The System $K_2O-H_4P_2O_7-H_2O$ at 0 and 25° C

A. William Frazier,* Robin M. Scheib, and James R. Lehr

On heating at 500° C, K_2HPO_4 yielded $K_4P_2O_7$, and from this salt $K_4P_2O_7 \cdot 3H_2O$, $K_3HP_2O_7 \cdot 3H_2O$, $K_2H_2P_2O_7$, $K_2H_2P_2O_7 \cdot 0.5H_2O$, $K_3H_5(P_2O_7)_2$, and $KH_3P_2O_7 \cdot H_2O$ were prepared. The optical properties and X-ray diffraction patterns of the several potassium pyrophosphates were determined, and their solubilities at 0 and 25° C were measured. Measurements were made also of solubilities at 25° C in the system $K_2O-H_3PO_4-H_4P_2O_7-H_2O$.

Solutions of ammonium polyphosphates are relatively concentrated liquid fertilizers that are effective sources of plant food nitrogen and phosphorus. Addition of potassium chloride to these solutions to prepare "complete" fertilizer solutions is not considered desirable because potassium chloride is not soluble enough to form a high analysis solution (Potts et al., 1961; Young, 1968). Although suspension fertilizers with physical properties of viscous liquids (Scott et al., 1967) can be prepared in which relatively large amounts of small crystals of potassium chloride and other solid salts are maintained in suspension, the chloride lowers the grade of the product. A considerable portion of the condensed phosphates in ammonium polyphosphate fertilizers is pyrophosphate, and a study of the solubility of the potassium pyrophosphates at 0 and 25° C was made as part of the exploration of the use of potassium in polyphosphate fertilizer solutions and suspensions.

PREPARATION OF POTASSIUM PYROPHOSPHATES

On heating, reagent K_2HPO_4 yielded tetrapotassium pyrophosphate, $K_4P_2O_7$, contaminated with potassium carbonate. The pyrophosphate exists as dimorphs. The low temperature dimorph, β form, which is reported by Thilo and Dostal (1959) and is carried in the ASTM powder diffraction files, was formed at 400° C. Its crystallite size was too small for detailed optical studies, but chromatographic examination showed all the phosphate to be pyrophosphate. Its chemical composition and those of the other preparations are listed in Table I. The optical properties of the other salts encountered in this study are listed in Table II.

Heating the low temperature dimorph of $K_4P_2O_7$ at 500° C, or heating K_2HPO_4 at 500° C for 20 hr (Osterheld and Audrieth, 1952), produced the high temperature dimorph or α form. Dehydration of $K_4P_2O_7 \cdot 3H_2O$ at 105° C also produced the α form. The optical properties of this form were reported by Lehr et al. (1967), and its X-ray diffraction pattern is listed in Table III. Both dimorphs of $K_4P_2O_7$ are stable at room temperature but are very hygroscopic.

Dipotassium pyrophosphate was prepared from the product of heating K_2HPO_4 at 500° C for 20 hr by dissolving the material to form its saturated aqueous solution, acidifying the solution to pH 3 with glacial acetic acid, and adding ethanol slowly with stirring to precipitate $K_2H_2P_2O_7 \cdot 0.5H_2O$ mixed with some $K_2H_2P_2O_7$ and potassium acetate. (When the ethanol was added rapidly the major component of the precipitate was anhydrous $K_2H_2P_2O_7$.) The acetate was removed by washing the precipitate with fresh ethanol and the dipotassium pyrophosphate was dissolved in water to prepare solutions saturated at 25° C from which other potassium pyrophosphates were prepared for optical, X-ray, and chemical characterization.

Treatment of the saturated solution of $K_2H_2P_2O_7$ with cation-exchange resin produced an acidic solution that deposited crystals of $KH_3P_2O_7 \cdot H_2O$ on cooling to 0° C. Addition of more $K_2H_2P_2O_7$ to this same acidic solution at room temperature precipitated $K_3H_5(P_2O_7)_2$.

