[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Ammonium Oxide and Ammonium Hydroxide. Heat Capacities and Thermodynamic Properties from 15 to 300°K.[1]

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It has been shown that ammonium oxide crystallizes as a pure compound to within 0.02 mole % even at the two eutectic regions where it is present. Ammonium hydroxide was shown to be pure to within 0.05% at the two eutectic regions where it is an equilibrium phase. These are upper limits for solid solutions under the above conditions, and these two compounds must crystallize in very pure form at their normal melting points. The heats of fusion of $(NH_4)_2O$ and NH_4OH were found to be 2352 and 1568 cal. mole^{-1} at their respective melting points, 194.32 and 194.15°K. The heat capacity of $(NH_4)_2O$ was measured from 15 to 273°K., and that of NH_4OH from 15 to 293°K. Sharp double maxima occur in the heat capacity curve of ammonium oxide in the region near 52°K. These show the characteristics of coöperative phenomena and are believed to be due to angular motions of NH_4 groups. The gradual transition was studied in detail and total heats through the region were measured. The $(F^0 - H_0^0)/T$, S, $(H^0 - H_0^0)/T$ and C_p functions have been tabulated for $(NH_4)_2O$ and NH_4OH to 300°K. The heat of the reaction $NH_3(g) + NH_4OH(l) = (NH_4)_2O(l)$ was found to be $\Delta H^0_{25} = -559.8$ cal. mole^{-1}. The entropy changes in the reactions: $NH_3(g) + H_2O(l) = NH_4OH(l)$ and $NH_3(g) + NH_4OH(l) = (NH_4)_2O(l)$ were computed from the third law of thermodynamics and the values were found to agree accurately with values of ΔS obtainable from isothermal data available at 298.16°K. The entropies of $(NH_4)_2O$ and NH_4OH are 63.94 and 39.57 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K. It is concluded that $(NH_4)_2O$ and NH_4OH approach zero entropy at low temperatures and thus all hydrogen bonds and other structural details must be essentially ordered in the crystalline states of these substances at low temperatures.

This paper reports a low temperature thermodynamic investigation of ammonium oxide and ammonium hydroxide. The work is a portion of the series of investigations in this Laboratory on possible non-equilibrium disorder in the solid state at low temperatures due to random hydrogen bonding.

Preparation.—Pure dry ammonia was prepared from C.P. ammonium chloride and potassium hydroxide, as described by Overstreet and Giauque,[2] and then mixed with the necessary amounts of pure water to make ammonium oxide or ammonium hydroxide. The determination of the exact composition will be discussed below.

Freezing point composition data for the ammonia–water system have been obtained by Pickering,[3] Rupert,[4] Smits and Postma,[5] Postma[6] and Elliott.[7]

Apparatus.—It was planned to use a calorimeter which has been given the laboratory designation Gold Calorimeter II[8a,b]; however, it was found that a crack had developed in the heavy gold bottom.

The cause of this is worth noting. During the first fifteen years, of the some 25-year period in which this calorimeter has been used, a thermocouple was soldered to the bottom and diffusion of lead into the gold was responsible for the cracking. This possibility was reduced in later calorimeters of this type by welding one or two platinum thermocouple wells to the gold. These wells were filled with either Rose's or Wood's alloy.

It was expected that the platinum tube would afford some protection to the gold. A tube of this type was used on Gold Calorimeter II during approximately the last ten years it was in use but there was evidence that the Rose's alloy diffused through the platinum tube in both this and in another similar calorimeter. Gold Calorimeter IV[9] was removed from its surrounding lead–copper protective cylinder and installed in place of Gold Calorimeter II which was scrapped. Otherwise the apparatus and standard thermocouple were substantially those which have been described previously as Gold Calorimeter II. Wood's alloy had been used in the platinum thermocouple well of Gold Calorimeter IV.

The standard thermocouple, which has the laboratory designation W, and which was originally calibrated in 1926, was compared with the vapor pressure of hydrogen at 14.70, 16.02, 18.21 and 20.41°K. (b.p. 20.37°). The results averaged 0.06 ± 0.02° low. It was also compared with the vapor pressure of nitrogen at 63.15° (T.P.), 64.97, 70.76 and 77.32°K. (b.p. 77.34°). The results averaged 0.07 ± 0.02° low. Appropriate corrections were made at these and other temperatures.

One defined calorie was taken as 4.1840 absolute joules. 0°C. = 273.16°K. The molecular weights were taken as 35.048 and 52.080 for NH_4OH and $(NH_4)_2O$, respectively.

Filling the Calorimeter.—In previous work it has been a simple matter to distil volatile pure substances into the calorimeter from a closed system. In this case the ammonia distilled in first and it was impractical to make the water rich residue follow it. An attempt to distil ammonia into water which had been placed in the calorimeter proved impractical because the lower density of the solution, formed near the surface, made mixing slow. The dilute solution could not be cooled much below the ice point during this procedure because separation of ice could have caused damage to the calorimeter due to expansion. It is quite practicable to produce convection stirring in such calorimeters, by heating the bottom section, when density differences are small but they were too great in the present case.

It was finally necessary to cool the ammonia solution to a low temperature to reduce the pressure and introduce the liquid through a fine stainless steel capillary. It was not possible to maintain composition accurately during this procedure so that excess ammonia was used and then removed by pumping out small increments until the composition of pure compound was approximated. This could be ascertained by measuring the amount of heat required for eutectic melting after each increment of ammonia was removed. The total amounts in the calorimeter were determined by distilling them out and weighing at the end of the measurements. All weights were corrected to vacuum. Before solidifying the liquids, helium gas was always admitted when the temperature was near the melting point, so that essentially all of the ammonia gas was swept into the calorimeter.

The helium gas, a small amount of which also served to improve thermal conduction, was pumped out at a low temperature before measurements were made on the liquid state. The protective copper–lead cylinder, which enclosed the calorimeter, was then kept at a higher temperature than the calorimeter at all times to avoid possible distillation effects.

The Densities of Ammonium Oxide and Ammonium Hydroxide.—In order to know the amounts of $(NH_4)_2O$ and NH_4OH which could be held by the calorimeter, and also for calculating the gas space in connection with vaporization corrections, it was necessary to know the densities approximately. Densities of ammonia water solutions near ordinary temperatures are tabulated in the I.C.T.[10] These were

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[1] This work was supported in part by The Office of Naval Research, United States Navy.

