

interest in biological studies. Living tissue is colloidal and undoubtedly has a great affinity for water. A portion of the water in the tissue would not freeze at low temperatures and this factor might be of interest in studying the behavior of living tissue at low temperatures.

#### Summary.

1. Finely divided material causes a depression of the freezing point of a liquid when the liquid exists in the film or capillary condition in the solid material.

2. The freezing-point depression due to solid material and that due to material in solution are additive.

3. The concentration of the soil solution cannot be measured by the freezing-point method except at very high moisture contents.

Further investigations on the freezing point and other methods of studying the soil solution will be published later.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY.]

### EQUILIBRIUM IN THE SYSTEM AMMONIA:AMMONIUM NITRATE:AMMONIUM THIOCYANATE.

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The object in view in undertaking this work was to investigate the vapor pressure and solubility relations in the ternary system ammonia: ammonium nitrate: ammonium thiocyanate. In order to show the limiting values of this system, the two binary systems ammonia: ammonium nitrate, and ammonia: ammonium thiocyanate have been included. At the working temperatures, ammonium nitrate and thiocyanate are both solids with practically no vapor pressure, and hence the binary system composed of these two salts falls out of consideration. We have therefore determined (1), the vapor pressures up to two atmospheres and (2), the solubility relations, of the ternary system at 0°, 10° and 20°; and the corresponding values, so far as they have not been previously determined, in the binary systems ammonia: ammonium nitrate and ammonia: ammonium thiocyanate.

It is well known that when either of the two salts mentioned is treated with dry ammonia at atmospheric pressure and room temperature or below, deliquescence takes place and a clear solution of the salt and ammonia results. Similar deliquescence occurs in the ternary system composed of the two salts with ammonia. Either salt may serve, therefore, as an absorbent for free ammonia, particularly when it is desirable to avoid the presence of water, and the ammonia can be recovered again by warming or by reducing the pressure. It seemed not unlikely that

mixtures of the two salts might have greater absorbing power for ammonia than either one alone, and to determine this, a knowledge of the vapor pressures in the ternary system as well as in the two binary systems was necessary. The subject has some interest from a technical standpoint on account of the possibility of extracting ammonia from its mixtures with nitrogen and hydrogen in the production of synthetic ammonia, where it is desirable to exclude moisture.

The ternary system is somewhat simplified by the fact that neither of the two salts forms a solid compound with the other, or with ammonia, at ordinary temperatures. If both salts are present as solids in equilibrium with solution and vapor, the system is univariant, and at a fixed temperature, both pressure and concentration of solution have definite values. With excess of only one salt, the system is divariant and at a given temperature, the ratio between the salts in solution may vary, but for each ratio, there is a definite vapor pressure. In a solution without excess of either salt, there are three variables: to define this system completely, temperature, pressure, and the ratio between the two salts must be arbitrarily fixed.

In the binary systems under consideration, Kuriloff<sup>1</sup> has determined the solubility of ammonium nitrate in ammonia over a wide range of temperature, and his results have been confirmed by Kendall and Davidson.<sup>2</sup> Bradley and Alexander<sup>3</sup> and Foote and Hunter,<sup>4</sup> have determined the solubility of thiocyanate. The vapor pressure of solutions containing thiocyanate in ammonia has been determined by Foote and Hunter,<sup>5</sup> between 0° and 40° up to 1 atmosphere. No systematic determination of the relation between vapor pressure and composition has been made with ammonium nitrate and ammonia and no data whatever exist for the ternary system.

### Vapor Pressures.

In principle, the method consisted in fixing the pressure of ammonia in the system and determining the composition of the solution which came into equilibrium with ammonia at this pressure and the desired temperature. This principle was used in a previous article<sup>6</sup> but the details of the method have since been considerably improved. The generator used for producing dry ammonia is described separately in a note.<sup>7</sup> The pressure in the generator was kept slightly greater than the pressure of the solutions.

<sup>1</sup> Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

<sup>2</sup> Kendall and Davidson, *THIS JOURNAL*, **42**, 1141 (1920).

<sup>3</sup> Bradley and Alexander, *ibid.*, **34**, 15 (1912).

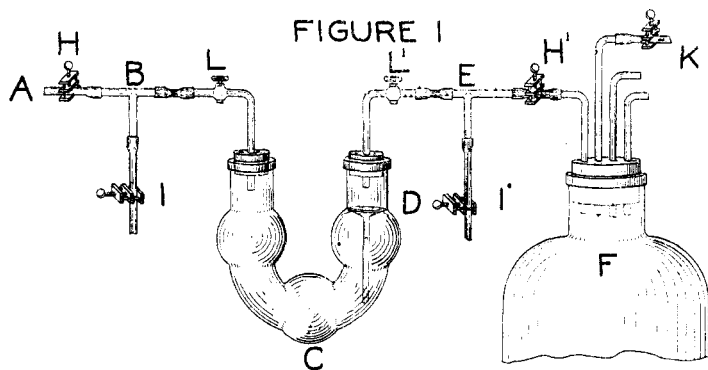
<sup>4</sup> Foote and Hunter, *ibid.*, **42**, 69 (1920).

