

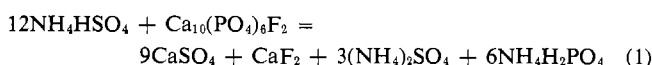
# The System $\text{NH}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$ at $25^\circ\text{C}$

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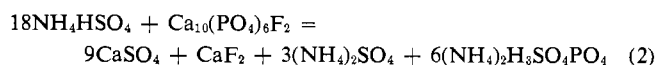
Measurements of solubility in the system  $\text{NH}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$  at  $25^\circ\text{C}$  showed that a major solid phase is the double salt  $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$ . The data are useful in indicating the most practical

conditions for operation of a fertilizer process based on the reaction of ammonium bisulfate with phosphate rock.

Phosphate rock reacts with aqueous solutions of ammonium bisulfate to produce mixtures of insoluble calcium sulfate and fluoride and soluble ammonium sulfate and phosphate. The minimum amount of the acid sulfate is indicated by the equation



but this reaction would not be expected to go to completion. The maximum effective amount of the acid sulfate is indicated by the equation



The double salt  $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$  has the same composition as  $\text{NH}_4\text{HSO}_4 \cdot \text{NH}_4\text{H}_2\text{PO}_4$ , so that equation 2 represents an excess of  $\text{NH}_4\text{HSO}_4$ , and the optimum ratio of  $\text{NH}_4\text{HSO}_4$  to apatite lies between those of equations 1 and 2. As part of an investigation of the production of fertilizer materials by the reaction of ammonium bisulfate with phosphate rock, a brief study was made of solubility in the acid region of the system  $\text{NH}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$  at  $25^\circ\text{C}$ .

The system  $\text{NH}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$  has been studied by Berlin and Mantsev (1933), Uno (1940), and Mishchenko and Chepelevetskii (1965), and the system  $\text{NH}_3\text{-SO}_3\text{-H}_2\text{O}$  was studied by Locuty and Laffitte (1934). To extend the information on the four-component system into regions pertinent to the reaction of phosphate rock with ammonium bisulfate, 12 mixtures in the system were equilibrated at  $25^\circ\text{C}$  for 2 months. In five of the mixtures the solid phases comprised three salts, and in the other seven the solid phases comprised two salts.

The equilibration mixtures were prepared from superphosphoric acid (80%  $\text{P}_2\text{O}_5$ ), sulfuric acid, ammonium sulfate, monoammonium orthophosphate, and water; all salts and acids were reagent grade. The solid phases were examined petrographically, and the compositions of the mixtures were adjusted when necessary to provide the desired solid phases before the 2 month equilibration was started.

The optical properties of most of the solid phases are described by Winchell and Winchell (1964), but three of the solid

phases— $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$ ,  $\text{NH}_4\text{H}_5(\text{PO}_4)_2$ , and  $(\text{NH}_4)_3\text{H}_9(\text{PO}_4)_4$ —have not been described thoroughly. Homogeneous preparations of each salt were characterized chemically, optically, and by X-ray. The compositions of the preparations are shown in Table I, their optical properties are listed in Table II, and their X-ray powder diffraction data are shown in Table III. The single-crystal X-ray data for  $\text{NH}_4\text{H}_5(\text{PO}_4)_2$  have been reported (Norbert and Andre, 1970).

The compositions of the equilibrated liquid phases are shown in Table IV, together with data reported by other investigators. The results are plotted in Figure 1 as projections on the  $\text{P}_2\text{O}_5\text{-SO}_3\text{-(NH}_3 + \text{H}_2\text{O)}$  face of the four-component system.

With the exception of points A and B in Table IV and Figure 1, our results are in excellent agreement with those of the previous investigators. Berlin and Mantsev (1933) placed at A the composition of the invariant-point solution with which  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $\text{NH}_4\text{HSO}_4$ , and  $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$  are in equilibrium, whereas we found the invariant point at B. The boundary of the  $\text{NH}_4\text{H}_2\text{PO}_4$  region, FYX, appears to intersect the boundary of the  $(\text{NH}_4)_2\text{SO}_4$  region, WJD, near J, the location of the univariant-point solution reported by Uno (1940), but this point was not located in the present study.

