molecules involved, in which the individual molecules cannot rotate. It is shown that the calculated rates for the reactions of nitric oxide with oxygen, chlorine and bromine agree excellently with experiment, whereas previous theories have been in error by a factor of 10^9. It is shown that the negative temperature dependence of the nitric oxide–oxygen reaction is a natural consequence of the theory. Our calculations indicate that the $2NO + H_2$ reaction may be more complicated than has been supposed.

PRINCETON, N. J. RECEIVED MARCH 23, 1935

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

The Heat Capacity and Vapor Pressure of Solid and Liquid Nitrous Oxide. The Entropy from its Band Spectrum

BY R. W. BLUE[1] AND W. F. GIAUQUE

In recent years a series of low temperature calorimetric investigations on the entropies of diatomic gases has been reported from this Laboratory. The entropy values calculated by use of the third law of thermodynamics have been compared in each case with very accurate values obtained by calculations based on band spectra data.

Some six years ago, when the interpretation of band spectra reached a stage in its development that permitted accurate and detailed information about the quantum levels of polyatomic molecules, we began an extension of the above work which is expected to include most of the gases boiling below ordinary temperatures. Measurements on several polyatomic substances have been completed. In this paper results on nitrous oxide are presented.

In the case of many diatomic gases the agreement between the third law and spectroscopic values of the entropy has been so excellent as to provide perhaps the best experimental verification of the third law of thermodynamics. However, there are three diatomic gases, hydrogen, nitric oxide, carbon monoxide, in which $\int_0^T C_p \mathrm{d} \ln T$ obtained from the measurements gives less than the known entropy. The deviation in the case of hydrogen has been accurately explained in terms of the lack of equilibrium between the ortho and para states. Johnston and Giauque[2] offered the explanation that the discrepancy of about $^1/_2R \ln 2$ in the case of nitric oxide was due to two forms of the polymer N_2O_2 in the solid state. The difference in the polymer was assumed to arise from a residual effect of the λ doublets known from both theory and experiment to exist in NO molecules. Later Clayton and Giauque[3] proved that a discrepancy of about $R \ln 2 = 1.377$ occurred in the case of carbon monoxide. They offered the explanation that this molecule, structurally resembling nitrogen, has ends so nearly alike that the crystal lattice fails to discriminate at high temperatures. At very low temperatures slow rate prevents the readjustment to an ordered arrangement which characterizes the state of zero entropy. They called attention to the fact that this is a general characteristic of molecules with two or more isotopic atoms occupying otherwise equivalent positions. They predicted that it would occur in cases of low polarity when somewhat similar atoms, or groups of atoms, occupied two or more molecular positions without producing great dissymmetry.

This explanation would serve equally well in the case of the nitric oxide polymer and is preferable to that offered by Johnston and Giauque.

The problem of understanding the circumstances through which lack of equilibrium sometimes invalidates the practical application of the third law is of considerable importance. The treatment of the lack of equilibrium in hydrogen,[4a,b] the zero point entropy of which was first correctly calculated by Giauque and Johnston, is an excellent example of what may be done when the statistical situation is understood. Moreover, we believe that methods can be developed for detecting and quantitatively correcting many such cases.

With this in mind we have studied the case of nitrous oxide, the structure of which was unknown at the beginning of this investigation, but which

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[1] Shell Research Fellow, Academic year 1931–1932.

[2] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[3] Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

[4] (a) Giauque and Johnston, *ibid.*, **50**, 3221 (1928); (b) Giauque, *ibid.*, **52**, 4816 (1930).

has since been determined from its band spectrum by Plyler and Barker.[5] They show that this molecule is linear with the atomic arrangement NNO. The status of the practical application of the third law to this substance is shown by the fact that we could not predict in advance whether it would or would not act like CO and NO with respect to lack of orientation equilibrium. Lack of crystal discrimination between the ends of NNO would lead to a discrepancy of -1.377 in the measured entropy. Since the completion of these measurements, some three years ago, Clusius[6] has published the results of a similar investigation in which he finds a discrepancy of 1.09 ± 0.2 E. U. Clusius believes that this molecule belongs to the classification suggested by Clayton and Giauque.

The investigation presented in this paper shows that the measured entropy is 1.14 ± 0.1 E. U. less than the value obtained from its band spectrum. This may be compared with the theoretical value of 1.377 based on complete lack of discrimination between the ends of the molecule.

