutions of invariant composition and three stable solid phases were required for equilibrium with saturated solutions with univariant compositions. The results are shown in Table VI.

When plotted as the ternary system $(NH_4)_2O$–K_2O–$(P_2O_5 + H_2O)$, as in Figure 1, the data in Table VI fall in about the same region as those in Table V and lie between the lines of constant value of $(NH_4)_2O + K_2O$ of 20 and 32%. The fields of stability of the different salts overlap considerably, so that the plot adds very little information to that provided by Table VI.

The system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O has been studied at 0° (Farr and Williard, 1971) but not at 25°. To permit comparison with the five-component ammonium potassium system, a brief study was made of the four-com-

Table IV. X-Ray Powder Diffraction Data[a]

d, Å	I/I$_0$	d, Å	I/I$_0$	d, Å	I/I$_0$	d, Å	I/I$_0$
$(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$; mole ratio N:K, 0.61 to 0.74							
7.08	5	3.56	25	3.04	45	2.27	9
6.17	4	3.52	11	2.99	100	2.18	2
6.01	33	3.39	10	2.95	4	2.15	1
5.45	2	3.36	7	2.86	5	2.13	1
5.03	10	3.26	3	2.82	3	2.08	1
4.81	29	3.20	2	2.46	20	1.99	2
4.04	8	3.17	1	2.40	9	1.91	6
3.92	1	3.11	5	2.39	21		
3.82	21	3.08	15	2.28	5		
$(NH_4,K)_2H_2P_2O_7$; mole ratio N:K, 1.9 to 3.0							
7.18	2	3.59	100	2.94	2	2.28	13
6.96	3	3.48	50	2.85	24	2.24	4
6.41	18	3.42	28	2.83	39	2.23	9
5.45	54	3.34	39	2.51	2	2.22	2
4.99	9	3.26	9	2.50	5	2.18	2
4.90	3	3.24	16	2.39	14	2.15	3
4.64	62	3.19	65	2.36	1	2.13	3
4.59	8	3.05	9	2.34	2	1.98	7
3.88	1	3.02	59	2.32	17	1.96	8
3.65	5	2.97	38	2.29	5	1.82	8
$(NH_4,K)_3HP_2O_7 \cdot H_2O$; mole ratio N:K, 1.0 to 2.8							
9.27	16	3.74	5	3.02	6	2.33	2
8.09	55	3.63	3	2.94	5	2.26	5
7.27	5	3.57	4	2.92	3	2.22	2
5.86	40	3.53	6	2.91	11	2.07	3
5.34	9	3.48	6	2.89	5	2.04	5
4.97	16	3.34	100	2.87	7	2.02	3
4.63	13	3.27	34	2.82	15	1.96	9
4.45	4	3.25	16	2.70	7	1.93	4
4.37	9	3.18	12	2.67	15	1.89	6
4.24	3	3.16	3	2.61	2	1.88	11
4.18	6	3.10	46	2.54	16		
4.03	13	3.08	27	2.47	9		

[a] Data obtained with X-ray diffractometer with CuKα radiation, γ = 1.54178 Å. Intensities measured as peak heights above background and expressed as percent of strongest line.

Table V. Solubility in the System NH_3-K_2O-$H_4P_2O_7$-H_2O at 25°

Saturated liquid phase				Solid phase[a]
	Composition, %			
pH	$(NH_4)_2O$	K_2O	P_2O_5	
6.26	21.4		36.6	A, B
6.50	18.0	5.8	36.8	A, B, C
6.80	15.2	10.0	34.8	A, C
7.70	9.5	19.1	31.7	A, C
8.60	6.6	25.4	31.3	A, C
4.98	19.7		40.2	B, D
4.95	14.2	9.0	40.8	B, D, E
4.90	11.3	12.9	39.9	C, E
5.00	9.7	14.6	39.1	C, E
5.1	9.1	16.2	39.6	C, E, G
5.3	8.1	17.6	38.9	C, G
5.5	7.4	18.6	37.8	C, G
5.7	6.4	20.1	37.2	C, G
6.0	3.9	25.2	36.2	C, G
6.9	3.2	26.6	32.6	C, J
5.80	16.6	6.3	38.4	B, C
5.50	16.4	6.8	40.0	B, C
5.15	16.3	7.1	41.8	B, C, E
5.00	15.9	7.0	41.1	B, E
4.60	11.3	9.6	38.4	D, E
4.20	9.1	9.6	35.8	D, E
2.50	5.9	13.1	39.7	D, E
2.50	5.6	14.0	39.9	D, E
4.7	7.8	15.9	38.8	E, G
4.3	6.8	15.6	37.6	E, G
3.9	6.0	15.2	36.8	E, G
2.35	5.2	14.6	40.3	E, G
1.98	—	19.4	33.6	G, H
8.5	6.6	28.5	34.0	C, J
6.5	2.6	27.8	36.0	C, G, J
6.70	1.8	28.2	34.5	G, J
6.65	—	29.8	33.4	G, J
10.2	—	37.6	29.0	J, K