Addition of KOH to the saturated solution of $K_2H_2P_2O_7$ at room temperature precipitated either $K_3HP_2O_7 \cdot 3H_2O$ or $K_4P_2O_7 \cdot 3H_2O$, depending upon the amount of KOH added.

Table I. Preparations of Potassium Pyrophosphates

	Composition, wt %			Mol/mol P_2O_5	
	K_2O	P_2O_5	H_2O, diff	K_2O	H_2O
$KH_3P_2O_7 \cdot H_2O$	20.3	60.5	19.2	0.51	2.50
	20.8	60.3	18.9	0.52	2.47
Stoichiometric	20.12	60.64	19.24	0.50	2.50
$K_3H_5(P_2O_7)_2$	30.1	58.2	11.7	0.78	1.59
	30.3	60.0	9.7	0.76	1.28
Stoichiometric	30.05	60.37	9.58	0.75	1.25
$K_2H_2P_2O_7 \cdot 0.5H_2O$	35.9	53.5	10.6	1.01	1.56
	36.1	53.6	10.3	1.02	1.52
Stoichiometric	35.80	53.94	10.26	1.00	1.50
$K_2H_2P_2O_7$	37.1	55.0	7.9	1.02	1.13
	36.4	54.0	9.6	1.02	1.40
Stoichiometric	37.06	55.85	7.09	1.00	1.00
$K_4P_2O_7 \cdot 3H_2O$	48.9	37.1	14.0	1.99	2.98
	48.2	36.4	15.4	2.00	3.34
Stoichiometric	49.01	36.93	14.06	2.00	3.00
$K_4P_2O_7$	57.1	43.1	Nil	2.00	0.00
Stoichiometric	57.03	42.97	0.00	2.00	0.00

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Table II. Optical Properties of Potassium Pyrophosphates

Compound	Crystal system, class and habit	Refractive indices	Optical properties[a]
$K_4P_2O_7 \cdot 3H_2O$	Monoclinic, $2/m$. Rods elongated along c, tabular on (100) and modified by (110), {111}, and small {101}	$\alpha = 1.482$ $\beta = 1.487$ $\gamma = 1.491$	Biaxial (−), $2V$ large (83°), OAP $\perp 010$, $Z = b$, $\beta \sim 90°$, X$\wedge c = 39°$, $d = 2.23$
$K_3HP_2O_7 \cdot 3H_2O$	Monoclinic, $2/m$. Plates tabular on (100), elongated along c and modified by {110}, (111), ($\overline{1}1\overline{1}$), ($\overline{1}1\overline{1}$), ($1\overline{1}1$), and small (001)	$\alpha = 1.466$ $\beta = 1.468$ $\gamma = 1.481$	Biaxial (+), $2V =$ 40° (43°), $OAP =$ 010, $Z\wedge c = 19.5°$ in acute β. $\beta = 99°$. $d = 2.17$
$K_2H_2P_2O_7 \cdot 0.5H_2O$	Monoclinic, $2/m$. Plates tabular on (100), elongated along b and modified by {101}, {011}, and small {110}. Also prisms with prominent {110} and (001) and small {011} and {101}	$\alpha = 1.463$ $\beta = 1.482$ $\gamma = 1.483$	Biaxial (−), $2V =$ 24° (25°), X$\wedge c =$ 23° in obtuse β. $\beta = 98°$, $b = $ Y, $OAP = 010$. Strong dispersion, $r < V$. $d = 2.32$
$K_2H_2P_2O_7$	Monoclinic, $2/m$. Rod crystals elongated along c, tabular on (010), and modified by {111} and {110}	$\alpha = 1.463$ $\beta = 1.465$ $\gamma = 1.510$	Biaxial (+), $2V =$ 25° (25°). $d =$ (2.40), $b = $ X, $Z\wedge c = 8°$, $\beta = 97°$, $d = 2.39$
$K_3H_5(P_2O_7)_2$	Orthorhombic, mmm. Plates tabular on X-Y plane	$\alpha = 1.471$ $\beta = 1.505$ $\gamma = 1.515$	Biaxial (−), $2V =$ 65° (59°). $d = 2.40$
$KH_3P_2O_7 \cdot H_2O$	Monoclinic, $2/m$. Plates tabular on (100), elongated along b, and modified by {101} and {011}	$\alpha = 1.469$ $\beta = 1.482$ $\gamma = 1.491$	Biaxial (−), $2V =$ 75° (79°). $OAP =$ (100), X$\wedge c = 1°$ in acute β, $\beta = 108°$. $d = 2.20$
$KH_5(PO_4)_2$	Monoclinic, $2/m$. Plates tabular on (100), elongated along b and modified by (001), {011}, and small (010)	$\alpha = 1.458$ $\beta = 1.474$ $\gamma = 1.502$	Biaxial (+), $2V =$ 70° (76°). X $= b$, $OAP \perp$ (010), $Z\wedge c =$ 30° in acute β. $\beta = 113°$. $d = 2.21$