<sup>5</sup> *Loc. cit.*

<sup>6</sup> Foote and Hunter, *loc. cit.*

<sup>7</sup> *THIS JOURNAL*, **43**, 1179 (1921).

The delivery tube of the generator was connected to the vapor-pressure apparatus (Fig. 1; not drawn to scale) at A. This connection leads through the T tube B and a glass tube provided with a stopcock at L to the absorption tube C. The branch of the T tube was closed by a thick-walled rubber tube and screw clip at I. The absorption tube consisted of a 3-bulb U-tube of about 100 cc. capacity. In the limb of this tube



away from the generator, a glass valve D was placed as a necessary precaution against spattering. Connections on this side of the absorption tube led through the stopcock L' and the T tube E to the bottle F, of about 6 liters capacity. Through a rubber stopper, fastened securely, there were 4 tubes connected to this bottle: (1) from the absorption tube; (2) to the suction pump; (3) to mercury pressure columns; (4) to manometer. Screw clips were placed at the points H, H', I, I' and K (to the pump).

The temperature was regulated by placing the absorption tube in a large tank of water which was held at the desired temperature. If the determination was to be made at a pressure of ammonia equal to 1 atmosphere, the screw-clip I' was left open during the passage of ammonia. For reduced pressures, I' was closed and the reduction of pressure obtained by a suction pump. The pressure in the large bottle F was kept constant by allowing air to bubble in through 2 pressure columns of mercury in series, the height of which could be varied. For pressures greater than one atmosphere, the screw clip K was closed and the connections on the mercury columns reversed. Thus, after creating a pressure of ammonia as much greater than atmospheric as the vertical height of the mercury pressure columns, the excess ammonia escaped by bubbling out through these columns. The total length of the two columns was about 850 mm. By making the proper connections and suitably inclining the columns, it was found possible to maintain any desired pressure from 90 mm. to about 1600 mm. Repeated tests on the apparatus have convinced us that there was no leakage sufficient to affect the results. Minor leaks in the apparatus beyond the absorption tube would have no effect on the results. For determination at the lower temperatures, a U-tube not shown in the diagram, was inserted in the apparatus in front of the absorption bulb and kept at the same temperature as the latter. Thus the ammonia reached the absorption tube already cooled to the working temperature.

The salts used, which were the purest we could obtain, were recrystallized and dried till they showed no trace of moisture.

The absorption tube containing the salts in known amount, and with connecting tubes inserted, was weighed and connected in the train of apparatus. The clips at I and I' were closed and the clips at H and H' and Stopcock L' opened. By cautiously opening Stopcock L, a current of ammonia of suitable velocity was allowed to sweep through the apparatus, the pressure being regulated, as described above, by the inclina-

tion of the mercury pressure columns. The passage of ammonia was continued till the weight remained constant. The weight of ammonia could thus be determined after correcting for the air displaced by ammonia and it was unnecessary to analyze the solution. The same material could be used for a series of determinations, at different pressures, though new material was used for each day's run, as on long standing in contact with ammonia at considerable pressure, the rubber stoppers appeared to absorb an appreciable amount of ammonia.

In the following tables, the results of the vapor pressure determinations are given. For each series, two or more samples of salt were used to eliminate errors so far as possible. In all cases, the values at atmospheric pressure are the average of two or more closely agreeing duplicates. The first value given in each table is for the saturated solution and the vapor pressures are extrapolated from near-by values. The barometric readings were corrected for temperature.

The results obtained for the binary system ammonia: ammonium nitrate are given in Table I; and for the binary system with thiocyanate in Table II. In the latter system, the results at pressures of ammonia below atmospheric are those of Foote and Hunter.<sup>1</sup> In the ternary system, vapor-pressure determinations were carried out using the following molecular proportions of the two salts: 3  $\text{NH}_4\text{NO}_3$ :1  $\text{NH}_4\text{CNS}$  (Table III); 1  $\text{NH}_4\text{NO}_3$ :1  $\text{NH}_4\text{CNS}$  (Table IV); 1  $\text{NH}_4\text{NO}_3$ :3  $\text{NH}_4\text{CNS}$  (Table V).

In all these tables, Col. 1 gives the observed vapor pressure of the solution whose composition is shown in the succeeding column. In the

TABLE I.  
Ammonia : Ammonium Nitrate.