[a] Determined microscopically. A = $(NH_4)_4P_2O_7$; B = $(NH_4)_3HP_2O_7 \cdot H_2O$; C = $(NH_4,K)_3HP_2O_7 \cdot H_2O$, mole ratio N:K, 1.0 to 2.8; D = $(NH_4)_2H_2P_2O_7$; E = $(NH_4,K)_2H_2P_2O_7$, mole ratio N:K, 1.9 to 3.0; G = $K_2H_2P_2O_7$; H = $K_3H_5(P_2O_7)_2$; J = $K_3HP_2O_7 \cdot 3H_2O$; K = $K_4P_2O_7 \cdot 3H_2O$.

ponent ammonium system at 25°; the results are shown in Table VII. From these results, the data on the system K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 25° (Frazier *et al.*, 1972), and the data in Table VI, it is apparent that the total plant-nutrient content (N + P_2O_5 + K_2O) of the saturated solution can be increased significantly by adding potassium phosphate to an ammonium phosphate solution, but not by adding ammonium phosphate to a potassium phosphate solution. Thus, a saturated ammonium phosphate solution with pH 6.3 (Table VII) contains 51.9% total plant nutrient, whereas an invariant-point solution in the five-component system with pH 6.3 (Table VI) contains 56.1% total plant nutrient. On the other hand, a saturated potassium phosphate solution with pH 6.40 (Table V of Frazier *et al.*, 1972) contains 63.6% total plant nutrient, whereas an invariant-point solution in the five-component system with pH 6.49 (Table VI) contains 65.2% total plant nutrient.

The salt $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$ did not form in the pyrophosphate system at 25°, but did appear in the potassium portion of the orthopyrophosphate system; in the ammonium portion of the system the anhydrous form of this salt was stable. Both $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$ and its anhydrous form appeared in the five-component system, and it was apparent that 25° is close to the transition point between these two forms. At 25° the anhydrous salt

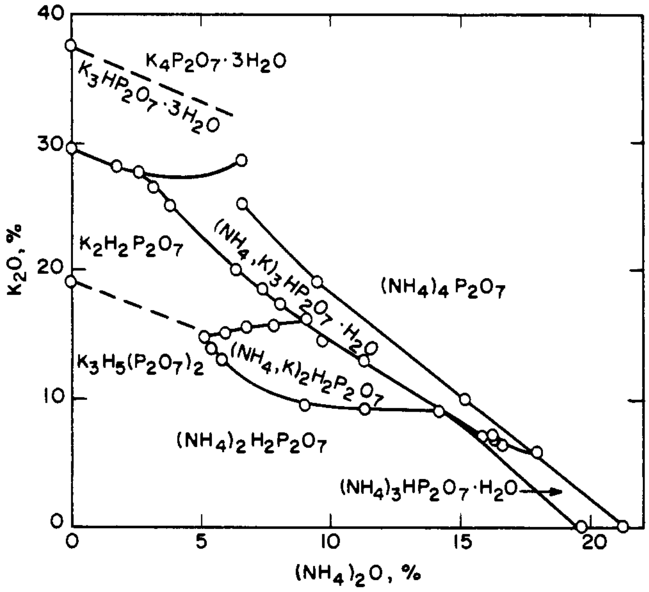

Figure 1. The system NH_3-K_2O-$H_4P_2O_7$-H_2O at 25° projected on the $(NH_4)_2O$-K_2O-(P_2O_5 + H_2O) face.

Table VI. Solubility in the System NH_3–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O at 25°

Saturated liquid phase						
	Composition, %				Pyro P_2O_5, % of total P_2O_5	
			P_2O_5			
pH	$(NH_4)_2O$	K_2O	Total	Ortho		Solid phase[a]
7.18	12.4	14.9	34.0	14.2	58	A, C, L
6.65	16.1	8.9	36.9	13.0	65	A, C, L
6.30	19.6	5.5	40.1	13.5	66	A, B, C, L
6.00	18.7	5.7	39.0	12.3	68	B, C, L
5.93	18.5	6.5	40.3	18.0	55	B, C, L, M
5.88	18.8	5.0	41.2	16.3	60	B, C, M
5.28	16.9	5.5	42.3	9.6	77	B, C, M
5.18	16.6	6.8	42.6	9.1	79	B, C, E, M
5.10	17.3	5.4	42.6	8.6	80	B, E, M
6.95	11.2	16.5	34.5	17.5	49	C, L. M
6.30	15.7	9.7	37.7	17.8	53	C, L. M
6.13	16.9	8.0	38.9	17.9	54	C, L, M
4.55	9.8	13.5	39.9	6.8	83	D, E, M
5.08	9.9	14.3	40.7	5.8	86	C, E, M
4.95	13.5	16.3	41.2	4.8	88	C, M
5.18	11.1	17.9	39.2	4.7	88	C, M
6.10	8.5	22.7	33.6	10.0	70	C, M
7.40	3.6	27.4	32.8	10.1	69	C, J, M
6.95	3.1	27.4	34.0	7.2	79	C, J, M
6.49	2.7	27.7	36.0	5.0	86	C, G, J, M
6.23	3.3	26.3	36.1	5.8	84	C, G, M
5.45	7.3	16.9	38.7	5.8	85	C, G, M
5.11	9.3	16.2	40.1	4.7	88	C, G, M
5.10	9.9	15.9	41.0	6.7	84	C, F, G, M
4.75	8.5	12.4	39.9	4.9	88	F, G, M
4.0	—	6.9	10.2	10.2	0	M
6.1	—	17.7	18.1	18.1	0	M
7.9	—	35.0	29.2	29.2	0	M, N
10.1	—	34.1	25.5	25.5	0	N