[a] Calculated values for $2V$ are in parentheses. All values for densities are calculated from the composition and refractive indices by the Gladstone–Dale relationship (Larsen and Berman, 1934).

An attempt to prepare $KH_3P_2O_7$ by dehydrating $KH_5(PO_4)_2$ thermally by a method reported by Silber and Brun (1965) was unsuccessful, and when $KH_3P_2O_7 \cdot H_2O$ was heated under vacuum at 102° C, the temperature specified, it melted and reverted to $KH_5(PO_4)_2$. A well-crystallized preparation of $KH_5(PO_4)_2$ was obtained by saturating 83% phosphoric acid (60% P_2O_5) with KH_2PO_4. The optical properties of $KH_5(PO_4)_2$ are included in Table II. Unlike its ammonium analog (Frazier et al., 1971), $KH_5(PO_4)_2$ does not decompose in acetone or alcohol and is not hygroscopic in the usual laboratory atmosphere.

Except for α- and β-$K_4P_2O_7$ and $KH_3P_2O_7 \cdot H_2O$, all the potassium pyrophosphates reported here are relatively stable in the usual laboratory atmosphere. The chemical compositions in Table I clarify reported discrepancies (Jolly, 1968) in the compositions and degrees of hydration of the salts. The X-ray powder diffraction data for α-$K_4P_2O_7$ and KH_3-$P_2O_7 \cdot H_2O$ are reported in Table III; the X-ray data for the other salts encountered in this study agree well with those listed in the literature (ASTM, 1970; Brun, 1968).

SOLUBILITY MEASUREMENTS

The equilibration mixtures were prepared from the recrystallized potassium pyrophosphates and distilled water. Each of the invariant point solutions was prepared by treating mixtures of the saturated solutions and solid salts with KOH

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

$KH_3P_2O_7 \cdot H_2O$				α-$K_4P_2O_7$			
d, Å	I	d, Å	I	d, Å	I	d, Å	I
7.13	44	2.673	12	9.24	47	2.618	6
6.44	12	2.657	10	6.80	19	2.520	12
5.77	11	2.591	48	5.00	26	2.487	16
5.23	88	2.550	2	4.60	6	2.446	18
4.94	10	2.505	14	4.32	16	2.413	11
4.48	12	2.486	2	3.78	10	2.345	6
4.27	11	2.387	6	3.57	12	2.291	10
4.12	57	2.373	10	3.49	18	2.262	12
3.85	8	2.337	3	3.27	8	2.233	5
3.74	6	2.320	21	3.21	4	2.201	2
3.64	25	2.281	6	3.12	2	2.170	4
3.56	49	2.272	13	3.079	45	2.152	10
3.51	39	2.240	6	3.045	5	2.099	6
3.44	20	2.210	8	3.011	42	1.978	15
3.25	40	2.188	10	2.951	27	1.959	9
3.24	47	2.138	10	2.888	100	1.944	7
3.22	100	2.118	3	2.758	28	1.787	7
3.20	15	2.091	14	2.742	5	1.722	12
3.022	35	2.059	14	2.716	7	1.658	7
2.969	20	1.995	4	2.694	25	1.645	5
2.903	4	1.926	3	2.662	27	1.614	2
2.821	19	1.878	13				
2.750	4						

