

4. A critical examination of the results obtained by Schlamp lends no support to the view that ternary salts in this solvent ionize according to a binary process.

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[CONTRIBUTION FROM THE BUREAU OF SOILS AND THE FIXED NITROGEN RESEARCH LABORATORY.]

VAPOR PRESSURE OF LITHIUM NITRATE: AMMONIA SYSTEM.¹

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In recent work on the absorption of ammonia from a mixture of hydrogen and nitrogen gases used in ammonia synthesis the desirability of employing as absorbent some substance other than water became evident. A number of good absorbents for ammonia are known, but each has its disadvantages for our purpose. Liquid absorbents seem more desirable than solid but only two other than water which meet most of the requirements have been mentioned in the literature. The desirable qualities in an absorbing liquid are that its water vapor pressure be low over a considerable range in temperature and that the vapor pressure of ammonia vary considerably over a short range in temperature. The liquid should be non-corrosive to ordinary metals so that it can be used as a circulating medium and should not cause any obstruction in the pipes, valves, or other parts of the system.

Solid ammonium nitrate treated with anhydrous ammonia liquefies, giving a liquid rich in ammonia and remaining liquid over considerable range in temperature. This is the well known Divers Solution² and has been studied by Kuriloff.³ Similarly, ammonium thiocyanate forms a liquid with ammonia as first noted by Bradley and Alexander⁴ and this has been studied by Foote and Hunter,⁵ who have shown some of the desirable properties of this liquid for the purpose we have in mind; namely, the removal of ammonia from a mixture of gases and its subsequent recovery free from these gases. However, a serious draw-back to the use of these liquids is that they attack metals rapidly.

In searching for a suitable liquid absorbent we have investigated substances listed by Franklin and Kraus,⁶ as very easily soluble, easily soluble, and miscible in liquid ammonia. A number of these were eliminated as undesirable for our purpose merely by inspection, but quite a number

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² *Chem. News*, **27**, 37.

³ Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

⁴ Alexander, *THIS JOURNAL*, **34**, 15 (1914).

⁵ Foote and Hunter, *ibid.*, **42**, 69 (1920).

⁶ Franklin and Kraus, *Am. Chem. J.*, **20**, 820.

were tested to determine whether, as with ammonium nitrate, a liquid formed on treatment of the solid with anhydrous ammonia gas. In carrying out these tests 10 g. of the substance was placed in an absorbing bottle and a stream of dried ammonia gas from a liquid ammonia cylinder was passed through the bottle. If evidences of liquefaction were shown after 10 or 15 minutes' treatment this was continued until the entire mass became liquid or no further change was observed in the material. If no change was observed a small amount of water was added and ammonia was passed through again. In some cases small amounts of moisture did cause liquefaction of the mass with high absorption of ammonia. One cc. of the liquid thus obtained was titrated with a standard sulfuric acid solution to determine roughly the amount of ammonia absorbed. The following substances shown in Table I were tested with positive results.

TABLE I.

Subs.	On addition of NH ₃ .	Water added. Cc.	1 cc. of sol. at 24° neut'd 0.95 N H ₂ SO ₄ . Cc.	Remarks.
NH ₄ I	Insoluble	10	14.1	
NH ₄ Br	Insoluble	15	15.9	
Ca(NO ₃) ₂ ·4H ₂ O	Soluble	5	18.5	Viscous at 24°
Zn(NO ₃) ₂ ·H ₂ O	Sludge formed	3	19.2	White suspension
NaNO ₂	Insoluble	12	14.7	Not completely sol.
KNO ₂	Insoluble	10	12.0	Not very sol. with H ₂ O
Pb(NO ₃) ₂	Insoluble	Insol.		
LiNO ₃	Soluble		26.0	Slightly cloudy
HgNO ₃	Pasty mass	Insol.		
UO ₂ (NO ₃) ₂ ·6H ₂ O	Deliquesces	Insol.		Color change yellow to orange
Cu(NO ₃) ₂	Pasty mass	10	14	Color change blue to indigo
NH ₄ Cl	Insoluble	10	14	Partly soluble
Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O	Soft mass	10		H ₂ O gave no further action
KI	Insoluble	10	15.8	
NaI	Partly soluble	3	19.2	Suspension
NaBr	Insoluble	9	16.0	
AgNO ₃	Pasty then solid	10	15.0	
Lactose	Insoluble	10	13.4	
Sr(NO ₃) ₂	Insoluble	6	10.4	

Of the substances thus tested, lithium nitrate appears to have the highest absorptive value, and hence we have determined the total vapor pressure of seven solutions of lithium nitrate in pure and aqueous ammonia.

