[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF YALE UNIVERSITY AND THE RUSSELL SAGE LABORATORY OF THE RENNSELAER POLYTECHNIC INSTITUTE.]

EQUILIBRIUM IN THE SYSTEM AMMONIA-AMMONIUM THIOCYANATE.[1]

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It recently became desirable to find absorbents other than water for free ammonia and in this connection the system of ammonia and ammonium thiocyanate has been investigated.

When dry ammonia gas is passed over dry ammonium thiocyanate at room temperature, deliquescence takes place and a clear, nearly colorless solution of the salt and ammonia results. This fact was first mentioned in the literature by Bradley and Alexander,[2] who determined the solubility of the salt in the liquid over a wide range of temperature and the composition of some of the solid phases.

Our work has been concerned chiefly with the vapor pressure of the liquid phase, but we have also determined the solubility of ammonium thiocyanate in the liquid over a limited range of temperature, and the specific conductance of several solutions at 0°.

Vapor Pressure.

At a given temperature, the vapor pressure of a solution composed of ammonium thiocyanate and ammonia is a function of its composition, varying between the value for the solution saturated with thiocyanate on the one hand and that of liquid ammonia on the other. We have determined vapor pressures at 5 temperatures from 0° to 40° between the limits of the saturated solution and the liquid having a vapor pressure of one atmosphere; and we have also determined the vapor pressure of saturated solutions alone at a number of very low temperatures.

Vapor Pressures from 0° to 40°.

The method used for determining vapor pressures between 0° and 40° consisted in passing pure ammonia gas at a known pressure through a known weight of thiocyanate until no further change in weight occurred. In this way the composition of the liquid corresponding to a known pressure of ammonia was found instead of the more usual method of determining the vapor pressure of a liquid having a known composition. The method is exceedingly simple and gave consistent results.

Dry ammonia was obtained by warming a strong aqueous solution and passing the gas through two towers, the first containing quicklime

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[1] A part of this work was carried out in 1911 by one of us and the rest more recently by both at the request of the Division of Chemistry of the National Research Council. The authors are indebted to Dr. John Johnston for some valuable suggestions regarding the work.

[2] THIS JOURNAL, 34, 15 (1912).

and the second fused caustic potash in sticks. The ammonium thiocyanate used was a C. P. product which we recrystallized and dried.

For the determinations, a weighed amount of the salt was placed in an absorption U-tube provided with a glass valve to prevent spattering. The temperature was kept constant by placing the tube in a suitable tank, and when necessary, the ammonia, before entering the U-tube, first passed through a coil immersed in the tank to insure its having the right temperature. For determinations at atmospheric pressure, the excess of ammonia gas passed directly into the atmosphere after leaving the U-tube; for pressures below atmospheric, a tube led from the U-tube into a large bottle in which a constant diminished pressure was maintained. The diminished pressure was produced by a water pump; it was kept constant by admitting air to the bottle after passing through a column of mercury, the height of which could be varied. At low pressures, it was found better to use two mercury tubes in series, each cutting down the pressure by half. This prevented the mercury from spattering too violently. The pressure never varied over a millimeter in a determination. A manometer connected with the bottle gave the pressure readings. Equilibrium between the gas and liquid usually was complete in about 20 minutes. A series of determinations at varying pressures could be carried out with one sample of thiocyanate. The vapor pressure of the saturated solution was obtained either by extrapolation (at 0°) or experimentally by reducing the pressure until crystals of thiocyanate just began to appear and then increasing it slightly until they just dissolved. This also gave the composition of the saturated solution. There is a small error in the results due to the fact that ammonia vapor partly displaces air when the liquid in the U-tube is weighed. In the most unfavorable case, this error only amounted to about 0.1% in the composition of the liquid.

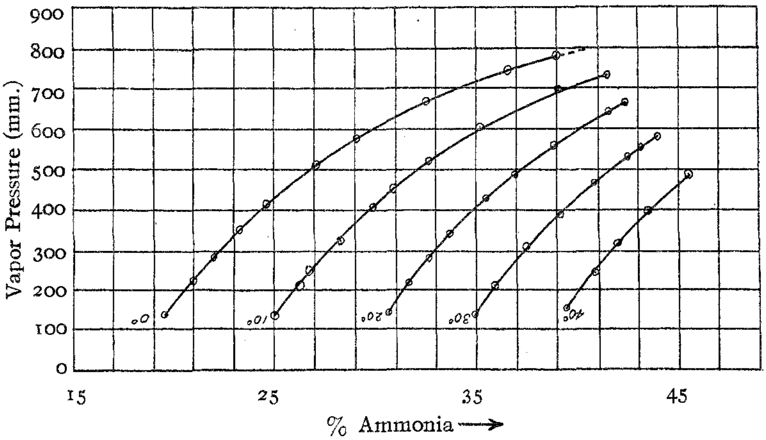

Fig. 1.

