[Contribution from the Chemical Laboratory of the University of California]

Ammonia. The Heat Capacity and Vapor Pressure of Solid and Liquid. Heat of Vaporization. The Entropy Values from Thermal and Spectroscopic Data

By Roy Overstreet and W. F. Giauque

In a former communication, Giauque, Blue and Overstreet[1] showed that the existing low temperature calorimetric data on ammonia lead to an entropy value about one cal./deg. per mole greater than the value obtained from band spectrum observations. The purpose of this research has been to obtain accurate calorimetric data in the hope of eliminating the discrepancy. As was expected, the inconsistency was found to be due chiefly to the inaccuracy of the existing calorimetric data.

Preparation of Ammonia.—The ammonia used in this investigation was prepared by the action of a saturated solution of potassium hydroxide on c. p. ammonium chloride. The gas was subjected to a preliminary drying by conducting it slowly through a vertical glass column, approximately one meter in length, containing broken sticks of potassium hydroxide. The ammonia issuing from the column was condensed over sodium in one of a series of glass distillation bulbs by means of solid carbon dioxide in ether. Approximately 250 cc. of liquid was prepared in this manner. After standing over sodium for twelve hours, the substance was then distilled five times. In each case the first 10 cc. of distillate and the final 10 cc. portion was discarded. Following each distillation, the gas was cooled to the temperature of liquid air and the line was evacuated to 10^{-5} mm.

The amount of liquid-soluble solid-insoluble impurity was estimated to be not more than one mole in one hundred thousand. This estimate was made on the assumption that the slight rise in heat capacity below the melting point was due to premelting. The single high observation given later in Table IV was confirmed by several measurements, not included, over smaller temperature intervals just below the melting point.

Apparatus.—The measurements were carried out in Gold Calorimeter II[2] which was rebuilt and described by Blue and Giauque.[3] A full description of a calorimeter of this type has been given by Giauque and Egan.[4]

The temperature scale was obtained from the copper-constantan thermocouple of laboratory designation "W."[5] The thermocouple, which was originally compared with a hydrogen gas thermometer, has been compared frequently with the oxygen and hydrogen vapor pressure thermometers. The latest comparison, made after the completion of this work, gave the following corrections to be added to the original calibration made nine years before: 0.01° at the boiling point of oxygen, 90.13° K., 0.11° at the melting point of oxygen, 54.39° K., 0.13° at the 43.76° K. transition of oxygen, 0.15° at the boiling point of hydrogen 20.37° K. and 0.17° at the triple point of hydrogen, 13.95° K. These corrections were employed in the temperature scale used in this research. The gold resistance thermometer-heater, used for greater calorimetric precision and accuracy, was calibrated continuously during the measurements by comparison with the thermocouple.

The Vapor Pressure of Ammonia.—The vapor pressure was determined by means of a manometer which could be connected directly with the calorimeter. A cathetometer was used as a comparison instrument with a standard meter mounted in the manometer case. The vapor pressure observations on solid ammonia from 176.92°K. to the melting point, 195.36°K., have been represented by the equation

$$\log_{10} P \text{ (int. cm. Hg)} = -1630.700/T + 9.00593 \quad (1)$$

For liquid ammonia from 199.26 to 241.59°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -1612.500/T - 0.012311\,T + 0.000012521T^2 + 10.83997 \quad (2)$$

In Table I the observed values are compared with those given by equations 1 and 2. The pressure observations are corrected to international centimeters of mercury by means of data given in the "I.C.T."[6] The standard acceleration of gravity was taken as 980.665 cm./sec.². The gravitational acceleration, 979.973 cm./sec.² has been determined for this location by Sternewarte.[7] Because of the high relative accuracy, which could be obtained with the resistance thermometer, the temperatures for the liquid are given to 0.001°. The absolute error may be as high as several hundredths of a degree.

From equation 2 the boiling point was calculated to be 239.68°K.

The deviations given in the third column of Table I were calculated by assuming that the temperature observations were correct. The deviations given in the fourth column of the table were calculated assuming that the pressures were correct.