Some Comments on Accuracy Requirements.—It may be well to point out that in making trustworthy decisions on questions where such amounts of entropy as $R \ln 2$ or $^1/_2R \ln 2$ are involved, calorimetric data with an accuracy of a few tenths of a per cent. should be obtained. The total amount of entropy is usually of the order of magnitude of 50 E. U. Thus a result based on calorimetric data which may be in error by several per cent. cannot be accepted as proving a discrepancy of about an entropy unit. That a probable error calculation is not justifiable is shown by the existence of a great many cases of fair internal consistency in inaccurate low temperature heat capacity measurements. Such amounts of entropy as $R \ln 2$, etc., have long had sound theoretical implications of several kinds. It is therefore unfortunate that many cases occur in the literature where such differences have been reported and do not exist, where correct agreement has been found but not proved by fortuitous cancellation of large errors and where entropy values have agreed in contradiction to fact. The series of investigations of the entropies of gases in this Laboratory was started with the realization of the importance of ± 0.1 E. U. and it is believed that this accuracy has been attained in all cases.

Nitrous Oxide.—Nitrous oxide containing no impurities not readily removed by fractionation is manufactured commercially for anesthetic purposes. A cylinder of commercial nitrous oxide was connected to a vacuum-tight fractionating system and the gas was passed over phosphorus pentoxide before being collected in a distilling bulb; 250 cc. of solid nitrous oxide was condensed by means of liquid air and the system was then evacuated to 10^{-5} mm. The nitrous oxide was then liquefied and distilled through a vacuum-jacketed fractionating column. A large end fraction was discarded. The material was then sublimed into another distilling bulb, the initial and final portions being discarded. It was again cooled to the temperature of liquid air and evacuated to 10^{-5} mm. The impurity was estimated to be not more than one part in one hundred thousand on a molal basis. This estimate was obtained from the heat capacity results given below. It was calculated on the assumption that the slight rise in heat capacity below the melting point was due to premelting.

Apparatus.—The measurements were carried out in the apparatus which has been described[7] previously as gold calorimeter II. However, the apparatus was rebuilt and a new protective lead and copper cylinder of greater heat capacity was installed to stabilize further the temperature of the calorimetric surroundings. The built-in hydrogen liquefier was eliminated from the new apparatus. Liquid hydrogen was prepared in the laboratory liquefier and transferred into the calorimetric apparatus when needed. The apparatus for volumetric measurement of the amount of gas used has been described by Giauque and Johnston,[8] who also gave a detailed discussion of the accuracy of calorimetric measurement at various temperatures. The value of the entropy obtained from the measurements should be reliable to within two-tenths of one per cent. The temperatures were measured and heat introduced by means of a gold resistance thermometer-heater. The resistance thermometer was calibrated during measurements by means of copper-constantan thermocouple "W" which had been compared with a hydrogen gas thermometer.[9a,b] The thermocouple was soldered to the bottom of the calorimeter. It has been compared frequently with the oxygen and hydrogen vapor pressure thermometers by previous workers in this Laboratory. Following its installation in the rebuilt apparatus it was again checked against the vapor pressure of oxygen with a maximum deviation of 0.03°, which is within the limit of error of the original calibration.

The Vapor Pressure of Nitrous Oxide.—The apparatus is arranged so that a manometer can be connected with the calorimeter for measurements of vapor pressure. This arrangement for measuring vapor pressure has the advantage that the considerable amount of material in the calorimeter automatically thermostats itself at fixed points such as the melting point. This cannot be done very satisfactorily in the type of apparatus in which the temperature is held constant by a bath, or, for example, by a metal block of considerable heat capacity.

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(5) Plyler and Barker, *Phys. Rev.*, **38**, 1827 (1931).

(6) Clusius, *Z. Elektrochem.*, **40**, 99 (1934).

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

(8) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

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

The vapor pressure measurements were made by using a cathetometer as a comparison instrument in connection with a standard meter mounted in the manometer case. The observations have been represented by the following equations: for solid nitrous oxide from 148.48°K. to the melting point 182.26°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -(1286/T) + 9.13061 - 0.0014038\,T \quad (1)$$

For liquid nitrous oxide from 182.26 to 185.85°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -(893.56/T) + 6.72158 \quad (2)$$

The observed and calculated values are given in Table I. All the pressure observations are corrected to international centimeters of mercury by means of data given in the "I. C. T."[10] 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.[11] The temperatures are given to 0.001° only because of the high relative accuracy. The absolute values may be in error by several hundredths of a degree.