[2] R. Overstreet and W. F. Giauque, THIS JOURNAL, **59**, 254 (1937).

[3] S. U. Pickering, *J. Chem. Soc.*, **63**, 141 (1893).

[4] F. Rupert, THIS JOURNAL, **31**, 866 (1909); **32**, 748 (1910).

[5] A. Smits and S. Postma, *Z. anorg. Chem.*, **71**, 250 (1911).

[6] S. Postma, *Rec. trav. chim.*, **39**, 515 (1920).

[7] L. D. Elliott, *J. Phys. Chem.*, **28**, 887 (1924).

[8] (a) W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) R. W. Blue and W. F. Giauque, *ibid.*, **57**, 991 (1935).

[9] J. D. Kemp and W. F. Giauque, *ibid.*, **59**, 70 (1937).

[10] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 59.

supplemented by two measurements, accurate to about 2%, by means of a rough calibration on a measuring bulb. NH_4OH = 0.89 at 205°K.; $(NH_4)_2O$ = 0.82 at 203°K. Linear interpolation was sufficiently accurate for the several intermediate compositions.

Proof that Ammonium Oxide and Ammonium Hydroxide Crystallize as Pure Compounds and Not as Solid Solutions in the Eutectic Regions.—When the calorimeter contained an excess of ammonia, over the amount corresponding to $(NH_4)_2O$, a heat of fusion of the NH_3–$(NH_4)_2O$ eutectic was observed at about 181°K. Postma[6] gives 180.6°K. for the $(NH_4)_2O$–NH_3 eutectic temperature and Rupert[4] found 179.1°K.

The eutectic heat of fusion was reduced linearly when increments of ammonia gas were removed at higher temperatures followed by resolidification and fusion. This linearity would be expected whether or not the eutectic consisted of solid solutions, provided that all of the solid solutions had the composition corresponding to the eutectic equilibrium. In a case where non-equilibrium solid solutions persisted at the eutectic temperature small deviations from linearity would be possible. When sufficient ammonia had been removed the NH_4OH–$(NH_4)_2O$ eutectic appeared and the heat of fusion increased linearly as additional increments of ammonia were removed. The $(NH_4)_2O$–NH_4OH eutectic temperature was about 187.2°K. Postma[6] found 187.4°K. and Rupert[4] reported 186.1°K.

When each of the linear curves was drawn to zero heat of fusion they were coincident within a few tenths of a calorie per mole of $(NH_4)_2O$. This shows that the $(NH_4)_2O$ phase in equilibrium with the eutectic on the NH_3 side was identical to within an accuracy of about 0.02 mole % with the $(NH_4)_2O$ phase in the eutectic on the NH_4OH side. We believe that no case is known where such a situation corresponds to other than a pure compound and it is very difficult to imagine that a solid solution of fixed composition could be in equilibrium with two liquid phases of widely different compositions at the same temperature. Accordingly we conclude that pure $(NH_4)_2O$ is the equilibrium phase in each of the two eutectics where it is present. The eutectic melting data as a function of ammonia removed are given in Table I and the intersection of the two straight lines at zero heat of fusion is shown in Fig. 1. 1.9421 moles of $(NH_4)_2O$ was in the calorimeter during this experiment.

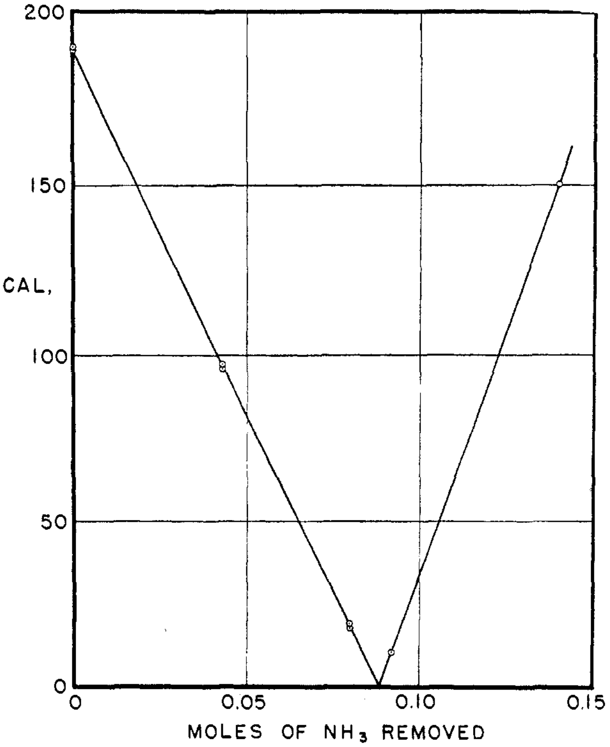

Fig. 1.—Heats of fusion of NH_3–$(NH_4)_2O$ eutectic and $(NH_4)_2O$–NH_4OH eutectic: 1.9421 moles of $(NH_4)_2O$ in the calorimeter.

Table I

Heats of Fusion of Eutectic Phases as a Function of Ammonia Removed

1.9421 moles $(NH_4)_2O$ in calorimeter

Total moles NH_3 removed	Eutectic heat of fusion, cal.	Euctectic phases
0	190.2	$(NH_4)_2O$–NH_3
	188.9	
.0429	97.2	$(NH_4)_2O$–NH_3
	95.6	
.0802	19.0	$(NH_4)_2O$–NH_3
	17.7	
.0920	9.8	NH_4OH–$(NH_4)_2O$
	10.2	
.1398	150.1	NH_4OH–$(NH_4)_2O$

The purity of the NH_4OH phase was not investigated in such detail but it was shown in the following manner: an eutectic heat of fusion of 10 cal. was obtained at about 173°K. This indicated an excess of water in the sample which contained 3.1498 moles of NH_4OH.