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(1) Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

(2) Giauque and Wiebe, This Journal, **50**, 101 (1928).

(3) Blue and Giauque, *ibid.*, **57**, 991 (1935).

(4) Giauque and Egan, *J. Chem. Phys.*, in press.

(5) (a) Giauque, Buffington and Schulze, This Journal, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. I, 1926.

(7) Sternewarte, Landolt, Börnstein and Roth, "Physikalische chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

TABLE I

VAPOR PRESSURE OF AMMONIA

Boiling point 239.68°K. 0°C. = 273.10°K.

T, °K.	P, obsd., int. cm. Hg.	P, obsd. − P, calcd.	T, measd. − T, calcd.	
176.92	0.615	0.000	0.00	Solid
181.13	1.010	.003	−.03	Solid
183.17	1.266	−.002	.02	Solid
186.00	1.735	.002	−.01	Solid
189.03	2.398	.003	−.01	Solid
191.85	3.206	−.001	.00	Solid
195.360	4.558	.000	.000	Triple point
199.262	6.188	−.001	.003	Liquid
203.114	8.261	−.001	.002	Liquid
206.587	10.608	.000	.000	Liquid
210.811	14.181	−.003	.001	Liquid
214.420	18.017	.003	−.002	Liquid
218.354	23.126	.006	−.004	Liquid
224.246	32.980	.008	−.004	Liquid
229.205	43.725	−.010	.004	Liquid
234.840	59.284	−.009	.003	Liquid
241.585	83.535	−.010	.002	Liquid

A summary of observations on the melting point temperature is given in Table II. Observation 1 was a single determination. Observations 2 and 3 were taken consecutively over a period of about two hours. Observations 4, 5 and 6 were taken consecutively over a period of approximately five hours. Table III contains a summary of the more recent determinations of the melting and boiling points of ammonia.

TABLE II

MELTING POINT OF AMMONIA

0°C. = 273.10°K.

Observation	% melted	T, °K. Resistance thermometer	T, °K. Thermocouple	P, int. cm. Hg
1	20	195.350	195.36	4.557
2	15	195.355	195.36	4.559
3	25	195.358	195.37	4.557
4	5	195.360	195.35	4.560
5	15	195.361	195.35	4.558
6	30	195.364	195.36	4.559
		Accepted values	195.36	4.558

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF AMMONIA

M. p., °K.	B. p., °K.	Observer
....	239.90	Keyes and Brownlee[8] (1918)
195.40	239.75	Cragoe, Meyers and Taylor[9] (1920)
....	239.74	Henning and Stock[10] (1921)
195.5	....	Eucken and Karwat[11] (1924)
195.36	239.68	This research

As may be seen from Table III the melting and boiling point temperatures agree fairly well with those obtained by Cragoe, Meyers and Taylor[9] and by Henning and Stock.[10] The latter authors did not make observations at the melting point but by substituting the observed triple point pressure in their vapor pressure equation the value 195.39°K. is found as compared to the present observation of 195.36°K.

The present value obtained for the boiling point is 0.07° below that of Cragoe, Meyers and Taylor and 0.06° below that of Henning and Stock.

The agreement is perhaps all that can be expected when one considers the possible errors of the several experimenters. The gas thermometer scale calibration by Giauque, Buffington and Schulze,[5a] of the thermocouple used in the present work, was estimated by those authors to be accurate to ±0.05°. However, high relative accuracy was obtained by means of the resistance thermometer which was read with a scale giving about 10^4 mm. per degree. The resistance thermometer was calibrated by comparison with the thermocouple at frequent intervals over a wide temperature range.

The value, 4.558 cm., given for the triple point pressure is in good agreement with an observation of Bergstrom[11a] who obtained 4.55 cm. Also by putting the melting point observation of the present research in the vapor pressure equation of Henning and Stock one obtains the value 4.55 cm. The observation, 4.49 cm., of Cragoe, Meyers and Taylor is evidently in error. Putting their value for the melting point, 195.40°K., into their vapor pressure equation one obtains 4.53 cm.