TABLE I

VAPOR PRESSURES OF NITROUS OXIDE

(Boiling Point 184.59°K.)

T, °K.	P obs., int. cm. Hg	$P_{\text{calcd.}}$	$T_{\text{meas.}} - T_{\text{calcd.}}$
148.476	1.821	1.823	+0.008 Solid
151.903	2.831	2.828	− .009 Solid
155.478	4.375	4.376	+ .002 Solid
159.268	6.802	6.801	− .001 Solid
163.279	10.536	10.543	+ .006 Solid
167.529	16.560	16.565	+ .003 Solid
172.317	26.655	26.652	− .001 Solid
177.218	42.195	42.193	− .001 Solid
182.258	65.895	65.896	+ .000 Triple point
182.889	68.579	68.568	− .003 Liquid
183.802	72.453	72.450	− .001 Liquid
184.738	76.647	76.680	+ .007 Liquid
185.848	81.892	81.952	− .006 Liquid

The vapor pressure values given in the third column of Table I were calculated by assuming that the temperature observations were correct. The calculated temperatures of column four assumed that the pressures were correct.

Table II contains a summary of the observations on the melting point temperature. Two series of measurements were taken about a week apart. Series I extended over a period of 10 hours, Series II over a period of 18 hours. The per cent. of the material which had been melted at the time of each observation is given.

TABLE II

MELTING POINT OF NITROUS OXIDE

T, °K. resistance thermometer	T, °K. thermocouple	Percentage melted	Remarks
182.257	182.26	0.3	Series I
182.260	182.27	3	I
182.261	182.27	6	I
182.260	182.28	20	I
182.267	182.28	80	I
182.260	182.26	0.5	Series II
182.258	182.25	5	II
182.261	182.25	20	II
182.265	182.26	50	II
182.268	182.26	80	II
	182.26 Accepted value		

Table III contains a summary of measurements of the melting and boiling points for nitrous oxide.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF NITROUS OXIDE

Melting point, °K.	Boiling point, °K.	Observer
173	....	Faraday[12] (1845)
158	....	Natterer[13] (1845)
...	183.4	Regnault[14] (1862)
...	181	Wills[15] (1874)
171	183.3	Ramsay and Shields[16] (1893)
...	183.7	Grunmach[17] (1904)
...	186	Hunter[18] (1905)
167	183.3	Guye and Drouginine[19] (1910)
182.5	184.4	Burrell and Robertson[20] (1915)
...	183.6	Bergstrom[21] (1922)
182.4	....	Clusius, Hiller and Vaughen[22] (1930)
182.26	184.59	This research

Measurement of Amount of Nitrous Oxide.— The amount of nitrous oxide used in the calorimetric measurements was measured volumetrically in a bulb of about 5 liters capacity. It was thermostated at 25.00°. The apparatus and procedures have been described previously.[8] The amount of material was measured both before and after the calorimetric observations. The two determinations checked to 0.01%. The constants used in the volumetric measurements are as follows:[10]

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(10) "International Critical Tables," McGraw-Hill Book Co., New York, 1926.

(11) Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-Chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

(12) Faraday, *Phil. Trans.*, **135**, 155 (1845).

(13) Natterer, *Ann.*, **54**, 254 (1845).

(14) Regnault, *Mem. Acad.*, **26**, 535 (1862).

(15) Wills, *J. Chem. Soc.*, **27**, 21 (1874).

(16) Ramsay and Shields, *ibid.*, **63**, 833 (1893).

(17) Grunmach, *Ann. Physik*, **15**, 401 (1904).

(18) Hunter, *Z. physik. Chem.*, **53**, 441 (1905).

(19) Guye and Drouginine, *J. chim. phys.*, **8**, 473 (1910).

(20) Burrell and Robertson, THIS JOURNAL, **37**, 2692 (1915).

(21) Bergstrom, *J. Phys. Chem.*, **26**, 876 (1922).

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

d_s (0° C., 1 A_n) = 1.9778 g./liter.
$1 + \lambda$ = 1.0074 = coefficient of deviation from Boyle's law at one atmosphere.
α = 0.00375 = coefficient of thermal expansion at 12.5°.
Molecular weight = 44.016.

