note that the only catalysts which have been effective (ferric chloride, boron fluoride, and aluminum chloride)[6] for the amination reaction all show a strong tendency to form coördination complexes.

Summary

1. The sodium, ammonium, trimethylammonium, pyridinium, guanidinium, hydroxylammonium, lead, and silver salts of hydroxylamine-O-sulfonic acid have been prepared.

2. All of these substances were found to be more or less unstable, yielding various nitrogenous decomposition products suggesting the intermediate formation of the radical NH or NH_2^+.

3. An interpretation of the mechanism of the amination of aromatic rings by hydroxylamine-O-sulfonic acid and its catalysis by aluminum chloride has been suggested on the basis of the chemical behavior of these salts.

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[Contribution from the Chemical Research Division, Department of Chemical Engineering, Tennessee Valley Authority]

The System Ammonia–Phosphoric Acid–Water at 75°

By J. C. Brosheer and J. F. Anderson, Jr.

In an experimental study of the preparation of ammonium phosphate fertilizers there became apparent a need for reliable data on the solubility relationships in the system ammonia–phosphoric acid–water at temperatures up to 75°. The Russian investigators, Muromtsev,[1] Muromtsev and Nazarova,[2] and Volfkovich, Berlin and Mantsev,[3] have reported solubility measurements at 0, 25 and 50° that are consistent and apparently reliable. The data of D'Ans and Schreiner[4] at 25° and of Jänecke[5] at 0 and 25° agree fairly well with the data of the Russian investigators. Buchanan and Winner[6] have determined the solubilities of monoammonium and diammonium phosphates in water at temperatures up to 110.5 and 70°, respectively; their results for monoammonium phosphate agree well with the Russian data, but their results for diammonium phosphate appear to be low at 0 and 25° and slightly high at 50°. Although Jänecke[7] has reported solubilities in the system ammonia–phosphoric acid–water at high temperatures, as indicated by the temperature at which a trace of solid phase existed in experimental compositions in sealed glass bulbs, his measurements are not adequate to define the solubility relationships at 75°.

The present paper extends the data in the literature to include solubilities in the system ammonia–phosphoric acid–water at 75°. Presented also are a few measurements made at 60°. The solubilities were determined by analysis of the saturated liquid phases, and the compositions of solid phases were determined either by microscopic examination or by Schreinemakers'[8] method of residues.

Measurements

The materials were reagent grades of phosphoric acid, monoammonium phosphate, diammonium phosphate and aqua ammonia. The purity of the salts was such that recrystallization was demonstrably without effect on their solubility.

Equilibrium between the components was established in a bath maintained at 75.00 (or 60.00) ± 0.05°. The thermometer used was calibrated against a thermometer certified by the National Bureau of Standards. Although equilibrium apparently was reached within twenty-four hours, the charges were rotated in the bath for at least three days.

Most of the charges were held in 300-ml. glass-stoppered bottles, 51 mm. in diameter, that were rotated end over end at 2 r. p. m. in the bath. When equilibrium was attained, the bottles were returned to the vertical position until the charges had settled. Liquid-phase samples were transferred, in heated pipets, to weighing bottles which were immediately stoppered and cooled. Samples of the wet solid phase were transferred similarly in small glass thimbles that were manipulated by platinum wires.

Charges in which the vapor pressure of ammonia prevented accurate sampling from open bottles (last 8 equilibria, Table II) were placed in 200-ml. equilibration flasks of the design shown in Fig. 1. After introduction of the charge, arm A was sealed, and the flask was revolved in the bath with axis CE horizontal. When equilibrium was attained, the flask was rotated about arms A and B to bring tip E uppermost. Protective cap L was removed from tip E, and the sampling bulb (Fig. 1), with stopcock F open and bulb J evacuated, was seated and fastened on standard-taper joint D. Tip E, which extended into the bore of stopcock F, was broken by a momentary partial closing of F, and stopcock G was opened simultaneously. The liquid-phase sample thus was filtered through fritted-glass filter K and collected in bulb J. When sampling was complete, stopcock F was closed and the flask and sampling bulb were removed from the bath as a unit. The cooled sample bulb was separated from the flask, and both the liquid-phase and the wet solid-phase samples were weighed and analyzed.

Aliquots of hydrochloric acid solutions of the samples from either of the equilibration vessels were analyzed for ammonia by addition of alkali and distillation into standard acid; similar aliquots were analyzed for phosphoric acid by double precipitation as magnesium ammonium

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(1) B. A. Muromtsev, *Kalii U. S. S. R.*, No. 1, 36-39 (1937).

(2) B. A. Muromtsev and L. A. Nazarova, *Bull. acad. sci. U. R. S. S.*, No. 1, 177–184 (1938).

(3) S. I. Volfkovich, L. E. Berlin and B. M. Mantsev, *Trans. Sci. Inst. Fertilizers Insectofungicides U. S. S. R.*, **153**, 228–241 (1940).

(4) J. D'Ans and O. Schreiner, *Z. physik. Chem.*, **75**, 95–107 (1910).

(5) E. Jänecke, *ibid.*, **127**, 71–92 (1927).

(6) G. H. Buchanan and G. B. Winner, *Ind. Eng. Chem.*, **12**, 448–451 (1920).

(7) E. Jänecke, *Z. physik. Chem.*, **A177**, 7–16 (1936).

(8) F. A. H. Schreinemakers, *ibid.*, **11**, 75 (1893).

phosphate and ignition to magnesium pyrophosphate. Compositions prepared in the bottles were sampled in duplicate, and the results for the liquid-phase samples were accepted only when they checked within 5 parts per thousand. Since compositions prepared in the special flasks could not be sampled conveniently in duplica. duplicate aliquots of the individual samples were analyzed.

Results

The solubility data obtained at 75° are listed in Tables I and II and are plotted, together with data reported in the literature for the 0, 25 and 50° isotherms, in Fig. 2.

The salt $NH_4H_5(PO_4)_2$ apparently is not formed at 75° with phosphoric acid concentrations of less than 86%. The fields of stability of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ at 75° are essentially those that might be deduced from the data at lower temperatures.

TABLE I

SOLUBILITIES IN THE SYSTEM NH_3–H_3PO_4–H_2O AT 75°

Solid phases determined by microscopic examination

Satd. soln., wt.% NH_3	Satd. soln., wt.% H_3PO_4	Solid phase	Satd. soln., wt.% NH_3	Satd. soln., wt.% H_3PO_4	Solid phase
6.70	73.56	A[a]	10.54	49.73	A
6.67	72.85	A	11.09	51.06	A
6.75	63.86	A	11.34	51.61	A
6.87	58.11	A	11.52	52.00	A
6.98	54.81	A	12.07	53.25	A
7.02	54.67	A	12.50	54.07	A
7.25	49.79	A	13.04	55.05	A
7.23	47.96	A	13.14	55.79	A
7.48	45.25	A	14.10	57.68	A
7.71	44.42[b]	A	14.34	58.19	A
7.81	44.54	A	14.39	58.41	A
7.80	44.68	A	14.61	58.55	A
8.11	44.91	A	14.89	59.23[c]	A + B
8.20	45.11	A	14.70	56.85	B
8.53	45.31	A	14.47	53.04	B
9.22	47.02	A	14.24	49.93	B
9.27	47.17	A	13.82	46.48	B
9.60	47.93	A	13.58	43.66	B
9.72	48.05	A	13.38	41.53	B
9.90	48.13	A	13.42	39.13	B
			13.38	38.69[d]	B

[a] A = $NH_4H_2PO_4$; B = $(NH_4)_2HPO_4$. [b] Solubility of $NH_4H_2PO_4$ in water; average of three determinations. [c] Average of five determinations. [d] Corresponds closely to solubility of $(NH_4)_2HPO_4$ in water.

Previous investigators of the system ammonia–phosphoric acid–water at 0, 25 and 50° have stated that the solid phase in equilibrium with highly ammoniacal saturated solutions is $(NH_4)_3PO_4 \cdot 3H_2O$. As shown in Table II and Fig. 2, however, the solid phase in equilibrium with ammoniacal saturated solutions at 75° is $(NH_4)_7H_2(PO_4)_3$, which may be expressed as $(NH_4)_3PO_4 \cdot 2(NH_4)_2HPO_4$. This material crystallized in much finer grains than did either $NH_4H_2PO_4$ or $(NH_4)_2HPO_4$; neither isolation of the pure salt nor determination of its optical properties was attempted because it was assumed that the results obtained would not warrant the effort, particularly since the decomposition pressure of this material at

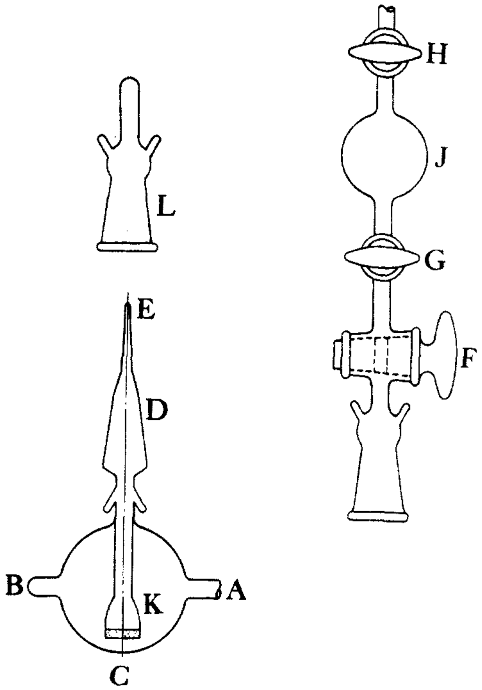

Fig. 1.—Equilibration flask and sampling bulb for use under pressure.

TABLE II

SOLUBILITIES IN THE SYSTEM NH_3–H_3PO_4–H_2O AT 75°

Solid phases determined by Schreinemakers'[8] method of residues

Satd. soln., wt.% NH_3	Satd. soln., wt.% H_3PO_4	Wet solids, wt.% NH_3	Wet solids, wt.% H_3PO_4	Solid phase
7.08	85.49	9.13	85.05	A[a]
		10.80	84.51	
6.85	80.35	10.27	81.78	A
		10.65	82.04	
6.72	75.24	10.81	79.95	A
		11.00	80.18	
13.55	38.46[b]			B + C
12.88	35.61	21.28	54.48	C
		20.04	51.37	
12.47	33.02	18.54	47.40	C
		16.73	43.31	
12.08	29.57	18.01	44.31	C
		16.22	39.79	
11.91	27.16	17.26	41.49	C
		17.78	42.71	
11.98	25.74	15.43	34.65	C
11.83	22.60	17.96	40.06	C
11.94	20.86	16.58	34.36	C
12.15	14.96	18.58	36.69	C
13.47	8.86	18.45	28.64	C
15.40	5.36	20.36	27.80	C
20.47	1.92	23.91	26.24	C
23.73	1.09	27.90	42.51	C

[a] A = $NH_4H_2PO_4$; B = $(NH_4)_2HPO_4$; C = $(NH_4)_7H_2(PO_4)_3$ or $(NH_4)_3PO_4 \cdot 2(NH_4)_2HPO_4$. [b] Average of four determinations. The tie-lines connecting this composition with the compositions of the corresponding wet solids intersected the NH_3-H_3PO_4 boundary between the composition $(NH_4)_2HPO_4$ and $(NH_4)_7H_2(PO_4)_3$.