The results which were obtained are given below. The values at the highest (atmospheric) pressure are in every case the average of two closely agreeing duplicates. By "per cent. of ammonia" is meant the weight of it in 100 weights of solution. The values in the fourth column at each temperature show the percentage of the vapor pressure of pure ammonia exerted by the vapor of each solution. They are discussed later. The vapor pressures of pure ammonia, P_{NH_3}, at each temperature, are taken from Keyes.[1]

$T = 0°$. $P_{NH_3} = 3255$ mm.

NH_3. %.	NH_3 molec. %.	Vapor pressure. p.	$p/P \times 100$.
44.48	78.15	762	23.41
43.00	77.11	677	20.80
42.04	76.41	615	18.89
40.77	75.45	551	16.93
39.42	74.39	489	15.02
36.93	72.33	388	11.92
34.98	70.61	323	9.92
31.57	67.32	233	7.16
27.47	62.84	154	4.73
25.06	59.89	120	3.69
23.3[a]	.....	105	.....

$T = 10°$. $P_{NH_3} = 4656$ mm.

NH_3. %.	NH_3 molec. %.	Vapor pressure. p.	$p/P \times 100$.
38.98	74.04	765	16.43
37.71	73.00	688	14.78
37.32	72.67	648	13.92
35.68	71.25	572	12.28
34.17	69.86	496	10.65
33.14	68.88	448	9.62
31.35	67.09	377	8.10
28.79	64.35	295	6.34
24.95	59.74	202	4.34
22.51[b]	56.46	167	3.59

$T = 20°$. $P_{NH_3} = 6480$ mm.

NH_3. %.	NH_3 molec. %.	Vapor pressure. p.	$p/P \times 100$.
33.39	69.12	756	11.67
32.38	68.13	682	10.52
31.36	67.10	620	9.57
30.26	65.96	560	8.64
28.52	64.05	473	7.30
27.07	62.36	415	6.40
25.13	59.98	340	5.25
22.43	56.37	259	4.00
21.64[b]	55.22	237	3.66

$T = 30°$. $P_{NH_3} = 8808$ mm.

NH_3. %.	NH_3 molec. %.	Vapor pressure. p.	$p/P \times 100$.
29.06	64.65	764	8.67
28.18	63.66	685	7.78
26.61	61.82	589	6.69
24.84	59.61	514	5.84
23.18	57.40	437	4.96
21.57	55.11	371	4.21
20.84	54.03	346	3.93
19.99[b]	52.73	316	3.59

$T = 40°$. $P_{NH_3} = 11722$ mm.

NH_3. %.	NH_3 molec. %.	Vapor pressure. p.	$p/P \times 100$.
24.62	59.32	748	6.38
23.17	57.38	658	5.61
22.03	55.78	587	5.01
20.56	53.61	503	4.29
18.50[b]	50.34	411	3.51

[a] Extrapolated for the saturated solution.

[b] Saturated solution.

The vapor pressures are plotted in Fig. 1.

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[1] THIS JOURNAL, 40, 25 (1918).

Vapor Pressures at Low Temperatures.

The vapor pressures of solutions of ammonia saturated with ammonium thiocyanate were determined over the range from —78° to +20°. A glass bulb containing an excess of the solid salt was connected with a mercury manometer and the pressures were obtained over the range indicated. The bulb was immersed in a bath of solid carbon dioxide and alcohol and measurements of the vapor pressures were made as the bath warmed. The temperature readings were taken with an ordinary toluene thermometer.