$T = 0^\circ$ .			$T = 10^\circ$ .			$T = 20^\circ$ .		
$P_{\text{NH}_3} = 3255 \text{ mm.}$			$P_{\text{NH}_3} = 4656 \text{ mm.}$			$P_{\text{NH}_3} = 6480 \text{ mm.}$		
$p$ .	Mol. % $\text{NH}_3$ .	$\frac{100 p}{\bar{P}_{\text{NH}_3}}$	$p$ .	Mol. % $\text{NH}_3$ .	$\frac{100 p}{\bar{P}_{\text{NH}_3}}$	$p$ .	Mol. % $\text{NH}_3$ .	$\frac{100 p}{\bar{P}_{\text{NH}_3}}$
364	58.62	10.9	533	56.90	11.4	703	54.90	11.0
390	60.63	12.0	552	58.05	11.9	770	56.76	11.9
406	61.24	12.5	594	60.17	12.8	843	58.43	13.0
441	62.52	13.6	663	62.10	14.2	947	60.79	14.6
403	64.46	15.2	762	64.22	16.4	1031	62.49	15.9
573	66.82	17.6	852	66.07	18.3	1112	63.78	17.2
673	69.26	20.7	910	67.24	19.5	1170	64.49	18.1
763	71.13	23.5	952	68.00	20.4	1253	65.70	19.3
864	73.18	26.6	1112	70.40	23.9	1331	66.98	20.5
969	74.86	29.8	1254	72.29	26.9	1420	68.13	21.9
1064	76.24	32.7	1379	73.76	29.6	1495	69.08	23.0
1166	77.54	35.8	1484	74.93	31.9	1582	70.04	24.4
1261	78.58	38.7	1600	76.10	34.4			
1375	79.77	42.3						
1496	80.87	46.0						
1609	81.86	49.4						

<sup>1</sup> *Loc. cit.*

column headed  $100 p/P_{\text{NH}_3}$ , the relation between the observed vapor pressure and the vapor pressure of pure ammonia at the same temperature, is given. The vapor pressures of pure ammonia are those determined by Keyes and Brownlee.<sup>1</sup>

TABLE II.  
Ammonia : Ammonium Thiocyanate.

$T = 0^\circ.$			$T = 10^\circ.$			$T = 20^\circ.$		
$P_{\text{NH}_3} = 3255 \text{ mm.}$			$P_{\text{NH}_3} = 4656 \text{ mm.}$			$P_{\text{NH}_3} = 6480 \text{ mm.}$		
$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$
105	58.15	3.2	167	56.46	3.6	236	55.22	3.6
120	59.89	3.7	201	59.74	4.3	258	56.37	4.0
154	62.84	4.7	294	64.35	6.3	339	59.98	5.2
232	67.32	7.1	376	67.09	8.1	413	62.36	6.4
322	70.61	9.9	446	68.88	9.6	471	64.05	7.3
387	72.33	11.9	494	69.86	10.6	558	65.96	8.6
487	74.39	15.0	570	71.25	12.2	618	67.10	9.5
549	75.45	16.8	646	72.67	13.9	680	68.13	10.5
613	76.41	18.2	688	73.00	14.8	753	69.12	11.6
675	77.11	20.7	770	74.15	16.5	774	69.68	11.9
763	78.18	23.5	872	75.42	18.7	876	71.14	13.5
872	79.42	26.8	980	76.57	21.0	989	72.48	15.3
973	80.44	29.9	1086	77.60	23.3	1106	73.65	17.1
1091	81.61	33.5	1194	78.53	25.6	1193	74.72	18.4
1198	82.52	37.1	1309	79.32	28.1	1301	75.55	20.1
1314	83.41	40.3	1440	80.36	30.9	1417	76.39	21.8
1424	84.25	43.7	1552	81.06	33.3	1543	77.16	23.8
1545	85.11	47.5						

TABLE III.  
Ammonia : Ammonium Nitrate : Ammonium Thiocyanate.  
 $3 \text{ NH}_4\text{NO}_3 : 1 \text{ NH}_4\text{CNS}.$

$T = 0^\circ.$			$T = 10^\circ.$			$T = 20^\circ.$		
$P_{\text{NH}_3} = 3255 \text{ mm.}$			$P_{\text{NH}_3} = 4656 \text{ mm.}$			$P_{\text{NH}_3} = 6480 \text{ mm.}$		
$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % $\text{NH}_3.$	$\frac{100 p.}{P_{\text{NH}_3}}$
297	60.39	9.1	416	58.65	8.9	538	55.26	8.1
307	60.92	9.4	440	59.84	9.5	598	57.52	9.2
374	63.94	11.5	464	60.61	10.0	652	59.14	10.0
459	66.90	14.1	556	63.30	11.9	763	61.42	11.8
558	69.46	17.2	654	65.66	14.0	871	63.27	13.4
657	71.51	20.2	763	67.86	16.3	986	65.19	15.2
771	73.52	23.7	876	69.77	18.8	1103	66.85	17.0
895	75.47	27.5	989	71.52	21.2	1216	68.40	18.8
1018	77.05	31.3	1100	72.93	23.6	1331	69.81	20.5
1148	78.51	34.4	1182	73.72	25.4	1443	70.96	22.2
1289	79.96	39.6	1223	74.30	26.3	1571	72.17	24.1
1420	80.83	43.6	1387	75.92	29.8			
1565	82.40	47.9	1531	77.20	32.9			

<sup>1</sup> Keyes and Brownlee, *THIS JOURNAL*, **40**, 25 (1918).

TABLE IV.

Ammonia : Ammonium Nitrate : Ammonium Thiocyanate.