The Heat Capacity of Nitrous Oxide.—The heat capacity results are given in Table IV. In calculating energy, 1.00042 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie (15°).

Heat capacity values picked from a smooth curve are given in Table V. The results are compared with those of Eucken and Hauck[23] and of Clusius, Hiller and Vaughen.[22]

In each case the above authors have given values taken at ten degree intervals from smooth curves through their data. The deviations from the present results are given in per cent.

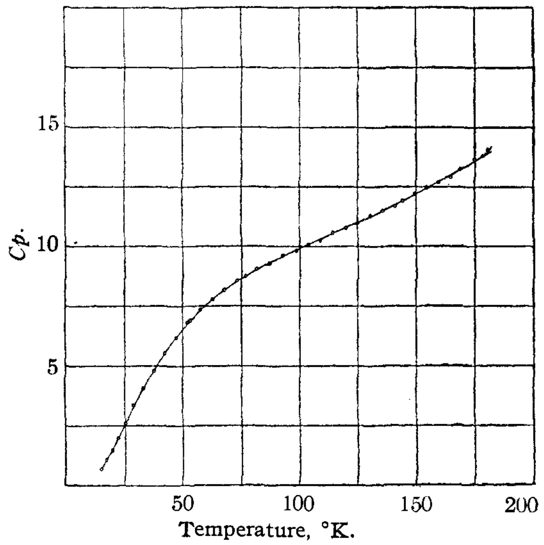

Fig. 1.—Heat capacity in calories per degree per mole of nitrous oxide.

TABLE IV

HEAT CAPACITY OF NITROUS OXIDE

(Molecular weight, 44.016)

Series I, 2.915 moles; II, 2.959; III, 2.891; IV, 2.886

T, °K.	ΔT	C_p cal./deg./mole	Series
15.17	2.462	0.692	III
17.59	2.360	1.070	III
19.95	2.248	1.480	III
22.62	3.083	1.997	III
25.81	3.220	2.602	III
29.34	3.785	3.335	III
33.38	4.258	4.059	III
37.83	4.550	4.785	III
42.61	4.448	5.529	III
47.22	4.591	6.165	III
52.02	4.965	6.827	III
53.31	3.575	6.910	III
57.35	4.870	7.35	III
63.03	4.667	7.78	III
68.05	5.244	8.17	III
73.54	5.736	8.55	III
76.67	4.627	8.74	III
81.57	5.165	9.03	III
87.06	5.651	9.29	III
92.69	5.592	9.59	III
98.34	5.583	9.83	III
103.75	5.094	10.08	III
109.12	5.491	10.24	III
114.65	5.460	10.57	III
120.29	4.633	10.78	III
125.22	4.943	11.00	III
130.44	5.155	11.31	III
135.84	5.359	11.50	III
141.07	4.661	11.69	III
144.57	4.723	11.92	I
149.60	5.013	12.21	I
154.71	4.799	12.47	I
159.66	4.737	12.69	I
164.82	5.095	12.91	I
169.10	4.805	13.26	I
174.90	4.500	13.62	I
178.50	2.119	13.81	I
180.75	2.005	14.06	I
182.26	Melting point		
183.55	1.937	18.57	IV
183.71	1.631	18.51	II
184.59	Boiling point		
185.40	1.583	18.60	II
185.59	1.884	18.57	IV
187.13	1.557	18.58	II

The data are shown in Fig. 1.

TABLE V

HEAT CAPACITY OF NITROUS OXIDE

(Molecular weight, 44.016)

Values taken from smooth curve through observations

T, °K.	C_p cal./deg./mole	Deviation C. H. and V. − B. and G., %	Deviation E. and H. − B. and G., %
20	1.51	−0.7	
30	3.46	.9	
40	5.13	2.9	
50	6.52	2.0	
60	7.56	1.2	
70	8.32	0.8	
80	8.95	− .1	
90	9.44	− .5	0.1
100	9.90	− .7	.8
110	10.32	− .4	1.3
120	10.77	.2	1.7
130	11.25	.4	0.9
140	11.72	.9	− .2
150	12.19	1.4	− .1
160	12.71	1.9	.5
170	13.30	2.3	1.9
180	13.98	2.1	
185	18.57		

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(23) Eucken and Hauck, *Z. physik. Chem.*, **134**, 161 (1928).

