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# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 69

MAY 17, 1947

NUMBER 5

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

## The Entropy of Nitromethane. Heat Capacity of Solid and Liquid. Vapor Pressure, Heats of Fusion and Vaporization

BY W. M. JONES AND W. F. GIAUQUE

This paper presents the results of a calorimetric investigation of nitromethane extending from 13 to 300°K. The low temperature measurements were made about five years ago following the publication of the spectroscopic observations of Wells and Wilson,<sup>1</sup> but it was not possible to complete the calculations until recently.

**Apparatus and Method.**—The measurements were made in a vacuum calorimeter which has the laboratory designation Gold Calorimeter IV. The calorimeter has been described by Kemp and Giauque,<sup>2</sup> and a more detailed description of a similar calorimeter has been given by Giauque and Egan.<sup>3</sup>

A gold resistance thermometer gave high precision in the temperature measurements. The reference standard for temperature was a copper-constantan thermocouple with the laboratory designation W-21. This thermocouple had been calibrated in terms of a helium gas thermometer through the laboratory standard thermocouple W-22 as an intermediate. The junction of thermocouple W-21 was attached to the calorimeter by means of a platinum well filled with Wood's metal. To make sure that the calibration had not altered with time, the thermocouple was checked at several fixed thermometric points. Hydrogen was condensed to liquid in the calorimeter and later oxygen was similarly liquefied and solidified. At the boiling point of hydrogen, 20.37°K., the thermocouple read 0.01° high. At the upper transition point of oxygen, 43.76°K., the temperature was 0.02° low. At the triple point of oxygen, 54.39°K., the reading was 0.02° high and at the boiling point, 90.13°K., the temperature given

(1) A. J. Wells and E. B. Wilson, Jr., *J. Chem. Phys.*, **9**, 314 (1941).

(2) J. D. Kemp and W. F. Giauque, *THIS JOURNAL*, **59**, 79 (1937).

(3) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

by the thermocouple was 0.02° low. As all of these observations are within the accuracy of measurement, the original calibration was left unaltered. The ice point has been taken to be 273.10°K.

**Preparation of Nitromethane and Measurement of Amount.**—A sample of approximately 500 cc. of nitromethane was supplied through the courtesy of the Commercial Solvents Corporation. In accordance with a suggestion from the Commercial Solvents Corporation, all glassware used in connection with the handling of the nitromethane was cleaned with cleaning solution. This was because there is some basis for suspecting that the alkali in glass may cause slight decomposition of nitromethane. A portion of this sample was distilled into the calorimeter at low pressures and preliminary measurements of the melting point showed the presence of considerable impurity. The material was then dried for twenty-four hours with anhydrous calcium sulfate "Drierite" and distilled at 10 cm. pressure to prevent decomposition. The distillation was made in a column packed with glass helices and equivalent to 25 plates. An intermediate fraction was selected for the measurements.

Measurements of the variation of the melting point with the fraction melted led to an estimate of 0.30 mole per cent. impurity. These measurements will be discussed in detail below in connection with the determination of the melting point. We consider such a large amount of impurity to be quite unsatisfactory and it is much larger than anything that has been considered acceptable in the related series of entropy investigations carried out previously. In the present case, the increasing pressure of war work made it necessary to proceed in haste or give up the work.

The nature of the impurity is unknown, but

there is some question as to whether the material was properly dried. In previous work on other substances used in this series, phosphorus pentoxide has been used for drying even when it has been necessary to carry out the drying by contact at low temperatures to avoid reaction.

The nitromethane was measured in a weighing bottle which could be attached to the apparatus by means of a standard ground glass joint. The weights were corrected to vacuum. The molecular weight was taken as 61.042.

The heat capacities of the solid, the melting point determination, and the determinations of the heat of fusion were made with a sample weighing 144.0830 g. or 2.3604 moles. The sample used for the heat capacities of the liquid, the vapor pressures, and the heats of vaporization contained 141.7546 g. or 2.3222 moles.

**The Heat Capacity of Nitromethane.**—The heat capacity data are given in Table I. The defined calorie, equal to 4.1833 international joules, has been used. Values of the heat capacity read from smooth curves at even values of the temperature are given in Table II. At 15°K., the error may be 5%, and at 20°K., about 1%. Above 35°K., the values recorded in Table II should be correct to 0.2% except for the short region where the premelting caused by impurity is appreciable. The ordinary methods employed in the correction of heat capacities just below the melting point, for the premelting effect, could not be used because it was found that the apparent percentage of impurity calculated on the basis of Raoult's law for an impurity soluble in liquid, but not in solid nitromethane, rose as more nitromethane was melted. Thus, the heat capac-

TABLE I  
HEAT CAPACITY OF NITROMETHANE. OBSERVED VALUES  
0°C. = 273.10°K.

