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Solubility in the System Aluminum Phosphate–Phosphoric Acid–Water

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RECEIVED APRIL 19, 1954

Solubilities were determined in the system $AlPO_4$–H_3PO_4–H_2O at 25, 50 and 75°. Although the liquid phases reached equilibrium in less than 5 months, many of the solid phases apparently did not reach equilibrium. The solid phases are $AlPO_4 \cdot xH_2O$, in which x is less than 3 and decreases with increase in temperature; an intermediate acid salt that is probably $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$; and an acid salt, $AlPO_4 \cdot 2H_3PO_4$. The system is similar to the system $FePO_4$–H_3PO_4–H_2O. The aluminum salts are considerably more soluble, however, than the corresponding iron salts.

Iron and aluminum occur in rock phosphate and must be reckoned with in acidulation processes for converting the rock to fertilizer. The formation of iron and aluminum compounds in phosphate systems is a part of the chemistry of the acidulation processes.

Solubilities in the system iron phosphate–phosphoric acid–water have been reported.[1-6] Quantitative information on the corresponding aluminum phosphate system was lacking, however, when the present determinations of solubilities at 25, 50 and 75° were made. Bailer[1] reported that Erlenmeyer found only two aluminum phosphates, $AlPO_4 \cdot 2H_2O$ and $AlPO_4 \cdot 2H_3PO_4$.

TABLE I

THE SYSTEM $AlPO_4$–H_3PO_4–H_2O AT 25°

Liquid phase, %				Wet solids, %				
Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Solid phase
0.00	0.00	0.00	0.00	14.29[a]	19.59	33.65	...	$AlPO_4 \cdot xH_2O$
0.04	1.06	0.10	1.38	16.76	23.58	40.10	0.34	$AlPO_4 \cdot xH_2O$
0.46	5.09	1.11	6.13	11.00	17.46	26.31	2.97	$AlPO_4 \cdot xH_2O$
1.06	8.46	2.54	9.64	11.23	20.13	26.86	6.21	$AlPO_4 \cdot xH_2O$
1.07	8.68	2.56	9.93	7.60	16.00	18.18	7.49	$AlPO_4 \cdot xH_2O$
2.01	11.90	4.82	12.56	5.78	16.41	13.83	11.54	$AlPO_4 \cdot xH_2O$
2.19	12.37	5.25	12.86	16.93	28.25	40.50	6.46	$AlPO_4 \cdot xH_2O$
2.25	14.01	5.39	15.01	13.85	25.60	33.14	8.72	$AlPO_4 \cdot xH_2O$
2.24	14.02	5.37	15.04	12.11	23.97	28.97	9.81	$AlPO_4 \cdot xH_2O$
3.03	16.81	7.25	17.38	6.80	20.51	16.26	15.25	$AlPO_4 \cdot xH_2O$
4.50	22.57	10.76	22.51	14.42	30.31	34.49	14.14	$AlPO_4 \cdot xH_2O$
4.23	23.21	10.12	23.91	6.75	24.75	16.16	21.19	$AlPO_4 \cdot xH_2O$
4.66	23.74	11.15	23.81	11.92	28.21	28.52	16.03	$AlPO_4 \cdot xH_2O$
5.46	26.32	13.06	25.85	11.07	30.16	26.48	20.36	$AlPO_4 \cdot xH_2O$
6.17	28.18	14.77	27.03	14.83	42.05	35.49	29.54	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.15	29.94	14.71	29.52	...	...	...	...	....
7.31	33.13	17.48	31.69	12.62	34.93	30.20	23.96	Metastable
7.32	34.20	17.51	33.15	15.07	44.94	36.05	33.08	Metastable
7.40	34.65	17.71	33.61	16.98	47.61	40.62	33.09	Metastable
6.03	32.56	14.42	33.37	6.49	32.36	15.53	32.20	$AlPO_4 \cdot xH_2O$
7.65	35.15	18.31	33.82	16.35	45.56	39.13	31.47	Metastable
8.58	36.48	20.54	34.86	14.19	39.51	33.95	27.27	Metastable
7.93	36.52	18.96	35.19	17.42	47.94	41.68	32.69	Metastable
6.57	35.75	15.71	36.74	15.56	46.69	37.22	34.55	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
8.51	38.32	20.35	36.57	8.51	38.26	20.37	36.46	Metastable
7.44	37.00	17.80	36.78	12.17	42.24	29.11	34.93	Metastable
8.84	39.07	21.15	36.95	10.29	39.12	24.61	34.23	Metastable
6.41	37.17	15.33	39.00	13.48	45.31	32.24	36.65	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.49	38.47	15.52	40.65	13.15	46.08	31.46	38.34	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.45	38.85	15.44	41.23	14.21	47.11	33.99	37.73	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.29	42.79	15.06	46.98	16.37	49.64	39.16	37.06	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.28	43.09	15.02	47.42	14.85	48.51	35.52	38.44	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.14	45.84	14.70	51.48	10.64	47.07	25.45	44.54	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
5.93	46.78	14.19	53.18	10.05	48.51	24.05	47.65	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.03	49.44	14.42	56.68	8.95	50.27	21.41	52.20	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
6.73	53.15	16.10	60.45	11.55	52.15	27.63	49.80	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
7.25	54.57	17.35	61.40	12.29	54.24	29.41	51.25	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$

[a] Slightly exceeds the $AlPO_4$ equivalent of the P_2O_5.