The Heat Capacity of Ammonia.—The heat capacity results are given in Table IV. For the calculation of energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie. The data are shown in Fig. 1. The heat capacity of ammonia has been measured by Eucken and Karwat[11] and by Clusius, Hiller and Vaughen.[12] In Table V are recorded heat capacity values picked from a smooth curve through the observations. Since Eucken and Karwat have prepared a similar table, deviations from their data are included. Deviations from the data of Clusius, Hiller and Vaughen are not included, since their investigations were carried out, for the most part, at temperatures below 20°K. However, their data at higher temperatures are too high by

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(8) Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918).

(9) Cragoe, Meyers and Taylor, *ibid.*, **42**, 206 (1920).

(10) Henning and Stock, *Z. Physik*, **4**, 226 (1921).

(11) Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924).

(11a) Bergstrom, *J. Phys. Chem.*, **26**, 358 (1922).

(12) Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **B8**, 427 (1930).

approximately the same percentages as those given for Eucken and Karwat in Table V.

TABLE IV

HEAT CAPACITY OF AMMONIA

Molecular weight 17.031; 0°C. = 273.10°K.

Series I, II, III and IV 4.3558 moles. Series V 4.3321 moles.

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
15.04	0.780	0.176	130.87	5.038	8.152
15.71	1.097	.200	135.80	4.726	8.484
17.26	1.714	.237	140.47	4.502	8.714
19.75	2.960	.358	145.32	4.987	8.972
22.74	3.007	.529	150.23	4.673	9.304
26.08	3.588	.750	155.35	5.073	9.594
29.74	3.462	1.013	160.40	4.824	9.866
33.46	3.883	1.313	165.58	5.263	10.16
37.78	4.664	1.666	170.85	4.984	10.45
42.32	4.423	2.031	175.86	4.732	10.77
46.79	4.413	2.391	180.99	5.125	11.10
51.23	4.490	2.758	186.16	4.861	11.45
56.11	5.246	3.173	191.09	4.612	11.94
61.24	4.965	3.567	195.36	Melting point	
65.47	3.789	3.913	197.84	3.733	17.54
69.69	4.511	4.217	202.31	4.944	17.60
74.63	5.185	4.563	207.28	4.798	17.71
79.56	4.674	4.926	212.32	5.072	17.75
84.05	4.296	5.234	217.42	4.915	17.89
88.70	4.902	5.535	219.59	4.870	17.90
93.44	4.755	5.831	222.60	5.134	17.94
98.32	5.083	6.172	225.02	4.754	17.96
103.24	4.750	6.447	227.94	5.134	18.02
107.87	4.454	6.743	229.93	4.655	18.02
112.71	4.979	7.044	233.15	5.016	18.05
117.55	4.666	7.356	234.76	4.563	18.05
119.50	4.175	7.491	238.33	4.897	18.12
122.11	4.419	7.621	239.68	Boiling point	
125.97	4.565	7.858			

TABLE V

HEAT CAPACITY OF AMMONIA

Molecular weight 17.031, 0°C. = 273.10°K.

Values taken from smooth curve through observations

T, °K.	C_p	Deviation %. E. and K.—This research	T, °K.	C_p	Deviation %. E. and K.—This research
20	0.368	−4.4	140	8.699	4.7
30	1.033	0.8	150	9.272	4.6
40	1.841	8.9	160	9.846	4.3
50	2.663	13.6	170	10.42	3.8
60	3.474	10.2	180	11.03	3.2
70	4.232	7.6	190	11.71	2.0
80	4.954	6.0	200	17.58	4.6
90	5.612	5.4	210	17.75	2.9
100	6.246	5.3	220	17.90	1.5
110	6.877	5.1	230	18.03	0.7
120	7.497	4.8	240	18.12	0.5
130	8.102	4.8			

Heat of Fusion.—Determinations of the heat of fusion of ammonia are given in Table VI. With the temperature slightly below the melting point, heat was added until all of the substance was melted and the liquid heated slightly above the melting point. Correction was made for the $\int C_p dT$ and the premelting effect. It is interesting to compare the value for the heat of fusion obtained in this research with that calculated by Eucken and Donath[13] from measurements of the heat of sublimation and heat of vaporization near the melting point. By a small extrapolation of their heat of condensation measurements, they have calculated the difference between the heat of sublimation and the heat of vaporization at the melting point to be 1380 ± 8 cal. Considering the large quantities of heat dealt with, the agreement between their value and the value of this research is good.