T, °K.	$\Delta T$	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	Series
13.17	0.794	0.698	II
14.25	0.903	0.795	II
15.94	2.231	1.042	II
20.20	6.075	2.119	II
24.07	1.519	3.131	II
26.53	3.328	3.736	II
30.08	3.626	4.615	II
33.84	3.891	5.546	II
37.92	4.137	6.507	II
42.69	5.368	7.372	II
47.72	4.621	8.171	II
52.08	4.098	8.816	II
56.00	3.760	9.342	II
59.98	4.170	9.743	II
64.35	4.574	10.20	II
68.31	2.416	10.53	I
69.12	4.948	10.61	II
72.08	5.060	10.84	I
74.28	5.331	11.04	II
77.53	5.617	11.31	I
79.40	4.930	11.44	II

82.98	5.234	11.62	I
88.51	5.764	12.02	I
94.61	6.254	12.35	I
100.66	5.897	12.62	I
106.51	5.599	12.94	I
112.76	6.890	13.21	I
119.53	6.528	13.51	I
125.86	6.256	13.79	I
131.81	5.945	14.06	I
138.36	6.565	14.39	I
147.85	4.952	14.72	I
153.22	5.730	15.01	I
158.87	5.515	15.26	I
164.31	5.336	15.50	I
169.60	5.162	15.72	I
175.04	5.612	16.01	I
181.05	5.989	16.31	I
187.02	5.797	16.51	I
193.09	6.187	16.80	I
199.27	5.978	17.10	I
203.99	5.794	17.28	I
209.97	5.578	17.69	I
215.80	5.407	18.02	I
221.53	5.732	18.49	I
226.56	4.148	18.95	I
226.85	4.614	18.79	I
230.93	4.421	19.52	I
235.46	4.113	21.03	I
244.73	Melting point		
249.75	4.275	24.99	III
254.22	4.218	24.96	III
258.61	4.152	25.00	III
262.22	2.664	24.98	III
265.00	2.623	24.98	III
269.39	5.542	25.08	III
275.11	5.417	25.12	III
280.77	5.322	25.18	III
286.20	4.762	25.24	III
291.71	5.154	25.30	III
297.12	4.616	25.28	III

TABLE II  
HEAT CAPACITY OF NITROMETHANE. VALUES TAKEN  
FROM SMOOTH CURVES THROUGH THE DATA  
0°C. = 273.10°K.

T, °K.	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	T, °K.	$C_p$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
15	0.89	160	15.31
20	2.07	170	15.75
30	4.59	180	16.19
40	6.90	190	16.63
50	8.53	200	17.08 <sup>a</sup>
60	9.76	210	17.53 <sup>a</sup>
70	10.70	220	17.98 <sup>a</sup>
80	11.47	230	18.43 <sup>a</sup>
90	12.10	240	18.88 <sup>a</sup>
100	12.62	250	24.96
110	13.10	260	25.01
120	13.56	270	25.08
130	14.01	280	25.17
140	14.45	290	25.26
150	14.88	300	25.35

<sup>a</sup> Values corrected for premelting.

ity value given in Table II for 240°K. is an extrapolation; however, the uncertainty should not be greater than 1%. This does not imply that there is a corresponding uncertainty in the entropy value to be calculated below since an entropy increment not assigned to  $\int C_p d \ln T$  will be accounted for when the assumed premelting effect is applied to the heat of fusion.

In measuring the heat capacity of the liquid care was taken to prevent distillation from the calorimeter by keeping the surrounding lead-copper block warmer than the calorimeter. A pressure of about 1 cm. of helium was present in the system to prevent distillation during cooling and to ensure thermal equilibrium at low temperatures.

The small volume above the nitromethane in the calorimeter and the small variation of vapor pressure with temperature made it unnecessary to correct either for the amount of material in the gas space or for the thermal effect due to vaporization accompanying the rise in vapor pressure during a heat capacity determination.

The heat capacity of liquid nitromethane has been measured over the range 15–60° by Williams.<sup>4</sup> He obtained somewhat different values when calcium chloride or phosphorus pentoxide were used for drying the sample. Within the short range in which the present experiments overlap those of Williams, his values for material dried with phosphorus pentoxide are about 3% lower. However, whereas this investigation shows that the heat capacity increases with temperature above the melting point, Williams' values for material dried with phosphorus pentoxide pass through a well-defined minimum about 30°, and when calcium chloride was used for drying, he found that the heat capacity was still decreasing at 60°.