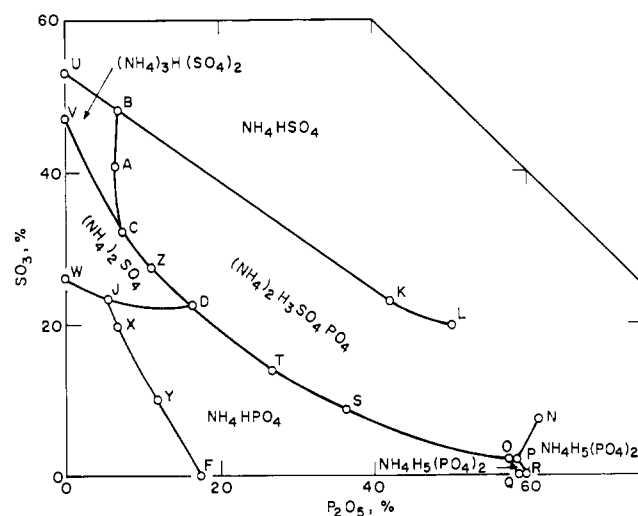


Figure 1. The system  $\text{NH}_3\text{-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$  at  $25^\circ\text{C}$ , projected on the  $(\text{NH}_3 + \text{H}_2\text{O})\text{-P}_2\text{O}_5\text{-SO}_3$  face

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**Table I. Composition of Preparations**

Compound	Composition, %				Moles/mole P <sub>2</sub> O <sub>5</sub>		
	NH <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O (diff.)	NH <sub>3</sub>	SO <sub>3</sub>	H <sub>2</sub> O
NH <sub>4</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>2</sub>	7.7	...	66.2	26.1	0.97	...	3.11
Stoichiometric	7.99	...	66.63	25.37	1.00	...	3.00
(NH <sub>4</sub> ) <sub>3</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>4</sub>	11.1	...	63.0	25.9	1.47	...	3.24
Stoichiometric	11.53	...	64.07	24.40	1.50	...	3.00
(NH <sub>4</sub> ) <sub>2</sub> H <sub>3</sub> SO <sub>4</sub> PO <sub>4</sub>	14.7	35.2	30.6	19.5	4.01	2.04	5.02
Stoichiometric	14.80	34.79	30.84	19.57	4.00	2.00	5.00

**Table II. Optical Data**

Compound	Crystal system	Refractive indices	Optical properties <sup>a</sup>
(NH <sub>4</sub> ) <sub>3</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>4</sub>	Monoclinic, 2/m (100) tablets modified by {011} and small (001). Sometimes elongated along c	α = 1.479 β = 1.519 γ = 1.521	Biaxial (-), 2V = 30° (25°) OAP = 010, XΔc = 45° in obtuse β. b = Y, d = 1.86
NH <sub>4</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>2</sub>	Monoclinic, 2/m. Rods elongated along c and plates tabular on (100), modified by {110}, (111), (11̄1), (1̄1̄1), and sometimes (001) and {011}	α = 1.460 β = 1.502 γ = 1.515	Biaxial (-), 2V = 60° (57°) OAP = 010, ZΔc = 24° in acute β. Y = b, β = 96°, d = 1.92
(NH <sub>4</sub> ) <sub>2</sub> H <sub>3</sub> SO <sub>4</sub> PO <sub>4</sub>	Monoclinic, 2/m. Prisms exhibiting prominent (100) and (010) modified by {111} and {101}. Can be tabular on either (100) or (010)	α = 1.478 β = 1.484 γ = 1.518	Biaxial (+), 2V = 47° (46°) OAP ⊥ (010), XΔc = 17° in acute β. Z = b, β = 107°, d = 2.11

<sup>a</sup> Values of 2V in ( ) are calculated by Johannsen's equation and values of density are calculated by the Gladstone-Dale equation (Larsen and Berman, 1934).

**Table III. X-Ray Powder Diffraction Data**

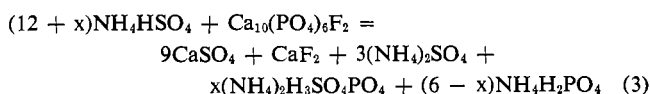
CuKα radiation, λ = 1.54178 Å. Intensities measured as peak heights above background and expressed as percent of strongest line

