Density and Vapor Pressure of Nitromethane 26° to 200°C.

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The density of nitromethane between 25° and 200° C. and its vapor pressure between 130° and 200° C. have been determined experimentally. Within these limits, the density is represented by the equation

$$d = 1.1615 - 1.1952 \times 10^{-3}t - 1.553 \times 10^{-6}t^2$$

and the vapor pressure by the equation

$$\log_e P = 10.8210 - 3905.39/(t + 260)$$

where d is in grams per cc., P in atm., and t in ° C.

NITROMETHANE is one of the materials used in experiments designed to evaluate combustion and detonation theories (1, 3). Dependable values for its physical properties are desirable over a considerable range of temperatures.

Density measurements of nitromethane have been extended from 30° to 200° C. and vapor pressure from 130° to 200° C. Density data were also obtained at 24° C. to establish the consistency of the higher temperature data with earlier measurements in the 20° to 30° C. range by Toops (5), who used a pycnometer capable of high precision at room temperature. The apparatus used in the work reported here was designed to contain liquid nitromethane, a potentially explosive material, at temperatures above its normal boiling point of 101° C. and at the vapor pressures corresponding to these temperatures. This type of apparatus is capable of a precision of slightly better than 0.1% in density.

EXPERIMENTAL

Samples. One series of measurements was made on sample I obtained by drying Eastman spectro grade nitromethane over calcium sulfate and distilling near 30° C.

Because the apparatus used considerable quantities of liquid, most of the measurements were made with Eastman spectro grade nitromethane degassed by freezing and melting under vacuum (sample II).

Sample I was analyzed by gas chromatography and by mass spectrometry. The major impurity by both methods was nitroethane, found by gas chromatography to be not more than 0.05 mole %. Mass spectrometry indicated 0.5 mole % nitroethane, 0.04 mole % nitropropane, and 0.01% unidentefied material. The H_2O content by Karl Fischer titration was 0.02 wt. %. If the gas chromatographic analysis is taken, the sample is 99.9 mole % nitromethane. The effect of 0.5 mole % nitroethane would be to change the density of the sample 0.05% at 25° C.

Sample II contained, according to mass spectrometric analysis, 2.6 mole % nitroethane, 0.6 mole % nitropropane, 0.4 mole % propanenitrile, 0.01% unidentified material. The H_2O content by Karl Fischer titration was 0.04 wt. %.

Both samples became colored after exposure to temperature above 140° C., but the amount of colored material was so small that it was not found in the analysis.

Apparatus and Procedure. The volume of the sample was measured in a calibrated enclosure (Figure 1) consisting of a section of high-pressure tubing closed at one end with a cone seal and at the other by a high-pressure valve. The tubing and valve are surrounded by a thick-walled steel cylinder held at constant temperature (±0.05°) by an accurate control system which has been described (6). The temperature of the tube was measured directly with a chromel-alumel thermocouple calibrated against a plat-
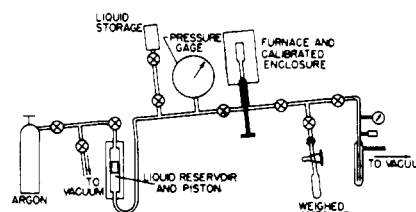

Figure 1. Apparatus for determining the density and vapor pressure of nitromethane

inum resistance thermometer and could be read to the nearest 0.01° C.

The valve connects the enclosure to a manifold of high-pressure tubing, which contains, in order, a source of compressed argon, a cylinder for storing the nitromethane, equipped with a piston and polyethylene-propylene "0" ring seal to separate the argon from the liquid sample, a 10-inch Bourdon-type pressure gage accurate to 1 p.s.i., the enclosure valve, a series of weighed glass ampoules, only one of which is shown in Figure 1, and a vacuum system. All packing materials except the piston ring are Teflon.

In an experiment, the steel cylinder which surrounds the calibrated volume enclosure is brought to the temperature at which the density is to be measured and the apparatus evacuated to about 0.01 torr. Nitromethane is then forced slowly into the apparatus by compressed argon acting on the opposite side of the piston. The pressure is followed as a function of time. The pressure rises gradually until the liquid begins to fill the hot region. At this time, it holds steady at the vapor pressure until the hot region is filled, then rises again gradually. During this filling period, the temperature of the enclosure decreases as a result of the entry of colder liquid, but is gradually restored by the control system. When the temperature is again constant and the pressure somewhat greater than the vapor pressure, the valve is closed, excess liquid drained back into the cylinder, and the manifold evacuated. The valve is then opened and the nitromethane frozen out in a weighed ampoule immersed in liquid nitrogen. The increase in weight of the ampoule was divided by the volume of the enclosure at the temperature of the determination to obtain the density in grams per cubic centimeter. The vapor pressure was the midpoint of the pressure plateau during the filling period. The density was obtained for the temperature of the enclosure at the time the valve was closed.