 $1 \text{ NH}_4\text{NO}_3 : 1 \text{ NH}_4\text{CNS.}$ 

$T = 0^\circ.$			$T = 10^\circ.$			$T = 20^\circ.$		
$P_{\text{NH}_3} = 3255 \text{ mm.}$			$P_{\text{NH}_3} = 4656 \text{ mm.}$			$P_{\text{NH}_3} = 6480 \text{ mm.}$		
$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$
215	59.96	6.6	296	57.42	6.4	384	54.78	5.9
224	60.56	6.9	314	58.52	6.7	402	55.88	6.2
252	62.16	7.7	342	59.83	7.3	422	56.62	6.5
304	64.52	9.3	396	61.80	8.5	483	58.52	7.4
364	66.78	11.2	469	64.14	10.0	576	61.14	8.9
463	69.72	14.2	567	66.72	12.2	665	63.13	10.2
551	71.68	16.9	667	68.78	14.3	759	64.82	11.7
662	73.68	20.3	768	70.46	16.5	876	66.46	13.5
761	75.26	23.4	859	71.70	18.4	991	68.08	15.3
862	76.72	26.5	984	73.35	21.1	1107	69.58	17.1
970	78.02	29.1	1104	74.70	23.7	1232	70.99	19.0
1093	79.36	33.6	1225	75.98	26.3	1331	72.00	20.5
1211	80.50	37.2	1340	77.05	28.8	1443	73.02	22.2
1337	81.60	41.1	1448	78.04	31.1	1560	74.08	24.1
1449	82.50	44.5	1574	78.98	33.8			
1560	83.26	47.9						

TABLE V.

Ammonia : Ammonium Nitrate : Ammonium Thiocyanate.

 $1 \text{ NH}_4\text{NO}_3 : 3 \text{ NH}_4\text{CNS.}$ 

$T = 0^\circ.$			$T = 10^\circ.$			$T = 20^\circ.$		
$P_{\text{NH}_3} = 3255 \text{ mm.}$			$P_{\text{NH}_3} = 4656 \text{ mm.}$			$P_{\text{NH}_3} = 6480 \text{ mm.}$		
$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$	$p.$	Mol. % NH <sub>3</sub> .	$\frac{100 p.}{P_{\text{NH}_3}}$
96	52.84	2.9	122	48.50	2.6	177	46.48	2.7
100	53.00	3.1	173	53.83	3.7	180	47.23	2.8
118	55.52	3.6	217	57.04	4.7	229	51.04	3.5
136	57.36	4.2	296	61.17	6.4	293	54.73	4.5
154	59.01	4.7	382	64.30	8.2	361	58.14	5.6
170	60.23	5.2	457	66.47	9.8	451	60.72	6.9
200	62.28	6.1	561	68.87	12.0	548	63.28	8.4
240	64.67	7.4	663	70.69	14.2	652	65.48	10.0
297	67.08	9.1	761	72.24	16.3	761	67.34	11.7
364	69.27	11.2	872	73.72	18.7	879	69.53	13.6
447	71.46	13.7	984	75.02	21.1	993	70.99	15.3
543	73.38	16.7	1097	76.24	23.6	1098	72.16	17.0
649	75.16	20.0	1132	76.64	24.3	1211	73.30	18.7
772	77.07	23.7	1231	77.52	26.4	1328	74.37	20.5
878	78.38	27.0	1342	78.40	28.8	1436	75.25	22.2
999	79.64	30.7	1454	79.26	31.2	1577	76.31	24.3
1114	80.72	34.2	1560	80.04	33.5			
1234	81.78	37.9						
1354	82.76	40.6						
1472	83.63	45.2						
1580	84.43	48.8						

### Solubility.

The solubility results were somewhat simplified from the fact that only the simple salts were present as solid phases. Solid addition products with ammonia and double salts do not form between  $0^{\circ}$  and  $20^{\circ}$ . This has been shown by Kuriloff<sup>1</sup> and Kendall and Davidson<sup>1</sup> in regard to ammonia addition products with ammonium nitrate, and by Bradley and Alexander<sup>1</sup> in regard to the thiocyanate, and we have confirmed their results. That no double salt formed was shown in the following manner. To a solution containing both salts in anhydrous ammonia, finely ground nitrate was added till the solution was nearly saturated, and then an excess of coarse crystals. Finely ground thiocyanate was then added in excess. In this way it was possible, by physical examination, to note that an excess of each salt was present. This solution was decanted and divided into two portions. To one, a small excess of nitrate and large excess of thiocyanate were added; to the other, the reverse. The samples thus prepared were used for solubility determinations and the composition of the solution found to be the same in each case. The residues were analyzed to determine that the relative amounts of the salts in excess had been as described above. Had there been double salt formation, the composition of these solutions would have differed, since in one case the solution would have been in equilibrium with a mixture of double salt and nitrate and in the other, with double salt and thiocyanate.

Starting from the two component solution saturated with ammonium nitrate alone, the curve has been determined showing the solubility of ammonium nitrate in ammonia with increasing amounts of thiocyanate; and a similar curve shows the solubility of thiocyanate in ammonia with increasing amounts of nitrate. The two curves intersect at a univariant point at which the solution is in equilibrium with both solid phases and vapor.