[a] Patterns obtained with proportional counter, X-ray diffractometer, Cu Kα radiation, $\lambda = 1.54178$ Å, with $MgAlO_3$ as internal standard and scanned at 0.25° 2θ/min. Intensities measured as peak heights above background and expressed as percent of strongest line.

Table IV. The System $K_2O-H_4P_2O_7-H_2O$

No.	Equilibration time days[a]	pH	K_2O	P_2O_5 Total	P_2O_5 Ortho[b]	Solid phase
				Results at 0° C		
1	4	0.1	11.8	35.3	4.2	$KH_3P_2O_7 \cdot H_2O$
2	2	0.1	11.2	35.1		$KH_3P_2O_7 \cdot H_2O$
3	2	0.2	11.3	32.4	2.9	$KH_3P_2O_7 \cdot H_2O$
4	4	0.43	11.0	29.9		$KH_3P_2O_7 \cdot H_2O + K_3H_5(P_2O_7)_2$
5	4	0.70	11.6	29.0		$K_3H_5(P_2O_7)_2$
6	4	1.43	13.2	26.5		$K_3H_5(P_2O_7)_2$
7	4	2.10	16.5	27.8	0.6	$K_3H_5(P_2O_7)_2 + K_2H_2P_2O_7 \cdot 0.5H_2O$
8	30	5.00	19.9	26.2		$K_2H_2P_2O_7 \cdot 0.5H_2O$
9	30	5.52	22.8	27.8		$K_2H_2P_2O_7 \cdot 0.5H_2O$
10	30	6.29	27.6	30.5		$K_2H_2P_2O_7 \cdot 0.5H_2O + K_3HP_2O_7 \cdot 3H_2O$
11	30	7.30	26.9	25.9		$K_3HP_2O_7 \cdot 3H_2O$
12	30	9.42	32.8	25.5		$K_3HP_2O_7 \cdot 3H_2O$
13	30	10.45	37.6	27.9		$K_3HP_2O_7 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$
14	30	11.90	37.7	28.2		$K_4P_2O_7 \cdot 3H_2O$
15	30	12.52	37.1	27.7		$K_4P_2O_7 \cdot 3H_2O$
16	30	>14.0	37.2	27.9		$K_4P_2O_7 \cdot 3H_2O$
17	30	>14.0	37.6	27.8		$K_4P_2O_7 \cdot 3H_2O$
				Results at 25° C		
18	1	0.6	14.4	42.7	3.2	$K_3H_5(P_2O_7)_2$
19	1h	1.1	15.5	38.1	0.8	$K_3H_5(P_2O_7)_2$
20	2h	1.0	15.5	34.5	1.8	$K_3H_5(P_2O_7)_2$
21	5h	1.0	15.7	35.0	1.9	$K_3H_5(P_2O_7)_2$
22	1h	1.98	19.4	33.6	1.6	$K_3H_5(P_2O_7)_2 + K_2H_2P_2O_7 \cdot 0.5H_2O$
23	2h	1.95	19.7	34.0	2.2	$K_3H_5(P_2O_7)_2 + K_2H_2P_2O_7 \cdot 0.5H_2O$
24	5h	1.95	20.2	34.9	2.4	$K_3H_5(P_2O_7)_2 + K_2H_2P_2O_7 \cdot 0.5H_2O$
25	6	3.70	20.5	30.3		$K_2H_2P_2O_7 \cdot 0.5H_2O$
26	30	6.10	27.2	31.8		$K_2H_2P_2O_7 \cdot 0.5H_2O$
27	30	6.65	29.8	33.4	0.5	$K_2H_2P_2O_7 \cdot 0.5H_2O + K_3HP_2O_7 \cdot 3H_2O$
28	30	8.10	30.8	27.5		$K_3HP_2O_7 \cdot 3H_2O$
29	30	8.74	32.8	27.3		$K_3HP_2O_7 \cdot 3H_2O$
30	30	10.2	37.6	29.0		$K_3HP_2O_7 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$
31	30	12.1	37.9	28.3		$K_4P_2O_7 \cdot 3H_2O$
32	30	13.7	37.2	27.3		$K_4P_2O_7 \cdot 3H_2O$
33	30	>14.0	38.9	3.5		$K_4P_2O_7 \cdot 3H_2O$