Various heat content data on the ammonia water system enable a rough estimate of the heat of fusion of the H_2O–NH_4OH eutectic as about 2000 cal. for the amount of eutectic associated with one mole of ice. The observed 10 cal. heat of fusion of the amount of eutectic in the calorimeter corresponds to only 0.005 mole of ice and a requirement of 0.005 mole of NH_3 to make pure NH_4OH. Thus an accurate heat of fusion is not of great importance. An amount of 0.0133 mole of ammonia was added, followed by convection stirring of the solution, solidification and finally eutectic melting. The eutectic melting near 173°K. had disappeared completely and a heat of fusion of 35 cal. appeared at the $(NH_4)_2O$–NH_4OH eutectic temperature. This corresponds to 0.0105 mole of excess ammonia, compared to 0.0083 mole calculated. The agreement is probably within the limit of error and in any case indicates that the NH_4OH phase is a pure compound to within about 0.05%.

The Melting Points of Ammonium Oxide and Hydroxide.—The melting points were determined by adding increments of energy and waiting at least two hours for equilibrium. Although observations were made as a function of the amount melted the freezing point composition curves are so flat that the NH_4OH in the $(NH_4)_2O$ and *vice versa* produced very small effects.

The results are given in Table II.

Heats of Fusion of $(NH_4)_2O$ and NH_4OH.—The heats of fusion of ammonium oxide and hydroxide were measured by

TABLE II

MELTING POINTS OF $(NH_4)_2O$ AND NH_4OH

Melted, %	Resistance thermometer, T, °K.	Thermocouple
	NH_4OH	
8	194.123	194.15
25	194.152	194.18
43	194.156	194.15
60	194.162	194.15
79	194.153	194.15
91	194.160	194.14
Accepted value		194.15
Other observers	Rupert[4] (1910)	193.8
	Postma[6] (1920)	194.1
	$(NH_4)_2O$	
14	194.319	194.32
30	194.323	194.34
45	194.317	194.31
61	194.318	194.32
76	194.319	194.32
92	194.325	194.32
Accepted value		194.32
Other observers	Rupert[4] (1910)	194.1
	Postma[6] (1920)	194.3

starting below the $(NH_4)_2O$–NH_4OH eutectic temperature and heating somewhat beyond the melting points which were only about seven degrees above the eutectic temperature. Corrections were made by means of the heat capacities and for the fusion of the small amounts of the other eutectic phases present. The data are given in Table III.

TABLE III

HEATS OF FUSION OF $(NH_4)_2O$ AND NH_4OH AT THEIR MELTING POINT

NH_4OH		$(NH_4)_2O$	
Initial T, °K.	ΔH, cal. mole^{-1}	Initial T, °K.	ΔH, cal. mole^{-1}
186.07	1565	186.20	2352
186.25	1568	185.75	2352
185.63	1569	185.84	2351
Accepted values	1568 ± 3		2352 ± 3

TABLE IV

HEAT CAPACITY OF AMMONIUM HYDROXIDE

3.1288 moles NH_4OH + 0.0105 mole $(NH_4)_2O$ in calorimeter. Results have been corrected to pure NH_4OH by subtracting C_p of $(NH_4)_2O$, cal. deg.$^{-1}$ mole^{-1} NH_4OH

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
15.39	0.443	87.22	9.28	194.15°	= m.p.
17.22	.620	93.36	9.94	197.12	28.36
18.94	.805	99.24	10.56	201.38	28.74
20.81	1.022	105.00	11.15	206.38	29.15
22.83	1.262	110.70	11.74	211.61	29.62
25.33	1.572	116.31	12.29	216.93	30.10
28.10	1.924	122.01	12.86	222.37	30.60
31.03	2.309	127.82	13.40	227.89	31.09
34.27	2.761	133.68	13.94[a]	233.47	31.60
37.79	3.250	139.60	14.46[a]	239.13	32.12
41.97	3.794	145.62	15.03[a]	244.84	32.63
46.66	4.399	151.71	15.58[a]	250.62	33.17
51.45	5.033	157.84	16.19[a]	256.44	33.65
56.17	5.627	164.04	16.71[a]	262.35	34.19
61.17	6.259	170.26	17.29[a]	268.28	34.69
66.28	6.892	176.34	17.81[a]	274.12	35.15
71.19	7.477	182.47	18.38[a]	279.81	35.62
76.33	8.073	186.76	23.70[b]	285.33	36.06
81.71	8.666			290.21	36.39

[a] Temperature rise obtained from thermocouple. [b] Eutectic heat absorption, ΔT = 2.248°

TABLE V

HEAT CAPACITY OF AMMONIUM OXIDE

1.9391 moles $(NH_4)_2O$ +0.0030 mole NH_4OH in calorimeter. Results have been corrected to pure $(NH_4)_2O$ by subtracting C_P of NH_4OH, cal. deg.$^{-1}$ mole^{-1} $(NH_4)_2O$

Series I

T, °K.	C_P	T, °K.	C_P	T, °K.	C_P
14.53	1.000	58.05	11.39	122.86	19.46
16.13	1.314	61.98	11.55	128.84	20.13
17.83	1.661	66.37	12.02	134.89	20.82[a]
19.63	2.059	71.47	12.70	141.10	21.48[a]
21.65	2.533	76.80	13.43	147.34	22.20[a]
24.11	3.129	82.32	14.19	153.66	22.90[a]
26.74	3.784	88.31	15.02	159.85	23.58[a]
29.39	4.492	94.08	15.80	166.13	24.21[a]
32.29	5.274	99.76	16.56	172.42	24.87[a]
35.73	6.303	105.40	17.29	178.59	25.48[a]
39.80	7.557	111.14	18.04	183.70	26.07[a]
43.68	8.883	116.96	18.74	186.94	28.49[b]
47.42	10.42				

Series II

T, °K.	ΔT	C_P	T, °K.	ΔT	C_P
22.15	3.192	2.661	51.65	0.0077	281.
25.37	3.205	3.436	51.66	.0052	429.
28.52	3.070	4.243	51.67	.0074	301.
31.70	3.220	5.111	51.69	.0310	71.33
35.10	3.559	6.110	51.77	.127	13.73
39.14	4.522	7.353	51.90	.136	12.50
43.20	3.538	8.670	52.20	.435	12.52
46.20	2.371	9.837	52.65	.463	12.95
48.55	2.263	11.02	53.11	.476	14.01
49.97	0.521	12.00	53.88	1.030	12.53
50.46	.450	12.51	55.02	1.253	11.77
50.84	.289	12.97	56.28	1.239	11.48
51.13	.279	13.50	57.51	1.211	11.36
51.40	.260	14.59	58.91	1.567	11.35
51.58	.0864	21.93	60.98	2.572	11.45
51.63	.0255	76.75			

Series III

T, °K.	ΔT	C_P	T, °K.	ΔT	C_P
50.46	0.509	12.48	53.00	0.1262	13.52
50.87	.292	13.01	53.13	.1235	13.84
51.46	.877	25.49	53.26	.1203	14.26
51.97	.1245	12.40	53.38	.1240	13.66
52.10	.1253	12.34	53.58	.2778	12.84
52.22	.1236	12.55	53.87	.2812	12.43
52.35	.1221	12.72	54.20	.3779	12.10
52.48	.1210	12.83	54.62	.4712	11.93
52.60	.1307	13.09	55.19	.6580	11.71
52.74	.1297	13.17	55.77	.5132	11.56
52.87	.1270	13.48			

Series III above m.p. 194.32°K.

