[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

The System NH_4Cl–NH_4NO_3–H_2O at 0.4, 25 and 50°

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In conjunction with some studies on ammonium nitrate it was found necessary to determine the solubility relationships in the ternary system NH_4Cl–NH_4NO_3–H_2O.

Although considerable work has been done on the reciprocal salt pairs NH_4NO_3–(K,Na,Li)Cl by Rengade,[1] Wurmser,[2] Perman,[3] Perman and Saunders,[4] Perman and Harrison,[5] and Jänecke,[6] both in aqueous solution and in the fused state, no information is available on the system NH_4Cl–NH_4NO_3–H_2O beyond the statement by Perman and Harrison that in the similar systems (NH_4, Li)(NO_3,Cl) no isomorphous mixtures or double salts were formed. Further, Perman and Dawkins[7] and Bowen[8] found in the system NH_4NO_3–NH_4Cl no solid solutions or double salts. From these random facts it was to be expected that in the system NH_4Cl–NH_4NO_3–H_2O no complexes or solid solutions were to be encountered, as was actually found to be the case.

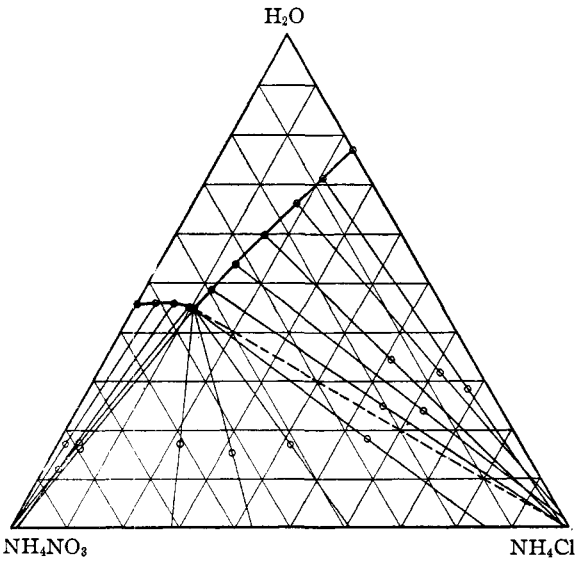

Fig. 1.—The system NH_4Cl–NH_4NO_3–H_2O at 0.4°.

Experimental

The salts employed were Baker and Adamson reagent grade ammonium chloride and ammonium nitrate recrystallized once from distilled water. Mixtures to yield a desired composition were weighed into 100-cc. oil sample bottles, the latter

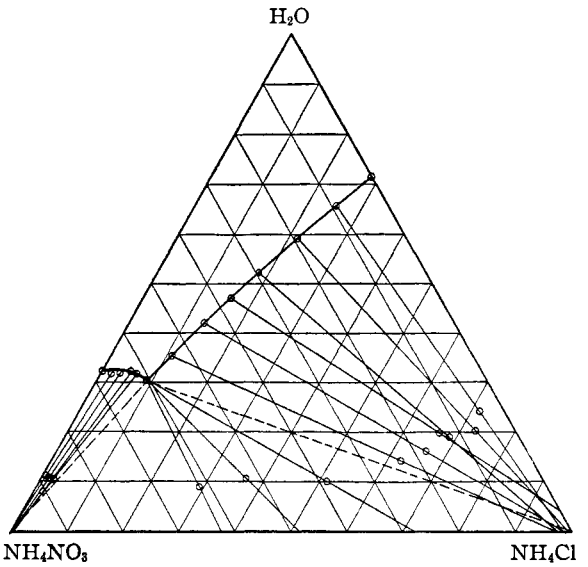

Fig. 2.—The system NH_4Cl–NH_4NO_3–H_2O at 25°.

stoppered, sealed, and rotated for about eighteen hours at the desired temperature in a Freas thermostat of large capacity. Temperatures were

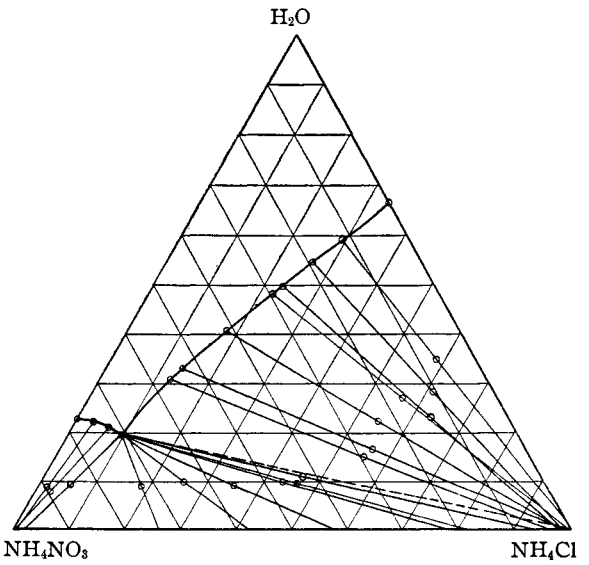

Fig. 3.—The system NH_4Cl–NH_4NO_3–H_2O at 50°.

controlled at 0.4 and 50° to within 0.1°, while at 25 to ± 0.02°.