TABLE VI

HEAT OF FUSION OF AMMONIA

Temperature interval	Corrected heat, input/mole	$\int C_p dT$	ΔH
193.688–196.684	1402.4	50.9	1351.5
193.638–195.919	1388.3	36.4	1351.9
193.416–196.539	1403.5	52.0	1351.5
		Mean	1351.6 ± 0.2
Eucken and Karwat[11]			1426
Eucken and Donath,[13] from heats of sublimation and heat of vaporization			1380 ± 8
From vapor pressure equations of this research, assuming a Berthelot gas			1376

Heat of Vaporization.—The heat of vaporization was measured by adding energy and determining the amount of gas evolved. The ammonia was vaporized against a constant pressure, which was slightly above atmospheric pressure. A small correction was applied to obtain the value corresponding to 760 mm. A summary of the data is given in Table VII. Osborne and Van Dusen[14] have measured the heat of vaporization of ammonia through the range −42 to +52°. The value 5573 interpolated from their data is in excellent agreement with the value obtained in this research.

It has been of interest to calculate the heat of fusion and the heat of vaporization from the vapor pressure data. This has been done by assuming that Berthelot's equation of state can be used to correct for gas imperfection. The values are included in Tables VI and VII. The agreement with the experimental values is sufficiently close to justify the use of Berthelot's equation for the calculation of the entropy correction for the actual to the ideal gas states.

[13] Eucken and Donath, *Z. physik. Chem.*, **124**, 181 (1926).

[14] Osborne and Van Dusen, THIS JOURNAL, **40**, 14 (1918).