These solutions were prepared by saturating c. p. recrystallized lithium nitrate with ammonia at different temperatures. The method used for determining the vapor pressure was a static one, and the apparatus is shown in Fig. 1. The solution was introduced into a bulb connected to a manometer and placed in a thermostat. Stirring

was accomplished by an electromagnetic arrangement consisting of a small plate of sheet platinum attached to a platinum wire carrying on its upper end an iron nail coated

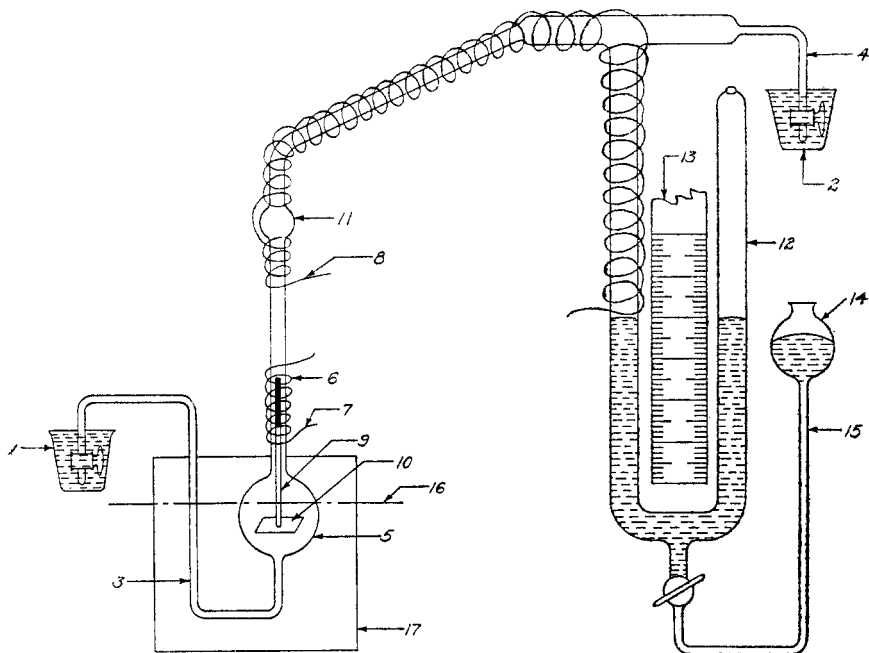


Fig. 1.—Vapor pressure apparatus; Nos. 1 and 2, mercury seals; Nos. 3 and 4, capillary tubes and cocks; No. 5, glass bulb; No. 6, iron nail (coated with glass); No. 7, solenoid; No. 8, heating wire; No. 9, glass rod; No. 10, platinum foil and wire; No. 11, safety bulb; No. 12, glass manometer; No. 13, meter stick; No. 14, mercury leveling bulb; No. 15, rubber capillary tube; No. 16, liquid level; No. 17, thermostat.

with glass, to prevent corrosion. Movement of the stirrer was accomplished by interrupted current through a solenoid on the outside of the glass tubing just about the height of the upper end of the iron nail. Other features of the apparatus require no special description. Samples of the material used were drawn off through a capillary for analysis for ammonia and for nitrates.

The range of the measurements was from -14° to 35° , and the results of these measurements are shown in Fig. 2.