[a] Unless specified h, hours. [b] P_2O_5 present as orthophosphate.

or with H-form cation-exchange resin (IR-120) to establish the proper composition. The solid phases had already been identified and characterized microscopically, and the presence of the two appropriate stable solid phases was sufficient evidence that each invariant point mixture had been established.

The approach to equilibrium was monitored by periodic microscopic examination of the solid phases. When all the crystals had attained euhedral morphology, it was assumed that the mixture was practically at equilibrium, and the equilibration period proper was started. When microscopic examination showed that no changes were occurring in the crystal forms or relative abundance of the solid phases, it was assumed that equilibrium had been attained, and the liquid phases were sampled and analyzed.

The equilibration mixtures were held at 0.0 ± 0.5° C or at 25 ± 1° C for times that depended on the pH, because the rate of hydrolysis of pyrophosphate to orthophosphate is significant at pH values below 4. To accelerate equilibration at 25° C, mixtures with pH 2 or below were agitated vigorously for the equilibration times shown in Table IV. Mixtures with pH 2 to 4 were shaken several times a day, and those with pH above 4 were shaken occasionally. The pH values of the 0° C equilibration mixtures are those of por-

tions of the liquid phases that had warmed to 25° C. The solid phases were identified petrographically, and those listed in Table IV were present in the respective mixtures throughout the entire equilibration times. The results are presented graphically in Figures 1 and 2.

The orthophosphate contents of some of the equilibration mixtures were determined chromatographically. The relatively high rates of hydrolysis at 25° C of pyrophosphate to orthophosphate at low pH are shown by the data for entries 19 to 24 in Table IV. The significant orthophosphate contents of these solutions cast some doubt on the validity of their solubility data, but pyrophosphate would not be expected to persist long under these conditions. The data for entry 27, with pH 6.65 that is fairly typical of fertilizer solutions, indicate that hydrolysis of pyrophosphate would be slow in the usual polyphosphate fertilizer solution.
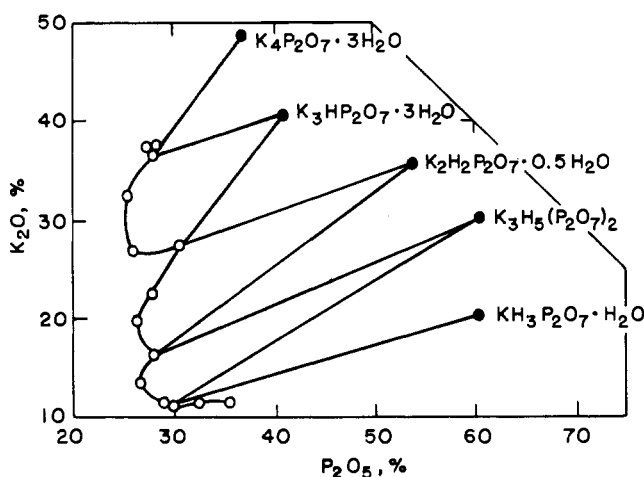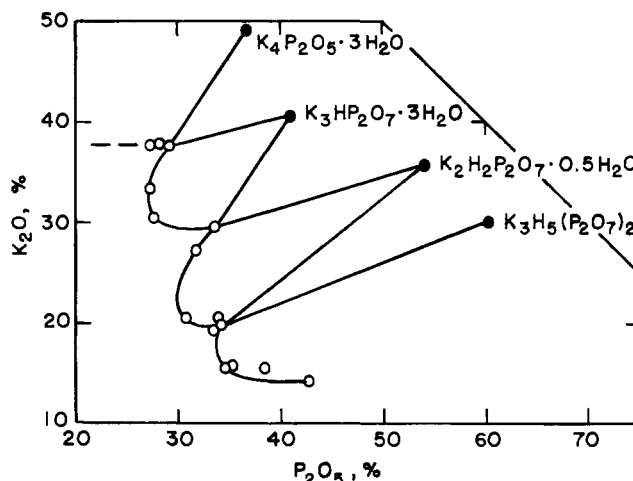
Data on the system $K_2O-H_4P_2O_7-H_2O$ at 25° C and those on the system $K_2O-H_3PO_4-H_2O$ reported by Berg (1937) were used in preparing the equilibration mixtures in the system $K_2O-H_3PO_4-H_4P_2O_7-H_2O$. These mixtures were prepared from reagent KOH, H_3PO_4, and KH_2PO_4, and recrystallized $K_2H_2P_2O_7 \cdot 0.5H_2O$ in the proportions to provide the solid phases known to exist in the two ternary systems. The composition of each mixture was adjusted so that at least

Table V. The System $K_2O-H_3PO_4-H_4P_2O_7-H_2O$ at 25° C

| | | Saturated solution Composition, wt % | | |
| | | P₂O₅ | | |
pH	K₂O	Total	Orthoᵃ	Solid phase
2.8	20.6	32.0		$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O$
3.5	20.2	29.7		$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O$
4.15	21.2	29.3	4.7	$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O$
5.38	25.4	31.1	4.1	$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O$
6.03	29.1	32.9	5.5	$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O$
6.40	30.1	33.7	5.7	$KH_2PO_4 + K_2H_2P_2O_7 \cdot 0.5H_2O + K_3HP_2O_7 \cdot 3H_2O$
6.65	30.3	32.2	5.1	$KH_2PO_4 + K_3HP_2O_7 \cdot 3H_2O$
7.24	30.2	30.4	8.5	$KH_2PO_4 + K_3HP_2O_7 \cdot 3H_2O$
7.80	31.5	29.3	13.4	$KH_2PO_4 + K_3HP_2O_7 \cdot 3H_2O$
8.10	32.7	29.3	15.8	$KH_2PO_4 + K_3HP_2O_7 \cdot 3H_2O$
8.90	35.6	30.5	22.2	$KH_2PO_4 + K_2HPO_4 \cdot 3H_2O + K_3HP_2O_7 \cdot 3H_2O$
9.20	35.9	30.0	21.6	$K_2HPO_4 \cdot 3H_2O + K_3HP_2O_7 \cdot 3H_2O$
9.50	37.8	30.4	21.0	$K_2HPO_4 \cdot 3H_2O + K_3HP_2O_7 \cdot 3H_2O$
10.05	39.1	30.9	20.6	$K_2HPO_4 \cdot 3H_2O + K_3HP_2O_7 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$
11.08	37.8	28.8	15.2	$K_2HPO_4 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$
12.15	39.6	27.3	16.9	$K_2HPO_4 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$
13.05	44.8	26.1	22.3	$K_2HPO_4 \cdot 3H_2O + K_4P_2O_7 \cdot 3H_2O$

ᵃ P₂O₅ present as orthophosphate.

Figure 1. The system $K_2O-H_4P_2O_7-H_2O$ at 0° C

Figure 2. The system $K_2O-H_4P_2O_7-H_2O$ at 25° C

one orthophosphate and one pyrophosphate was present as a stable solid phase; more complex mixtures containing three stable solid phases were prepared to establish the invariant points in the system. After equilibration at 25° C for 3 weeks in a water bath, the solid phases were identified and characterized microscopically and measurements were made of the pH, composition, and distribution of phosphate species in the liquid phases. The results are shown in Table V and Figure 3.