Heat of Fusion.—The heat of fusion of nitrous oxide was measured in the usual manner. Starting somewhat below the melting point heat was added until all of the material was melted and the liquid heated somewhat above the melting point. Correction was then made for the $\int C_p \mathrm{d}T$ and the small premelting effect.

TABLE VI

HEAT OF FUSION OF NITROUS OXIDE

(Molecular weight, 44.016)

Temperature interval	Corrected heat input/mole	$\int C_p \mathrm{d}T$	ΔH cal./mole	Mean
181.825–185.588	1630.7	67.2	1563.5	1563.0 ± 0.5
181.814–185.524	1629.4	66.9	1562.5	

Heat of Vaporization.—The heat of vaporization was measured by adding energy and accepting the gas evolved in the measuring bulb. The pressure was maintained constant to about a millimeter of mercury by an automatic regulator. A summary of the data is given in Table VII.

TABLE VII

HEAT OF VAPORIZATION OF NITROUS OXIDE

Boiling point, 184.59°K.; Molecular weight, 44.016

Amount evaporated, mole	Time of energy input, minutes	ΔH at 760 cal./mole
0.17882	50	3954
.21654	60	3956
.21428	60	3956
.19030	54	3964
.21366	60	3958
	Mean	3958 ± 3 cal.
From vapor pressure equation, assuming a Berthelot gas		3972

It is of interest to calculate the heat of vaporization from the vapor pressure data. This has been done by assuming that Berthelot's equation of state can be used for correcting for gas imperfection. The resulting value is 3972 cal./mole. This includes a Berthelot correction of −116 cal. to the value calculated by assuming an ideal gas. For this reason we can, as usual, give no weight to the vapor pressure value in connection with the entropy determination. However, the agreement of the two values may be used to justify Berthelot's equation which will be used to make a small entropy correction for the actual to the ideal gas states. It is also of interest to compare our calorimetric measurements with the work of Eucken and Donath.[24] They measured directly the heat of condensation of nitrous oxide gas to the solid at the temperatures 136.9 and 159.4°K. In Table VIII results and details of our calculation are summarized. The change in heat content of the gas was calculated from spectroscopic constants given later in this paper. Berthelot's equation of state and the thermodynamic equation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

were used in calculating heat content change due to gas imperfection.

TABLE VIII

CALCULATED HEAT OF SUBLIMATION OF NITROUS OXIDE

	Heat of sublimation	
	$T =$ 136.9°K.	$T =$ 159.4°K.
$\int_{T(\text{sublimation})}^{182.26} C_{p(\text{solid})}\, \mathrm{d}T$	578	305
ΔH_{Fusion}	1563	1563
$\int_{182.26}^{184.59} C_{p(\text{liquid})}\, \mathrm{d}T$	43	43
$\Delta H_{\text{vaporization}}$	3958	3958
$\int_{P=1}^{P=0} \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P$ (Berthelot gas)	+32	+32
$H_{T\,\text{sub.}} - H_{184.59°\text{K}}$ (Spectroscopic)	−365	−195
$\int_{P=0}^{P(\text{sublimation})} \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P$ (Berthelot gas)	−0	−4
	5809	5702 cal./mole
Measurements of Eucken and Donath	5815	5698

The agreement between the work of Eucken and Donath[24] and the present research is remarkably good. It may also be mentioned that the work of Giauque and Wiebe[7] on hydrogen chloride was in similar good agreement with condensation measurements of Eucken and Donath on this substance. It may be noted that the calculation, by Clusius, of the entropy of nitrous oxide was based to the extent of about 75 per cent. on the above work of Eucken and Donath.

The Entropy from Calorimetric Data.—The entropy was calculated in the usual way by graphical integration of $\int_0^T C_p \,\mathrm{d}\ln T$ plus the entropies of fusion and vaporization. The calculation is summarized in Table IX. The entropy correction for gas imperfection was made by using Berthelot's equation of state and thermodynamics[7]

$$\Delta S = 27RT_c^3P/32\,T^3P_c \qquad (3)$$

T_c = 334.6°K. and P_c = 71.7 atmospheres[1d]

$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 0.11$ E. U. at the boiling point

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(24) Eucken and Donath, *Z. physik. Chem.*, **124**, 181 (1926).