**Melting Point of Nitromethane.**—The melting point was observed as a function of the fraction melted by introducing measured amounts of energy and waiting for equilibrium. The temperatures were plotted against the reciprocal of the fraction melted and the curve extrapolated to give the melting point, which was found to be  $244.73 \pm 0.05^\circ\text{K}$ . The value given by the "International Critical Tables" is  $243.9^\circ\text{K}$ . The melting point observations are given in Table III.

TABLE III  
EQUILIBRIUM TEMPERATURE AS A FUNCTION OF THE FRACTION OF NITROMETHANE MELTED  
0°C. = 273.10°K.

Fraction melted	T, °K., Thermocouple	T, °K., Resistance thermometer
0.175	244.01	244.00
.379	244.31	244.31
.590	244.46	244.46
.801	244.50	244.55

Accepted value  $244.73 \pm 0.05$

(4) J. W. Williams, *THIS JOURNAL*, **47**, 2644 (1925).

The last three observations fall approximately on a straight line as would be expected for an ideal solution; however, the first observation indicates a considerable deviation from Raoult's law in the more concentrated solutions of impurity in nitromethane. From the slope of the straight line mentioned above the impurity is calculated to be 0.3 mole per cent.

**Heat of Fusion of Nitromethane.**—The results of the heat of fusion measurements on nitromethane are summarized in Table IV. As usual, the measurements started at a temperature somewhat below the melting point and ended somewhat above it. The results were corrected for  $\int C_p dT$  and for the amount of premelting that had occurred at the starting temperature. The premelting was known from the heat capacity measurements.

TABLE IV  
HEAT OF FUSION OF NITROMETHANE  
Melting point 244.73°K., calories per mole

Temp. interval, °K.	Corrected heat input	Pre-melting	$\int C_p dT$	$\Delta H$ Fusion
237.322–248.735	2538.9	21.9	240.5	2320
238.081–248.614	2518.3	24.2	223.3	2319
238.093–246.993	2475.7	24.2	182.7	2317
				Mean 2319 $\pm$ 3

**Vapor Pressure of Nitromethane.**—Since an accurate knowledge of vapor pressure is essential to the entropy interpretation, several measurements were made near 25°. The vacuum insulated calorimeter was very well suited for maintaining constant temperature for a long period of time and it was as usual connected to a manometer 1.6 cm. i. d. The data of Cawood and Patterson<sup>5</sup> were used for correcting for capillary depression. The standard acceleration of gravity was taken as 980.665 cm. sec.<sup>-2</sup>, and the local acceleration of gravity used was 979.973 cm. sec.<sup>-2</sup>.<sup>6</sup> The apparatus could not be used for vapor pressure measurements above room temperature because there was no protection against condensation; however, such measurements were not essential to our work.

The data are given in Table V. The calculated value given for 298.10°K. was obtained from a plot of  $\log P$  against  $1/T$ .

TABLE V  
VAPOR PRESSURE OF NITROMETHANE NEAR 25°C.  
0°C. = 273.10°K.

T, °K., resistance thermometer	P obs. inter. cm.
296.503	3.356
297.957	3.644
298.908	3.822

Vapor pressure calculated for 298.10°K. = 3.666 cm.

The value calculated for 298.1°K. from the va-

(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).  
(6) Landolt, Börnstein and Roth, "Physik. chem. Tabellen," Verlag Julius Springer, Berlin, 1923.

por pressure equation given by Williams<sup>4</sup> is 3.682 cm. which is in good agreement with the present value.

**Heat of Vaporization of Nitromethane.**—Measured quantities of heat were introduced electrically and the nitromethane was passed through a system of capillaries and condensed at essentially zero pressure in small weighed bulbs cooled with liquid air. The pressure, and thus the temperature at which vaporization occurred, was maintained practically constant by manual control of stopcocks in the capillary system. The room was maintained sufficiently warm so that no condensation could occur until the nitromethane reached the condensing bulb. Corrections were made for heat exchange between the calorimeter and its surroundings and for the small  $\int C_p dT$ . Weights were corrected to vacuum. The heats of vaporization are corrected to 298.10°K., using gas heat capacities from the extrapolated data of Pitzer and Gwinn.<sup>7</sup> The results are given in Table VI.

