

The Systems $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C

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The 25 °C solubility isotherms of the systems $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ were determined from pH 4 to 10. The $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system is characterized by saturation fields of $(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, and a new double salt, $2(\text{NH}_4)_2\text{SO}_3\cdot\text{NH}_4\text{H}_2\text{PO}_4$ [$(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$]. Five invariant points were obtained: $(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}\text{-(NH}_4)_2\text{HPO}_4\text{-(NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$ at pH 8.33, $\text{NH}_4\text{H}_2\text{PO}_4\text{-(NH}_4)_2\text{HPO}_4\text{-(NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ at pH 5.40, $\text{NH}_4\text{H}_2\text{PO}_4\text{-(NH}_4)_2\text{S}_2\text{O}_5\text{-(NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ at pH 5.32, $(\text{NH}_4)_2\text{HPO}_4\text{-(NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}\text{-(NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ at pH 5.47, and $(\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}\text{-(NH}_4)_2\text{S}_2\text{O}_5\text{-(NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ at pH 5.38. The same invariant points were encountered in the system with SO_3 ; however, $(\text{NH}_4)_2\text{SO}_4$ also was a saturating phase. Optical data are given for the sulfite salts encountered in this study and for the dimorphic forms of $(\text{NH}_4)_2\text{SO}_3$ (anhydrous). X-ray and infrared data for the double salt $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ also are given. The solubility data showed that ammonium orthophosphates have potential as sulfur dioxide absorbents, but other data, such as vapor pressure, will be required before their potential can be realistically evaluated.

The solubilities of SO_2 and SO_3 in ammonium phosphate solutions are of considerable interest because of the potential these solutions have as absorbers for sulfur oxides in pollution abatement systems. Stauffer's process (17) involves an SO_2 absorption step using sodium phosphate solution and subsequently produces elemental sulfur from spent solutions by H_2S reduction. A similar process substituting the more weakly basic ammonium cation and producing byproduct ammonium sulfate, a desirable fertilizer material, will have different solubility characteristics which may provide unique scrubber properties.

Solubility data of the ternary system $\text{NH}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ have been reported extensively in the literature (2-4, 6, 8-10, 16). Data also have been reported for the quaternary system $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-H}_2\text{O}$ and its component ternary systems (12-15). Likewise the system $\text{NH}_3\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ has been reported previously (1, 5, 16). The intermixing of these systems to give the 25 °C solubility isotherms of the systems $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ over the pH range of about 4-10 has now been accomplished and is reported here.

Experimental Section

The equilibrium mixtures were prepared and adjusted as necessary by using $(\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, and gaseous NH_3 and SO_2 . The sulfite salts used in this study were prepared in the laboratory from NH_3 and SO_2 . The other salts used were reagent grade.

Special precautions were taken to minimize oxidation of sulfite. All samples and reagents were prepared in a glovebox under N_2 gas by using freshly boiled distilled water which had been deaerated with nitrogen. As an additional precaution, 0.1% *p*-phenylenediamine (17), an antioxidant, was added to the starting solutions. All sampling procedures also were performed

in a glovebox. If oxidation occurred with these precautions, the quantity was within the error limit of the total sulfur analysis and could not be detected.

The samples in Teflon-lined, screw-capped, glass tubes were allowed to equilibrate in a 25 ± 0.5 °C bath equipped with a rotating sample holder. The samples were equilibrated for 1 month after petrographic analysis showed that two or three euhedral solid phases were present in samples of the quaternary system and that three or four were present in samples of the five-component system. These solutions were chosen so that all of the invariant point compositions and at least one composition lying on each of the phase boundaries connecting the invariant points would be obtained after equilibration. When a phase boundary was extensive, two or more points were obtained. In some samples the crystals of $(\text{NH}_4)_2\text{S}_2\text{O}_5$ were slightly rounded; however, this was due to slight dissolution caused by loss of SO_2 vapor when the samples were opened. After the initial equilibration period, the solid phases were checked again and, if still present in an euhedral condition, the equilibrium liquid phases were analyzed for total sulfur by barium sulfate precipitation, SO_2 by iodine titration, NH_3 by NaOH distillation, and P_2O_5 by the alkalimetric quimociac method. These analyses were repeated at 2-week intervals until they checked within analytical error. At this time the pH of the samples were measured. Most of the samples required from 1 to 2 months to reach equilibrium.