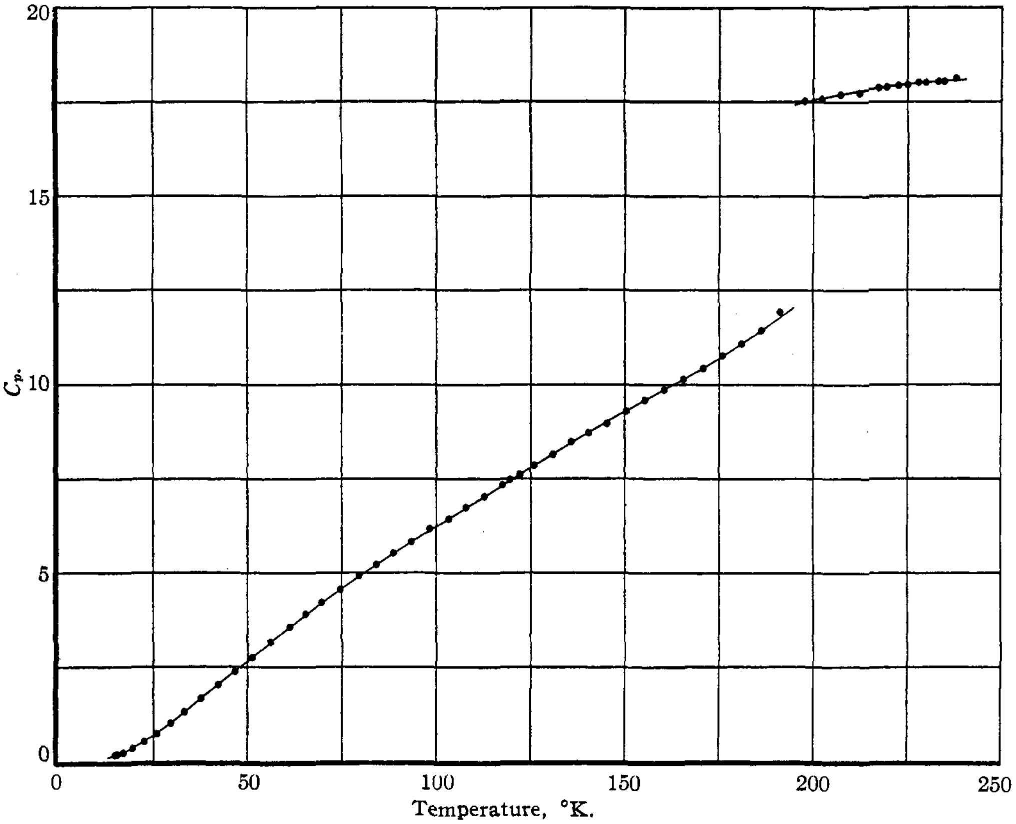

Fig. 1.—Heat capacity in calories per degree per mole of ammonia.

TABLE VII

HEAT OF VAPORIZATION OF AMMONIA

Boiling point 239.68°K. 0°C. = 273.10°K. Molecular weight 17.031

Amount evaporated, mole	Total of energy input, min.	ΔH at 760 mm. cal./mole
0.32400	100	5586
.39086	120	5590
.39197	120	5570
.36888	100	5581
.33913	100	5573
.38839	110	5589
.37590	100	5575
	Mean	5581
Osborne and Van Dusen		5573
From vapor pressure equation 2, assuming a Berthelot gas		5614

Measurement of Amount of Ammonia.—All amounts were measured gravimetrically. The gas vaporized during the heat of vaporization runs was absorbed in 6 N sulfuric acid and weighed. The absorption bulbs were of 110-cc. capacity. All necessary precautions were taken to avoid loss of moisture from the bulb to the outside or the gain of moisture in the bulb from the outside. Following the heat of vaporization runs, the remainder was absorbed in a large absorption bulb (800 cc.) containing 6 N sulfuric acid and weighed. The small amount of gas remaining in the apparatus was calculated from the pressure and volume.

The Entropy from Calorimetric Data.—The entropy was calculated by graphical integration of $\int_0^T C_p \, d \ln T$ plus the entropies of fusion and vaporization. The entropy correction for gas imperfection was made using Berthelot's equation of state and the thermodynamic equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{from which}$$

$$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$$

$$T_c = 406.0\text{°K.}^{15} \text{ and } P_c = 112.3 \text{ atmospheres}^{15}$$

Then $\Delta S = 0.07$ e. u. at the boiling point of ammonia. The entropy calculation is summarized in Table VIII.

The Entropy of Ammonia from Spectroscopic Data.—The translational entropy of ammonia was obtained from the Sackur–Tetrode equation

$$S_T = 3/2R \ln M + 5/2\, R \ln T - R \ln P + 5/2\, R + R \ln (2\pi k)^{3/2}/h^3N^{5/2} + R \ln R \quad (3)$$

$$= 3/2R \ln M + 5/2\, R \ln T - R \ln P + 4.967 - 16.024 + 8.757 \quad (4)$$

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(15) Çardoso and Giltay, *Arch. sci. phys. nat. Geneve*, **34**, 20 (1912)

TABLE VIII

CALCULATION OF THE ENTROPY OF AMMONIA

0–15°K., Debye function $hc\nu/k$ = 210	0.056
15–195.36°K., Graphical	10.16
Fusion 1351.6/195.36	6.919
195.36–239.68°K., Graphical	3.646
Vaporization 5581/239.68	23.29
Entropy of actual gas at boiling point	44.06 ± 0.10 cal./deg. per mole
Correction for gas imperfection	0.07
Entropy of ideal gas at boiling point	44.13