The volume of the enclosure was calibrated with distilled and degassed water, for which densities and vapor pressures are well known (2). Three calibration experiments were made before and four after the measurements on nitromethane. The data were plotted and interpolations made graphi-

cally. Owing mainly to thermal expansion, the volume increases from 5.550 cc. at 25° C. to 5.610 cc. at 204° C. The calibration data fit a straight line with a standard deviation of 0.06%. The root-mean-square difference between the water equilibrium temperatures observed and the temperature corresponding to observed vapor pressure is 1.3° C. The uncertainty thereby introduced is discussed in the next section of this paper.

RESULTS AND DISCUSSION

Experimental data for the two series of density measurements are listed in chronological order for each sample in Table I and plotted in Figure 2. Data for the purified sample I lie systematically above those for sample II. Included for comparison in Figure 1 are three points obtained by Toops (5).

Quadratic equations for density in grams per cubic centimeter *vs.* temperature in ° C. were obtained by applying the method of least squares to the observed data. The two points near 98° C. observed for sample II were omitted. The equations obtained for the purified sample (sample I) and for sample II, respectively, are as follows:

$$d_I = 1.1615 - 1.1952 \times 10^{-3}t - 1.553 \times 10^{-6}t^2 \quad (1)$$
$$d_{II} = 1.1520 - 1.1395 \times 10^{-3}t - 1.665 \times 10^{-6}t^2 \quad (2)$$

The two series of density measurements differ in magnitude because they represent samples of different purity. However, the precision of the measurements depends only on the apparatus and procedure used, inasmuch as the samples were qualitatively the same. Since a greater quantity of sample II was available, more data could be obtained for this sample and a better estimate could be made from this series of the standard deviation of a single measurement from the values calculated from Equation 2. This standard deviation, 0.078%, is representative of the precision obtained for both series of measurements, and was found as follows:

$$s\% = 100 \left[\frac{\Sigma \left(\frac{d_{obsd.} - d_{calcd.}}{d_{obsd.}} \right)^2}{n - 3} \right]^{1\;2}$$

where n represents the number of measurements. All the measurements for sample II were utilized, except the two anomalous measurements at 97.5° and 99.6° C. (Note that no such anomalous data point was found for sample I at 98.2° C.)

The values of the experimental and calculated densities used to calculate the standard deviation contained one figure beyond those tabulated in Table I.

The density at 25° C. calculated from Equation 1 is 0.06% less than that observed by Toops (5). This difference is about what the authors would expect on the basis of the difference in composition of the samples and the precision of their measurements. The thermal expansion coefficient at 25° C., as calculated from Equation 1, is about 10% less than that calculated by Toops. Although this difference is in the direction which would be expected on the basis of relative compositions, it seems more likely ascribable to the added uncertainties in Equation 1 near the end of its applicable temperature range.

Experimental data for the vapor pressures are tabulated in Table II. No difference was observed between the two samples. The data fit the Antoine equation

$$\log_e P = 10.8210 - 3905.39/(t + 260) \quad (3)$$

Table I. Density of Nitromethane

| Temperature, ° C.	Density, Observed G./Cc.	Density, Calculated
	Sample I	Equation 1
24.2	1.1320	1.1317
98.2	1.0280	1.0291
159.6	0.9327	0.9312
203.1	0.8540	0.8547
	Sample II	Equation 2
131.8	0.9725	0.9728
132.7	0.9712	0.9714
149.2	0.9456	0.9449
149.1	0.9466	0.9450
170.8	0.9091	0.9088
170.1	0.9102	0.9100
189.9	0.8747	0.8755
189.9	0.8749	0.8755
97.5	1.0185	1.0250
64.6	1.0704	1.0714
64.8	1.0708	1.0711
64.7	1.0707	1.0713
99.6	1.0156	1.0220
33.6	1.1116	1.1118
31.2	1.1149	1.1148
22.0	1.1270	1.1261
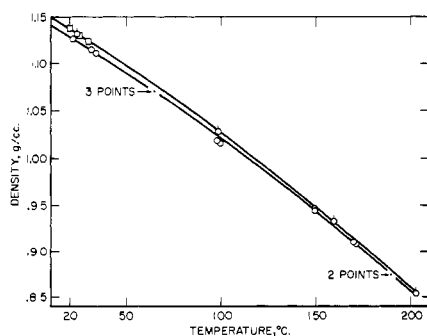
Figure 2. Density of nitromethane
vs. temperature