After the present solubility measurements were completed, Guérin and Martin[7] reported somewhat

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(1) A. Bailer, thesis, Stuttgart, 1930.

(2) E. B. Brutskus, *Trans. Sci. Inst. Fertilizers and Insectofungicides* (*U.S.S.R.*), **137**, 110 (1937).

(3) F. K. Cameron and J. M. Bell, *J. Phys. Chem.*, **11**, 363 (1907).

(4) S. R. Carter and N. H. Hartshorne, *J. Chem. Soc.*, **123**, 2223 (1923).

(5) S. R. Carter and N. H. Hartshorne, *ibid.*, 363 (1926).

(6) R. F. Jameson and J. E. Salmon, *ibid.*, 28 (1954).

(7) H. Guérin and R. Martin, *Compt. rend.*, **234**, 1777 (1952).

TABLE II

THE SYSTEM $AlPO_4$–H_3PO_4–H_2O AT 50°

Liquid phase, %				Wet solids, %				
Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Solid phase
0.01	0.05	0.01	0.06	8.75	12.73	20.93	0.23	$AlPO_4 \cdot xH_2O$
0.10	3.60	0.24	4.78	6.25	11.92	14.96	4.44	$AlPO_4 \cdot xH_2O$
0.36	6.35	0.86	8.07	6.20	13.71	14.83	7.01	$AlPO_4 \cdot xH_2O$
0.65	8.62	1.55	10.66	5.84	15.27	13.98	9.85	$AlPO_4 \cdot xH_2O$
1.14	11.39	2.72	13.55	4.49	15.23	10.74	12.40	$AlPO_4 \cdot xH_2O$
1.73	14.77	4.14	17.07	7.05	20.20	16.87	14.34	$AlPO_4 \cdot xH_2O$
1.89	15.39	4.51	17.63	9.48	27.37	22.68	19.56	Metastable
3.70	22.53	8.85	24.00	...	...	...	...	....
4.79	27.02	11.45	28.10	11.31	44.89	27.05	40.24	Metastable
6.02	31.44	14.41	31.83	12.38	42.62	29.63	35.03	Metastable
6.84	34.65	16.36	34.70	8.50	36.13	20.33	33.54	Metastable
7.31	36.02	17.49	35.68	8.67	36.68	20.75	33.97	Metastable
7.47	37.69	17.87	37.67	11.52	42.76	27.56	36.90	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
7.74	38.82	18.52	38.72	12.27	44.36	29.36	37.66	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
7.47	43.71	17.88	45.98	12.26	47.57	29.35	42.10	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
7.55	46.27	18.07	49.37	11.88	48.52	28.43	44.16	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
7.52	47.18	18.00	50.68	11.90	48.79	28.47	44.49	$AlPO_4 \cdot H_3PO_3 \cdot 3H_2O$
7.90	50.86	18.91	55.02	13.11	50.89	31.38	45.05	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
8.42	52.98	20.14	56.97	12.18	52.72	29.14	49.37	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
8.63	54.22	20.65	58.28	9.93	55.26	23.75	57.22	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O + AlPO_4 \cdot 2H_3PO_4$
6.26	55.60	14.97	64.73	9.78	59.54	23.41	63.39	$AlPO_4 \cdot 2H_3PO_4$
2.09	60.05	5.00	78.89	6.47	61.77	15.47	72.85	$AlPO_4 \cdot 2H_3PO_4$