$R = 1.9869$ cal./deg. per mole. The values of all natural constants are those given in the "I. C. T."[6] The remaining entropy was evaluated by means of the equation

$$S = R \ln Q + RT \, \mathrm{d} \ln Q/\mathrm{d}T \qquad (5)$$

where $Q = pe^{-\epsilon/kT}$ summed over all states. p is the *a priori* probability and ϵ the energy of the state. For the rotational entropy the approximation

$$Q_R = \frac{1}{\sigma} \times \frac{8\pi^2}{h^3} \times (2\pi kT)^{3/2} \, (I_1I_2I_3)^{1/2} \qquad (6)$$

was used, where σ is the symmetry number and I_1, I_2 and I_3 are the principal moments of inertia. Therefore

$$S_R = R/2 \ln I_1I_2I_3 + 3/2 \, R \ln T + R \ln \frac{8\pi^2}{h^3} \cdot (2\pi k)^{3/2} + 3/2R - R \ln \sigma \qquad (7)$$

$$= R/2 \ln I_1I_2I_3 + 3/2 \, R \ln T - R \ln \sigma + 267.65 \qquad (8)$$

The moments of inertia have been taken from the observations of Wright and Randall[16] on the pure rotation spectrum of ammonia. Since the molecule is a symmetrical top

$$I_1 = I_2 = 2.782 \times 10^{-40} \text{ g. cm.}^2$$
$$I_3 = 4.33 \times 10^{-40} \text{ g. cm.}$$

The vibrational entropy was calculated by means of equation 5. Ammonia has four normal vibrational frequencies. ν_2 and ν_4 have double *a priori* weights. ν_1 and ν_3 are single. $\nu_1 = 3335$ cm.$^{-1}$ [17] $\nu_3 = 948$ cm.$^{-1}$ [18] $\nu_4 = 1631$ cm.$^{-1}$ [17] ν_2 has never been observed spectroscopically. However, since it is known to be the largest frequency and does not contribute to the entropy below 298.1°K., an estimate of Howard[19] $\nu_2 = 3450$ cm.$^{-1}$ was assumed.

From the above equations and data the entropy of the ideal gas at the boiling point was calculated to be 44.10 cal./deg. per mole. The contribution due to vibration was only 0.05 cal./deg. per mole. The value at 298.1°K. was found to be 45.91 cal./deg. per mole. These values are compared with the experimental results in Table IX.

In making the above calculations the nuclear spin entropy has been ignored. Since the hydrogen atom has a spin of $^1/_2$ and nitrogen a spin of 1 unit, the amount $R \ln 24 = 6.31$ cal./deg. per mole must be added to obtain the absolute entropy which has been included in Table IX for the sake of completeness. The values which do not include the nuclear spin contribution are the ones which should be used in ordinary thermodynamic calculations or compared with experimental values obtained from the ordinary application of the third law of thermodynamics.

TABLE IX

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPY VALUES OF AMMONIA

	Cal./mole/deg.			
	Spectroscopic		Experimental	
T, °K.	Absolute	Less nuclear spin entropy	Actual	Corrected to ideal state
239.68	50.41	44.10	44.06	44.13
298.1	52.22	45.91	...	45.94

As may be seen from Table IX the value obtained from the third law of thermodynamics is in excellent agreement with that obtained with the assistance of spectroscopic data.

Lewis and Randall[20] have given an equation for the free energy change in the reaction

$$1/2 \, N_2 + 3/2 \, H_2 = NH_3(g)$$

By means of this equation and the known entropies of nitrogen, N_2, $S_{298.1} = 45.79$[21] and hydrogen, H_2, $S_{298.1} = 31.23$[22] a value of 46.0 cal./deg. per mole is obtained for the entropy of ammonia at 298.1°K. This value is in excellent agreement with the experimental value 45.94 cal./deg. per mole.

We thank Dr. C. C. Stephenson for assisting with the measurements and many of the calculations.

Summary

The heat capacity of solid and liquid ammonia has been determined over their respective ranges from 15°K. to the boiling point. The melting and boiling points were found to be 195.36 and 239.68°K., respectively.

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[16] Wright and Randall, *Phys. Rev.*, **44**, 391 (1933).

[17] Shaefer and Matossi, "Das ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 250.

[18] Barker, personal communication to Wright and Randall.

[19] Howard, *J. Chem. Phys.*, **3**, 207 (1935).

[20] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 557.

[21] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

[22] Giauque, *ibid.*, **52**, 4816 (1930).