Upper curve represents Equation 1 for sample I (purified). Lower curve represents Equation 2. Circles represent these experimental data. Squares represent the data of Toops (5)

Table II. Vapor Pressure of Nitromethane

Temperature, ° C.	Vapor Pressure, Observed Atm.	Vapor Pressure, Equation 3
	Sample I	
159.9	4.56	4.57
203.0	10.89	10.87
	Sample II	
131.8	2.38	2.35
132.8	2.38	2.41
172.6	6.16	6.01
149.3	3.57	3.59
149.2	3.57	3.59
170.7	5.78	5.78
170.1	5.65	5.70
190.0	8.47	8.52
189.9	8.47	8.50

(P in atm., t in ° C.). The standard deviation for an individual measurement is 0.06 atm. calculated from values extended one figure beyond those tabulated in Table II.

The deviation of the water vapor pressures determined in the calibration from the values found in Dorsey (2) for the corresponding temperatures introduces a systematic uncertainty into the nitromethane vapor pressure of about 0.06 atm. at 100° and 0.5 atm. at 200° C. apart from the much smaller random uncertainty represented by the standard deviation of 0.06 atm. However, the agreement between the vapor pressures determined and those extrapolated from the work of McCullough et al. is considerably closer.

At 131.8° C., the pressure calculated from Equation 3 is 0.023 atm. greater than that calculated from the Antoine equation of McCullough et al. (4). Extrapolation of their Cox equation gives pressures slightly greater (0.13 atm. at 187° C.) than those calculated from Equation 3. Toops (5) also gives constants for the Antoine equation, which are not very different from those given by McCullough et al.

The change in density with composition can be estimated from the differences between the densities of samples I and II, as represented by Equations 1 and 2. Since the difference in purity between samples I and II is about 3 mole %, the authors would expect the density measured by Toops to be about 0.1% higher than the density of sample I.

Detonation and combustion experiments, which require relatively large quantities of nitromethane, are usually made with samples having considerable amounts of impurities. An estimate of the density of a particular sample can be made by assuming the specific volumes of its components additive in proportion to the weight fraction of each component. The additivity method is only approximate and does not completely account for the difference between samples I and II but is helpful in indicating the trend. When the density and thermal expansion are involved in the analysis of detonation and combustion experiments, it seems worthwhile to make some allowance for the effect of impurities if the densities of these impurities are known.

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The Critical Temperature, Critical Pressure, and Vapor Pressure of Argon

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The vapor pressure of argon has been measured in a glass equilibrium cell over the range 114.40° to 150.65° K. The critical temperature and critical pressure, determined by observing the formation and the disappearance of the meniscus, were 150.65 ± 0.02° K. and 47.92 ± 0.05 atm., respectively. The results obtained have been compared with published data, and an empirical equation has been developed to represent what are believed to be the most reliable vapor pressure data over the range 90° to 150.65° K.

ALTHOUGH several investigations of the vapor pressure and critical constants of argon have been made, the reported data are in considerable disagreement. In fact, the reported critical temperatures differ by as much as 5° K. and the critical pressures by several atmospheres. Therefore, as part of an extensive study of vapor-liquid equilibrium in the helium-argon system (6), the critical temperature, critical pressure, and the vapor pressure of argon were determined. The results are compared with corresponding data published in the literature. A correlation equation which describes the vapor pressure of argon from 90° K. to the critical point is given.

EXPERIMENTAL

The cryostat and glass equilibrium cell used are shown in Figure 1. The equilibrium cell (capacity, 8 cc.) was

very similar to one used by Eakin, Ellington, and Gami (4) for dew-point and bubble-point measurements except that no mechanism for stirring was provided. A constant temperature was maintained by removing heat from the propane cryostat through the copper cooling tube, T, which was cooled at its upper end by liquid nitrogen boiling at atmospheric pressure. The vapor pressure cell, G, and the power end of the cooling tube, which was rapidly circulated through the cooling tube and around the cell by the propellers, S3, located inside the cooling tube.

The temperature of the equilibrium cell was measured using a copper-constantan (Driver-Harris Advance brand) thermocouple, A, located on the outside wall of the cell as shown in Figure 1. E.m.f. measurements were made using a Leeds and Northrup Type K-3 potentiometer and Type 9834 DC electronic null detector. Readings could be made to ±0.1 μv. corresponding to ±0.005°. The thermocouple was calibrated in place against a platinum

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