TABLE IX

CALCULATION OF ENTROPY OF NITROUS OXIDE

0–14°K., Debye function $hc\nu/k$ = 127	0.214
14–182.26°K., graphical	16.792
Fusion 1563.0/182.26	8.576
182.26–184.59°K., graphical	0.223
Vaporization 3958/184.59	21.442
Entropy of actual gas at boiling point	47.25 ± 0.10 E. U.
Correction for gas imperfection	0.11
Entropy of ideal gas at boiling point	47.36

The above experimental result may be compared with an accurate value for the entropy obtained from band spectra data and the familiar equations

$$S_{\text{Trans.}} = 3/2\, R \ln M + 5/2\, R \ln T - R \ln P - 2.300 \quad (4)$$

$$S_{\text{Rot.}} = R \ln IT + 177.676 \quad (5)$$

$$S_{\text{Vib.}} = R \sum_{v_1,\, v_2,\, v_3} \left[\frac{x}{1 - e^x} - \ln\, (e^x - 1) \right] \quad (6)$$

where $x = hc\nu/kT$ and the vibration designated as v_2 has a weight of two in summing the three types of vibration.

Plyler and Barker[5,25] give for the moment of inertia of nitrous oxide $I = 66.0 \times 10^{-40}$ g. cm.^{2}. Their work proves that the molecule is linear and NNO. They summarize the vibrational energy levels in the equation

$$S_{\text{Vib.}} = 1288.7v_1 + 588.3v_2 + 2237.9v_3 - 3.3v_1^2 - 2.2v_2^2 + 3.0l^2 - 13.8v_3^2 - 10v_1v_2 - 26.7v_1v_3 - 13.5v_2v_3 \text{ cm.}^{-1} \quad (7)$$

In this equation, which is of a type proposed by Dennison,[26] values of l depend on v_2. The possible values are, l equal to v_2 or less than v_2 by all possible even integers, excluding negative values. Thus $v_2 = 0, l = 0$; $v_2 = 1, l = 1$; $v_2 = 2, l = 2$ or 0. The *a priori* probability is $p = 2$ for every value of l other than zero, in which case $p = 1$. Since we shall confine our calculations to ordinary temperatures or lower, it will be sufficiently accurate to ignore the anharmonic terms. With this approximation in the above equation we take $v_1 = 1285.4$, $v_2 = 589.1$ (double weight), and $v_3 = 2224.1$ cm.$^{-1}$ and find the entropy at the boiling point 184.59°K., less the amount due to the nuclear spin of nitrogen to be 48.501 cal./deg./mole. At 298.1 the corresponding value is 52.581 E. U. This value, which is the one to be used in ordinary calculations based on the third law of thermodynamics, is less than the absolute entropy by $R \ln 9$ due to the nuclear spin of the two nitrogen atoms. The absolute entropies are 52.867 and 56.947 E. U. at 184.59 and 298.1°K., respectively.

The entropy at 298.1° has been calculated previously by Rodebush,[27] by Badger and Woo,[28] and by Kassel.[29] Our value agrees closely with those of the above authors except that of Rodebush, which is about 0.2 E. U. low due to the use of an erroneous moment of inertia originally given by Plyler and Barker[5] and corrected at a later date. We have used their revised[25] vibrational constants which differ slightly from those used by Kassel, who also calculated $(F^\circ - E_0^\circ)/T$, H and C_p to 1500°K. However, the difference is probably within the limit of error of Equation 7.

In Table X the experimental and spectroscopic values have been compared. The experimental value given for 298.1°K. has been obtained by using the spectroscopic data for the gas above the boiling point.

TABLE X

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPIES OF NITROUS OXIDE

	Spectroscopic		Experimental	
T, °K.	Absolute	Less nuclear spin entropy	Actual gas	Corrected to ideal state
184.59	52.867	48.501	47.25 ± 0.1	47.36 E. U.
298.1	56.947	52.581	....	51.44

Since the extrapolation of the heat capacity measurements at low temperatures did not include recognition of nuclear spin effects, comparison should be made between the values in columns three and five of Table X. It may be seen that the experimental value is 1.14 E. U. too low. This result indicates that the NNO molecules remain in the solid state at low temperatures with lack of discrimination between the nitrogen and oxygen ends. As mentioned above, the largest discrepancy based on our explanation would be $R \ln 2 = 1.377$ E. U.

The fact that the discrepancy is 0.24 = (1.377 − 1.14) E. U. less than the maximum amount indicates that some approach to orderly arrangement in the crystal has been made.