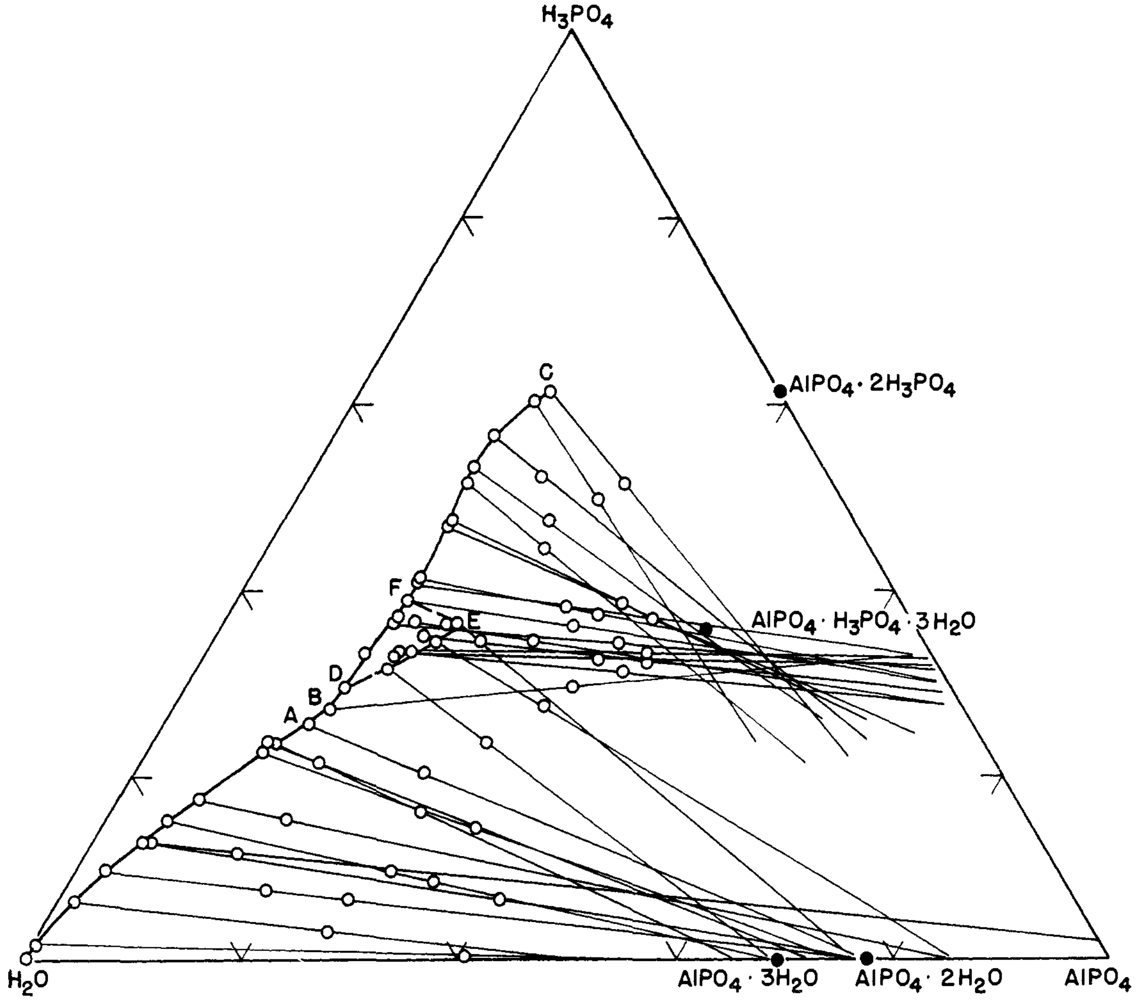

Fig. 1.—The system $AlPO_4$–H_3PO_4–H_2O at 25°.

TABLE III

THE SYSTEM $AlPO_4$–H_3PO_4–H_2O AT 75°

Liquid phase, %				Wet solids, %				
Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Al_2O_3	P_2O_5	$AlPO_4$	H_3PO_4	Solid phase
0.00	0.25	0.00	0.35	19.18	27.02	45.88	0.44	$AlPO_4 \cdot xH_2O$
0.05	3.77	0.11	5.12	7.55	15.01	18.07	6.20	$AlPO_4 \cdot xH_2O$
0.17	6.35	0.41	8.44	6.91	14.99	16.54	7.41	$AlPO_4 \cdot xH_2O$
0.54	10.36	1.29	13.27	6.37	17.08	15.24	11.34	$AlPO_4 \cdot xH_2O$
1.24	15.21	2.96	18.63	7.67	22.62	18.36	16.48	$AlPO_4 \cdot xH_2O$
2.65	22.76	6.33	26.33	7.39	26.16	17.69	21.90	$AlPO_4 \cdot xH_2O$
3.16	24.86	7.56	28.25	8.33	28.73	19.94	23.65	$AlPO_4 \cdot xH_2O$
4.14	29.02	9.90	32.11	9.99	32.58	23.89	25.79	$AlPO_4 \cdot xH_2O$
4.58	30.72	10.95	33.62	10.09	33.76	24.13	27.22	$AlPO_4 \cdot xH_2O$
5.65	34.67	13.51	37.01	8.30	35.77	19.85	33.35	$AlPO_4 \cdot xH_2O$
5.95	35.01	14.23	36.91	8.90	36.50	21.30	33.28	$AlPO_4 \cdot xH_2O$
6.35	36.15	15.19	37.71	6.84	36.70	16.37	37.51	$AlPO_4 \cdot xH_2O$
8.13	41.77	19.46	42.04	11.79	43.26	28.20	37.07	$AlPO_4 \cdot xH_2O$
9.39	44.37	22.46	43.22	10.95	44.95	26.20	41.01	$AlPO_4 \cdot xH_2O + AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
9.38	46.16	22.45	45.70	14.46	49.55	34.60	40.61	$AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$
9.37	49.10	22.42	49.78	11.39	50.29	27.24	47.54	$AlPO_4 \cdot H_3PO_5 \cdot 3H_2O$
8.26	50.52	19.77	53.87	10.16	54.40	24.30	55.58	$AlPO_4 \cdot 2H_3PO_4$
7.36	53.03	17.61	59.07	9.98	54.23	23.89	55.68	$AlPO_4 \cdot 2H_3PO_4$
6.44	55.04	15.42	63.61	9.32	55.39	22.31	58.55	$AlPO_4 \cdot 2H_3PO_4$
6.02	56.29	14.41	66.14	9.77	59.52	23.38	63.39	$AlPO_4 \cdot 2H_3PO_4$
4.09	58.29	9.78	72.63	9.41	62.06	22.51	67.60	$AlPO_4 \cdot 2H_3PO_4$

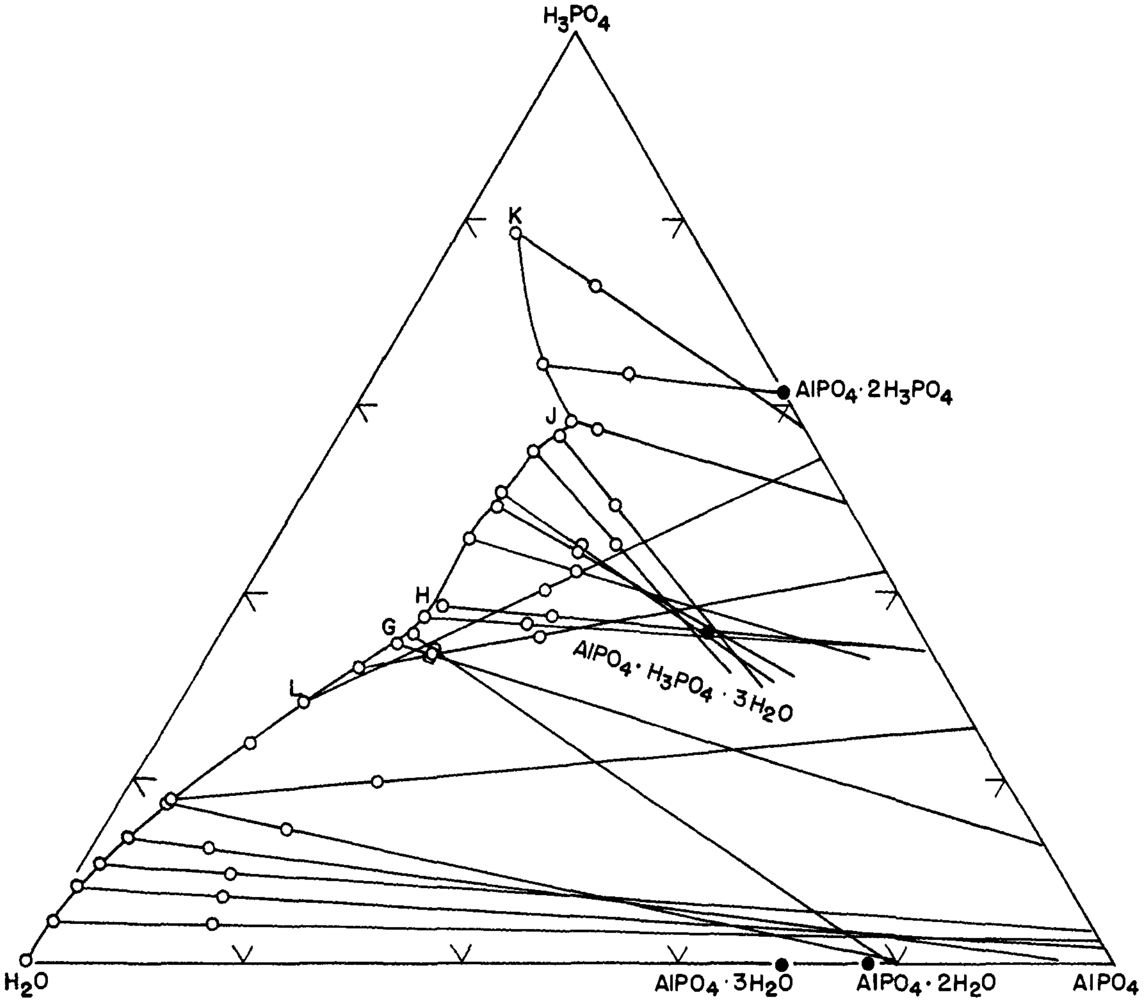

Fig. 2.—The system $AlPO_4$–H_3PO_4–H_2O at 50°.

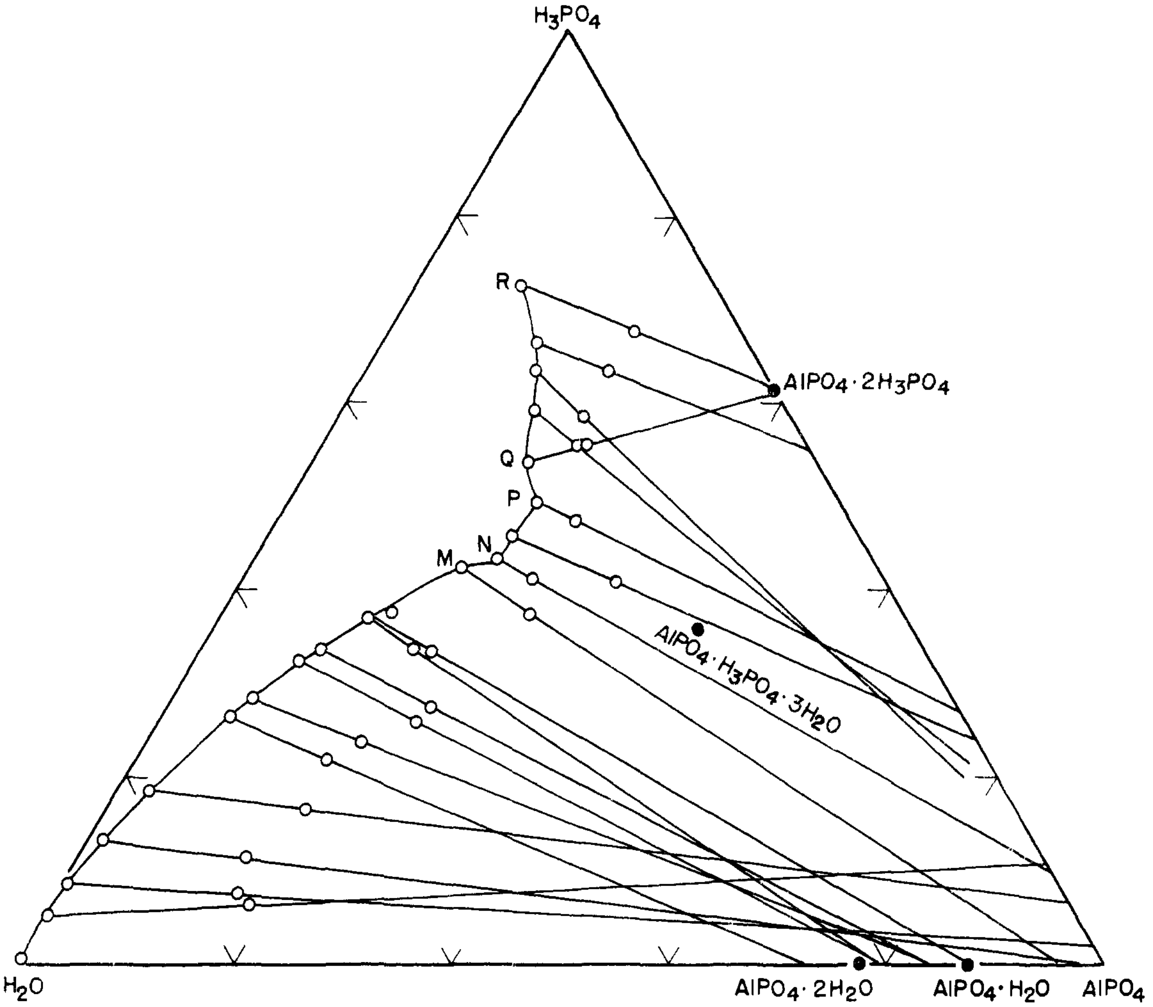

Fig. 3.—The system $AlPO_4$–H_3PO_4–H_2O at 75°.

higher solubilities of aluminum phosphate from their study of the system at 60°. They concluded that the stable solid phases are $AlPO_4·3.5H_2O$, $AlPO_4·2H_2O$, $2AlPO_4·H_3PO_4·3.5H_2O$, $AlPO_4·H_3PO_4·0.5H_2O$ and $AlPO_4·2H_3PO_4$. The brevity of their paper—essentially a summary statement of conclusions—precludes an independent, direct appraisal of its content. The thermal stabilities that Guérin and Martin reported for aluminum phosphates are incompatible, however, with the stabilities found in unpublished work by TVA.

Solubility Measurements

Cylindrical solubility flasks containing slurries of aluminum phosphate in aqueous solutions of phosphoric acid were rotated end-over-end in a water-bath. When the liquid phases reached equilibrium, the mixtures were allowed to settle. Samples of the clear supernatant liquors and of the wet solids were analyzed. The compositions of the solid phases were determined by Schreinemakers' method of residues.[8]

Materials.—Aluminum phosphate that was prepared by precipitation from solutions of aluminum salts and alkali metal phosphates could not be washed free of extraneous ions from the reagents. A satisfactory aluminum phosphate was prepared in batches by dissolving grade 5A aluminum metal (99.85 to 99.89% Al) in phosphoric acid. A 120-g. charge of aluminum turnings was refluxed with 35% phosphoric acid in a mole ratio H_3PO_4:Al of 1.5. The reaction required several days.

The suspension of aluminum phosphate was decanted from the small residue of metal, diluted to 13 liters, and allowed to settle for several days. The supernatant liquor was decanted, and the precipitate was washed on a filter. The precipitate was washed twice more by decantation and was again filtered and washed.

The product always contained a little free acid; when dried at 105° it contained about 31% Al_2O_3 and 44% P_2O_5. The mole ratio Al_2O_3:P_2O_5 ranged from 0.975 to 0.995. The composition corresponded approximately to $AlPO_4·2.3H_2O$. The detectable impurities, as found spectrographically, were Fe_2O_3, <0.02; SiO_2, <0.04; MgO, <0.02; and CaO, <0.01%.

The phosphoric acid used in the study was of reagent grade.

Procedure.—The thermoregulators in the water-bath were set in accordance with thermometers that were calibrated by the National Bureau of Standards. The control limits were 25 ± 0.05°, 50.0 ± 0.1°, and 75.0 ± 0.2°.

The initial content of solid phase in the equilibration mixtures was 15 to 20%. The compositions were adjusted several times in the first 2 months to maintain the desired consistency.

A set of mixtures was assumed to be at equilibrium when the composition of the clear liquor above several partly settled suspensions was constant in two successive monthly samples. The liquid phases apparently reached equilibrium at each temperature in less than 5 months.

When the solids in the equilibrated mixtures approached their maximum degree of settling—usually after 3 weeks—samples of the clear supernatant liquors were withdrawn in

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(8) F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

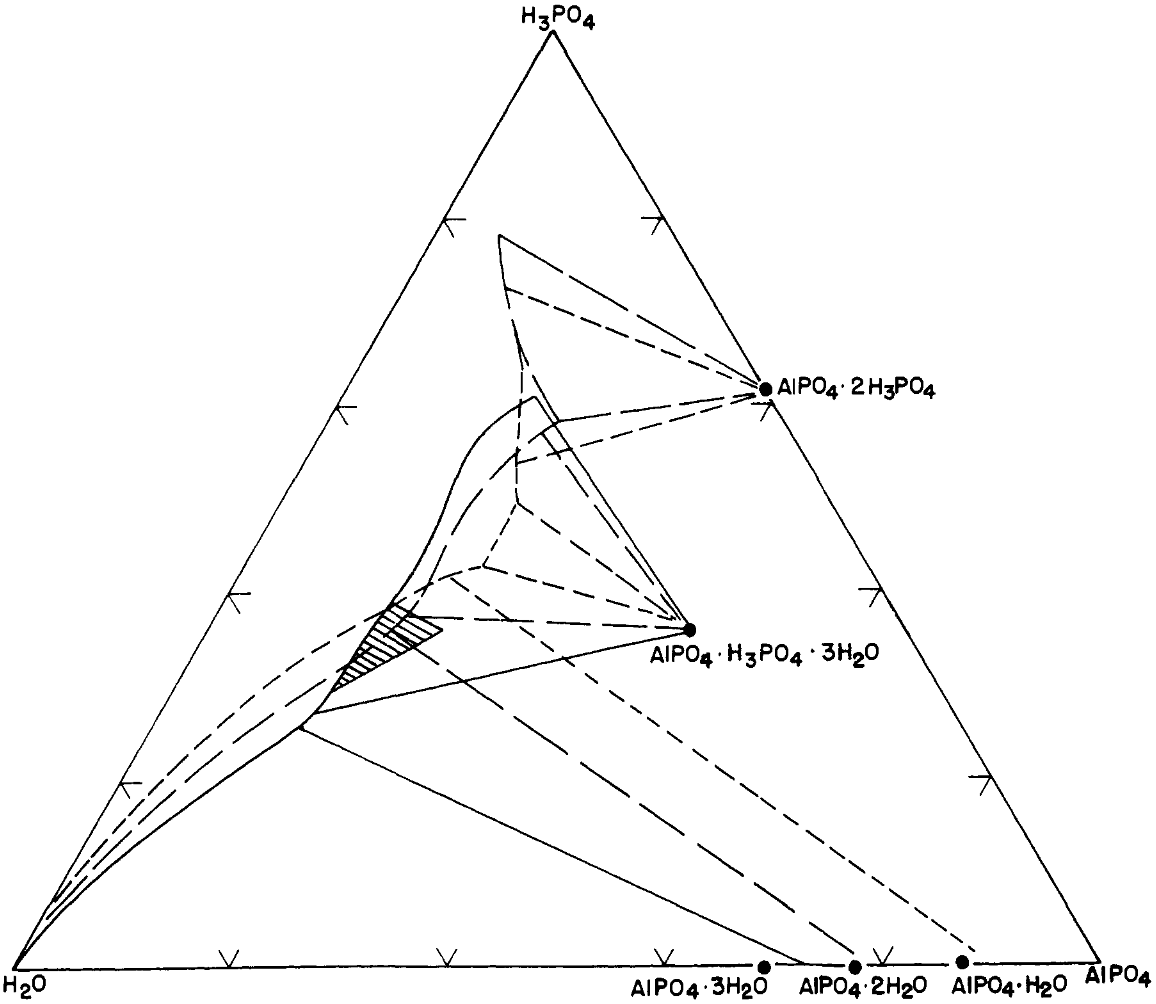

Fig. 4.—The system $AlPO_4$-H_3PO_4-H_2O: ——, 25°; — —, 50°; - - -, 75°.

pipets that were preheated to the equilibration temperature. The samples were weighed, and aliquots for analysis were taken by conventional volumetric technique. The rest of the supernatant liquor was siphoned off and discarded. Samples of the wet solid phases were dipped out in tared glass cups, which then were bottled and weighed. The solids were dissolved in hydrochloric acid.

Aliquots of the diluted samples were analyzed for aluminum by precipitation with 8-hydroxyquinoline.[9] Phosphorus in the samples from the 25° isotherm was determined by precipitation and ignition of magnesium ammonium phosphate.[10] Phosphorus in the 50 and 75° samples was determined alkalimetrically[11] by titration of precipitated ammonium molybdophosphate with a solution of sodium hydroxide that was standardized against a National Bureau of Standards sample of rock phosphate.

Solubility Isotherms

Identification of the solid phases proved difficult. They generally were of such small particle size that they did not settle well from the viscous liquid phases. Variations in the composition of different samples of the solids from the same equilibration flask indicated that many of the solid phases were not at equilibrium. Bailer[1] encountered a similar difficulty with solid phases in the system iron phosphate–phosphoric acid–water.

Primary data on the compositions of liquid and solid phases at the three temperatures are shown in Tables I, II and III. The tabulated compositions of the saturated liquid phases are averages of duplicate determinations in which the values for Al_2O_3 and P_2O_5 checked within five parts per thousand. Most of the values listed for the solid phases are averages of two determinations that gave about the same tie-line between the saturated liquid and the wet solids.

The 25° isotherm, Fig. 1, consists of two branches. There probably is a third branch at higher acid concentrations, as in the other isotherms. The branch from the H_2O corner to A is that of $AlPO_4 \cdot xH_2O$, where x apparently is between 2 and 3. Branch BC is that of an intermediate acid salt whose composition approximates $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$. The region in the triangular area DEF corresponds to metastable solutions in which the solid phases may be $AlPO_4 \cdot xH_2O$, $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$, or mixtures of the two.

The 50° isotherm, Fig. 2, consists of three branches. The branch from the H_2O corner to

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[9] G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **3**, 91 (1929).

[10] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **19**, 59 (1937).

[11] Association of Official Agricultural Chemists, "Methods of Analysis," 7th Ed., 1950, pp. 9–10.

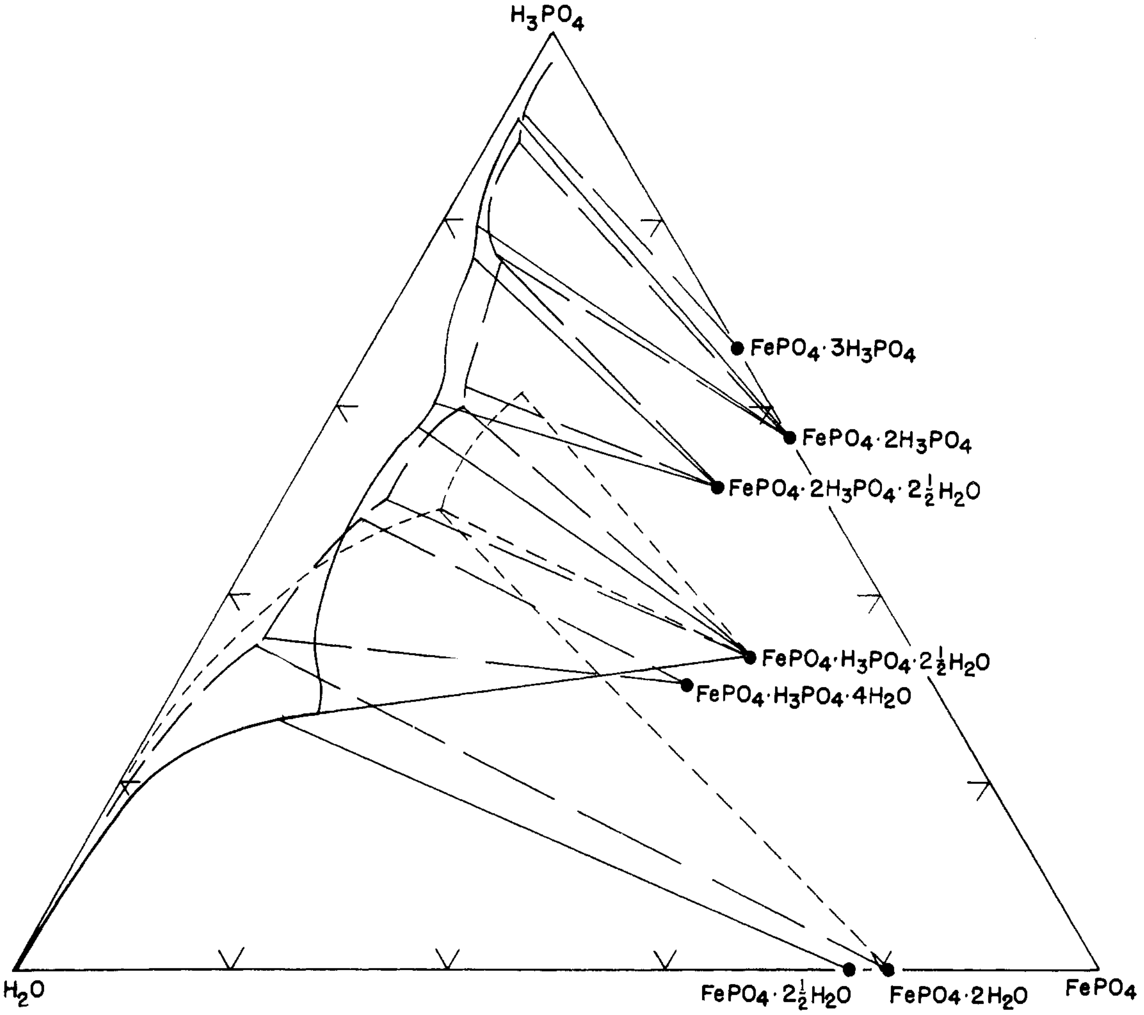

Fig. 5.—The system $FePO_4$–H_3PO_4–H_2O: ——, 25°, Jameson and Salmon[6]; — —, 40°, Bailer[1]; - - - -, 80°, Brutskus.[2]

G is that of $AlPO_4 \cdot xH_2O$, where x is close to 2. Branch HJ is that of an intermediate acid salt, presumably the $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$ that was indicated also in the 25° isotherm. Branch JK is that of $AlPO_4 \cdot 2H_3PO_4$. Portion LG of the solubility curve apparently corresponds to metastable solutions in which either $AlPO_4 \cdot xH_2O$, $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$, or mixtures of the two may exist, as in the corresponding, larger region in the 25° isotherm.

The 75° isotherm, Fig. 3, also consists of three branches. The branch from the H_2O corner to M is that of $AlPO_4 \cdot xH_2O$, where x is less than 2. Branch NP is that of an intermediate acid salt—probably $AlPO_4 \cdot H_3PO_4 \cdot 3H_2O$. Branch QR is that of $AlPO_4 \cdot 2H_3PO_4$.

A comparison of the three isotherms, as in Fig. 4, shows that $AlPO_4 \cdot xH_2O$ has a negative temperature coefficient of solubility and the intermediate acid salt a positive coefficient, whereas the solubility of $AlPO_4 \cdot 2H_3PO_4$ is practically unaffected by increase of the temperature from 50 to 75°. With increase in temperature, the $AlPO_4 \cdot xH_2O$ and $AlPO_4 \cdot 2H_3PO_4$ branches increase at the expense of the intermediate branch.

The isotherms are similar in shape to those shown in Fig. 5 for the system $FePO_4$–H_3PO_4–H_2O at 25, 40 and 80°. The iron salts are considerably less soluble, however, than the aluminum salts. The tertiary phosphates, RPO_4, and the primary phosphates, $RPO_4 \cdot 2H_3PO_4$ or $R(H_2PO_4)_3$, appear as solid phases in both systems. Solid phases corresponding to the secondary phosphates, $R_2(HPO_4)_3$ or $2RPO_4 \cdot H_3PO_4$, do not appear in either system. The intermediate acid salt, $RPO_4 \cdot H_3PO_4$, that appears in both systems may be a salt of a dimeric phosphoric acid, $H_6P_2O_8$, in which the iron or aluminum replaces half of the hydrogen ions to form $RH_3P_2O_8$.

Acknowledgment.—The Reynolds Metals Company, Sheffield, Ala., contributed the high-purity aluminum metal from which the aluminum phosphate was prepared. R. L. Dunn and Mrs. Inez Jenkins Murphy made most of the chemical analyses.

Wilson Dam, Alabama