The heat of fusion is 1351.6 cal./mole. The heat of vaporization at the boiling point is 5581 cal./mole.

The vapor pressure of solid and liquid ammonia has been measured and the data have been represented by the equations: solid ammonia 176.92 to 195.36°K. $\log_{10} P$ (int. cm. Hg) $= 1630.700/T + 9.00593$; liquid ammonia 199.26 to 241.59°K. $\log_{10} P$ (int. cm. Hg) $= -1612.500/T - 0.012311\,T + 0.0000125217T^2 + 10.83997$.

The molal entropy of the gas at the boiling point has been calculated by means of the third law of thermodynamics and the experimental data. The value found, 44.13 ± 10 e, u., is in excellent agreement with the value 44.10 e, u. calculated from spectroscopic data.

From band spectrum data the entropy of ammonia at 298.1°K. and 1 atmosphere was calculated to be 45.91 cal./deg. per mole.

The above entropy value, which should be used in ordinary thermodynamic calculations, does not include the nuclear spin entropy. The absolute entropy is 52.22 cal./deg. per mole.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Relative Atomic Weight of Oxygen from Air and Water Determined by an Interchange Reaction

BY THOMAS O. JONES AND NORRIS F. HALL

An important difference in the composition of oxygen from the air and from water has been brought to light recently both in America and in Japan,[1] and this has been confirmed subsequently[2] by others. Various somewhat questionable assumptions and methods incident to the earlier papers have been discussed by Smith and Matheson,[2] but there seems little doubt of the reality of the difference, which readily accounts for certain otherwise unexplained results of workers other than the discoverers.[3] All of the results referred to above were obtained by burning elementary hydrogen with different sorts of oxygen, and electrolytic methods were generally employed to produce one or both of the gases.

We have now demonstrated this important effect by a method which involves neither electrolysis nor combustion, and which may prove practical for the preparation of large quantities of water abnormal as to its O^{18} content. The equilibrium between water and oxygen

$$2H_2O^{16} + O_2^{18} = 2H_2O^{18} + O_2^{16}$$

if established at low temperatures would, according to Dole,[1a] account for the observed difference. On the other hand, it is found, using the methods outlined by Urey and Greiff,[4] that at *high* temperatures the constant of this reaction closely approaches unity (at 1000°A., K is 1.0038, at 1500°A., K is 1.0002, at 2500°A., K is 1.0004), and that the departure of oxygen from a perfectly random atomic distribution in the three molecular forms is negligible in this temperature range.

Consequently, at 1500°A., for example, the O^{18}/O^{16} ratio of a sample of water in equilibrium with a large excess of air should be *the same* as in the air within 0.1 γ (water density at 25°) and within 0.09 γ at 2000°A. These differences are less than the probable error of the density determination. If then a sample of ordinary water were vaporized, heated with excess air and recondensed, its density should measurably increase, provided (a) air oxygen is really heavier and (b) there is an approach to equilibrium. The D/H ratio should remain unaffected.

Assuming that 7 γ is the correct value of the Dole effect for surface water, the equilibrium density increases to be expected are roughly

TABLE I

T, °A.	γ	Ref.
223	1.2	1a
273	4.8	1a
293	5.7	1a
373	6	2b
575	6.7	2b
1500	6.9	This paper
2000	6.91	

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[1] (a) Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Chem. Phys.*, **4**, 268, 1936 (6 γ); (b) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36, 414 (1936) (7 γ).

[2] (a) Greene and Voskuyl, THIS JOURNAL, **58**, 693 (1936) (6 γ); (b) Hall and Johnston, *ibid.*, **58**, 1920 (1936) (6.6 γ); (c) Smith and Matheson, *Bur. Standards J. Research*, **17**, 625 (1936) (8.6 γ).

[3] (a) Hall and Jones, THIS JOURNAL, **58**, 1915 (1936) and the present paper; (b) Dole[1] and THIS JOURNAL, **58**, 580 (1936); (c) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 419 (1936).

[4] Urey and Greiff, THIS JOURNAL, **57**, 321 (1935).