T, °K.	C_P	T, °K.	C_P	T, °K.	C_P
196.82	47.21	223.36	49.97	251.63	52.76
201.08	47.66	228.55	50.56	257.78	53.31
205.86	48.22	234.14	51.12	264.00	53.83
211.08	48.70	239.90	51.66	270.16	54.32
217.74	49.43	245.65	52.21		

[a] Temperature rise from thermocouple. [b] Includes eutectic heat ΔT = 2.373.

The Heat Capacities of $(NH_4)_2O$ and NH_4OH.—The heat capacities of ammonium oxide containing 0.155 mole % of NH_4OH, and ammonium hydroxide containing 0.33 mole % of $(NH_4)_2O$ were measured and corrected for the foreign phases present. The correction was assumed additive in the case of the liquids and while this is only approximately true the correction is so small that any error is negligible. The results are summarized in Tables IV and V. The entire range above 15°K. was investigated since each run began where the previous run terminated. The temperature rise in each run may be estimated from the spacing. All measurements made in temperature regions where there was an appreciable vapor pressure were corrected for vaporization heat by means of pressure observations on a 2-mm. capillary manometer. The temperatures and volumes of the small gas space in the calorimeter and its connecting tube were known at all times. The densities of the liquids have been given above.

The heat capacities recorded as C_p in Tables IV and V are $C_{(\text{sat. vapor})}$ except for the effect of a very small pressure of helium gas on the solid at low temperatures. However, the correction to obtain C_p by means of the following equation is within the limit of error below a vapor pressure of one atmosphere.

$$C_{P(1\ \text{atm.})} = C_{(\text{sat.})} + T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{\text{sat}} - T\int_{P(\text{sat})}^{1\ \text{atm.}} \left(\frac{\partial^2 V}{\partial T^2}\right) \mathrm{d}P$$

Over the 60° regions below the melting points of both NH_4OH and $(NH_4)_2O$, the resistance thermometer showed evidence of a small amount of strain which was relieved when small fractions of the substances were melted. It is for this reason that the measurements so designated in Tables IV and V were obtained in terms of the standard thermocouple. One possibility was that crystallization was accompanied by some slow internal rearrangement which caused expansion after the initial solidification. To check this point about 5% of the solid NH_4OH sample was melted and allowed to cool slowly by radiation. It required about 26 hours to resolidify the melted portion. Subsequent measurements showed that the strain persisted.

The Anomaly in the Heat Capacity of $(NH_4)_2O$.—Figure 2 shows two maxima which occurred in the heat capacity of ammonium oxide. They are typical of the maxima which have been reported for other compounds containing hydrogen in NH_4 and other groups, such as NH_4Cl,[11a,b] NH_4NO_3,[12] $(NH_4)_2SO_4$[12,13] CH_4.[14] The energy absorption is believed to be due to an increase in angular motion and the narrow high maxima are typical of coöperative molecular action. Other examples with more than one maximum are HBr[16] with three, HI[16] and NH_4I[11b] with two. We have considered that angular motions in more than one crystal plane were a plausible explanation for multiple maxima. In the present case an additional possibility would appear to be present since the two NH_4 groups may play different roles within the structure.

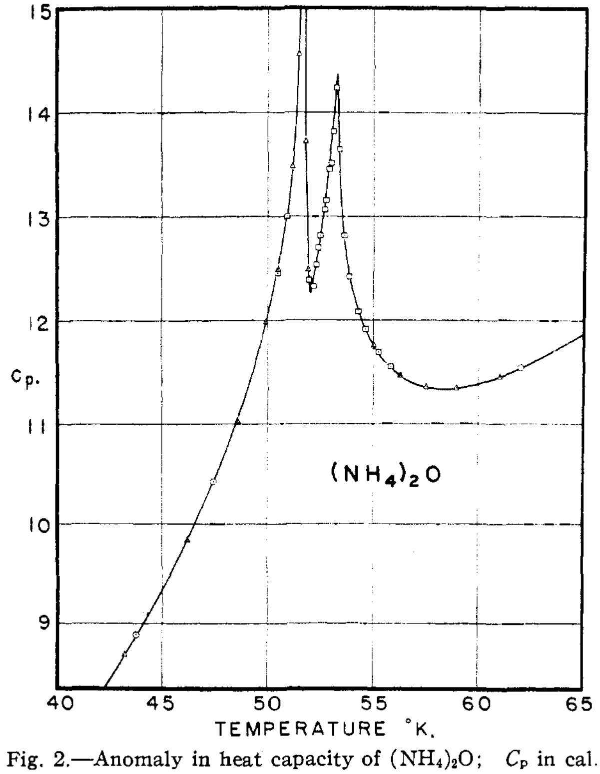

Fig. 2.—Anomaly in heat capacity of $(NH_4)_2O$; C_p in cal. mole^{-1} degree^{-1}: ⊙, series I; ◬, series II; ⊡, series III.

Details of the heat measurements through the anomalous region are given in Table V. The short runs in Table V were designed to give the shape of the curve rather than high accuracy. The few long runs measure the total heat absorption through the region. They are given in Table VI.

TABLE VI

HEAT ABSORBED BY $(NH_4)_2O$ IN THE ANOMALOUS REGION NEAR 52°K.

Run	Temperature interval, °K. (made in series 1, Table V)	ΔH, cal. mole^{-1}
1	49.385–52.607	51.5
2	52.612–56.248	44.8
	(made after series 3, Table V)	
3	49.946–56.354	90.8
	Calcd. from Runs 1 + 2	
	50–55	74.8
	Calcd. from Run 3	
	50–55	74.5

The resistance thermometer showed a small amount of strain near the lower maximum but this disappeared when the transition was complete. There is evidently a volume change associated with the gradual transition.