The solubility determinations were carried out in glass-stoppered bottles which were shaken in an ordinary solubility tank. Equilibrium was reached after an hour's shaking. The samples for analysis were withdrawn through a plug of glass wool into a weighed specimen tube. Since the vapor pressures of the solutions are high at room temperature, causing appreciable evaporation, it was found necessary to cool the entire apparatus used for drawing out the sample. In this way, the loss by evaporation was small and the effect was decreased by withdrawing large samples and using aliquot parts for analysis. Ammonia was determined by titration in the usual way, preliminary experiments having shown that the presence of thiocyanate did not affect the end-point, using congo red as indicator. Thiocyanate was determined by the Volhard method. Ammonium nitrate was in all cases determined by difference; the values are omitted from the table.

The solubility results for the three temperatures are given in Table VI.

<sup>1</sup> *Loc. cit.*

TABLE VI.  
SOLUBILITY.

System Ammonia : Ammonium Nitrate : Ammonium Thiocyanate.

$T = 0^\circ.$			$T = 10^\circ.$			$T = 20^\circ.$		
Wt. % NH <sub>3</sub> .	Wt. % NH <sub>4</sub> CNS.	Solid phase.	Wt. % NH <sub>3</sub> .	Wt. % NH <sub>4</sub> CNS.	Solid phase.	Wt. % NH <sub>3</sub> .	Wt. % NH <sub>4</sub> CNS.	Solid phase.
22.88	77.12	NH <sub>4</sub> CNS	22.70	77.30	NH <sub>4</sub> CNS	21.35	78.65	NH <sub>4</sub> CNS
20.96	69.88	NH <sub>4</sub> CNS	20.11	71.49	NH <sub>4</sub> CNS	19.59	75.72	NH <sub>4</sub> CNS
19.60	64.95	NH <sub>4</sub> CNS	17.85	64.66	NH <sub>4</sub> CNS	18.12	70.24	NH <sub>4</sub> CNS
19.10	61.65	{ NH <sub>4</sub> CNS NH <sub>4</sub> NO <sub>3</sub>	17.27	61.68	{ NH <sub>4</sub> CNS NH <sub>4</sub> NO <sub>3</sub>	17.08	66.04	{ NH <sub>4</sub> CNS NH <sub>4</sub> NO <sub>3</sub>
19.00	61.80	{ NH <sub>4</sub> CNS NH <sub>4</sub> NO <sub>3</sub>	17.30	61.61	{ NH <sub>4</sub> CNS NH <sub>4</sub> NO <sub>3</sub>	15.22	60.05	{ NH <sub>4</sub> NO <sub>3</sub> NH <sub>4</sub> CNS
19.97	59.97	NH <sub>4</sub> NO <sub>3</sub>	18.52	56.37	NH <sub>4</sub> NO <sub>3</sub>	15.19	59.95	{ NH <sub>4</sub> NO <sub>3</sub> NH <sub>4</sub> CNS
22.62	51.41	NH <sub>4</sub> NO <sub>3</sub>	21.87	44.53	NH <sub>4</sub> NO <sub>3</sub>	17.73	54.37	NH <sub>4</sub> NO <sub>3</sub>
23.70	44.58	NH <sub>4</sub> NO <sub>3</sub>	23.06	34.53	NH <sub>4</sub> NO <sub>3</sub>	18.90	50.81	NH <sub>4</sub> NO <sub>3</sub>
24.27	40.80	NH <sub>4</sub> NO <sub>3</sub>	23.32	24.27	NH <sub>4</sub> NO <sub>3</sub>	20.37	42.38	NH <sub>4</sub> NO <sub>3</sub>
24.70	37.15	NH <sub>4</sub> NO <sub>3</sub>	23.32	21.70	NH <sub>4</sub> NO <sub>3</sub>	20.99	35.16	NH <sub>4</sub> NO <sub>3</sub>
24.66	33.05	NH <sub>4</sub> NO <sub>3</sub>	22.55	8.80	NH <sub>4</sub> NO <sub>3</sub>	21.20	29.64	NH <sub>4</sub> NO <sub>3</sub>
24.75	24.55	NH <sub>4</sub> NO <sub>3</sub>	21.91	None	NH <sub>4</sub> NO <sub>3</sub>	21.14	28.83	NH <sub>4</sub> NO <sub>3</sub>
24.22	9.64	NH <sub>4</sub> NO <sub>3</sub>				21.15	19.47	NH <sub>4</sub> NO <sub>3</sub>
23.13	None	NH <sub>4</sub> NO <sub>3</sub>				21.13	14.20	NH <sub>4</sub> NO <sub>3</sub>
						20.55	None	NH <sub>4</sub> NO <sub>3</sub>

The solubility and vapor-pressure results for one temperature are shown in the diagram, Fig. 2. Vapor pressures are plotted vertically from points in the triangle representing the composition by weight of the corresponding solutions. The curves AB and BC show the solubilities.

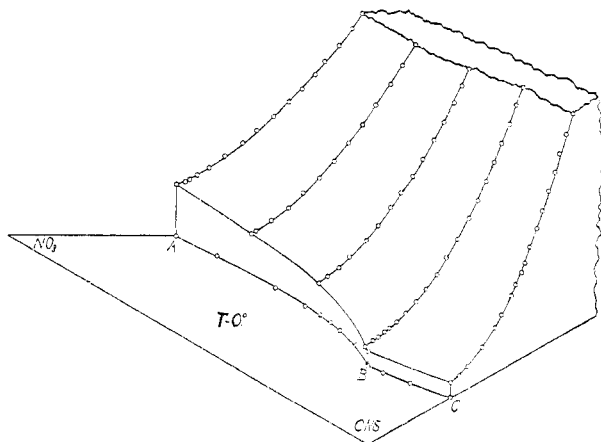


Fig. 2.