It may be well to remark once more that experimental discrepancies of the type discussed here do not weaken our confidence in the truth of the third law of thermodynamics. This law requires that equilibrium be maintained for all processes necessary to the attainment of the perfect crystalline state. When a discrepancy of the calculated amount is found it not only substantiates the above reasoning but supports the truth of the third law of thermodynamics.

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(25) Barker, *Phys. Rev.*, **41**, 369 (1932).

(26) Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).

(27) Rodebush, *Phys. Rev.*, **40**, 113 (1932).

(28) Badger and Woo, THIS JOURNAL, **54**, 3523 (1932).

(29) Kassel, *ibid.*, **56**, 1838 (1934).

We wish to thank Mr. Roy Overstreet for assistance with the experimental work.

Summary

The heat capacity of solid and liquid nitrous oxide has been determined over their respective ranges from 14°K. to the boiling point. The melting and boiling points were found to be 182.26 and 184.59°K., respectively.

The heat of fusion is 1563 cal./mole. The heat of vaporization at the boiling point is 3958 cal./mole.

The vapor pressure of solid and liquid nitrous oxide has been measured. The data have been represented by the equations: solid nitrous oxide 148.48 to 182.26°K., $\log_{10} P$ (int. cm. Hg) $= -(1286/T) + 9.13061 - 0.0014038T$; liquid nitrous oxide 182.26 to 185.85°K., $\log_{10} P$ (int. cm. Hg) $= -(893.56/T) + 6.72158$. The experimental data have been used to calculate the molal entropy of the gas at the boiling point. The value found, 47.36 ± 0.1 E. U., is 1.14 entropy units less than the value 48.501 E. U., calculated from spectroscopic data.

This difference is in good agreement with a similar discrepancy found by Clusius. The result indicates that NNO enters its crystal lattice without much discrimination between its ends. The similar case of carbon monoxide led Clayton and Giauque to predict that this situation was to be expected with molecules of low polarity and rather similar ends. The maximum discrepancy for two interchangeable atoms or groups is $R \ln 2 = 1.377$ E. U. The molal entropy of nitrous oxide at 298.1°K. and one atmosphere was found to be 52.581 E. U. (without nuclear spin entropy); the absolute entropy is 56.947 E. U. Each of the above values is based on band spectra data.

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Ammines of Thorium Bromide

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In a study of some reactions of thorium bromide it was noted that the halide combined with a relatively large amount of ammonia and further that even at room temperature the pressure of ammonia above a solid which had an approximate composition of an octammine was only a few millimeters of mercury. It seemed to be of interest to study the system of thorium bromide and ammonia, at 0° and at 25° up to pressures approximating two atmospheres, and to compare the data with those obtained by Chauvenet for thorium chloride. Chauvenet found[1] the following equilibrium to exist

$$ThCl_4 \cdot 18NH_3 \rightleftharpoons ThCl_4 \cdot 12NH_3 + 6NH_3$$

the decomposition pressure of the higher ammine being 1030.5 mm. at 0.1° and 1630.2 mm. at 8.1°.

The tensimetric method was employed, the apparatus resembling in general that used by Kraus[2] in the study of the vapor pressure of the system calcium and ammonia. It differed, however, in that a ground glass joint was used to connect the bulb containing the thorium bromide to a small glass spiral which led to the manometer and to a calibrated exhaustible tube with a reservoir of mercury by means of which a known amount of ammonia could be removed from the system. The glass spiral allowed the contents of the bulb to be agitated.

The preparation and purification of anhydrous thorium bromide has been previously described.[3] About 11 g. (0.02 mole) was introduced in the bulb, the bottom of which was flat allowing the salt to form a thin layer, and after ammonia had been condensed on the solid, which greatly increased in volume, it was allowed to stand for twenty-four hours. The liquid was then permitted to evaporate, a bath of ethyl chloride being used during the evaporation of the last of the ammonia. During this entire procedure the bulb was attached through the ground glass joint to the rest of the apparatus, a stopcock in which allowed the ammonia to escape. The ethyl chloride was replaced by an ice-bath and ammonia was allowed to issue until the pressure was approximately 1180 mm., a value that preliminary experiments had indicated as being the decomposition pressure

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[1] Chauvenet, *Ann. chim. phys.*, **23**, 275 (1911).

[2] Kraus, THIS JOURNAL, **30**, 661 (1908).

[3] Young, *ibid.*, **56**, 29 (1934).