The compositions of the equilibrium liquid phases along with the pH and solid phases in the systems $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C are shown in Tables I and II.

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

The solid-phase relationship in the four-component system $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C is shown in Figure 1. This projection of the intersections of crystallizing fields on the $\text{P}_2\text{O}_5\text{-SO}_2$ face is quite informative since the concentration of NH_3 varied only from 11.7 to 15.5% over the entire composition range when two or more solid phases existed in equilibrium. The isotherms on the diagram represent monovariant compositions in the system or the boundary line between two saturation fields. Invariant points are shown at the intersection of these isotherms. Dashed lines between the saturated fields and the solution field near the water corner were drawn from limited data and approximate bivariant points which are in equilibrium only with the one solid phase. Data along the 0% SO_2 line were taken from the literature (4, 16). Data along the 0% P_2O_5 line were obtained by interpolation of Vasilenko's data (13).

The 25 °C isotherms for the system $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ are characterized by saturation fields of five previously known compounds [$(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ (DAP), $\text{NH}_4\text{H}_2\text{PO}_4$ (MAP), $(\text{NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{S}_2\text{O}_5$] and one new double salt identified by chemical analysis of well-crystallized, homogeneous preparations as $2(\text{NH}_4)_2\text{SO}_3\cdot\text{NH}_4\text{H}_2\text{PO}_4$ [$(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$]. There are five invariant points in the system: one at pH 8.33 between $(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}\text{-(NH}_4)_2\text{HPO}_4\text{-(NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$ and four others at about pH 5.4, clustered tightly around the tiny field of

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

sample no.	pH	liquid-phase compositn, %				equilibrium solid phases ^b					
		SO ₂	P ₂ O ₅	NH ₃	H ₂ O ^a	NP	N ₂ P	N ₃ P	NS ₂	NS	N ₅ S ₂ P
1	5.78	4.82	29.32	12.57	53.29	✓	✓				
2	5.76	9.01	25.66	12.84	52.49	✓	✓				
3	5.60	21.46	16.45	13.57	48.52	✓	✓				
4	5.40	40.40	6.72	15.27	37.61	✓	✓				✓
5	5.40	40.38	6.59	15.31	37.72	✓	✓				✓
6	5.34	42.16	5.68	15.29	36.87	✓					✓
7	5.32	43.84	5.21	15.39	35.56	✓			✓		✓
8	5.32	43.82	5.21	15.30	35.67	✓			✓		✓
9	5.17	44.95	4.08	14.87	36.10	✓			✓		✓
10	4.67	47.21	2.12	13.96	36.71	✓			✓		✓
11	3.91	48.27	1.22	13.61	36.90	✓			✓		✓
12	8.80	9.87	12.94	11.73	65.46		✓	✓			
13	8.33	16.70	8.38	13.13	61.79		✓	✓		✓	
14	7.87	16.90	8.41	13.13	61.56		✓			✓	
15	6.66	18.96	9.72	13.21	58.11		✓			✓	
16	6.63	19.38	10.04	13.31	57.27		✓			✓	
17	5.90	27.07	9.86	13.94	49.13		✓			✓	
18	5.47	39.54	6.63	15.15	38.68		✓			✓	
19	5.47	39.54	6.62	15.16	38.68		✓			✓	
20	5.41	41.40	5.40	15.39	37.81					✓	✓
21	5.37	44.43	4.34	15.33	35.89					✓	✓
22	5.38	44.65	4.37	15.30	35.67					✓	✓
23	5.37	45.39	3.72	15.45	35.44				✓	✓	✓
24	5.34	47.65	1.36	15.08	35.91				✓	✓	✓
25	10.40	13.13	0.28	14.53	72.06			✓			
26	10.0	19.20	0.84	13.17	66.79			✓			
27	8.66	17.50	6.72	12.95	62.83			✓			

^a By difference, $(\text{H}_2\text{O}) = 100 - ((\text{NH}_3) + (\text{SO}_2) + (\text{P}_2\text{O}_5))$. ^b NP = $\text{NH}_4\text{H}_2\text{PO}_4$, N₂P = $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, NS₂ = $(\text{NH}_4)_2\text{S}_2\text{O}_5$, NS = $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and N₅S₂P = $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$.

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

sample no.	pH	liquid-phase compositn, %					equilibrium solid phases ^b						
		total S	SO ₂	SO ₃	P ₂ O ₅	NH ₃	H ₂ O ^a	NP	N ₂ P	N ₃ P	NS ₂	NS	N ₅ S ₂ P
1	5.69	4.73	0	11.81	22.50	13.34	52.35	✓	✓				
2	5.59	9.51	11.73	9.09	16.61	13.87	48.70	✓	✓				
3	5.56	12.02	17.90	7.64	13.80	14.23	46.43	✓	✓				
4	5.47	17.34	30.83	4.77	8.67	14.95	40.78	✓	✓				
5	5.38	20.80	38.10	4.32	6.15	15.50	35.93	✓	✓				
6	-	20.97	37.82	5.09	6.08	15.62	35.38	✓	✓				✓
7	-	21.37	39.16	4.42	5.70	15.59	35.13	✓					✓
8	5.33	21.27	39.20	4.12	5.47	15.70	35.51	✓					✓
9	5.30	22.40	41.44	4.14	5.07	15.78	33.57	✓			✓		✓
10	5.30	22.24	41.50	3.67	5.07	15.74	34.02	✓			✓		✓
11	5.10	22.37	42.08	3.27	3.90	15.26	35.49	✓			✓		✓
12	4.64	23.56	43.84	4.05	2.33	14.62	35.17	✓			✓		✓
13	3.44	24.03	44.99	3.77	1.15	14.11	35.97	✓			✓		✓
14	8.78	8.17	0	20.40	8.22	12.83	58.55		✓	✓			
15	8.69	9.33	5.31	16.65	7.06	13.55	57.42		✓	✓			
16	8.19	10.95	10.71	13.96	5.78	14.39	55.16		✓	✓		✓	
17	6.50	11.63	14.09	11.44	7.17	14.35	52.96		✓			✓	
18	5.87	14.19	22.38	7.47	8.57	14.52	47.07		✓			✓	
19	5.52	18.57	33.05	5.07	7.16	15.26	39.46		✓			✓	
20	5.45	20.18	36.66	4.57	5.91	15.58	37.28		✓			✓	
21	5.41	21.24	38.44	4.99	5.04	15.68	35.84					✓	✓
22	5.37	22.40	42.36	3.00	4.01	15.71	34.93				✓	✓	✓
23	5.35	22.77	42.26	4.05	3.91	15.75	34.04				✓	✓	✓
24	5.36	24.00	44.61	4.17	1.41	15.54	34.26				✓	✓	✓
25	5.34	24.96	46.17	4.62	0	15.36	33.85				✓	✓	✓
26	10.50	7.59	0	18.95	0.20	16.76	64.09			✓			
27	10.40	9.71	5.87	16.90	0.33	16.40	60.49			✓			
28	10.20	11.38	11.07	14.58	0.54	15.90	57.91			✓			
29	8.70	11.36	10.99	14.63	4.23	14.38	55.77			✓		✓	

^a $(\text{H}_2\text{O}) = 100 - ((\text{NH}_3) + (\text{SO}_2) + (\text{SO}_3) + (\text{P}_2\text{O}_5))$. ^b $(\text{NH}_4)_2\text{SO}_4$ was a saturating phase in all the samples. NP = $\text{NH}_4\text{H}_2\text{PO}_4$, N₂P = $(\text{NH}_4)_3\text{HPO}_4$, N₃P = $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, NS₂ = $(\text{NH}_4)_2\text{S}_2\text{O}_5$, NS = $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, and N₅S₂P = $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$.

$(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$. The invariant points are shown at the extremities of the $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ field. The salt concentration is near maximum, and the pH range is very small in the area represented by $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$. The region for the existence of $(\text{NH}_4)_2\text{S}_2\text{O}_5$ is surprisingly small.

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

The 25 °C solubility isotherm for the system $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ is plotted in Figure 2. This isotherm is very similar to that of the system $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, the main difference

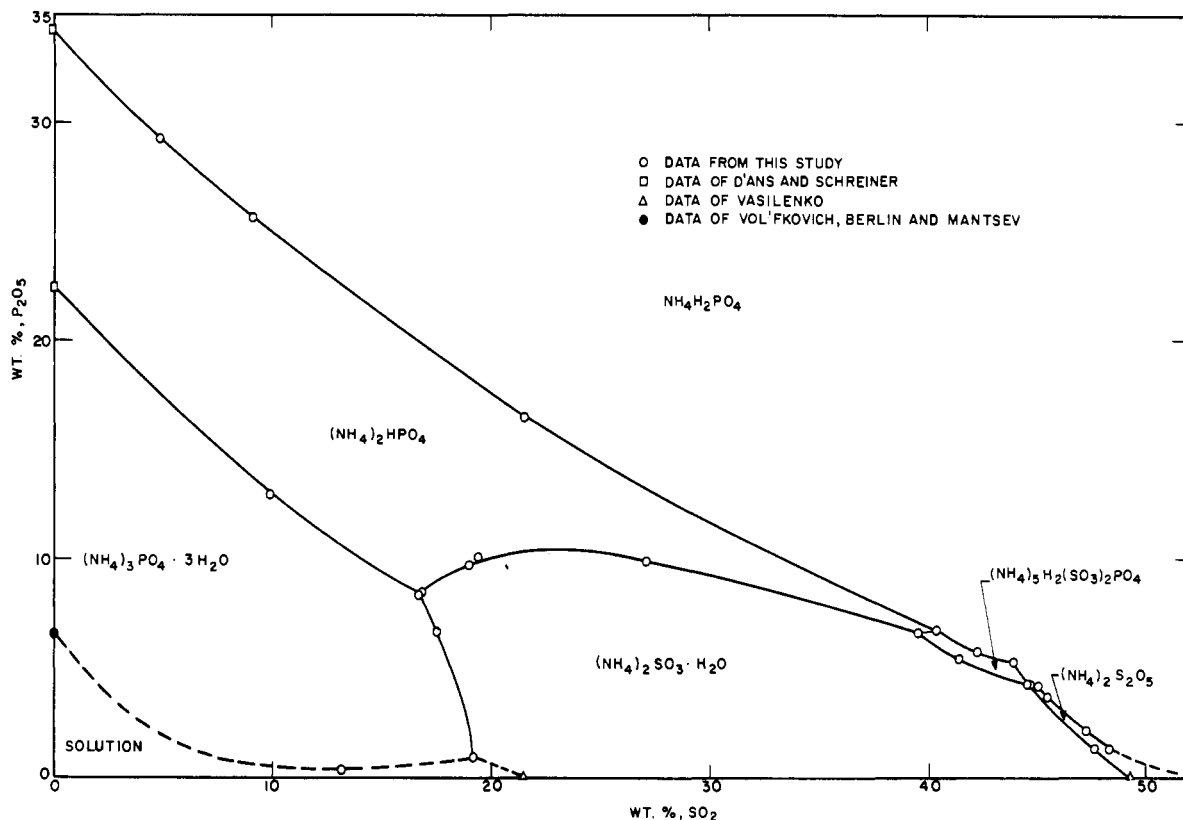


Figure 1. The system $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C.

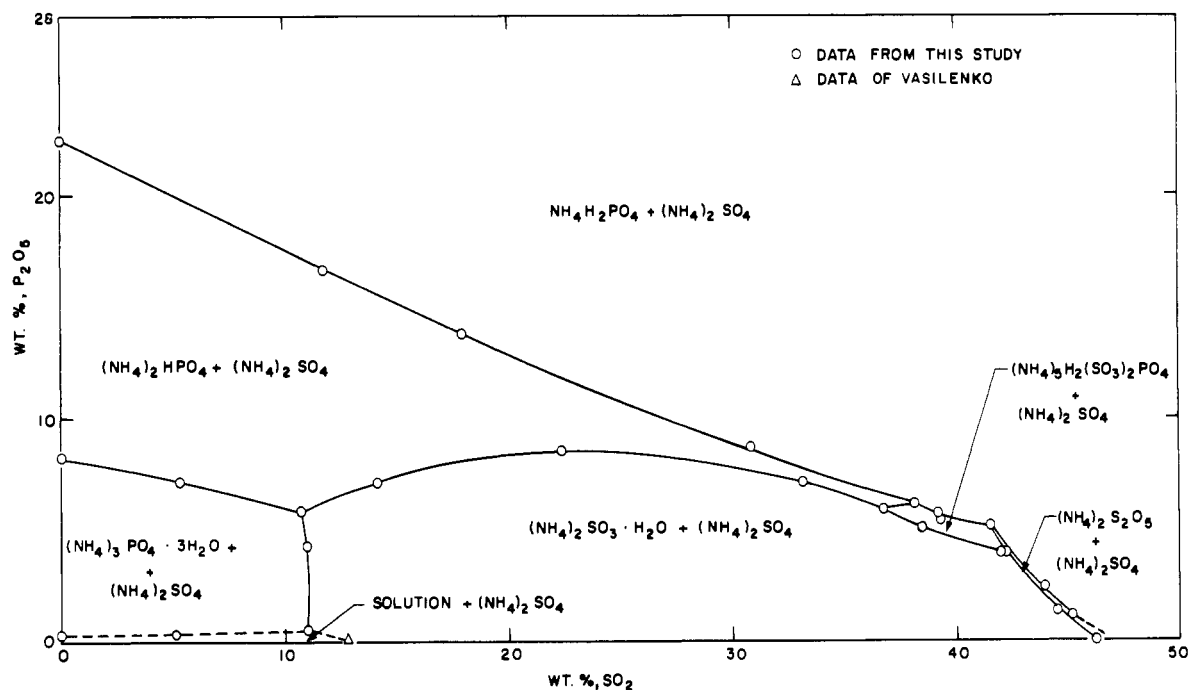


Figure 2. The system $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C.

being that $(\text{NH}_4)_2\text{SO}_4$ is a saturating phase over the entire phase system. The value of the $(\text{NH}_4)_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$ saturation point on the 0% P_2O_5 line was obtained by interpolation of Vasilenko's data (14).

Our data for the ternary point $(\text{NH}_4)_2\text{HPO}_4\text{-NH}_4\text{H}_2\text{PO}_4\text{-(NH}_4)_2\text{SO}_4$ at 25 °C agree well with those obtained by Vol'fkovich et al. (16). Data for the ternary point $(\text{NH}_4)_2\text{HPO}_4\text{-(NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O-(NH}_4)_2\text{SO}_4$, however, are not in good agreement. Vol'fkovich et al. give the composition of this point as 21.80% SO_3 , 6.8% P_2O_5 , and 12.8% NH_3 , whereas our data show a

composition of 20.40% SO_3 , 8.22% P_2O_5 , and 12.83% NH_3 . It appears that their sample may have been undersaturated with respect to $(\text{NH}_4)_2\text{HPO}_4$.

Samples which were originally prepared for points along the $(\text{NH}_4)_2\text{SO}_4\text{-(NH}_4)_2\text{S}_2\text{O}_5\text{-(NH}_4)_2\text{SO}_3\cdot\text{H}_2\text{O}$ saturation isotherm were initially heated to about 60 °C in order to speed up the equilibration. Upon cooling of the mixture in a 25 °C bath overnight, an unknown solid phase, U1, appeared in the samples. Preliminary results showed that this solid was biaxial (+) with refractive indices $\alpha \sim 1.521$, $\beta \sim 1.530$, and $\gamma \sim 1.559$. The

Table III. Composition of Preparations for Microscopic and X-ray Characterization

compd	compositn, wt %			
	NH ₃	SO ₂	P ₂ O ₅	H ₂ O (diff)
(NH ₄) ₅ H ₂ (SO ₃) ₂ PO ₄	24.3	37.2	18.7	19.8
calcd	24.52	36.89	20.44	18.15
(NH ₄) ₂ S ₂ O ₅	19.0	70.2		10.8
calcd	18.90	71.10		10.0
(NH ₄) ₂ SO ₃ ·H ₂ O	25.3	47.6		27.1
calcd	25.4	47.75		26.85
(NH ₄) ₂ SO ₃				
(monoclinic)	28.8	54.4		16.8
(hexagonal)	29.0	56.1		14.9
calcd	29.33	55.16		15.51

salt was still present in the samples after several weeks of equilibration at 25 °C. One of the samples in which this salt appeared contained no P₂O₅. Attempts to prepare the unknown salt were unsuccessful.