An inspection of the curves shows that lithium nitrate is very soluble in ammonia and that the vapor pressure of the ammonia is very much lowered by the presence of the dissolved salt. The curve is somewhat flatter where water is present and becomes steeper with an increase of ammonia. The curve for lithium nitrate containing no water shows a low vapor pressure of ammonia at 0° , and a pressure exceeding an atmosphere at 35° , thus giving a rather wide variation of pressure over a comparatively short range in temperature.

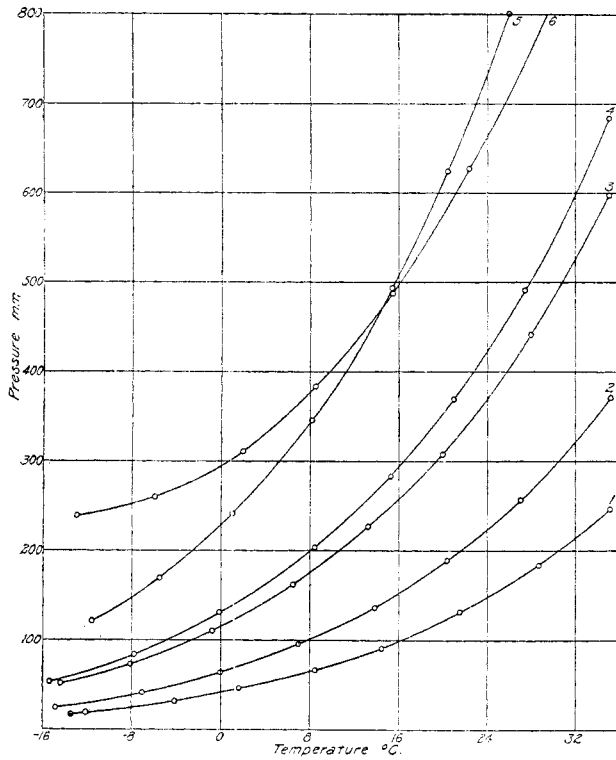


Fig. 2.—Vapor pressure of $\text{NH}_3:\text{LiNO}_3$ solutions.

1	{	17.98% NH_3	2	{	21.5% NH_3	3	{	23.3% NH_3
		45.72% LiNO_3			42.25% LiNO_3			18.04% LiNO_3
		36.30% H_2O			36.25% H_2O			58.66% H_2O
4	{	26.2% NH_3	5	{	38.43% NH_3	6	{	36.34% NH_3
		30.07% LiNO_3			55.51% LiNO_3			63.66% LiNO_3
		43.73% H_2O			6.06% H_2O			

TABLE II.

$\text{NH}_3:\text{LiNO}_3:\text{H}_2\text{O}$.

$\text{NH}_3, 17.98\%$; $\text{LiNO}_3, 45.72\%$; $\text{H}_2\text{O}, 36.30\%$.

Temp. °C.	Pressure mm.
-13.5	16.7
-12.15	19.64
-4.15	31.9
1.67	46.27
8.47	66.77
14.42	91.14
21.56	131.0
28.65	183.2
35.17	246.85

TABLE III.

$\text{NH}_3:\text{LiNO}_3:\text{H}_2\text{O}$.

$\text{NH}_3, 21.5\%$; $\text{LiNO}_3, 42.25\%$; $\text{H}_2\text{O}, 36.25\%$.

Temp. °C.	Pressure mm.
-14.85	24.54
-6.97	41.60
0.03	63.8
7.00	95.31
13.95	136.4
20.4	188.39
27.05	256.98
35.2	371.1
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TABLE IV.

NH ₃ :LiNO ₃ :H ₂ O	
NH ₃ ,23.3%; LiNO ₃ ,18.04%; H ₂ O,58.66%.	
Temp. °C.	Pressure mm.
-14.45	50.82
-8.10	73.7
0.75	110.2
6.45	161.9
13.35	225.23
20.00	307.97
28.00	441.75
35.10	598.09

TABLE V.