[a] Determined microscopically. A = $(NH_4)_4P_2O_7$; B = $(NH_4)_3HP_2O_7 \cdot H_2O$; C = $(NH_4,K)_3HP_2O_7 \cdot H_2O$, mole ratio N:P, 1.0 to 2.8; D = $(NH_4)_2H_2P_2O_7$; E = $(NH_4,K)_2H_2P_2O_7$, mole ratio N:P, 1.9 to 3.0; F = $(NH_4,K)_2H_2P_2O_7 \cdot 0.5H_2O$, mole ratio N:P, 0.61 to 0.74; G = $K_2H_2P_2O_7$; J = $K_3HP_2O_7 \cdot 3H_2O$; L = $(NH_4)_2HPO_4$; M = $(NH_4,K)H_2PO_4$; N = $K_2HPO_4 \cdot 3H_2O$.

dissolved very slowly in the region of the hemihydrate, and the hemihydrate dissolved very slowly in the region of the anhydrous salt.

As shown in Figure 1, mixed ammonium potassium salts were stable in the presence of salts with pure end-member compositions, in agreement with the optical and X-ray data that show that the mixed salts are not members of isomorphous series with the end members. The significant but definitely limited miscibility range of ammonium and potassium in the mixed crystalline salts indicates that the cations in these salts are held by three different types of bonds, one of which holds ammonium, another holds potassium, and a third can hold either ammonium or potassium.

Table VII. The System NH_3–H_3PO_4–$H_4P_2O_7$–H_2O at 25°

Saturated liquid phase					
	Composition, %			Pyro P_2O_5, % of total P_2O_5	
		P_2O_5			
pH	$(NH_4)_2O$	Total	Ortho		Solid phase[a]
6.8	21.9	36.1	14.2	61	N_4P_2, N_2P
6.3	22.9	39.6	14.4	64	N_4P_2, N_2P, N_3P_2
6.0	22.7	39.7	15.7	60	N_2P, N_3P_2
5.7	22.7	41.5	19.1	54	N_2P, N_3P_2, NP
5.4	20.9	41.6	12.7	50	N_3P_2, NP
5.0	20.5	42.6	10.4	76	N_3P_2, NP, N_2P_2
4.3	16.0	36.8	10.5	71	NP, N_2P_2

[a] NP = $NH_4H_2PO_4$, N_2P = $(NH_4)_2HPO_4$, N_2P_2 = $(NH_4)_2H_2P_2O_7$, N_3P_2 = $(NH_4)_3HP_2O_7 \cdot H_2O$, N_4P_2 = $(NH_4)P_2O_7$.

The data in Tables V and VI and the regions of stability of the different salts in Figure 1 indicate that in the pH range 5.5 to 7.0, that of most liquid fertilizers, the maximum concentration will reflect the solubility of $(NH_4,K)_3HP_2O_7 \cdot H_2O$. In concentrated ammonium polyphosphate solutions, this salt is the stable phase when the K_2O concentration is higher than 5.0%, and in concentrated potassium polyphosphate solutions, it is the stable phase when the N content is above 1.5%. A solution with grade 9-36-9 appears in the field of stability of $(NH_4,K)_3HP_2O_7 \cdot H_2O$, near the ammonium portion of the system; it has a pH of 6.3 to 6.7 and 50 to 65% of the total P_2O_5 is present as pyrophosphate. On cooling below 25°, however, this solution would deposit crystals of $(NH_4,K)_3HP_2O_7 \cdot H_2O$, $(NH_4)_2HPO_4$, and $(NH_4)_4P_2O_7$ or $(NH_4,K)H_2PO_4$. A solution with grade 8-32-8 probably would be satisfactorily stable at low temperatures usually encountered in storage of fertilizer solutions.

The results of the solubility measurements show that saturated solutions in the system NH_3–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O are more concentrated in total plant nutrients than are corresponding solutions in similar systems containing only ammonium or potassium. The increases in concentration are significant, and they may be large enough to warrant the use of a premium form of potassium, instead of potassium chloride, in the preparation of liquid fertilizers.

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Received for review December 18, 1972. Accepted February 14, 1973.