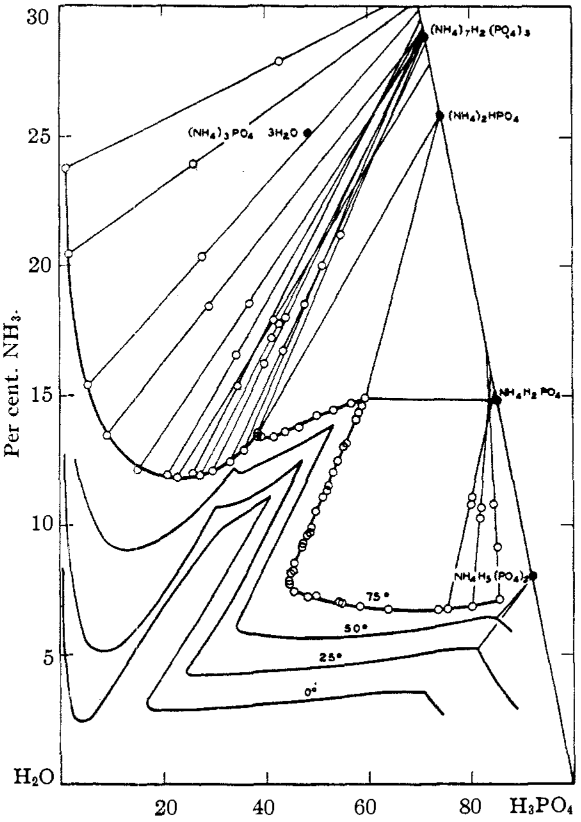

Fig. 2.—The system NH_3–H_3PO_4–H_2O. Compositions in weight per cent.; data for 0, 25 and 50° selected from the literature.

room temperature is not known and storage under another pressure of ammonia might result in change to either $(NH_4)_3PO_4$ or $(NH_4)_2HPO_4$. The compound $(NH_4)_7H_2(PO_4)_3$ has not been reported previously in the literature, but Passille[9] has reported data on the dissociation pressures of ammonium phosphates from which he assumed the existence of a compound, intermediate in composition between $(NH_4)_3PO_4$ and $(NH_4)_2HPO_4$, to which he assigned the formula $(NH_4)_5H(PO_4)_2$, or $(NH_4)_3PO_4 \cdot (NH_4)_2HPO_4$. Passille neither isolated nor analyzed this compound.

With respect to the last four equilibria in Table II, the vapor phase remaining in the equilibration flask with the wet solid phase probably contained enough ammonia to account for the failure of the corresponding tie-lines in Fig. 2 to extrapolate to the composition $(NH_4)_7H_2(PO_4)_3$. The tie-lines corresponding to the last two equilibria in Table II, on extrapolation, intersect the NH_3-H_3PO_4 boundary line at 30.24 and 30.61% NH_3, respectively, whereas $(NH_4)_3PO_4$ contains 34.27%, $(NH_4)_5H(PO_4)_2$ contains 30.29% and $(NH_4)_7H_2(PO_4)_3$ contains 28.86% NH_3. The evidence that neither $(NH_4)_3PO_4$ nor $(NH_4)_3PO_4 \cdot 3H_2O$ exists as a stable solid phase at 75° thus appears conclusive, although the possible existence at 75° of compounds or solid solutions more ammoniacal than $(NH_4)_7H_2(PO_4)_3$ is not excluded.

The data obtained at 60°, and listed in Table III, indicate that $(NH_4)_7H_2(PO_4)_3$ exists as a stable solid phase at 60° also.

TABLE III

SOLUBILITIES IN THE SYSTEM NH_3-H_3PO_4-H_2O AT 60°

Solid phases determined by Schreinemakers'[8] method of residues

Satd. soln., wt.%		Wet solids, wt.%		
NH_3	H_3PO_4	NH_3	H_3PO_4	Solid phase
12.74	41.24	18.32	55.17	B[a]
		18.11	54.77	
12.36	37.96	18.67	54.19	B
		19.08	55.61	
12.45	36.76	18.86	54.08	B
		18.21	52.85	
12.54	35.90	19.39	55.43	B
		19.57	55.46	
12.62	35.69	18.84	53.49	B + C
		19.15	53.89	
12.64	35.61	18.13	49.21	B + C
		20.06	55.46	
11.72	31.13	17.89	45.51	C
		17.94	44.87	
11.04	25.98	13.54	32.66	C
		15.59	36.62	

[a] B = $(NH_4)_2HPO_4$; C = $(NH_4)_7H_2(PO_4)_3$ or $(NH_4)_3PO_4 \cdot 2(NH_4)_2HPO_4$.

Summary

Solubilities in the system ammonia–phosphoric acid–water at 75° have been determined for concentrations of H_3PO_4 from 1.1 to 85.5%.

A solid phase previously unreported exists in equilibrium with saturated solutions more ammoniacal than those in equilibrium with diammonium phosphate. This solid phase, which has the composition expressed by the formula $(NH_4)_7H_2(PO_4)_3$, or $(NH_4)_3PO_4 \cdot 2(NH_4)_2HPO_4$, exists at both 75 and 60°.

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(9) A. de Passille, *Compt. rend.*, **199**, 356–358 (1934).