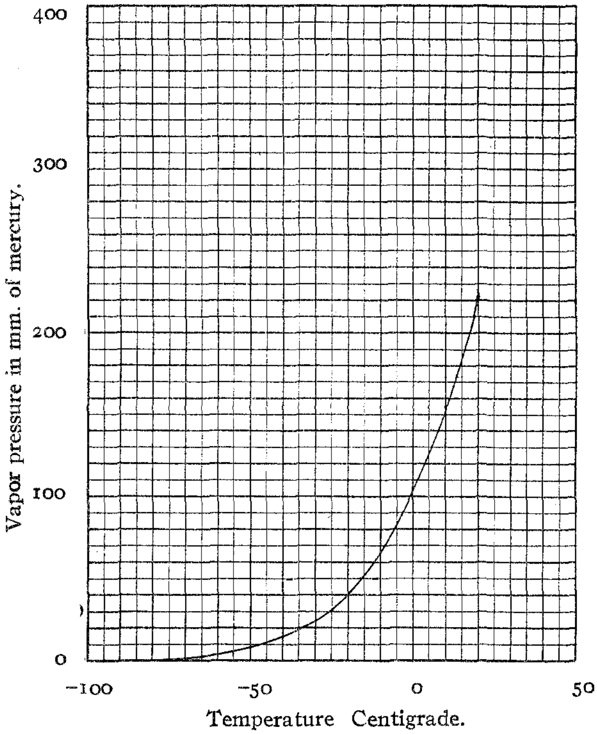

Fig. 2.—Vapor-pressure curve. Saturated solution of ammonium thiocyanate in ammonia.

The following values were obtained:

Temp. $T°$	Vapor pressure (mm.).
—78	1
—65	4
—50	9
—34	21
—23	34
—20	41
0	107
+20	225

These results are plotted in Fig. 2.

Solubility.

Several solubility determinations were made in the course of vapor-pressure determinations as described previously. A number of others were made in the following manner: A weighed quantity of solution, having a known composition, was sealed in a tube with a suitable weighed amount of thiocyanate. The mixture was heated until all dissolved, then cooled rapidly to form small crystals. On heating slowly in a water bath, the temperature could be determined at which the last of the crystals dissolved. At this temperature, the composition of the contents of the bulb is that of the saturated solution. The following results were obtained. Those marked with an asterisk were obtained during the vapor-pressure determinations.

Temperature. *T* °.	NH_3. %.	NH_4CNS. %.
2.8	23.13	76.87
10.0*	22.51	77.49
20.0*	21.64	78.36
23.3	21.48	78.52
30.0*	19.99	80.01
31.0	19.86	80.14
33.0	19.24	80.76
40.0*	18.50	81.50
49.8	16.67	83.33

Individual results are not without appreciable error but the two methods give results agreeing reasonably. The results have been plotted and a curve drawn through them from which the following results have been taken:

Temperature. *T* °.	NH_3. %.	NH_4CNS. %.
0	23.3	76.7
10	22.65	77.35
20	21.6	78.4
30	20.15	79.85
40	18.4	81.6
50	16.65	83.35

Bradley and Alexander[1] obtained results noticeably higher in thiocyanate. The two methods which we used in determining solubility gave results agreeing reasonably and we cannot believe they are far from the facts.

Discussion of the Results.

A glance at the results on vapor pressure between 0° and 40° will show that ammonium thiocyanate is exceedingly soluble in ammonia and that the vapor pressure of the latter has been greatly lowered by the dissolved salt. As an illustration, at 20°, the saturated solution contains 78.4% of thiocyanate and the vapor pressure is 237 mm. The vapor pressure of pure ammonia at this temperature is about 6500 mm. This lowering in vapor pressure is abnormally great and not of the same order that would be produced according to Raoult's law, even if the salt were completely dissociated. In the fourth column of the tables, the percentage of the vapor pressure of pure ammonia exerted by the vapor of each solution has been calculated. If Raoult's law held for the solutions, these values should equal the molecular percentages of ammonia in the second column. Depending on the temperature and concentration, the values

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[1] *Loc. cit.*

of vapor pressure calculated by Raoult's law are from about 3 to 15 times the values actually found.

In Fig. 3, the percentage values of vapor pressure, $(p/P) \times 100$, taken from the fourth column of the table, have been plotted (for 0°, 20° and 40°) as a function of composition. The values for the two intermediate temperatures are omitted as they tend to confuse the diagram. From the form of the curves, especially the one at 0°, it is evidently possible to estimate approximately the values for $(p/P) \times 100$ in more dilute solutions.

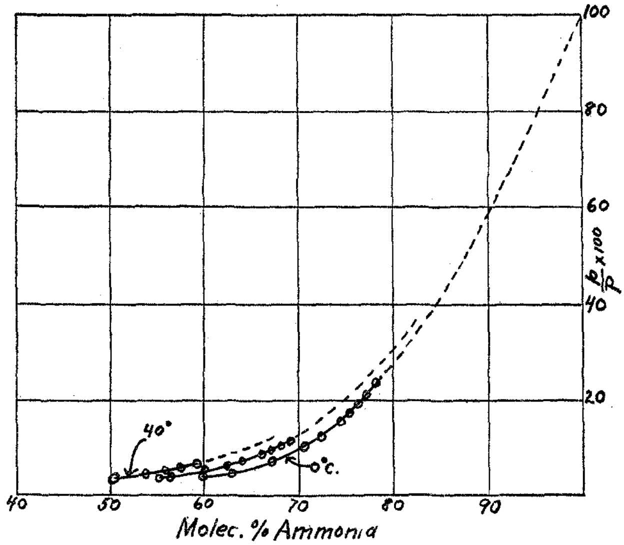

Fig. 3.