In general, the saturated solutions in the ortho–pyrophosphate system are somewhat more concentrated than those in the pyrophosphate system and considerably more concentrated than those in the orthophosphate system. In the pH range 6 to 7, in which most liquid fertilizers fall, the maximum fertilizer grade in the ortho–pyrophosphate system is 0-34-30 (%N-%P₂O₅-%K₂O) at pH 6.4 and that in the pyrophosphate system is 0-33-30 at pH 6.65. On the other hand, the maximum grade in the orthophosphate system is only about 0-20-20.

As shown in Table V, at pH 8 and above, more than half the phosphate in the saturated solutions in the ortho–pyrophosphate system is orthophosphate, whereas at low pH almost all the phosphate in solution is pyrophosphate. The near coincidence of the solubility curves in Figure 3 of the ortho–
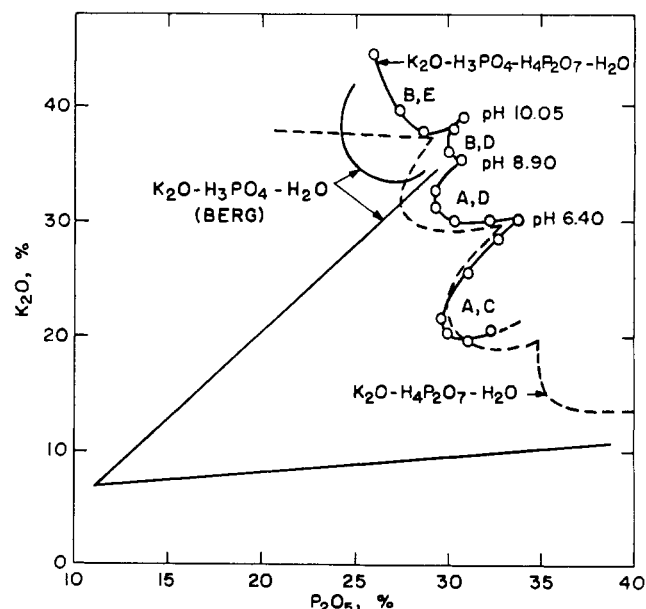

Figure 3. The system $K_2O-H_3PO_4-H_4P_2O_7-H_2O$ at 25° C. Solid phases: A = KH_2PO_4, B = $K_2HPO_4 \cdot 3H_2O$, C = $K_2H_2P_2O_7 \cdot 0.5H_2O$, D = $K_3HP_2O_7 \cdot 3H_2O$, E = $K_4P_2O_7 \cdot 3H_2O$

pyrophosphate system and the pyrophosphate system at pH 6.5 and below reflects the higher solubility of the pyrophosphates than that of monopotassium orthophosphate.

None of the "double salts" of potassium orthophosphate, such as $2K_2HPO_4 \cdot KH_2PO_4 \cdot H_2O$, that are described by Berg (1937) were observed in the ortho–pyrophosphate system, nor were any of the potassium ortho–pyrophosphates reported by Silber and Brun (1965). The mixed ortho–pyrophosphates are said to be formed under nearly anhydrous conditions or in melts of potassium hydroxide and polyphosphoric acid that would contain acids more highly condensed than pyrophosphoric.

The system $NH_3–K_2O–H_3PO_4–H_4P_2O_7–H_2O$ would include complete N–P–K polyphosphate fertilizer solutions that contain no chloride or other extraneous ions. A study is being made of solubilities in this quinary system in the continuing search for stable, high-analysis liquid fertilizers. In exploratory studies of the system, ammonia was added to some of the mixtures in Table V, and several new solid phases that contain both ammonia and potassium were observed.

These solid phases are being characterized to facilitate their identification in further studies of the system.

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