NH ₃ :LiNO ₃ :H ₂ O	
NH ₃ ,26.2%; LiNO ₃ ,30.07%; H ₂ O,43.73%.	
Temp. °C.	Pressure mm.
-15.4	52.86
-7.8	84.35
-0.10	131.81
8.4	203.09
15.23	283.43
21.00	369.72
27.5	491.54
35.1	683.10

TABLE VI.

NH ₃ :LiNO ₃ :H ₂ O	
NH ₃ ,38.43%; LiNO ₃ ,55.51%; H ₂ O,6.06%.	
Temp. °C.	Pressure mm.
-11.6	121.34
-5.5	169.64
1.03	242.08
8.17	345.39
15.39	493.04
20.45	623.82
27.57	862.7
34.4	1140.92

TABLE VII.

NH ₃ :LiNO ₃	
NH ₃ ,36.34%; LiNO ₃ ,63.66%.	
Temp. °C.	Pressure mm.
-13.0	239.32
-6.02	259.94
1.53	321.90
8.48	382.9
15.5	487.45
22.4	627.39
30.05	818.13
35.00	998.16

Solid phase.

Action on Metals.

Solutions of lithium nitrate in pure and aqueous ammonia were tested as to their action upon certain metals. After remaining in contact with machine steel and iron wire for several months no appreciable action had taken place. Nichrome wire placed in such solutions was not attacked but a nickel-steel alloy showed slight action after many months.

Use of Solution.

It appears from these results that a solution of lithium nitrate in liquid ammonia with a small addition of water would possess desirable quantities for the removal of ammonia from a mixture of gases such as hydrogen, nitrogen, and ammonia. The absorption could be carried out at a temperature around 0°, or somewhat lower and a large portion of ammonia released either by a comparatively small increase in temperature or by reduction in pressure. The presence of water vapor would not have to be considered if this were an undesirable constituent of the gas leaving the absorbing medium. One of the very desirable properties is that ordinary steel or iron could be used in the construction of apparatus for absorption of ammonia and for circulation of the liquid.

Summary.

1. A number of substances have been found to liquefy when treated with anhydrous ammonia gas or on the addition of small amounts of water.

2. The total vapor pressures of several mixtures of lithium nitrate, ammonia and water have been measured.

3. The lithium nitrate-ammonia solution could be used as an absorbent for ammonia, as in the synthetic process.

4. The corrosive action of such a solution on ordinary iron or steel is not appreciable after several months' contact.

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VAPOR PRESSURE OF AMMONIA-SALT SOLUTIONS.¹

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The work leading up to the study of lithium² nitrate:ammonia system also led us to consider calcium nitrate:, sodium iodide:, calcium chloride:, ammonia nitrate:, and ammonium thiocyanate:ammonia solutions. Ordinary crystalline calcium nitrate with four molecules of water forms a liquid with anhydrous ammonia gas, which is rather viscous at 24°. With the addition of water this solution becomes less viscous and offers the hope of meeting the requirements of an absorbent liquid. The measurements of vapor pressure were carried out in the same apparatus as used in the lithium nitrate experiments. The vapor pressures of two solutions of calcium nitrate, one of which contains 58.34% of water and the other

TABLE I (Curve 1).

$\text{NH}_3:\text{Ca}(\text{NO}_3)_2:\text{H}_2\text{O}$
 $\text{NH}_3, 19.18\%$; $\text{Ca}(\text{NO}_3)_2,$
 22.48% ; $\text{H}_2\text{O}, 58.34\%$.

Temp °C.	Pressure mm.
-14.5	34.8
- 9.3	48.1
- 2.2	73.2
5.3	110.2
15.1	181.7
21.15	242.0
29.5	354.0
36.35	474.0

TABLE II (Curve 2).

$\text{NaI}:\text{NH}_3:\text{H}_2\text{O}$
 $\text{NH}_3, 16.06\%$; $\text{NaI},$
 32.34% ; $\text{H}_2\text{O}, 51.60\%$.

Temp. °C.	Pressure mm.
-14.4	40.9
- 8.0	61.14
- 1.2	90.4
3.15	116.3
10.7	170.8
17.9	242.4
25.8	347.5
35.0	519.2

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² See preceding article by the authors.