Heat Capacity of Liquid Nitromethane from 35° to 200° C.

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The heat capacity of saturated liquid nitromethane (under its own vapor pressure) has been determined in an adiabatic calorimeter to a precision of 0.1% between 35° and 200° C., and may be represented in this range by the polynomial: $C_{sat} = 104.4_4 + 6.381_1 \times 10^{-2}t + 3.175_3 \times 10^{-4}t^2 - 8.131_8 \times 10^{-7}t^3 + 4.073_9 \times 10^{-9}t^4$ where C_{sat} is in joules/mole-° C. and t is in ° C.

NITROMETHANE IS used in experiments designed to evaluate combustion and detonation theories (*3, 4*). Dependable values for its thermodynamic properties are desirable over a considerable range of temperatures. Its heat capacity is used directly in the theories and indirectly in the derived thermodynamic quantities.

This paper reports measurements of the heat capacity of saturated liquid nitromethane (under its own vapor pressure) from slightly above room temperature to 200° C. Because of the potentially explosive nature of the nitromethane, the sample was made small, at some sacrifice of accuracy. Earlier work includes heat capacity measurements on liquid nitromethane, by Jones and Giauque (*8*) between −258° and 24° C., by Hough, Mason, and Sage (*7*) between 40° and 100° C., and by Williams (*13*) between 15° and 65° C.

EXPERIMENTAL

Materials. A sealed ampoule of nitromethane was furnished by E. E. Toops, Jr., Commercial Solvents Corp., from the batch prepared for his density measurements (*9*). He found the cryoscopic "purity" to be 99.99 mole % for his sample. A gas chromatographic analysis of the heat capacity sample showed an H_2O content of 0.015 weight % (0.059 mole %), nitroethane less than 0.01 weight % (0.008 mole %), and nitropropane less than 0.01 weight % (0.007 mole %).

The nitromethane sample used in this work is not the same as that used in the authors' density and pressure measurements (*1*). The new sample, prepared by a different procedure, was obtained because of disagreement between the results of different methods of analysis used to determine the purity of the "density" sample. The analyses of both samples are discussed critically below.

Method and Apparatus. The method consisted of determining the quantity of energy required to raise the temperature of the calorimeter and its contents by a small amount, usually about 10° C. The experiments were first made with the empty calorimeter, and the heat capacity of the sample was then obtained by difference between smoothed curves for the calorimeter with the sample and for the empty calorimeter. The details of the method follow those described by West (*10, 12*).

The apparatus used for the heat capacity measurements was adapted from apparatus previously described (*11, 12*). Some modifications were made to accommodate a sample of prudent size and to take advantage of the lower maximum temperature (*2*).

The sample container was a cylinder of 4.7679-cc. capacity at 22.3° C., capable of being attached to a sealed vacuum system and equipped with a cone seal that could be manipulated from outside the vacuum system. The sample of 3.8561 grams of nitromethane was transferred to the cylinder directly from its original ampoule by distillation within the closed, evacuated system. The quantity of sample resulted in a vapor space of 28% of the container volume at 35° C. and 6% at 200° C.

RESULTS

For each determination on the empty calorimeter, the initial temperature, final temperature, and energy increment were fitted to a polynomial by the method of Furukawa and Reilly (*5*), in such a manner as to minimize the difference between Q_{obsd}, the experimental energy increment, and Q_{calcd}, the energy increment calculated from the polynomial for the temperature range of the experiment. The resulting equation for the heat capacity of the empty calorimeter was

$$C_e = 15.964705 + 6.207663 \times 10^{-3}t - 5.965945\ t^{-1} \tag{1}$$

where C_e is in joules per degree and t is in °C. The standard deviation, s, of an individual determination was 0.031%, calculated as follows:

$$s = \{(n-k)^{-1} \Sigma\, [(Q_{obsd} - Q_{calcd})(Q_{obsd})^{-1}]^2\}^{1/2}$$

where n is the number of experiments and k is the number of constants in the polynomial.

An equation for the heat capacity of the calorimeter containing 3.8561 grams of nitromethane was calculated in the same way:

$$C_f = 22.573123 + 1.0259209 \times 10^{-2}t + 1.8666287 \times 10^{-5}t^2 - 6.102669t^{-1} \tag{2}$$

with a standard deviation for an individual determination of 0.027%. Coefficients are given to more figures than are warranted by the uncertainty of the data, to reduce round-off error and provide continuity in the calculations which follow.

The heat capacity of the empty calorimeter was first determined in a series of 28 measurements. Nine experiments were made to determine what allowance should be made for a slight change in the amount of metal in the calorimeter. These measurements agreed with the earlier results to within about 0.2% at 40° C. and 0.1% at 200° C. Thirty-two experiments were made on the calorimeter containing nitromethane.

The difference between Equations 1 and 2, divided by the mass of the sample (3.8561 grams), represents the heat capacity of the liquid-vapor system in the calorimeter. Smoothed values of the system heat capacity at intervals of 10° C. were calculated and tabulated in Table 1, column 2.

The following corrections were applied to each of these tabulated system values to obtain the heat capacity of the saturated liquid nitromethane, C_{sat}, as a function of temperature, at the corresponding vapor pressure:

Hoge's vapor-phase correction method (*6*) was applied to obtain the heat capacity of the saturated liquid in the calorimeter, shown in column 3 of Table I. The density and vapor pressure data of Berman and West (*1*) were

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Table I. Heat Capacities[a]

Temp., °C.	Liquid-Vapor System,[b] Joules/G.-Deg.	Saturated Liquid,[c] Joules/G.-Deg.	Nitromethane, C_{sat}, Joules/Mole-Deg.[d]
35	1.7554	1.7540	107.03
40	1.7626	1.7609	107.46
50	1.7777	1.7754	108.35
60	1.7937	1.7909	109.29
70	1.8105	1.8070	110.28
80	1.8283	1.8241	111.33
90	1.8471	1.8421	112.43
100	1.8669	1.8612	113.59
110	1.8876	1.8813	114.81
120	1.9092	1.9025	116.11
130	1,9319	1.9250	117.48
140	1.9555	1.9488	118.93
150	1.9800	1.9742	120.47
160	2.0056	2.0011	122.12
170	2.0321	2.0298	123.87
180	2.0595	2.0604	125.75
190	2.0880	2.0933	127.76
200	2.1173	2.1287	129.92

[a] All entries to one figure beyond last dependable figure. [b] Column 2 values derived from Equations 1 and 2. [c] Column 3 values obtained individually from column 2 values by applying vapor-phase correction. [d] Column 4 values obtained by applying the correction for H_2O content to column 3 values, converting the results to the molar basis, and fitting to a polynomial (Equation 4).

Table II. Comparison between This Work and Earlier Literature Values

	Heat Capacity, Cal./Mole-Deg.			
Temperature, ° C.	30	40	70	90
This work	25.48[a]	25.68	26.36	26.87
Hough, Mason, and Sage (*7*)		26.00	26.61	27.10
Jones and Giauque (*8*)	25.38			
Williams (*13*)		24.24	25.26	

[a] Extrapolated to compare with Jones and Giauque.

used for this correction. By arbitrarily setting the density and vapor pressure values at the positive and negative limits defined by their standard deviations and making the vapor-phase correction calculation with these limiting values in their four possible combinations, it was found that the standard deviations of 0.078% for density and 0.06 atm. for vapor pressure could introduce an uncertainty of not more than 0.02% at 100° C. and 0.005% at 200° C. into the calculated liquid heat capacity.

Corrections based on an ideal solution were made to the liquid heat capacities for the effect of impurities. Only the H_2O represents an impurity significant enough for this calculation:

$$C_{CH_3NO_2} = (C_{liq} - f\,C_{H_2O})(1 - f)^{-1} \tag{3}$$

where f is the weight fraction of H_2O present.

The effect of the 0.01 maximum weight % of nitroethane reported by the gas chromatograph is negligible, since it would introduce a change of only 0.0004% in the heat capacity.

In terms of a mole of 61.0406 grams, the molar heat capacity of saturated liquid nitromethane can be adequately represented (to 0.01% of the individual values obtained after the vapor-phase and impurity corrections) by

$$C_{sat}\,(\text{joules/mole-deg.}) = 104.44 + 6.3811 \times 10^{-2}t + 3.1753 \times 10^{-4}t^2 - 8.1318 \times 10^{-7}t^3 + 4.0739 \times 10^{-9}t^4 \tag{4}$$

All coefficients are given to five significant figures, one more than indicated by the uncertainty of the data (about 0.1%).

Table I, column 4, contains the smoothed values of C_{sat} derived from Equation 4 (in joules/mole-deg.).