The heat of vaporization at the normal boiling point has been measured by Phillips and Waterton,<sup>8</sup> Matthews,<sup>9</sup> and by Pitzer and Gwinn.<sup>7</sup> These observations may be compared with the present work by calculating the change of the heat of vaporization with temperature and pressure. In this calculation the extrapolated heat capacity and density data of Williams<sup>4</sup> were used, together with the gas heat capacity and data of state estimates of Pitzer and Gwinn.<sup>7</sup>

The comparison of the heat of vaporization measurements is made in Table VI. The agreement is better than might have been expected in view of the uncertainty of the data of state of the gas.

TABLE VI

## HEAT OF VAPORIZATION OF NITROMETHANE AT 298.1°K.

Moles vaporized	Time of energy input, minutes	$\Delta H$ vaporization at 298.1°K., cal. mole <sup>-1</sup>
0.21959	75	9144
.21599	75	9152
.21849	75	9141
.21603	75	9152

Mean value 9147  $\pm$  9

Calculated from the data of:

Waterton and Phillips.....	9181
Matthews.....	9156
Pitzer and Gwinn.....	9146

**The Entropy of Nitromethane.**—The entropy calculation from the calorimetric measurements is summarized in Table VII. In making the small correction for gas imperfection at a pressure of 0.04828 atmosphere and 298.1°K., it was felt that the use of Berthelot's equation was justified. The critical constants of nitromethane have not been observed; however, they can be estimated

with sufficient accuracy for the present purpose as  $T_c = 620^\circ\text{K.}$  and  $P_c = 80$  atm. This leads to  $S_{\text{ideal}} - S_{\text{actual}} = 0.010$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 298.10°K. Although it was justifiable to use the virial data given by Pitzer and Gwinn<sup>7</sup> at the boiling point to correct the heat of vaporization at that temperature, an attempt to extrapolate their equation a to 298.1° led to  $S_{\text{ideal}} - S_{\text{actual}} (P = 0.04828 \text{ atm.}) = 0.10$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. This value appears unreasonably high and indicates uncertainty in the extrapolation; thus this estimate was discarded.

TABLE VII

## CALCULATION OF THE ENTROPY OF NITROMETHANE FROM THE CALORIMETRIC MEASUREMENTS

0-13.50°K., extrapolation	0.246
13.50-244.73°K., graphical	26.384
Fusion, 2319/244.73	9.476
244.73-298.10°K., graphical	4.945
Vaporization 9147/298.10	30.684
Entropy of actual gas at 0.04828 atm. and 298.1°K.	71.74
$S_{\text{ideal}} - S_{\text{actual}}$	.01
Entropy of ideal gas at 0.04828 atm. and 298.10°K.	71.75
Compression to 1 atm. $R \ln 0.04828$	-6.02
Entropy of ideal gas at 1 atm. and 298.10°K.	65.73 $\pm$ 0.10 cal. deg. <sup>-1</sup> mole <sup>-1</sup>

The known molecular data on nitromethane are as follows: Brockway, Beach and Pauling<sup>10</sup> have given the N-O distance as 1.21  $\pm$  0.02 Å., the C-N distance as 1.46  $\pm$  0.02 Å., and the O-N-O angle as 127  $\pm$  3°.

Wells and Wilson<sup>1</sup> have assigned the fourteen vibrational frequencies (all except torsion) as 476, 599, 647, 921, 1097, 1153, 1384, 1413, 1449, 1488, 1582, 2965, 3048 (twice).

The H-C-N angle and the C-H distance are unknown and the usual assumptions of tetrahedral angles and C-H = 1.09 Å., as in methane, are made.

The principal moments of inertia calculated from the above data are 67.2  $\times 10^{-40}$ , 76.0  $\times 10^{-40}$ , and 137.9  $\times 10^{-40}$  g. cm.<sup>2</sup>.

The reduced moment of inertia for the internal rotation of the molecule is calculated to be 4.86  $\times 10^{-40}$  g. cm.<sup>2</sup>. No frequencies due to internal rotation have been observed; however, Pitzer and Gwinn<sup>7</sup> measured the heat capacity of nitromethane gas and concluded that the potential barrier was probably between 0 and 1100 cal. mole<sup>-1</sup> but might be in the range 8000-10,000 cal. mole<sup>-1</sup> and not outside these ranges. Their best estimate was stated to be 800 cal. mole<sup>-1</sup>.

De Vries and Collins<sup>11</sup> also measured the heat capacity of nitromethane gas. Their results

(7) Pitzer and Gwinn, *THIS JOURNAL*, **63**, 3313 (1941).

(8) Phillips and Waterton, *J. Chem. Soc.*, 2783 (1930).

(9) Matthews, *THIS JOURNAL*, **48**, 582 (1936).