Another new compound, U2, was obtained by heating an invariant point solution [(NH₄)₂SO₄-(NH₄)₂SO₃·H₂O-(NH₄)₂S₂O₅] in the system NH₃-SO₂-SO₃-H₂O at 25 °C to approximately 60 °C. This compound appeared to be stable at temperatures as low as 30–35 °C, but unlike U1 it redissolved readily upon cooling of the solution to 25 °C. The U2 salt was uniaxial (+) with refractive indices $n_{\omega} \sim 1.526$ and $n_{\epsilon} \sim 1.573$. Chemical analysis of several preparations of U2 were inconclusive as to its exact composition; thus it remained an unknown. However, the data indicate that it contained three anions and is an ammonium sulfate-ammonium sulfite-ammonium pyrosulfite triple salt.

The presence of U1 in the equilibrium cells prepared for points along the (NH₄)₂SO₄-(NH₄)₂SO₃·H₂O-(NH₄)₂S₂O₅ isotherm was incompatible with other data obtained for the system NH₃-SO₂-SO₃-P₂O₅-H₂O at 25 °C. Therefore, new samples prepared along this phase boundary were not heated and after 4 months of equilibration there was no evidence of other salts such as U1 or U2.

After more than 6 months of equilibration, a check of the original four samples which contained U1 showed that it had finally disappeared in two of the samples and was almost gone in the other two.

Discussion

The data in Figures 1 and 2 show that the buffering action of the phosphates gives them a tremendous built-in capacity for absorption of SO₂. As expected, the concentrations of SO₂ and P₂O₅ were slightly less in the system with sulfate than in the sulfate-free system. The concentration of sulfate or SO₃

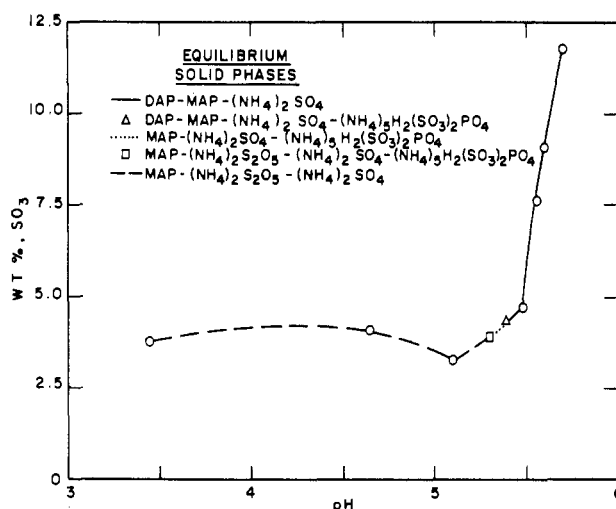


Figure 3. Relationship between sulfate solubility and pH in NH₄-P₂-O₅-SO₂-SO₃-H₂O system.

in the system NH₃-SO₂-SO₃-P₂O₅-H₂O was significantly less than that of SO₂, except above pH 8 where triammonium phosphate is a stable phase.

The data in Figure 3 and Table II show that the concentration of SO₃ is less than 5% in the saturated system at pH values below 5.5. This low solubility could provide a means for removal of ammonium sulfate before regenerating the scrubber solution when scrubbing stack gases with concentrated ammonium phosphate solutions.