d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>
(NH <sub>4</sub> ) <sub>2</sub> H <sub>3</sub> SO <sub>4</sub> PO <sub>4</sub>					
5.87	98	2.988	15	2.070	10
5.26	23	2.728	15	2.053	13
4.83	21	2.686	22	1.961	6
4.63	93	2.622	6	1.939(B)	12
4.07	68	2.409	10	1.904	12
3.77	86	2.294	21	1.738	6
3.66	10	2.225	10	1.691	6
3.49	93	2.194	16	1.675	6
3.29	100	2.105	7	1.508	7
3.23	56	2.093	7		
NH <sub>4</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>2</sub>					
6.15	34	2.714	9	1.914	3
5.09	100	2.689	9	1.865	3
4.92	19	2.540	17	1.834	3
4.73	18	2.456	4	1.696	17
3.85	41	2.421	5	1.650	4
3.84	30	2.330	11	1.638	3
3.83	52	2.292	1	1.610	3
3.57	40	2.245	4	1.594	4
3.10	58	2.047	21	1.579	3
3.07	28	2.000	15	1.552	4
2.939	5	1.961	3	1.541	3
2.831	10	1.940	3		
(NH <sub>4</sub> ) <sub>3</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>4</sub>					
5.92	15	3.28	11	2.304	7
5.81	100	3.19	11	2.139	6
5.57	6	3.14	48	2.025	23
5.30	44	2.994	20	1.962	16
5.16	25	2.907	28	1.940	17
5.05	92	2.752	10	1.936	12
4.46	36	2.582	35	1.917	8
3.78	74	2.576	31	1.798	13
3.69	16	2.520	9	1.468	7
3.32	60	2.389	9		

Chromatographic analysis showed that in the solution at L, only 47.4% of the phosphorus was present as orthophosphate, and in the solution at N, only 61% was orthophosphate; the rest of the phosphorus was present as condensed phosphates. The presence of condensed phosphate species near the P<sub>2</sub>O<sub>5</sub> corner of the system made it difficult to prepare equilibration mixtures in this region with the desired solid phases, and attempts to prepare mixtures in which NH<sub>4</sub>H<sub>9</sub>(PO<sub>4</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>H<sub>3</sub>SO<sub>4</sub>PO<sub>4</sub>, and NH<sub>4</sub>HSO<sub>4</sub> were in equilibrium were unsuccessful. Attempts to move along the line LN from either extremity invariably resulted in dissolution of one of the two solid phases.

The data for mixtures containing more than 50% P<sub>2</sub>O<sub>5</sub> are somewhat uncertain. The region of stability of (NH<sub>4</sub>)<sub>3</sub>H<sub>9</sub>(PO<sub>4</sub>)<sub>4</sub> is very small and that of NH<sub>4</sub>H<sub>9</sub>(PO<sub>4</sub>)<sub>2</sub> is much smaller than is indicated in Figure 1 because an increase in the phosphate concentration beyond 62% P<sub>2</sub>O<sub>5</sub> results in a marked increase in condensed phosphate species such as pyro-, tripoly-, and tetrapolyphosphates. These condensed phosphates both complicate the system and impart a high viscosity to the liquid phase.

In the treatment of phosphate rock with ammonium bisulfate, enough water must eventually be added to dissolve the ammonium sulfate and phosphate for separation from the insoluble calcium sulfate and fluoride. The soluble salts are those produced by the reaction



in which x ranges from 0 to 6. The amounts of water required to dissolve these salts, calculated from the data in Table IV and Figure 1, are shown in Table V. The results indicate that the most economical mole ratio NH<sub>4</sub>HSO<sub>4</sub>:Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub> is about 16 (or x = 4), which produces the most soluble mixture of ammonium salts and is sufficiently acidic to effect

Table IV. Solubility in the System  $\text{NH}_3\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$  at 25° C