DISCUSSION

The results of this work and of the experiments of Jones and Giauque (*8*) on 99.7 mole % nitromethane, Hough, Mason, and Sage (*7*) on 99.8 mole % nitromethane, and Williams (*13*) on P_2O_5-dried nitromethane, are summarized at four temperatures in Table II. Our value at 30° C. is extrapolated for comparison with that of Jones and Giauque.

Our results lie between those of Jones and Giauque and those of Hough, Mason, and Sage, 0.4% higher than the former and 1% lower than the latter. Jones and Giauque assumed that their major impurity was H_2O and presumably corrected their data accordingly; no determination was made of the content of higher nitroalkanes in their sample. An impurity correction based on nitroethane rather than H_2O would have increased their values about 0.2%. Considering the uncertainty of their correction and the fact that our figure is extrapolated beyond our experimental range, the agreement is good. Hough, Mason, and Sage assumed that their impurity, as reported by the supplier, had a heat capacity similar to that of nitromethane (presumably nitroethane), and estimated the quantity of this impurity from the refractive index of the sample. It is our experience that commercial and purified samples of nitromethane, as received, may contain up to 0.04% H_2O by weight, enough to account for about half the difference between our results and theirs. Williams assumed that his major impurity was H_2O, but the difference between his and the other results in Table II is larger than any impurity uncertainty. Williams found a heat capacity minimum at about 30° C., whereas Jones and Giauque found no evidence of such a minimum or of a negative value for dC/dt in the 15° to 30° C. range.

Analyses of Nitromethane Sample. It has been customary for investigators of nitromethane properties to report the degree of purity of their samples in terms of cryoscopic "purity," obtained by a convenient method which serves as a means of comparing different samples of a given compound but does not necessarily indicate their true purity or the content and nature of the impurities. In a calorimetric determination, however, a qualitative and quantitative estimate of all impurities is needed for correcting the experimental data to the values for the pure compound. For this reason, we had gas chromatographic and mass spectrometric analyses made of both the sample used in this work and the sample used for the density study reported by Berman and West (*1*). The analyses are assembled in Table III.

There was considerable disagreement for both samples between the results of the mass spectrometer and those of the gas chromatograph, whereas the cryoscopic "purity" results of Toops (*9*) correlated well with our gas chro-

Table III. Analyses of Nitromethane Samples Used for Density and Heat Capacity

Determination	"Density" Sample (*1*)	Calorimeter Sample
Cryoscopic "purity," mole %		99.99
Gas chromatograph		
Nitroethane, weight %	0.05 max.	0.01 max.
H_2O, weight %	0.02[a]	0.015
Mass spectrometer		
Nitroethane, mole %	0.5	0.4
Nitropropane, mole %	0.04	0.02

[a] By Karl Fischer titration.

matograph results. This agreement suggests that the gas chromatograph results are dependable and reaffirms the choice of these results made by Berman and West (*1*) for the "density" sample. The chromatographic determination also provides a comparison between the "density" sample and samples used in other nitromethane investigations, showing that it was of the same order of purity as samples used elsewhere.

PRECISION

The precision of the calorimetric measurements is estimated to be 0.12% at 40° C. and 0.09% at 200° C., obtained by combining the absolute standard deviations of the determinations on the empty and the full calorimeter and dividing by the heat capacity of the sample, as follows:

$$s_d = [(s_e C_e)^2 + (s_f C_f)^2]^{1/2} \ (C_f - C_e)^{-1}$$

where s_d, s_e, and s_f are, respectively, the per cent standard deviations of the combined measurement, the empty calorimeter measurement, and the full calorimeter measurement; C_e is the heat capacity of the empty calorimeter, and C_f that of the full calorimeter.

The maximum uncertainty in the calculated heat capacity of the liquid, derived from the uncertainties of the densities and vapor pressures, is at most 0.02%. In addition to this random error, a possible systematic error of 0.02% is introduced by the disagreement between analytical methods for the nitroethane content.

ACKNOWLEDGMENT

We thank E. E. Toops, Jr., for his kindness in supplying the calorimeter sample of nitromethane; Robert Leslie, who performed the chromatographic analysis; and William Dorko, who performed the mass spectrometric analysis.

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RECEIVED for review September 16, 1968. Accepted October 13, 1968. Work supported by the Bureau of Naval Weapons, Code RRRE-6.