Runs 1 and 2 make it possible to calculate separately the amounts of energy in the two peaks above the minimum of heat capacity between them. This was desirable in connection with the entropy calculation. Runs 1 and 2 have been combined in Table VI for comparison with run 3 on the basis of the arbitrary interval 50–55°K. The substance had cooled to only 49° before run 3. The value calculated from runs 1 and 2 was accepted for calculating the thermodynamic properties because it was obtained in a continuous series from liquid hydrogen temperatures. However, the 0.3 cal. mole^{-1} difference is probably within the experimental error.

The Heat of Formation of Ammonium Oxide from Ammonia and Ammonium Hydroxide.—The heat of the reaction

$$(NH_4)_2O(s) = NH_4OH(s) + NH_3(g) \qquad (1)$$

was measured in the following manner. After the removal of the small increments of NH_3 to prove that $(NH_4)_2O$ was a pure solid compound, the remaining substance was solidified. It was eventually possible to ascertain its composition accurately after its complete removal from the calorimeter. Several heat capacity measurements were made on the solid at temperatures below the eutectic to eliminate conceivable supercooling or premelting as sources of error. The total heat required to convert all of the solid to liquid at a temperature somewhat above the melting point of $(NH_4)_2O$ was then measured. This was followed by heat capacity measurements on the liquid at increasing temperatures until the vapor pressure of NH_3 reached a value slightly above one atmosphere.

A measured amount of heat was then added to

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[11] (a) F. Simon, *Ann. Physik*, **68**, 241 (1922); (b) F. Simon, O. Simson and M. Ruhemann, *Z. physik. Chem.* **129**, 339 (1927).

[12] J. L. Crenshaw and I. Ritter, *ibid.*, **B16**, 143 (1932).

[13] C. H. Shomate, THIS JOURNAL, **67**, 1096 (1945).

[14] K. Clusius and A. Perlick, *Z. physik. Chem.*, **B24**, 313 (1934).

[15] W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 2193 (1928).

[16] W. F. Giauque and R. Wiebe, *ibid.*, **51**, 1441 (1929).

evaporate a considerable amount of ammonia at constant pressure. The heat was added by means of the portion of the heater on the lower half of the calorimeter to ensure that ammonia gas leaving the calorimeter would not be superheated. This was absorbed in a glass weighing bulb containing 6 N sulfuric acid. The solution in the weighing bulb was protected by guard tubes against the transfer of water to or from the atmosphere. The ammonia reached the acid by means of a glass tip immersed in mercury to prevent the solution from being sucked back. A few measurements of vapor pressure were made as a function of composition and temperature. These were supplemented by temperature coefficients which could be calculated, with sufficient accuracy by means of the measured heats of vaporization. These data were used to determine the average temperature at which the ammonia gas left the calorimeter. Following the heat of vaporization measurement the substance was resolidified and the heat of fusion and the heat capacity were again measured from below the eutectic temperature to the condition existing at the end of the vaporization measurement.

The change of heat content of ammonia gas with pressure at constant temperature was calculated by means of the tables of the U. S. Bureau of Standards[17] which were extrapolated below their lower limit of about one third atmosphere. The heat capacity of the ideal gas was calculated from the spectroscopic observations on ammonia gas summarized by Herzberg.[18] A small correction was made for the effect of rotational stretching by means of the equations given by Wilson.[19]

These data gave the heat of Reaction 1 at the eutectic temperature. Essentially the method uses the pure solid phases in the eutectic as references for heat content. Since heat capacity data were available on all substances concerned the heat of the reaction

$$(NH_4)_2O(l) = NH_4OH(l) + NH_3(\text{ideal gas}) \qquad (2)$$

could be calculated at higher temperatures.

In calculating the value at 25° it was necessary to extrapolate the heat capacity data on $(NH_4)_2O$ above 273°K. but this should not cause appreciable error. The data are summarized in Table VII.

TABLE VII

HEAT OF THE REACTION

$(NH_4)_2O$(pure solid) = NH_4OH(pure solid) + NH_3(ideal gas)

Run	Moles at start $(NH_4)_2O$	Moles at start NH_4OH	Moles NH_3 removed	T vaporiz. av.	ΔH, cal. mole^{-1} NH_4OH formed
1	1.7296	0.2124	0.4255	255.5	$\Delta H_{187.4°K.} = 7532$
2	1.3041	.6379	.3085	258.2	$\Delta H_{187.4°K.} = 7523$

Run 1 was given no weight	ΔH of Reaction 2	
Values from this research	$\Delta H_{0°C.} = 5863$	$\Delta H_{25°C.} = 5598$
Scatchard, *et al.*,[20] plus Bureau of Standards Tables[16]	$\Delta H_{0°C.} = 5879$	$\Delta H_{25°C} = 5609$

During run no. 1 the heat leak into the calorimeter from the surrounding copper block seemed to be larger than the normal rate both at the beginning and end of the run. This could have been due to a small delayed heat effect from incomplete mixing within the calorimeter. On account of this small uncertainty Run 1 is given no weight, although it agrees rather well with Run 2.

A very small amount of water left the calorimeter with the ammonia. The tables of Scatchard, Epstein, Warburton and Cody[20] were used to make a correction of −0.7 cal. mole^{-1} in Run 2 for the weight and heat of vaporization of the water. The correction in Run 1 was negligible. The values of ΔH in Table VII attributed to Scatchard, *et al.*,[20] are based primarily on the calorimetric observations of Zinner.[21] They were calculated by combining the heat of mixing of the pure saturated liquids with data from the tables of the properties of pure ammonia given in the U. S. Bureau of Standards Tables,[17] and the properties of water from the tables of Keenan and Keyes.[22]

Heat Capacity of Some Aqueous Ammonia Solutions.—Incidental to the measurements of the heat of reaction discussed above, the heat capacity of aqueous ammonia at three concentrations was measured. As mentioned above, there was some evidence of incomplete mixing in these measurements, particularly at the concentration 0.6411 weight fraction of ammonia, however, any such effect should have had little influence on the heat capacity. The observed results are given in Table VIII. They should be accurate to 0.1%.