Aside from the effect of electrolytic dissociation and possibly the association of liquid ammonia, the abnormal lowering of vapor pressure caused by ammonium thiocyanate is probably due largely to ammonia addition products in solution. If the deviation from Raoult's law was due entirely to the last mentioned cause, the average composition of the compound in solution could be calculated by Callendar's equation[1]

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

in which p_0 and p represent, respectively, the vapor pressures of pure ammonia and of the solution, n and N the molecules of solute and of solvent, and a the molecules of solvent combined with solute. Taking 3 values at random from our results at 0°, the corresponding values of a are as follows:

x NH_3 mol. %.	a.
78.15	3.26
74.39	2.72
62.84	1.64

The values of a increase with increasing concentration of ammonia, which is to be expected, but they are undoubtedly too high as a part of

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[1] *Proc. Roy. Soc.*, 80A, 466 (1908); *Proc. Roy. Inst.*, 19, 485 (1909).

the abnormal lowering is due to dissociation of the thiocyanate in solution. That dissociation is present, is shown by the high conductance of the solutions. The following results were obtained at 0°:

NH_3 mol. %.	Specific conductance.
75.0	0.1979
68.9	0.1640
63.3	0.1395
59.7	0.1246
57.1	0.1110

The solutions contained such a high percentage of thiocyanate that the conductance decreases with increasing concentration of the salt but the values indicate considerable dissociation though the data are not sufficient to calculate the amount.

Association of liquid ammonia, if it exists, like dissociation of the thiocyanate or compound formation in solution, would cause lower vapor pressures than those calculated by Raoult's law since the molecular percentage of ammonia would be less. Calculation shows, however, that to account for the abnormal lowering in the present case, the liquid must be very highly associated and the association must increase as the concentration of ammonia decreases. It does not seem likely, therefore, that association of ammonia plays any considerable part in the abnormal lowering of vapor pressure in the present case.

The lowering in the vapor pressure of ammonia produced by water is much less than that produced by ammonium thiocyanate of equal molecular concentration.

With regard to the vapor pressures of saturated solutions, the ratio between them and the vapor pressure of ammonia at the same temperature increases slightly with temperature, reaching a practically constant value above 10°. This is shown in the following table:

Temp. T °.	p vapor pressure of saturated solution. Mm.	P NH_3 vapor pressure. Mm.	$(p/P) \times 100$.
—78	1	44	2.3
—65	4	112	3.6
—50	9	323	2.8
—34	21	735	2.85
—23	34	1210	2.81
—20	41	1393	2.94
0	107	3255	3.29
10	167	4656	3.59
20	237	6480	3.66
30	316	8808	3.59
40	411	11722	3.51

At higher temperatures, it is probable that the ratio would again decrease, due to the increasing solubility of thiocyanate.

Application of the Results.

As a means of condensing ammonia, ammonium thiocyanate could hardly displace water except when it is desirable to avoid the presence of water vapor. This is the case in the production of ammonia from nitrogen and hydrogen. From the data which have been given, it is possible to calculate at least approximately the efficiency of thiocyanate for this purpose, provided the pressure and composition of the equilibrium mixture of nitrogen, hydrogen and ammonia are known.

Assuming a mixture of the 3 gases containing 3 volume per cent. of ammonia at a total pressure of 100 atmospheres, which appears to be the minimum pressure used industrially, the percentage of ammonia which could be extracted at different temperatures is given in the table below. This table assumes that ammonium thiocyanate is in excess, so that the resulting liquid has the minimum vapor pressure.

Temp. T °.	NH_3 liquefiable. %.
0	95.4
10	92.7
20	89.6
30	86.1
40	82.0

The presence of nitrogen and hydrogen under high pressure might affect these values somewhat, but there are no data to show what the effect would be. A higher total pressure or a greater percentage of ammonia in the equilibrium mixture would of course increase the yields.

The liquid giving these high yields is saturated with ammonium thiocyanate and contains a relatively small percentage of ammonia. The liquid could be enriched in ammonia by some multiple system. As an illustration, at 10°, $^2/_3$ of the ammonia could be removed, giving a liquid containing 39% of ammonia instead of 22.5%. The remaining ammonia could then be removed, up to a maximum of 92.7%, by passing the gases through excess of thiocyanate.

Removal of ammonia from the liquid, when once the latter has been formed, offers no difficulty. It can be done by reducing the pressure or raising the temperature, or both. Provided the temperature is not raised sufficiently to melt the thiocyanate (150°), causing a partial transformation into thiourea, there seems no reason why the salt could not be used over again indefinitely.

Compared with the maximum amounts of ammonia which can be obtained from the equilibrium mixtures by simple refrigeration without the presence of thiocyanate, the results which have been given are striking. Assuming the same composition and pressure of the equilibrium mixture as above, and Regnault's values for the vapor pressure of liquid ammonia, the ammonia which can be recovered by refrigeration alone is given in the following table:

Temp. *T* °.	NH_3 recoverable by refrigeration. %.
0 and above	none
—10	6.0
—15	25.3
—20	39.0
—25	51.7
—30	62.0

If, however, refrigeration be adopted in the presence of ammonium thiocyanate, the results would be as follows:

Temp. *T* °.	NH_3 recoverable. %.
—20	98.1
—30	98.9
—50	99.6

In the practical application of this method for the absorption of ammonia, it will be found that the heat evolved by the absorption will use up a considerable quantity of the refrigerating substance. This can, however, be eliminated by carrying on the operation of absorption in several stages.

If the first absorption cylinder containing ammonium thiocyanate be maintained at 20°, the heat produced by the absorption can be easily removed by cooling with water. The ammonia recovered will represent 89.6% of the ammonia in the gas. If the second cylinder be maintained at 0°, a further quantity of ammonia equal to 5.8% will be removed. If a third cylinder be maintained at —20°, an additional quantity of ammonia represented by 2.7% of the total amount will be obtained. In the two latter stages, a system of heat interchangers may be used to maintain the efficiency of the refrigerating materials.

By such a system of absorbers it will be possible to remove 98.1% of the ammonia in the gas. Further, the heat produced by absorption of 89.6% of the ammonia will not require to be taken care of by refrigerating material.

Further work on this system combined with ammonium nitrate and with water is in progress.

Summary.

1. The vapor pressures of solutions of ammonium thiocyanate in ammonia have been determined at various temperatures between 0° and 40°.

2. The vapor pressures of a solution of ammonia saturated with ammonium thiocyanate have been determined between +20° and —78°.

3. The solubility of ammonium thiocyanate in ammonia has been found at temperatures ranging from 0° to 50°.

4. The specific conductance of several solutions at 0° has been measured.

5. The vapor pressures found are much lower than Raoult's law re-

quires. Probable causes of this abnormal lowering have been considered.

6. The practical application of the use of ammonium thiocyanate in the absorption of ammonia has been considered.

NEW HAVEN, CONN., and TROY, N. Y.

THE COPPER FLAME TEST FOR HALOGENS IN AIR.[1]

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The Beilstein[2] test for halogens depending on the green color which copper imparts to a colorless flame in which they are present has been widely used as a sensitive test for halogens and halogen compounds in air and in other gases. A usual procedure in such cases has been to feed the gas in question into a Bunsen flame in which a spiral copper wire or a copper gauze is suspended. It has been found that by a careful regulation of the flame as little as one part in a hundred thousand parts of air can be detected in this way.

Of late this method has been widely used, at least in the laboratory, for detecting toxic war gases in air, since they almost invariably contain halogens. The delicacy mentioned above is adequate for most war gases, but for certain of the more toxic ones, for example, mustard gas, 10- to 100-fold greater delicacy is desirable. The attempt was therefore made to increase the delicacy of the copper flame test sufficiently to meet these requirements.

This has been accomplished by the very simple expedient of making the test a *cumulative* one. The air in question is passed over a moderately heated copper spiral or gauze for some time—a longer time the lower the concentration of the halogen. After this period of accumulation the copper spiral is sharply heated in a suitable flame and the green tinge observed.

Apparatus and Procedure.

The apparatus used in this test is very simple; it consists merely of a quartz tube of about one cm. bore, in which is placed a roll of oxidized copper gauze 50 meshes to the linear inch, 10 to 11 cm. long, wound tightly around a stiff iron wire, which serves as a handle for the insertion and withdrawal of the roll from the tube. In addition a non-luminous Bunsen or acetylene flame is required.

To carry out a test the air in question is drawn through the tube, while

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[1] Published with the approval of Major General W. L. Sibert, Director, Chemical Warfare Service, U. S. A.

[2] Beilstein, *Ber.*, 5, 620 (1872); Noelting (interference of pyridine), *Ibid.*, 23, 3664 (1890); W. Lorenz, *Z. anal. Chem.*, 34, 42 (1895); Erdmann, *J. prakt. Chem.*, (2) 56, 36 (1897).