Ammonium nitrate is the solid phase along the curve AB, and ammonium thiocyanate along BC. At B, the solution is saturated with both salts. The diagrams for the other two temperatures are similar in type and are therefore omitted.



### Discussion of the Results.

From the results, it can be shown that a very simple relation exists between the vapor pressure of the solutions in the binary systems and in the ternary system. This relation may be expressed as follows. At the temperatures investigated curves of equal vapor pressure in the ternary system are straight lines which connect the points of equal vapor pressure in the binary systems. That is, the vapor pressure relation for these solutions is linear. This relation exists very closely at all temperatures and pressures investigated. By interpolating the results in Tables I to V, the composition of solutions showing equal vapor pressure may be derived. Table VII gives these values for the pressure 300 mm., 500 mm., etc., at the temperatures 0°, 10° and 20° for all systems. Col. 1 shows the vapor pressures exhibited by solutions containing the percentage of ammonia by weight expressed in the other columns. In Cols. 2 and 6, the solutes are pure nitrate and thiocyanate. In the other columns, the solutions contain the two salts in the molecular proportions indicated.

TABLE VII.  
COMPOSITION OF SOLUTIONS SHOWING EQUAL VAPOR PRESSURES.

<i>p.</i>	NH <sub>4</sub> NO <sub>3</sub> % NH <sub>3</sub>	3 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS % NH <sub>3</sub>	1 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS % NH <sub>3</sub>	1 NH <sub>4</sub> NO <sub>3</sub> : 3 NH <sub>4</sub> CNS % NH <sub>3</sub>	NH <sub>4</sub> CNS % NH <sub>3</sub>
<i>T</i> = 0°.					
300	.....	25.30	28.32	31.13	33.96
500	28.04	31.28	34.34	36.80	39.57
700	32.91	36.02	38.80	41.08	43.40
900	37.30	39.97	42.46	44.70	46.82
1100	41.10	43.32	45.73	47.85	49.90
1300	44.46	46.45	48.58	50.71	52.72
1500	47.25	49.20	51.30	53.40	55.57
<i>T</i> = 10°.					
300	.....	.....	22.92	25.92	28.92
500	.....	25.68	28.81	31.43	34.18
700	26.60	29.96	32.94	35.36	37.92
900	30.18	33.46	36.20	38.72	41.12
1100	33.42	36.43	39.10	41.55	44.20
1300	36.28	39.15	41.68	44.04	46.14
1500	39.07	41.60	44.24	46.32	48.30
<i>T</i> = 20°.					
300	.....	.....	.....	21.40	23.90
500	.....	.....	23.92	26.48	29.05
700	.....	24.42	27.63	30.40	32.75
900	23.95	27.44	30.52	33.28	35.80
1100	26.90	30.19	33.12	36.00	38.42
1300	29.68	32.78	35.48	38.20	40.82
1500	32.23	35.07	37.61	40.24	42.62

The isobars based on these data are shown in Figs. 3, 4 and 5, omitting those for which complete data do not exist. It will be noticed that the points in the ternary system lie nearly on the straight lines connecting

the points of equal vapor pressure in the binary systems. The greatest divergence is shown at low pressures at 20°. It is therefore, possible to derive directly the composition of the solution formed from any mixture

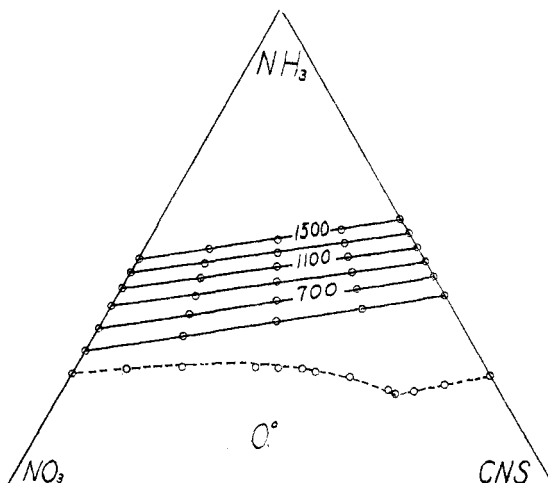


Fig. 3.

containing ammonium nitrate and thiocyanate in known proportions, at a given temperature and pressure, provided the composition of the binary systems showing this vapor pressure is known.

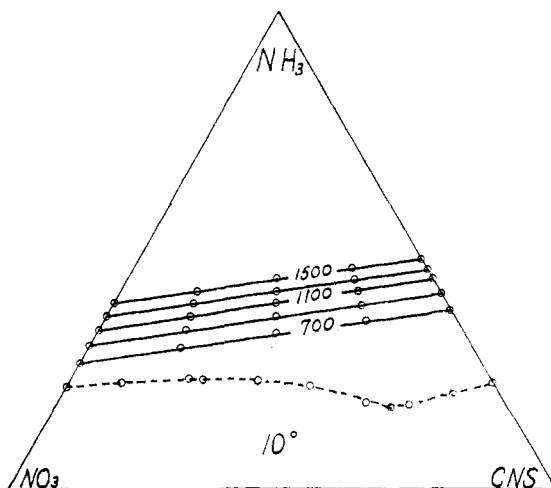


Fig. 4.

The isobars at each temperature are very nearly parallel. In consequence, when one isobar is known, it is possible, with a fair degree of accuracy, to derive the composition of all solutions exerting a given pres-

sure, provided the composition of any one solution is known at that pressure. Whether this generalization would extend far beyond the pressures investigated, our data do not show.

Reference to the values given in Tables I to V will show that the vapor pressures of these systems diverge very widely indeed from Raoult's law. In adjacent columns, the molecular per cent. of ammonia and the relation  $100 p/P_{\text{NH}_3}$  are expressed. By Raoult's law these values should be identical. Foote and Hunter,<sup>1</sup> in their discussion of this relation for

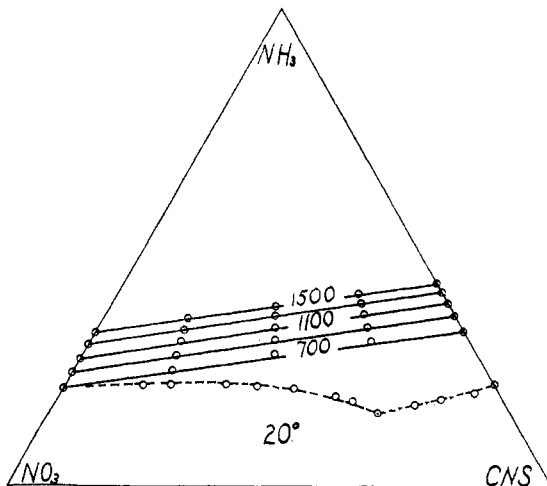


Fig. 5.

the thiocyanate solutions, have concluded that this deviation is due to two causes: (1) electrolytic dissociation; (2) the formation of addition products in solution. The vapor pressures are much lower than Raoult's law requires even if the salts were completely dissociated, and the abnormal lowering is doubtless due largely to addition products in solution. Assuming the deviation from Raoult's law to be entirely due to formation of addition products, the average composition of the compound in the ammonium nitrate solution may be calculated by the Callender formula used by Foote and Hunter for thiocyanate,

$$\frac{p_0 - p}{p_0} = n/N - an + n.$$

Here  $p_0$  and  $p$  represent the vapor pressures of solvent and solution, respectively;  $N$ , the molecules of solvent;  $n$ , the molecules of solute; and  $a$  the number of molecules of solvent combined with one molecule of solute. In Table VIII, the values of  $a$  have been calculated for a number of ammonium nitrate solutions, chosen at random from the experimental

<sup>1</sup> *Loc. cit.*

results at 0° in Table I, together with the values for thiocyanate solutions of the same molecular concentration.

TABLE VIII.  
MOLECULES OF SOLVENT (*a*) COMBINED WITH SOLUTE.  
 $T = 0^\circ$ .

Molec. per cent. NH <sub>3</sub> .	NH <sub>4</sub> NO <sub>3</sub> solution ( <i>a</i> ).	NH <sub>4</sub> CNS solution ( <i>a</i> ).
81.86	3.34	3.98
77.54	2.89	3.18
74.86	2.55	2.79
71.13	2.16	2.35
66.82	1.79	1.94

While these results for *a* are high, due to the effect of electrolytic dissociation on the vapor pressure, the table shows that compound formation is less in the nitrate solution. This is of course shown qualitatively by the fact that the vapor pressures of the nitrate solutions are higher than those of the thiocyanate of equal molecular concentration.

#### Application of the Results.

Footé and Hunter suggested the possibility of using ammonium thiocyanate to absorb ammonia when it is important to avoid the presence of water, as in the process for synthetic ammonia. In the system ammonia: ammonium thiocyanate, the maximum efficiency of absorption at a given temperature is obviously exhibited by the saturated solution, since it has the lowest vapor pressure. This solution also shows a greater efficiency than the saturated solution of ammonium nitrate for the same reason. In the ternary system containing both salts and ammonia, however, a series of saturated solutions has vapor pressures lower than that of the thiocyanate solution; and there is one solution in particular which has the lowest vapor pressure of all. This solution would therefore give the greatest efficiency in extracting ammonia. The determination of the proportions of nitrate and thiocyanate in this mixture is a matter of considerable interest.

Table IX expresses the vapor pressures of the saturated solutions for the two binary systems and for the three mixtures investigated in the ternary system.

TABLE IX.  
VAPOR PRESSURE OF SATURATED SOLUTIONS.

Solute.	0°.	10°.	20°.
NH <sub>4</sub> NO <sub>3</sub> .....	365	535	705
3 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS.....	297	418	530
1 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS.....	216	297	386
1 NH <sub>4</sub> NO <sub>3</sub> : 3 NH <sub>4</sub> CNS.....	96	122	177
NH <sub>4</sub> CNS.....	105	167	237

It has been previously shown that for solutions of the same ammonia concentration, the thiocyanate solution has the lowest vapor pressure.

