

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

VAPOR PRESSURE OF AMMONIA-SALT SOLUTIONS.<sup>1</sup>

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The work leading up to the study of lithium<sup>2</sup> 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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<sup>2</sup> See preceding article by the authors.

18.43% of water, were determined. These are shown in Curves 1 and 6, Fig. 1, and Tables I and VI. It may be seen that these solutions have qualities similar to those of lithium nitrate although the amount of am-

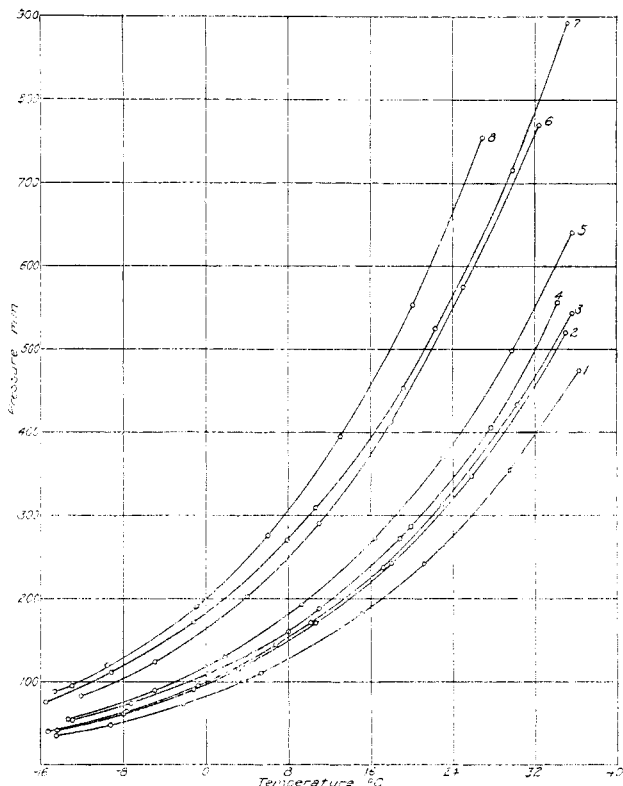


Fig. 1.—Vapor pressure of ammonia-salt solutions.

1	{ 22.48% $\text{Ca}(\text{NO}_3)_2$ 19.18% $\text{NH}_3$ 58.34% $\text{H}_2\text{O}$	2	{ 32.34% $\text{NaI}$ 16.06% $\text{NH}_3$ 51.60% $\text{H}_2\text{O}$	3	{ 0.18648 gm. $\text{NH}_4\text{CNS}$ 22.16% $\text{NH}_3$ (by wt.)
4	{ 33.7% $\text{NH}_4\text{NO}_3$ 18.82% $\text{NH}_3$ 47.48% $\text{H}_2\text{O}$	5	{ 12.9% $\text{CaCl}_2$ 22.9% $\text{NH}_3$ 64.2% $\text{H}_2\text{O}$	6	{ 55.8% $\text{Ca}(\text{NO}_3)_2$ 25.77% $\text{NH}_3$ 18.43% $\text{H}_2\text{O}$
7	{ 28.15% $\text{NH}_3$ 71.85% $\text{H}_2\text{O}$	8	{ 64.88% $\text{NaI}$ 26.92% $\text{NH}_3$ 8.20% $\text{H}_2\text{O}$		

monia absorbed is somewhat smaller. A solution of calcium nitrate and ammonia seems to possess no special advantages over the lithium nitrate except that of cheapness. However, it does possess one disadvantage, that the presence of carbon dioxide, if by any chance this should get into the gases being scrubbed for removal of ammonia, would cause the

formation of a precipitate which remains in suspension. With continued use this might become objectionable and have to be eliminated from the solution.

Vapor-pressure measurements were made on a calcium chloride-ammonia solution containing 64% of water. While solid calcium chloride absorbs ammonia it does not liquefy, but an absorbent solution is formed with the addition of water. Curve 5 and Table V show the results obtained from measurements with this solution. This shows it to be an absorbent of the same general character as the calcium nitrate but the solution possesses the disadvantage of being corrosive to metals.

TABLE III (Curve 3).  
 $\text{NH}_4\text{CNS}:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 22.16\%$ ;  $\text{NH}_4\text{CNS},$   
 0.18648 G. per cc.

Temp. °C.	Pressure mm.
-15.3	39.6
-8.03	62.0
-0.81	94.5
6.78	143.9
10.16	170.8
17.19	237.6
23.0	314.1
30.3	433.1
35.7	543.1

TABLE IV (Curve 4).  
 $\text{NH}_4\text{NO}_3:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 18.82\%$ ;  $\text{NH}_4\text{NO}_3,$   
 $33.7\%$ ;  $\text{H}_2\text{O}, 47.48\%$ .

Temp. °C.	Pressure mm.
-12.95	53.2
-7.25	73.5
0.10	109.0
7.98	159.5
10.95	188.0
18.80	272.5
27.72	405.0
35.20	555.7

Sodium iodide when treated with anhydrous ammonia gas changes to a creamy mass which on the addition of a little water forms a solution with a slight suspension, the character of which was not investigated but is probably due to impurity in the salt. Measurements were made on two solutions, one with 8.2% of water and the other with 51.6% of water. The results of these measurements are seen in Curves 2 and 8 and in Tables II and VII. The solution containing 8.2% of water crystallizes at  $-8^\circ$ .

TABLE V (Curve 5).  
 $\text{NH}_3:\text{CaCl}_2:\text{H}_2\text{O}$   
 $\text{NH}_3, 22.9\%$ ;  $\text{CaCl}_2, 12.9\%$ ;  
 $\text{H}_2\text{O}, 64.2\%$ .

Temp. °C.	Pressure mm.
-13.4	54.0
-5.01	88.6
1.8	129.8
2.45	136.5
9.27	193.1
16.42	272.6
23.06	370.1
29.75	498.2
35.60	640.3

TABLE VI (Curve 6).  
 $\text{NH}_3:\text{Ca}(\text{NO}_3)_2:\text{H}_2\text{O}$   
 $\text{NH}_3, 25.77\%$ ;  $\text{Ca}(\text{NO}_3)_2,$   
 $55.8\%$ ;  $\text{H}_2\text{O}, 18.43\%$ .

Temp. °C.	Pressure mm.
-12.1	82.6
-4.9	124.1
+3.97	202.3
11.0	291.1
18.0	413.0
25.0	575.3
32.4	782.7
....	....
....	....

TABLE VII (Curve 8).  
 $\text{NaI}:\text{NH}_3:\text{H}_2\text{O}$   
 $\text{NH}_3, 26.9\%$ ;  $\text{NaI}, 64.88\%$ ;  
 $\text{H}_2\text{O}, 8.2\%$ .

Temp. °C.	Pressure mm.
-14.6	87.52
-13.0	96.6
-9.6	120.3
-8.0	143.0
-0.9	190.3
6.0	276.0
13.07	394.8
20.07	551.8
26.9	753.8

Both ammonium nitrate and ammonium thiocyanate are substances that liquefy readily with anhydrous ammonia gas. Measurements made on two solutions of these salts are shown in Curves 3 and 4 and Tables III and IV. Curve 7 shows the vapor pressure of 28.15 % of ammonia in water simply for comparison.

#### Action on Metals.

Qualitative tests showed that solutions of ammonium nitrate and ammonium thiocyanate in ammonia attacked iron and steel and their alloys with great rapidity. Calcium chloride-ammonia solution was found to be corrosive to a less extent. Solutions of calcium nitrate and sodium iodide did not show immediate action, so that quantitative measurements were made with these solutions.

The results after 3 months showed that no loss occurred from the action of calcium nitrate on machine steel and nickel steel, but ordinary iron was rather badly attacked. Almost identical results were obtained with sodium iodide solutions. While vapor-pressure measurements indicate the possibility of using these solutions for absorbing ammonia from the hydrogen and nitrogen mixture of gases used in ammonia synthesis, it must not be forgotten that the action of hydrogen on halogen compounds or on the thiocyanate might result in introducing into the gas small amounts of halogen or sulfur compounds that would be detrimental to the life of the catalyst. Therefore, of this set of solutions calcium nitrate seems most promising for use as an absorbent for the ammonia.

#### Summary.

1. Vapor-pressure curves for solutions of several inorganic salts in ammonia have been constructed.
2. Solutions of ammonium nitrate in ammonia and ammonium thiocyanate are very corrosive to iron and steel; calcium chloride-ammonia is less corrosive, and calcium nitrate-ammonia and sodium iodide-ammonia show no immediate corrosive action.
3. Calcium nitrate-ammonia solutions seem the most promising of these solutions for practical use as an absorbent for ammonia in the synthetic process.

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