After equilibrium had been established, the

(1) Rengade, *Chim. et. Ind.*, **7**, 1090 (1922).
(2) Wurmser, *Compt. rend.*, **174**, 1466 (1922).
(3) Perman, *J. Chem. Soc.*, **121**, 2473 (1922).
(4) Perman and Saunders, *ibid.*, **123**, 841 (1923).
(5) Perman and Harrison, *ibid.*, **125**, 1709 (1924).
(6) Jänecke, *Z. angew. Chem.*, **41**, 916 (1928).
(7) Perman and Dawkins, *J. Chem. Soc.*, **125**, 1239 (1924).
(8) Bowen, *J. Phys. Chem.*, **30**, 726 (1926).

compositions of the saturated solution and solid phase were determined by the well-known method of "wet residues" of Schreinemakers. Chlorides were determined by Mohr's method, and ammonia by the formaldehyde method of Grissom.[9] The sodium hydroxide used was 0.2 *N* and was standardized against an ammonium chloride sample of known ammonia content.

Data and Results

The experimental results are given in Table I,

TABLE I

THE SYSTEM NH_4Cl–NH_4NO_3–H_2O

Saturated solution NH_4NO_3, %	Saturated solution NH_4Cl, %	Wet residue NH_4NO_3, %	Wet residue NH_4Cl, %	Solid phase
		0.4° Isotherm		
54.26	0	...	...	NH_4NO_3
50.53	3.39	81.43	1.33	NH_4NO_3
47.90	6.35	85.78	2.69	NH_4NO_3
45.67	9.28	78.48	3.72	NH_4NO_3
44.59[a]	10.37	...	...	NH_4NO_3 + NH_4Cl
39.44	11.75	20.48	54.85	NH_4Cl
32.71	13.51	13.84	62.28	NH_4Cl
24.39	15.81	14.21	51.18	NH_4Cl
15.52	18.39	6.76	61.48	NH_4Cl
8.01	20.58	3.31	67.99	NH_4Cl
0	23.09	...	...	NH_4Cl
		25° Isotherm		
67.73	0	...	...	NH_4NO_3
66.27	2.00	88.20	0.79	NH_4NO_3
64.73	3.82	88.00	1.34	NH_4NO_3
62.24	5.58	90.25	1.65	NH_4NO_3
61.68	6.97	87.65	2.28	NH_4NO_3
60.37[b]	9.36	...	...	NH_4NO_3 + NH_4Cl
53.49	11.08	23.31	62.22	NH_4Cl
44.50	13.60	17.99	66.03	NH_4Cl
36.99	15.80	13.63	66.29	NH_4Cl
29.57	18.20	12.49	68.74	NH_4Cl
19.05	21.81	7.09	72.75	NH_4Cl
9.14	25.21	4.12	71.60	NH_4Cl
0	28.33	...	...	NH_4Cl
		50° Isotherm		
77.39	0	...	...	NH_4NO_3
74.07	3.90	89.78	1.70	NH_4NO_3
72.09	7.08	89.61	2.83	NH_4NO_3
70.77[c]	9.24	...	...	NH_4NO_3 + NH_4Cl
56.54	12.98	29.45	55.60	NH_4Cl
53.03	14.27	27.22	56.14	NH_4Cl
41.45	18.04	23.37	54.39	NH_4Cl
29.54	22.24	16.34	56.50	NH_4Cl
26.66	23.44	13.50	63.75	NH_4Cl
18.99	26.20	10.43	61.16	NH_4Cl
11.22	29.36	6.60	58.70	NH_4Cl
0	33.50	...	...	NH_4Cl

[a] Mean of five determinations.
[b] Mean of three determinations.
[c] Mean of seven determinations.

and are shown graphically in Figs. 1, 2 and 3. These indicate no solid solutions or double salts in the range 0.4 to 50°.

These figures indicate also the effect of temperature on solubility. The solubility of ammonium nitrate is seen to increase with temperature much more than that of ammonium chloride; while the composition of the invariant mixture is seen to increase considerably in ammonium nitrate but decrease in ammonium chloride and water. As the ammonium chloride content is practically constant, the increase in concentration of the ammonium nitrate is primarily at the expense of the water.

Summary

1. Isotherms for the ternary system NH_4Cl–NH_4NO_3–H_2O have been determined at 0.4, 25 and 50°.

2. The results indicate no complex salt, solid solution, or hydrate formation in the range investigated.

CLEVELAND, OHIO RECEIVED APRIL 20, 1935

(9) Grissom, *J. Ind. Eng. Chem.*, **12**, 172 (1920).