The sulfite salts (NH₄)₅H₂(SO₃)₂PO₄, (NH₄)₂S₂O₅, and (NH₄)₂S-O₃·H₂O were prepared in pure form suitable for chemical analysis and microscopic characterization. These data are shown in Tables III and IV along with the data for the dimorphic forms of (NH₄)₂SO₃ (anhydrous) which were encountered in previous studies. The monoclinic (NH₄)₂SO₃ was prepared by reacting 100 g of NH₃, 20 g of SO₂, and 8 g of H₂O at 95 °C and 200 psi. The hexagonal form is readily obtained by subliming (NH₄)₂SO₃·H₂O and condensing the vapors on a cool surface.

Ammonium sulfite phosphate, (NH₄)₅H₂(SO₃)₂PO₄, dissolves incongruently in water with precipitation of (NH₄)₂SO₃·H₂O. On exposure at ambient conditions it evolves SO₂, resulting in a residue of (NH₄)₂HPO₄ and (NH₄)₂SO₃·H₂O.

Ammonium pyrosulfite, (NH₄)₂S₂O₅, is hygroscopic and on exposure at ambient conditions evolves SO₂, leaving a residue of (NH₄)₂SO₃·H₂O. A sample stored at 65–70 °C for 48 h was completely sublimed, except for a thin veneer of (NH₄)₂SO₄ which formed during the initial heating period and prevented further

Table IV. Optical Data of Ammonium Sulfites

compd	crystal system	refractive indices	optical properties ^a
(NH ₄) ₅ H ₂ (SO ₃) ₂ PO ₄	orthorhombic, <i>mmm</i> plates, tabular on 010, elongated along <i>c</i> and modified by {011}, {110}, and {111}; <i>a</i> : <i>b</i> : <i>c</i> = 1.21:1:2.75	$\alpha = 1.514$ $\beta = 1.527$ $\gamma = 1.551$	biaxial (+), $2V = 75-80^\circ (75^\circ)$, OAP = (001), $Z = a$, $d = (1.59)$
(NH ₄) ₂ S ₂ O ₅	orthorhombic, <i>mmm</i> rods, elongated along <i>c</i> , terminated by {011}, modified by an (<i>hk</i> 0) zone. <i>a</i> : <i>b</i> : <i>c</i> = 0.425:1:0.425	$\alpha = 1.564$ $\beta = 1.590$ $\gamma = 1.639$	biaxial (+), $2V = 70^\circ (74^\circ)$, dispersion strong, $r > v$, OAP = (001), $Z = a$, $d = (1.88)$
(NH ₄) ₂ SO ₃ ·H ₂ O	monoclinic, <i>2/m</i> ; highly modified prisms frequently elongated along <i>c</i> with prominent {110}	$\alpha = 1.492$ $\beta = 1.507$ $\gamma = 1.518$	biaxial (-), $2V = 75^\circ (80^\circ)$; OAP \perp (010); $Z \wedge c = 21^\circ$ in obtuse β ; $\beta = 100^\circ$, $d = (1.41)$
(NH ₄) ₂ SO ₃	monoclinic, <i>2/m</i> ; plates tabular on (010)	$\alpha = 1.533$ $\beta = 1.578$ $\gamma = 1.582$	biaxial (-), $2V = (33^\circ)$; OAP \perp plane of tabularity, $X = b$, $d = (1.57)$
(NH ₄) ₂ SO ₃	hexagonal, 6; hexagonal prisms tabular on (0001)	$\omega = 1.588$ $\epsilon = 1.531$	uniaxial (-), $d = (1.58)$

^a Values of $2V$ in parentheses are calculated by Johannsen's equation, and values of density are calculated by the Gladstone-Dale equation (7).

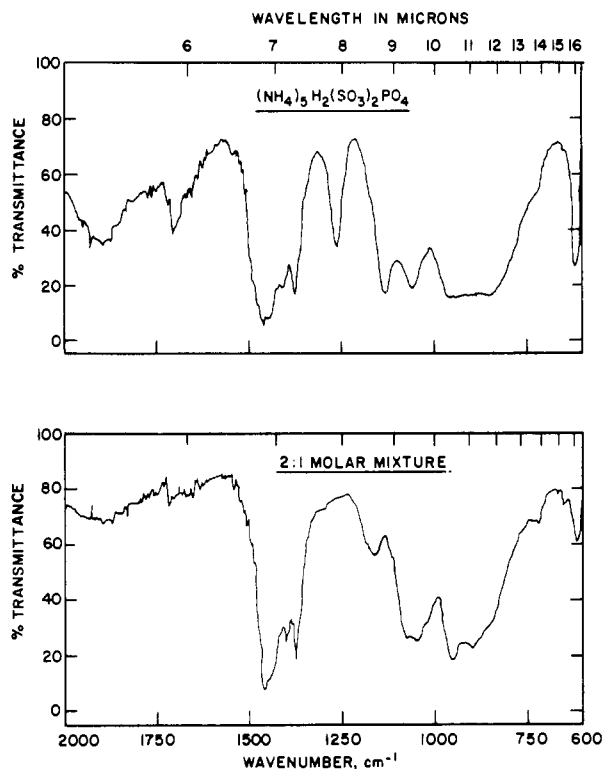


Figure 4. Infrared spectra of adduct $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ and 2:1 molar physical mixture of $(\text{NH}_4)_2\text{SO}_3\text{-H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$.

oxidation as $(\text{NH}_4)_2\text{S}_2\text{O}_5$ sublimed through the porous shell. A differential scanning calorimeter pattern showed that thermal decomposition started at 70 °C with evolution of a strongly acidic gas (SO_2). Heat continued to be absorbed at 130 °C, but the acidity of the gas decreased, indicating the loss of both ammonia and SO_2 . At 182 °C the sample was totally sublimed except for 0.7% residue of $(\text{NH}_4)_2\text{SO}_4$.

Infrared spectra of the double salt $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ were obtained from a mineral oil mull of the sample by using NaCl windows as the sample holder. The spectrum of a 2:1 molar physical mixture of $(\text{NH}_4)_2\text{SO}_3$ and $\text{NH}_4\text{H}_2\text{PO}_4$ also was obtained for comparison. The spectrophotometer used was a Beckman IR-8. The spectra are shown in Figure 4. The double salt has a distinct and unique peak at 1260 cm^{-1} , and the peaks occurring at approximately 620, 1700, and 1900 cm^{-1} appear to be more enhanced in the adduct spectrum than in the spectrum of the mixture. The peak which appears at 1170 cm^{-1} in the mixture also appears in the adduct but is enhanced and shifted to 1130 cm^{-1} . The X-ray powder diffraction pattern of $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4$ was obtained from a side-loaded mineral oil mull of the salt using spinel as an internal standard. The pattern showed no evidence of any of the salt decomposition products. Patterns obtained on several different samples of the salt gave reproducible values for d ; however, the relative intensities, I/I_0 , varied from sample to sample. The X-ray data are given in Table V.

Conclusions

The solubility data of the systems $\text{NH}_3\text{-SO}_2\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25 °C show that solutions of ammonium orthophosphates are good absorbers of sulfur dioxide. However, other data such as the vapor pressure of SO_2 and

Table V. X-ray Powder Diffraction Data for $(\text{NH}_4)_5\text{H}_2(\text{SO}_3)_2\text{PO}_4^a$

d , Å	I/I_0	d , Å	I/I_0
6.60	10	2.536	25
5.57	35	2.44	10
5.24	90	2.32	5
4.93	50	2.29	15
4.67	90	2.20	10
4.12	50	2.18	15
3.95	20	2.13	25
3.82	70	2.104	20
3.70	20	2.099	10
3.66	45	2.05	10
3.48	10	2.03	40
3.32	40	1.894	5
3.30	40	1.851	15
3.23	65	1.835	10
3.22	30	1.768	5
3.15	100	1.731	20
3.02	40	1.648	5
2.96	25	1.618	5
2.79	5	1.605	5
2.70	5	1.535	10
2.62	5	1.531	5
2.543	50		

^a Data obtained with X-ray diffractometer with Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å. Intensities measured as peak heights above background and expressed as percent of the strongest line.

NH_3 above the ammonium phosphate scrubber solutions will have to be determined before a realistic evaluation of their potential can be made.

The appearance of U1 and U2 in the sample solutions which had been heated indicates that at higher temperatures, saturation fields of these compounds will be encountered in the $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-H}_2\text{O}$ and $\text{NH}_3\text{-SO}_2\text{-SO}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ systems.

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