Point on figure	Composition of saturated soln., %			Solid phase <sup>a</sup>	Reference	Grams/100 g dry salt <sup>b</sup>			
	NH <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>			NH <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> O
Present work									
B	10.7	48.0	6.8	NPS, NS, N <sub>3</sub> S <sub>2</sub>	...	13.6	74.5	11.9	26.7
C	10.8	32.1	7.3	NPS, N <sub>3</sub> S <sub>2</sub> , N <sub>2</sub> S	...	17.9	65.3	16.8	66.1
D	10.3	22.4	16.2	NPS, N <sub>2</sub> S, NP	...	17.1	45.7	37.2	66.1
K	7.0	23.0	42.1	NS, NPS	...	7.5	30.2	62.3	7.1
L	6.9	19.7	50.1	NS, NPS	...	6.9	24.1	69.0	-0.3
N	5.1	7.1	61.1	NP <sub>2</sub> , NPS	...	5.2	8.9	85.9	1.8
O	6.0	1.9	57.6	NP, N <sub>3</sub> P <sub>4</sub> , NPS	...	6.8	2.6	90.5	13.9
P	6.0	1.8	58.3	NP <sub>2</sub> , N <sub>3</sub> P <sub>4</sub> , NPS	...	6.8	2.5	90.8	12.7
Q	5.7	...	58.8	NP, N <sub>3</sub> P <sub>4</sub>	...	6.6	0.0	93.4	15.1
R	5.6	...	59.8	N <sub>3</sub> P <sub>4</sub> , NP <sub>2</sub>	...	6.3	0.0	93.7	13.4
S	6.6	8.9	36.3	NP, NPS	...	9.7	16.1	74.2	47.7
T	7.7	14.2	26.9	NP, NPS	...	12.4	27.9	59.7	60.5
Published data									
F	4.3	...	17.6	NP	Uno (1940)	15.0	0.0	85.0	249.7
A	9.7	40.9	6.8	NPS, N <sub>3</sub> S <sub>2</sub> , NS	Berlin (1933)	14.0	72.4	13.6	44.3
J	11.3	23.2	5.7	NP, N <sub>2</sub> S	Uno (1940)	23.7	59.7	16.6	110.1
Y	7.3	10.3	12.0	NP	Uno (1940)	20.0	34.5	45.5	174.0
X	10.0	19.8	6.9	NP	Uno (1940)	22.8	55.5	21.7	128.3
Z	10.7	27.5	11.1	N <sub>2</sub> S, NPS	Berlin (1933)	17.9	56.4	25.6	67.5
U	11.4	53.3	...	NS, N <sub>3</sub> S <sub>2</sub>	Locuty (1933)	14.9	85.1	0.0	30.4
V	11.4	46.9	...	N <sub>2</sub> S, N <sub>3</sub> S <sub>2</sub>	Locuty (1933)	16.5	83.5	0.0	45.1
W	11.2	26.2	...	N <sub>2</sub> S	Locuty (1933)	25.9	74.1	0.0	130.9

<sup>a</sup> NS =  $\text{NH}_4\text{HSO}_4$ , NPS =  $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$ , N<sub>3</sub>S<sub>2</sub> =  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , N<sub>2</sub>S =  $(\text{NH}_4)_2\text{SO}_4$ , NP =  $\text{NH}_4\text{H}_2\text{PO}_4$ , N<sub>3</sub>P<sub>4</sub> =  $(\text{NH}_4)_3\text{H}_9(\text{PO}_4)_4$ , NP<sub>2</sub> =  $\text{NH}_4\text{H}_3(\text{PO}_4)_2$ . <sup>b</sup> Dry salt is assumed to contain only NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>.

Table V. Water Required to Dissolve Soluble Salts

Input mole ratio NH <sub>4</sub> HSO <sub>4</sub> : apatite <sup>a</sup>	Composition, wt %, of dry salts			Water, g, required to dissolve	
	NH <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Salts containing	
				100 g dry salts	100 g P <sub>2</sub> O <sub>5</sub>
12	18.8	22.1	39.2	190	485
13	18.4	26.7	35.4	151	426
14	18.1	30.4	32.3	118	365
15	17.8	33.6	29.7	90	303
16	17.6	36.2	27.5	66	240
17	17.4	38.5	25.6	67	262
18	17.3	40.5	24.0	67	280

<sup>a</sup> (12 + x) in equation 3.

complete dissolution of the phosphate rock. Ammoniation of this saturated solution yields an ammonium sulfate phosphate fertilizer with N-P-K grade of 21.2-10.7-0 (N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O grade 21.2-24.4-0) that requires the removal of only 5.5 lb of H<sub>2</sub>O per lb of P in the product (2.4 lb H<sub>2</sub>O per lb P<sub>2</sub>O<sub>5</sub>).

When x is 6, however, all the phosphate in the product is present as the complex salt  $(\text{NH}_4)_2\text{H}_3\text{SO}_4\text{PO}_4$ , and this salt may be considered as a mixture of  $(\text{NH}_4)_2\text{SO}_4$  and H<sub>3</sub>PO<sub>4</sub>. If the amount of water indicated in Table V is present, the

mixture may be considered that of  $(\text{NH}_4)_2\text{SO}_4$  and 66% aqueous H<sub>3</sub>PO<sub>4</sub>. Brief laboratory studies have shown that treatment of such a mixture with methyl or ethyl alcohol dissolves the aqueous phosphoric acid and leaves a residue of  $(\text{NH}_4)_2\text{SO}_4$ . Similar treatment of the dry salt produces the same residue and concentrated phosphoric acid. The two products then may be separated and used in any of several fertilizer processes. For example, the  $(\text{NH}_4)_2\text{SO}_4$  may be converted thermally to  $\text{NH}_4\text{HSO}_4$  and recycled to the initial acidulation step, the alcohol may be recovered by distillation and recycled, and the phosphoric acid may be used in a number of processes.

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