The addition of ammonium nitrate, however, decreases the amount of ammonia in the saturated solution and lower vapor pressures may be thus obtained. Solubility determinations show that the solution of maximum solubility contains the two salts in very nearly the proportions of 3 molecules thiocyanate to 1 of nitrate. The maximum divergence from this ratio in the temperature range investigated is about 2% at 20°. Vapor-pressure determinations had already been carried out for the solutions containing the two salts in the above molecular proportions. Since this mixture approximates closely that of maximum solubility, we have assumed that it gives the minimum vapor pressure. At 20°, where the difference is greatest, the vapor-pressure curve of saturated solutions indicates that the actual difference in vapor pressure is about 7 mm. which is not significant in the following calculations.

From the data expressed in Table IX, it is possible to calculate the comparative efficiency of nitrate, thiocyanate and mixtures of the two salts for condensing ammonia from a mixture of gases. Foote and Hunter,<sup>1</sup> assumed for calculation that the three gases, nitrogen, hydrogen and ammonia were at a total pressure of 100 atmospheres, and that the mixture contained 3 volume per cent. of ammonia. Under these conditions, the percentages of ammonia given below (Table X) could be extracted, assuming an excess of the solid phase or phases, so that the vapor pressures are those of the saturated solutions.

TABLE X.  
PERCENTAGE OF AMMONIA EXTRACTED FROM GAS MIXTURES.

Salt.	% NH <sub>3</sub> absorbed at 0°.	% NH <sub>3</sub> absorbed at 10°.	% NH <sub>3</sub> absorbed at 20°
NH <sub>4</sub> NO <sub>3</sub> .....	84.0	76.6	69.1
3 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS.....	87.0	81.7	76.8
1 NH <sub>4</sub> NO <sub>3</sub> : 1 NH <sub>4</sub> CNS.....	90.5	87.0	83.1
1 NH <sub>4</sub> NO <sub>3</sub> : 3 NH <sub>4</sub> CNS.....	95.8	94.7	92.2
NH <sub>4</sub> CNS.....	95.4	92.7	89.6

From Table X, it may be seen that the use of ammonium nitrate, in amounts up to about one-fourth of the total solid, increases the efficiency as an absorbing material, due to the greater solubility and consequent greater lowering of the vapor pressure. It will be observed that this mixture (1 NH<sub>4</sub>NO<sub>3</sub> : 3 NH<sub>4</sub>CNS) works nearly as efficiently at 20° as thiocyanate alone at 10°. These values are for the saturated solutions, containing relatively small percentages of ammonia. The liquid may be enriched by the same multiple system proposed by Foote and Hunter.

In the course of the experimental work, it was noted that ammonium thiocyanate absorbs ammonia with remarkable rapidity. Absorption by pure nitrate is considerably slower. The 3:1 mixture absorbs ammonia

<sup>1</sup> *Loc. cit.*

very rapidly indeed and qualitative observations indicate that no difficulty due to slow absorption would be experienced.

#### Summary.

1. Vapor pressures at  $0^\circ$ ,  $10^\circ$  and  $20^\circ$  have been determined for the two binary systems ammonia:ammonium nitrate, and ammonia:ammonium thiocyanate, and for three mixtures in the ternary system composed of the two salts mentioned and ammonia. The vapor-pressure range investigated was from the saturated solutions to those showing pressures of about 1600 mm.

2. Neither double salts nor solid addition products with ammonia form at  $0^\circ$  and above; but the saturated solutions are in equilibrium with the simple salts.

3. The solubility curves of ammonium nitrate and ammonium thiocyanate in the three-component system have been determined at  $0^\circ$ ,  $10^\circ$  and  $20^\circ$ , together with the univariant point at which these curves intersect.

4. The results show that at the temperatures investigated, curves of equal vapor pressure in the ternary system are very nearly straight lines which connect points of equal vapor pressure in the two binary systems.

5. The vapor pressures of the solutions are far below those required by Raoult's law.

6. At any temperature, the saturated solution containing the two salts approximately in the molecular ratio  $1 \text{ NH}_4\text{NO}_3 : 3 \text{ NH}_4\text{CNS}$  shows the lowest vapor pressure. This solution is therefore most efficient for absorbing ammonia from gas mixtures.

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## EQUILIBRIUM IN THE SYSTEM AMMONIA : WATER : AMMONIUM THIOCYANATE.

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In this investigation, as in the preceding article, we have determined (1) the vapor pressures up to about two atmospheres and (2) the solubility relations, in the ternary system, and the corresponding values, so far as necessary, in the three binary systems which enclose it. The temperatures chosen were  $10^\circ$ ,  $20^\circ$  and  $30^\circ$ .

The only solid phase at the temperatures of experiment is the thiocyanate. There is consequently no univariant system of the three components, but with excess of the salt, the system is divariant and at a given temperature a series of saturated solutions exists, which is limited by the saturated solution of the thiocyanate in water on the one side, and in ammonia, on the other. Like the preceding system, all the unsaturated solutions containing the three components are trivariant, and