TABLE VIII

HEAT CAPACITY OF AQUEOUS AMMONIA

X = weight fraction NH_3 in liquid, C_p in cal. deg.$^{-1}$ g.$^{-1}$

$X = 0.6411$		$X = 0.6123$		$X = 0.5883$	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
201.56	0.910	201.30	0.896	201.33	0.883
207.30	.923	207.13	.908	207.30	.897
213.40	.935	213.35	.921	213.72	.909
219.35	.947	219.76	.934	220.14	.924
225.14	.958	225.87	.947	226.42	.937
....	...	232.04	.960	232.63	.951
237.26	.981	238.18	.972	238.82	.964
243.37	.992	244.18	.983	245.09	.977
249.63	1.005	250.31	.996	251.46	.991
256.22	1.016	256.64	1.008	257.91	1.005

Table IX contains values taken from smooth curves through the data. These values, together with those corresponding to the concentrations X = 0.48596 ((NH_4OH). and

TABLE IX

HEAT CAPACITY OF AQUEOUS AMMONIA FROM 200 TO 260°K.

X = weight fraction NH_3 in liquid, C_p in cal. deg.$^{-1}$ g.$^{-1}$

T, °K.	$X = 0.6411$ C_p	$X = 0.6123$ C_p	$X = 0.5883$ C_p
200	0.907	0.893	0.880
210	.928	.914	.902
220	.948	.935	.923
230	.967	.955	.945
240	.987	.976	.967
250	1.005	.995	.988
260	1.023	1.014	1.009

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(17) U. S. Bureau of Standards Circular No. 142, April 19 (1923).

(18) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 295, 437.

(19) E. B. Wilson, Jr., *J. Chem. Phys.*, **4**, 526 (1936).

(20) G. Scatchard, L. F. Epstein, J. Warburton and P. J. Cody, *Refrig. Eng.*, **53**, 413 (1947).

(21) K. Zinner, *Z. gesamte Kälte-Ind.*, **41**, 21 (1934).

(22) J. K. Keenan and F. G. Ryes, "Thermodynamic Properties of Steam, Including Data for the Liquid and Solid Phases," John Wiley and Sons, Inc., New York, N. Y., 1936.

X = 0.65407 ($(NH_4)_2O$) at the same temperatures, serve to define the heat capacity as a function of composition between those compounds.

Smooth curves through the data for ammonium oxide and ammonium hydroxide are believed to represent the heat capacities to 0.1–0.2% at all temperatures above 35°K. except for the short runs in the region of the anomaly in $(NH_4)_2O$.

The error may be 1% at 20°K. and several per cent. at 15°K. principally because of decreasing sensitivity of the resistance thermometer. Values taken from the curves at even values of the temperature have been used to obtain the thermodynamic properties of ammonium oxide and ammonium hydroxide which are given in Tables X and XI.

Table X

The Thermodynamic Properties of Ammonium Oxide, Cal. Mole^{-1} Deg.$^{-1}$

T, °K.	C_p	S	$(H^0 - H^0_0)/T$	$-(F^0 - H^0_0)/T$
15	1.085	0.394	0.291	0.103
20	2.151	.847	.618	.229
25	3.344	1.453	1.042	.411
30	4.649	2.177	1.534	.643
35	6.075	2.999	2.079	.920
40	7.666	3.910	2.674	1.236
45	9.683	4.905	3.317	1.588
50	12.032	6.012	4.039	1.973
	Transition region			
55	11.776	7.444	5.032	2.412
60	11.388	8.439	5.565	2.874
70	12.491	10.269	6.468	3.801
80	13.873	12.027	7.307	4.720
90	15.246	13.741	8.113	5.628
100	16.592	15.417	8.895	6.522
110	17.889	17.060	9.654	7.406
120	19.108	18.669	10.391	8.278
130	20.268	20.245	11.107	9.138
140	21.392	21.788	11.802	9.986
150	22.485	23.301	12.477	10.824
160	23.562	24.787	13.137	11.650
170	24.616	26.247	13.781	12.466
180	25.654	27.683	14.411	13.272
190	26.667	29.098	15.031	14.067
194.32	Melting point			
200	47.552	43.168	27.962	15.206
210	48.603	45.513	28.920	16.593
220	49.659	47.798	29.838	17.960
230	50.695	50.029	30.723	19.306
240	51.685	52.208	31.576	20.632
250	52.617	54.337	32.400	21.937
260	53.491	56.418	33.194	23.224
270	54.310	58.452	33.961	24.491
280	55.075[a]	60.442	34.702	25.740
290	55.795[a]	62.387	35.417	26.970
298.16	56.355[a]	63.942	35.983	27.959
300	56.477[a]	64.290	36.108	28.182

[a] Extrapolated above 273°K.

Table XI

The Thermodynamic Properties of Ammonium Hydroxide, Cal. Deg.$^{-1}$ Mole^{-1}

T, °K.	C_p	S	$(H^0 - H^0_0)/T$	$-(F^0 - H^0_0)/T$
15	0.419	0.140	0.104	0.036
20	0.924	.325	.242	.083
25	1.533	.596	.439	.157
30	2.185	.933	.675	.258
35	2.860	1.320	.938	.382
40	3.536	1.747	1.222	.525
45	4.195	2.201	1.515	.686
50	4.845	2.679	1.818	.861
55	5.485	3.170	2.121	1.049
60	6.114	3.673	2.427	1.246
70	7.333	4.708	3.042	1.666
80	8.486	5.763	3.651	2.112
90	9.583	6.826	4.249	2.577
100	10.643	7.891	4.836	3.055
110	11.666	8.953	5.410	3.543
120	12.650	10.011	5.973	4.038
130	13.603	11.062	6.524	4.538
140	14.531	12.104	7.063	5.041
150	15.441	13.137	7.591	5.546
160	16.344	14.221	8.168	6.053
170	17.245	15.181	8.621	6.560
180	18.142	16.192	9.125	7.067
190	19.030	17.197	9.623	7.574
194.15	Melting point			
200	28.566	26.530	18.210	8.320
210	29.474	27.946	18.725	9.221
220	30.380	29.338	19.234	10.104
230	31.285	30.708	19.738	10.970
240	32.187	32.059	20.238	11.821
250	33.081	33.391	20.734	12.657
260	33.957	34.706	21.226	13.480
270	34.807	36.004	21.714	14.290
280	35.624	37.285	22.197	15.088
290	36.400	38.549	22.673	15.876
298.16	37.022	39.567	23.057	16.510
300	37.134	39.795	23.143	16.652

The Entropies of Ammonium Oxide and Ammonium Hydroxide.—The entropy calculations are summarized in Tables XII and XIII. In obtaining the entropy in the anomalous region of heat capacity of $(NH_4)_2O$ the calculation was made graphically except for the amount represented by the peaks above C_p = 12.32 cal. deg.$^{-1}$ mole^{-1}. In this case the center of gravity of $1/T$ was estimated and used along with the total energy

Table XII

Entropy of Ammonium Oxide, Cal. Deg.$^{-1}$ Mole^{-1}

0–15°K. Debye extrapolation	0.394
15–194.32°K.. graphical	29.308
Fusion 2352/194.32	12.104
194.32–273.16°K., graphical	17.279
Entropy of liquid at 273.16°K.	59.085
273.16–298.16°K., graphical extrap.	4.857
Entropy of liquid at 298.16°K.	63.94

Table XIII

Entropy of Ammonium Hydroxide, Cal. Deg.$^{-1}$ Mole^{-1}

0–15°K., Debye extrapolation	0.140
15–194.15°K., graphical	17.472
Fusion 1568/194.15	8.076
194.15–273.16°K., graphical	10.722
Entropy of liquid at 273.16°K.	36.410
273.16–298.16°K., graphical	3.157
Entropy of liquid at 298.16°K.	39.57

above the arbitrary cut off point. This energy could be obtained accurately from the long runs through the anomalous region.

Other entropy values which will be needed for the comparisons to be made below are

$H_2O(l)$, $S_{298.16} = 16.72$, $S_{273.16} = 15.14$ cal. deg.$^{-1}$ mole^{-1}
$NH_3(g, f = 1)$, $S_{298.16} = 46.03$, $S_{273.16} = 45.29$ cal. deg.$^{-1}$ mole^{-1}

The entropy and heat content of ammonia gas were calculated from the spectroscopic data summarized by Herzberg.[18] The natural constants used are those given by Du Mond and Cohen and listed by Rossini, Gucker, Johnston, Pauling and Vinal.[23] The moments of inertia of the ground state of the ammonia molecule, which were calculated in terms of the above constants, are the average of those obtained from the inversion doublets of the rotational levels.

$I_1 = I_2 = 2.815 \times 10^{-40}$ and $I_3 = 4.435 \times 10^{-40}$ g.cm.^{2}

The vibrational constants used were ν_1, 3335.9 (1/2), 3337.5 (1/2); ν_2, 931.58 (1/2), 968.08 (1/2); ν_3, 3414 (2); and ν_4, 1627.5 (2) cm.$^{-1}$. Harmonic oscillation was assumed since there is essentially no excitation above the states $\nu = 1$, and that only in ν_2 and ν_4. Since the inversion doublets of the rotational states have a separation of only about 0.8 cm.$^{-1}$, equal distribution was assumed and the symmetry number taken as three in calculating the entropy of ammonia. The entropy and heat content calculation were corrected for rotational stretching of the molecule by means of the equations given by Wilson.[19]

Comparison of the Third Law Data with Entropy Changes from the Free Energy Equation.—The free energy entropy, and heat content changes in the reaction

$$NH_4OH(l) + NH_3(l, \text{sat.}) = (NH_4)_2O(l) \qquad (3)$$

were obtained by graphical interpolation from the tables of Scatchard, *et al.*[20] These tables have been based on available data on the liquid–vapor composition and vapor pressure of the ammonia–water system, together with calorimetric observations of Zinner[21] on the heat of mixing liquid ammonia and water.

Data relating to the reaction

$$NH_3(g, f = 1) = NH_3(l, \text{sat.}) \qquad (4)$$

were obtained from Tables of the U. S. Bureau of Standards.[17] The tables for ammonia require a small correction below a pressure of 5 p.s.i.a. in obtaining data for the ideal gas state ($f = 1$). Since the heat of vaporization of ammonia is a large item in the heat of reaction we compared this quantity from the table with the more recent determination of Overstreet and Giauque.[2]

$$NH_3(l) = NH_3(g) \qquad (5)$$

Bur. Std' Tables[17] $\Delta H_{\text{b.p.}} = 5580$ mole^{-1}
Overstreet and Giauque $\Delta H_{\text{b.p.}} = 5581$ cal. mole^{-1}

For Reaction 3

Tables of Scatchard, *et al.*[20]
$\Delta F_{25}° = -434$ cal. mole^{-1}
$\Delta H_{25}° = -576$ cal. mole^{-1}
$\Delta S_{25}° = -0.475$ cal. deg.$^{-1}$ mole^{-1}

For Reaction 4

Data from Bureau of Standard's Tables[17] $\Delta F_{25}° = 1298$
$\Delta H_{25}° = -5032$
$\Delta S_{25}° = -21.230$

Combining Reactions 3 and 4

$$NH_4OH(l) + NH_3(g, f = 1) = (NH_4)_2O(l) \qquad (6)$$

$\Delta F_{25} = +864$
$\Delta H_{25} = -5609$
$\Delta S_{25} = -21.705$

If we accept the above value of ΔF for Equation 6 and combine it with the heat of reaction measured in the present research, $\Delta H_{25} = -5598$, the entropy change, $\Delta S_{25} = -21.67$ cal. deg.$^{-1}$ mole^{-1}. Applying the Third Law

$$63.94 - 39.57 - 46.03 = \Delta S_{25} = -21.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The almost exact all around agreement is somewhat fortuitous.

The free energy and entropy of the reaction

$$H_2O(l) + NH_3(l, \text{sat.}) = NH_4OH(l) \qquad (7)$$

may also be obtained by graphical interpolation in the tables of Scatchard, *et al.*[20] For Reaction 7

$\Delta F_{25}° = -1527$ cal. mole^{-1}
$\Delta H_{25}° = -2109$ cal. mole^{-1}
$\Delta S_{25}° = -1.953$ cal. deg.$^{-1}$ mole^{-1}

combining the data of Equations 4 and 7

$$H_2O(l) + NH_3(g, f = 1) = NH_4OH(l) \qquad (8)$$

$\Delta F_{25}° = -229$
$\Delta H_{25}° = -7141$
$\Delta S_{25}° = -23.18$

Applying the third law

$$39.57 - 16.72 - 46.03 = \Delta S_{25} = -23.18 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Again the exact agreement is somewhat fortuitous since the tables of Scatchard, *et al.*,[20] while carefully prepared, have utilized data which will not ensure this degree of accuracy. That this is so may be shown by using the tables at 0° to make the comparisons at that temperature.

For Reaction 7

Table of Scatchard, *et al.*[20] $\Delta F_0° = -1559$
$\Delta H_0° = -2122$
$\Delta S_0° = -2.06$

For Reaction 4

Data from Bureau of Standards' Tables[17] $\Delta F_0° = -751$
$\Delta H_0° = -5300$
$\Delta S_0° = -22.15$

Combining Equations 4 and 7

$$H_2O(l) + NH_3(g, f = 1) = NH_4OH(l) \qquad (8)$$

$\Delta F_0° = -808$ cal. mole^{-1}
$\Delta H_0° = -7422$ cal. mole^{-1}
$\Delta S_0° = -24.21$ cal. deg.$^{-1}$ mole^{-1}

Applying the Third Law

$$S_{NH_4OH(l)} - S_{H_2O(l)} - S_{NH_3(g, f=1)} = 36.41 - 15.14 - 45.29$$
$$\Delta S_0° = -24.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The discrepancy is 0.19 cal. deg.$^{-1}$ mole^{-1}. The present heat capacity measurements should lead to an entropy value of NH_4OH which is accurate to about 0.05 cal. deg.$^{-1}$ mole^{-1}.

The entropies of water and ammonia are accurately known, and the sign of the discrepancy is such that either ΔS from isothermal considerations is too small, or $\int_0^T C_p \, d \ln T$ for NH_4OH is too large. Considering the limits of error this latter situation

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(23) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, THIS JOURNAL, **74**, 2699 (1952).

is thermodynamically inadmissible and the error must come from the tables which give $\Delta S_{0°} = -24.21$ cal. deg.$^{-1}$ mole^{-1}. A similar test for Reaction 6 at 0° is as follows

For Reaction 3

Tables of Scatchard, *et al.* $\Delta F_{0°} = -436$
$\Delta H_{0°} = -579$
$\Delta S_{0°} = -0.52$

Combining the data of Reactions 3 and 4 for 0°

$$NH_4OH(1) + NH_3(g, f = 1) = (NH_4)_2O(1) \quad (6)$$

$$\Delta F_{0°} = 315 \text{ cal. mole}^{-1}$$
$$\Delta H_{0°} = -5879 \text{ cal. mole}^{-1}$$
$$\Delta S_{0°} = -22.67 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Applying the third law

$$S_{(NH_4)_2O(1)} - S_{NH_4OH(1)} - S_{NH_3(g, f=1)} = 59.09 - 36.41 - 45.29$$

$$\Delta S_{0°} = -22.61 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

This is excellent agreement again and yet the 0° comparison for reaction 8 shows an internal inconsistency in the combined tables of Scatchard, *et al.*,[20] and the Bureau of Standards.[17]

The free energy of formation of ammonia–water solutions, from the components, in the range 0–25° should be accurate.

$$\Delta F = RT \int \ln f_{NH_3} \, dN_{NH_3}$$

and at ordinary temperatures either the pressures of ammonia and water are low or when the pressure of ammonia is high there is essentially no water vapor present. Thus the fugacity, f, may be calculated from the properties of pure ammonia gas. Most of the data are in the form of total pressures and Scatchard, *et al.*,[20] have made a small correction for water vapor in terms of the Gibbs–Duhem equation. This should be an accurate procedure.

In order to find the source of the discrepancy the heat content tables of Scatchard, *et al.*, were carefully interpolated by means of graphical plots and the heat content values in the Bureau of Standards Ammonia Tables were extrapolated graphically from 5 p.s.i.a. to zero pressure. The changes in heat content between 0 and 25° for NH_4OH and $(NH_4)_2O$ were compared with the present heat capacity results. The similar value for $NH_3(g, f = 1)$, was obtained from the limiting values of the Bureau of Standards Tables and compared with the results of calculation based on the spectroscopic data given above.

The comparison is shown in Table XIV.

TABLE XIV

COMPARISON OF CALORIMETRIC DATA

$H_{25°} - H_{0°}$, cal. mole^{-1}

	This research	**Table of Scatchard, *et al.***
$(NH_4)_2O(1)$	1387	1425
$(NH_4OH(1)$	902	945
	Spectroscopic data	**Bureau of Standards tables**
NH_3(ideal gas)	219.7	210.2
$\Delta H_{25°} - \Delta H_{0°}$ Reaction 6	265	270

The sum of the second and third entries in Table XIV subtracted from the first entry gives $\Delta H_{25°} - \Delta H_{0°}$ for Reaction 6. The result has been given in Table XIV. Although the disagreement of the several terms is considerable the errors nearly cancel. However, a similar calculation for Reaction 8 involves the subtraction of the third from the second entry and this involves a discrepancy of 47 cal. mole^{-1}, which is equivalent to an error of 0.17 cal. deg.$^{-1}$ mole^{-1} in entropy at 273°K.

It is evident that the Bureau of Standard's Ammonia Tables[17] could be improved by making them consistent with the thermodynamic properties of ideal ammonia gas, which are very accurately known from spectroscopic data.

A principal weakness in the thermodynamic data of the ammonia–water system is due to the fact that Zinner[20] determined the temperature coefficient of the heat of mixing by measuring the heats of mixing over a range of temperature. It is very difficult to obtain accurate temperature coefficients by such a method. The preferred procedure is to measure the heat of reaction under the most favorable conditions and then obtain the temperature coefficients by means of heat capacity measurements. From the above comparisons it would appear that Zinner's measurements are fairly accurate near 25°.

Despite the minor discrepancies in available tables relating to ammonia and the ammonia–water system the over-all entropy agreement is good and we believe that it is safe to conclude that the entropies of ammonium oxide and ammonium hydroxide both approach zero at the absolute zero of temperature within 0.1 cal. deg.$^{-1}$ mole^{-1}. The hydrogen bonding and all other structural details must be essentially ordered in the crystalline states of these substances at low temperatures.

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