(10) Brockway, Beach and Pauling, *THIS JOURNAL*, **57**, 2693 (1935).

(11) De Vries and Collins, *ibid.*, **64**, 1224 (1942).

agree very well with those of Pitzer and Gwinn<sup>7</sup> and they conclude that the potential barrier restricting rotation is about but a little less than 800 cal. mole<sup>-1</sup>. Calculation of the potential barrier from their data leads to a value of about 600 cal. mole<sup>-1</sup>.

The calculation of the potential barrier from the entropy measurements reported here is given below. "I.C.T." constants are used for the statistical calculation.

TABLE VIII

## CALCULATION OF THE ENTROPY OF NITROMETHANE FROM MOLECULAR DATA

Ideal Gas State, $T = 298.1^\circ\text{K.}$ , $P = 1 \text{ atm.}$ cal. deg. <sup>-1</sup> mole <sup>-1</sup>	
Translation	38.25
External rotation	23.51
Vibration	1.88
Internal rotation (assumed free)	2.15
Entropy corresponding to free internal rotation	65.79
Entropy from calorimetric data	65.73
Reduction in entropy due to restriction of internal rotation	0.06

The entropy tables of Pitzer and Gwinn<sup>12</sup> show that the 0.06 cal. deg.<sup>-1</sup> mole<sup>-1</sup> corresponds to a six-fold potential barrier of 500 cal. mole<sup>-1</sup>, in good agreement with the values 800 and 600 cal. mole<sup>-1</sup>. The limits of accuracy of all the above determinations make values in the range 0-1000 cal. mole<sup>-1</sup> possible, but taking all the results together, the magnitude of the potential barrier

(12) Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

restricting the internal rotation in nitromethane would appear to be rather definitely established in the range of the above determinations.

The possibility that the value might lie in the range 800-10,000 cal. mole<sup>-1</sup> is definitely excluded by the entropy determination.

We thank Dr. Jerome Martin of the Commercial Solvents Corporation for supplying the sample of nitromethane and Drs. J. E. Gordon and L. Guttman for assistance with the calorimetric measurements.

## Summary

The heat capacity of solid and liquid nitromethane has been determined from 13 to 300°K.

The melting point is 244.73°K. (0°C. = 273.1°K.). The heat of fusion is 2319 cal. mole<sup>-1</sup>.

The vapor pressure at 25° was found to be 3.666 cm. and the heat of vaporization at this temperature as measured calorimetrically is 9147 cal. mole<sup>-1</sup>.

The observations were used to calculate the entropy of nitromethane in the ideal gas state at 298.1°K. and 1 atm. The value found was 65.73 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. As customary, this value does not include the entropy due to nuclear spin.

Combining the above entropy value with calculations based on available molecular data, the six-fold potential barrier restricting internal rotation in the nitromethane molecule is found to be 500 cal. mole<sup>-1</sup>, in good agreement with values of 800 and 600 cal. mole<sup>-1</sup> found by Pitzer and Gwinn, and De Vries and Collins, respectively, from measurements of heat capacity of the gas.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 14, 1946

CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1086j

## Crystal Structure of Sodium Borohydride

BY A. M. SOLDATE

The unexpected properties of sodium borohydride, such as its stability in vacuum at temperatures as high as 400°,<sup>1</sup> give interest to an investigation of its structure, hitherto unreported.

**Experimental Methods and Results.**—A sample of powdered sodium borohydride was kindly supplied by Dr. H. C. Brown of Wayne University, who reported it as being 98-99% pure. Specimens suitable for X-ray photography were obtained by sealing powdered material in thin-walled Pyrex capillaries about 0.5 mm. in diameter. To ensure adequate protection of this hygroscopic substance, the procedure was carried out over sulfuric acid in a sealed enclosure.

Powder photographs were made with copper

(1) Private communication from Dr. H. I. Schlesinger, The University of Chicago.

K $\alpha$  radiation filtered through nickel in a cylindrical camera with a 5-cm. radius. The twenty reflections observed were indexed on the basis of a cubic cell with  $a_0 = 6.15 \text{ \AA}$ . More precise lattice constant measurements using sodium chloride as an internal standard gave  $6.151 \pm 0.009 \text{ kX}$  for the value of  $a_0$ . No reflections with mixed indices were observed, the lattice is, therefore, face-centered.

The unit cell, being face-centered, must contain a multiple of four sodium borohydride molecules. It was assumed that the correct number of molecules in the unit cell is four. The density calculated with this assumption is 1.074 g./cc. No experimental value is known to us, but this value is a reasonable one. There are two ways in which the sodium and boron atoms can be arranged in the unit cell: