

Thermal Conductivity of Liquid Hydrazine (N₂H₄) at 293.2 Kelvin and 0.101 to 2.068 Megapascals

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DOI: 10.2514/1.38775

The thermal conductivity of liquid hydrazine was measured by the steady-state hot-wire method at 293.2 K and 0.101 MPa. Eight pure organic liquids were used as reference liquids to calibrate the experimental apparatus. The thermal conductivity was determined to be $\lambda = 0.32 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The present measurement is in agreement with one recent measurement. The present measurement disagrees with the most recent measurement as well as several previous measurements and estimation methods. The thermal conductivity was determined to change very little over the pressure range of 0.101 to 2.068 MPa. The present observed pressure dependence is in agreement with one previous pressure dependence measurement. The speed of sound in liquid hydrazine was measured to be $2092 \pm 12 \text{ m} \cdot \text{s}^{-1}$, in agreement with previous measurements. There are large inaccuracies obtained when estimating the thermal conductivity of hydrazine by using standard estimation methods that use speed-of-sound data.

Nomenclature

c_N	=	speed of sound, $\text{m} \cdot \text{s}^{-1}$
I_c	=	constant current, A
k	=	Boltzmann constant, $1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
L	=	path length, m
N_A	=	Avogadro constant, $6.02214 \times 10^{23} \text{ mol}^{-1}$
P	=	pressure, Pa
q	=	heat flux, $\text{J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
R	=	resistance, Ω
R_c	=	gas constant
T	=	temperature, K
V_f	=	voltage, V
V_η	=	molar volume, $\text{m}^3 \cdot \text{mol}^{-1}$
α, β	=	thermal conductivity constants of measurement cell
Δf	=	liquid resonance-frequency difference, Hz
λ	=	thermal conductivity, $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
v	=	specific volume, $\text{m}^3 \cdot \text{kg}^{-1}$
v_c	=	critical volume, $\text{m}^3 \cdot \text{kg}^{-1}$

I. Introduction

HYDRAZINE (N₂H₄) is a propellant often used in propulsion systems for orbital maneuvering on manned and unmanned spacecraft. The thermal properties of pure liquid hydrazine are of major interest when designing processing equipment, spacecraft, and propulsion engines. The thermal conductivity is an indispensable parameter in engineering work that involves heat transfer applications. It is also important to understand the pressure dependence of the thermal properties of hydrazine, because it is usually stored under pressure in orbit. Despite the importance of this thermal property, there is very little agreement in the literature among reliable data sources. The current literature disagrees by an order of magnitude from the first experimental measurements to the most recent measurements on the thermal conductivity of liquid hydrazine [1–5].

One problem measuring pure hydrazine is that hydrazine is hygroscopic and older samples could have potentially contained

other manufacturing impurities such as aniline. These impurities could potentially have major effects on the measured thermal conductivity of hydrazine. This is particularly true of water and ammonia impurities, as liquid water and liquid ammonia have large thermal conductivities compared with most liquids at 293.15 K and 0.101 MPa. Table 1 lists the several previous sources for the thermal conductivity value for liquid hydrazine in various solvents [1–5]. The thermal conductivity of hydrazine was determined previously by the Ralph M. Parsons Corporation [1]; however, the report is now out of print and there are few details on how the value was obtained. Bachmaier [2] measured the thermal conductivity of hydrazine/methanol mixtures. Once again, there was very little detail in the report on how this value was obtained or the purity of hydrazine used in the experiment. Safarov and Zaripova [3] measured the thermal conductivity of hydrazine–water mixtures as a function of temperature and pressure using a cylindrical bicalorimeter. They obtained a smaller thermal conductivity than the two older measurements for 90% hydrazine in water ($\lambda = 0.395 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) at 293 K. Their extrapolated 100% hydrazine value was $\lambda = 0.328 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 293 K and 0.101 MPa. The Safarov and Zaripova value agrees with the value in the most recent *Chemical Properties Handbook* [4] ($\lambda = 0.4008 - 1.5493 \times 10^{-4} T - 4.8625 \times 10^{-7} T^2$, where λ is in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and T is in Kelvin) at 293 K ($\lambda = 0.314 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). There is no reference in the handbook regarding the origin of the thermal conductivity value other than that it was based on unspecified experimental and calculated values. The most recent measurement from Grebenkov et al. [5] is an order of magnitude smaller than the older measurements at 295 K and 0.101 MPa ($\lambda = 0.0499 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). This value is on the low end of thermal conductivity of most measured liquids. Grebenkov et al. used a steady-state hot-wire method with anhydrous hydrazine.

For most pure liquids, the thermal conductivity can be estimated by using the modified Bridgman equation [6,7]:

$$\lambda = 2.8 \left(\frac{N_A}{V_\eta} \right)^{2/3} k c_N \quad (1)$$

In Eq. (1), N_A is Avogadro's number, V_η is the molar volume, k is Boltzmann's constant, and c_N is the speed of sound in the fluid. For liquid water, the speed of sound is $1496.70 \text{ m} \cdot \text{s}^{-1}$ at 298.15 K. The speeds of sound in hydrazine, monomethyl hydrazine (MMH), and unsymmetric dimethyl hydrazine (UDMH) were previously measured by Kretschmar, as discussed in [8–11] [$c_N = 2074 \text{ m} \cdot \text{s}^{-1}$ (N₂H₄), $1548 \text{ m} \cdot \text{s}^{-1}$ (MMH), and $1247 \text{ m} \cdot \text{s}^{-1}$ (UDMH)], at 298.15 K. The thermal conductivity of hydrazine estimated by the Bridgman equation is $0.569 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at

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Table 1 Previous determinations of the thermal conductivity of hydrazine

Reference	Purity	λ , $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	Method
[1]	95% N_2H_4 , 5% H_2O	0.50	Unknown measurement
[2]	Unknown	0.54	Unknown measurement
[3]	90% N_2H_4 , 10% H_2O	0.395	Cylindrical bicalorimeter
[4]	100% N_2H_4	0.314	Reference handbook [4]
[5]	Anhydrous N_2H_4	0.0499	Steady-state hot wire

298.15 K. The Bridgman equation suggests that the older measurements of thermal conductivity are correct, even though these older measurements have $\sim 5\%$ water added, which most likely increased the thermal conductivity measured.

Gibek and Maisonneuve [12] recently measured the speed of sound in liquid hydrazine by measuring the waterhammer over-pressure levels in flowing hydrazine pipes. They obtained a speed of sound of MMH of $1530 \text{ m} \cdot \text{s}^{-1}$ in good agreement with the Kretschmar value [10,11]. However, they measured a speed of sound of liquid hydrazine of $1293 \text{ m} \cdot \text{s}^{-1}$ at 298 K. This value is significantly lower than the Kretschmar value [10,11]. Using the Gibek and Maisonneuve [12] value for the speed of sound in hydrazine in Eq. (1) yields an estimated thermal conductivity value of $0.354 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. This estimated value is in agreement with the current measurements of the hydrazine thermal conductivity by Safarov and Zaripova [3].

This work investigated the thermal conductivity of hydrazine at 293.5 K and 0.101 to 2.068 MPa by using the steady-state hot-wire method [13]. The thermal conductivity apparatus was calibrated by using eight reference liquids that have well-known thermal conductivities [4,8]. The thermal conductivity was determined to be $\lambda = 0.32 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 293.5 K and 0.101 MPa, in agreement with the previous measurements of Safarov and Zaripova [3] and the recommended value in the *Chemical Properties Handbook* [4]. The pressure dependence of the thermal conductivity was found to not vary (within error of the experimental value) from 0.101 to 2.068 MPa. The observations are in agreement with the previous pressure trends observed by Safarov and Zaripova [3] for mixtures of hydrazine and water over the pressure range of interest.

The speed of sound in hydrazine at 293.5 K was measured using an ultrasonic interferometry technique [14]. The speed of sound in liquid hydrazine was found to be $2092 \pm 12 \text{ m} \cdot \text{s}^{-1}$. The value is in agreement with previous measurements of $2093 \text{ m} \cdot \text{s}^{-1}$ at 293.2 K [11]. The speed-of-sound result demonstrates that the Bridgman

equation does not yield an accurate estimate of the thermal conductivity for liquid hydrazine.

II. Experiment

A. Thermal Conductivity

The thermal conductivity apparatus was designed to closely follow ASTM International (ASTM) standards for the steady-state hot-wire method (see Fig. 1) [13]. The thermal conductivity cell consists of a 20.0-cm-long Pyrex glass tube that had a 6.5 mm radius with 2.45-mm-thick walls. For high-pressure measurements, the thermal conductivity cell consists of a 21.0-cm-long stainless steel 304L tube that has an inner diameter of 8.05 mm. The tube was threaded for a Teflon plug that had a silicon rubber o-ring seal. This plug allowed the cell to be sealed, thus preventing the hydrazine from reacting with air during testing. For high-pressure tests, a 0.25 in. stainless side arm was fitted with a valve that allowed the tube to be pressurized during testing. The helium (99.995%) pressure was changed from 0.101 MPa (14.7 psi) to 2.068 MPa (300 psi) during the experiments. A platinum wire (0.06 mm radius) was used as the resistance thermometer (100Ω and $0.00385 \Omega / ^\circ\text{C}$). The 4-lead wire was housed in a 1.63-mm-radius, 18.6-cm-long ceramic tube that was inserted through the center of the Teflon plug. Two lead wires were connected to a voltmeter to record the voltage during tests. The other two lead wires were connected to a constant current source and an ammeter. When the Teflon plug was screwed into place, the ceramic tube ran down the axis of the tube, as shown in Fig. 1.

The thermal conductivity cell was filled with the test liquid in a nitrogen-purged chemical-handling bag. The cell was filled completely with liquid to remove any dead space that might have potentially been filled with nitrogen gas. The cell was then sealed with the Teflon plug and placed into a temperature-controlled water bath at 293.2 K ($\pm 0.5 \text{ K}$) with a temperature stability at the set point of $\pm 0.005 \text{ K}$. With this setup, the effective heating path length through the test liquid to the temperature-controlled bath was 2.42 mm. A constant current I_c was placed on the platinum wire and the final voltage V_f was recorded. When the voltage reached a constant value ($\sim 3 \text{ min}$) the current was again changed. The change in temperature is then determined by Eq. (2):

$$\Delta T = \left[\left(\frac{V_f}{I_c} - 100 \Omega \right) / 0.385 \Omega \right] \text{K} + 273.15 \text{ K} \quad (2)$$

The hydrazine used in the experiment was purchased from Aldrich Chemicals (99.6% aniline-free). The purity of the calibration liquids was as follows: water (99.9%), dimethyl phthalate (greater than 99.9%), methanol (99.8%), 2-propanol (99.9%), ethanol (99.5%), carbon tetrachloride (99.9%), chloroform (99%), acetonitrile (99%), and acetone (99.8%).

B. Speed-of-Sound Measurements

The experimental setup is similar to that detailed by Han et al. [14] and will only be briefly described here. Two broadband lithium niobate transducers with a resonance frequency of 1.8–6 MHz were attached to a rectangular cell containing the test liquid. The cell was either a 1-cm-path-length quartz cuvette or a 3.5-cm-path-length square plastic bottle. One transducer (speaker) was swept through the frequency range at 1 kHz steps with an excitation voltage ranging from 0.25 to 2.5 V. Figure 2 shows a picture of the experimental setup

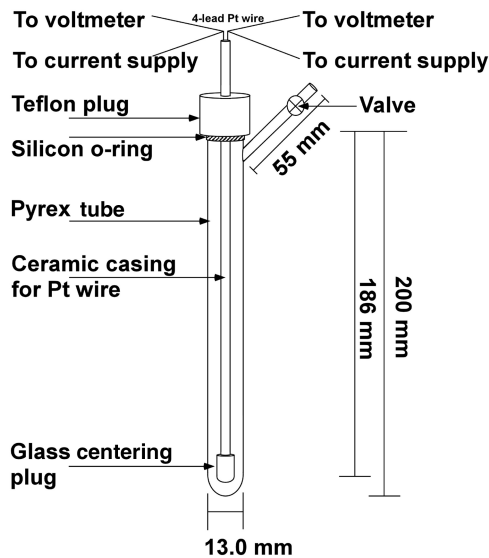


Fig. 1 Stainless steel experimental apparatus used in the thermal conductivity experiments. The glass-tube apparatus was similar in design, except that it lacked the side arm needed for pressurization.

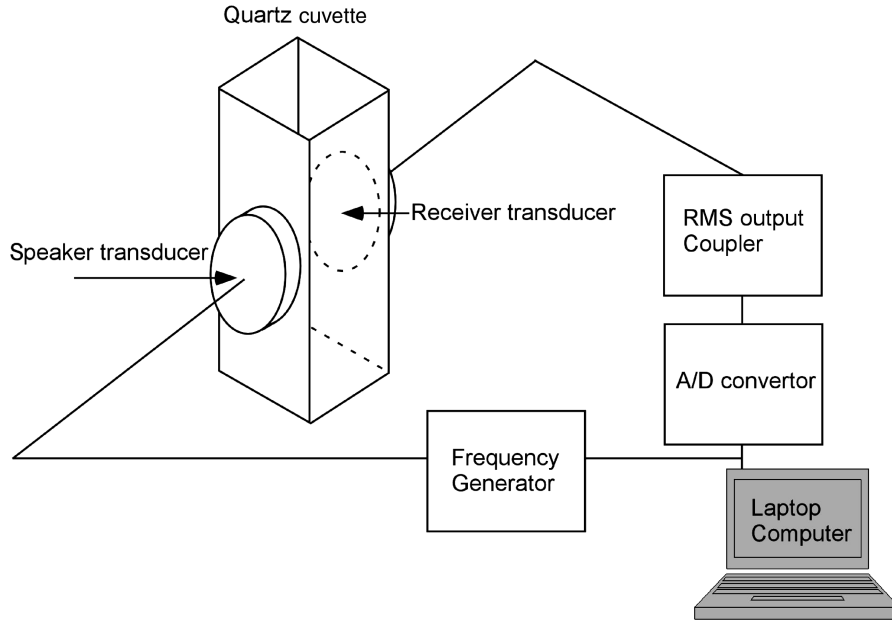


Fig. 2 Experimental setup for measuring the speed of sound by using ultrasound.

for the speed-of-sound measurements. A computer-controlled frequency generator sent the driver-frequency signal to the speaker transducer. The generated sound waves then traveled through the liquid in the sample cell. The standing sound wave in the sample cell was then picked up by the receiver transducer on the opposite side of the sample cell. The frequency signal on the receiver transducer was sent through a 10 dB amplifier and then through a high-pass frequency filter inside an output coupler. The root-mean-square amplitude of the signal was then sent to a transient digitizer and recorded by a computer. The amplitude of the standing wave in the cell has a frequency dependence based on the path length of the cell (L) and the speed of sound of the liquid in the cell. The liquid resonance-frequency difference Δf , the difference in frequency when the standing wave has a maximum peak amplitude on the receiver signal, can be related to the speed of sound in the liquid (c_N) by Eq. (3) [14]:

$$\Delta f = 2Lc_N \quad (3)$$

The liquid resonance-frequency difference varies slightly from peak to peak due to interference from the cell walls. Thus, an average of

several Δf throughout the driver-frequency scanning range had to be used to obtain the speed of sound.

The path lengths of the two different sample cells were calibrated with liquids that had known speeds of sound. Water, methanol, 2-propanol, acetone, and carbon tetrachloride were used to calibrate the cells.

III. Results

The thermal conductivity is defined from Fourier's law in heat transport:

$$q = -\lambda \nabla T \quad (4)$$

where q is the heat flux, ∇T is the temperature gradient, and λ is the thermal conductivity of the material. In the cylindrical symmetry of the experimental apparatus, the temperature gradient is approximately radial:

$$\nabla T \approx \frac{\Delta T}{\partial r} \quad (5)$$

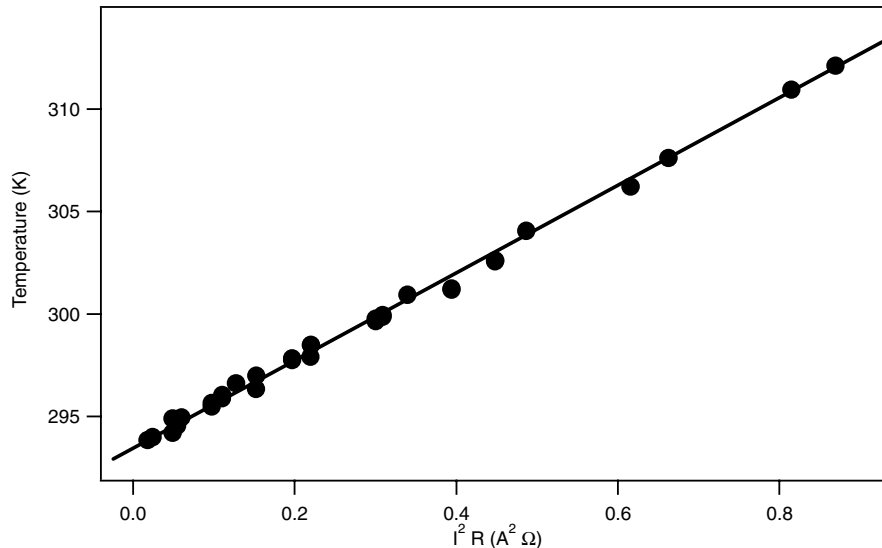


Fig. 3 Temperature as a function of applied current $I^2 R$ for a sample of water at 293.5 K.

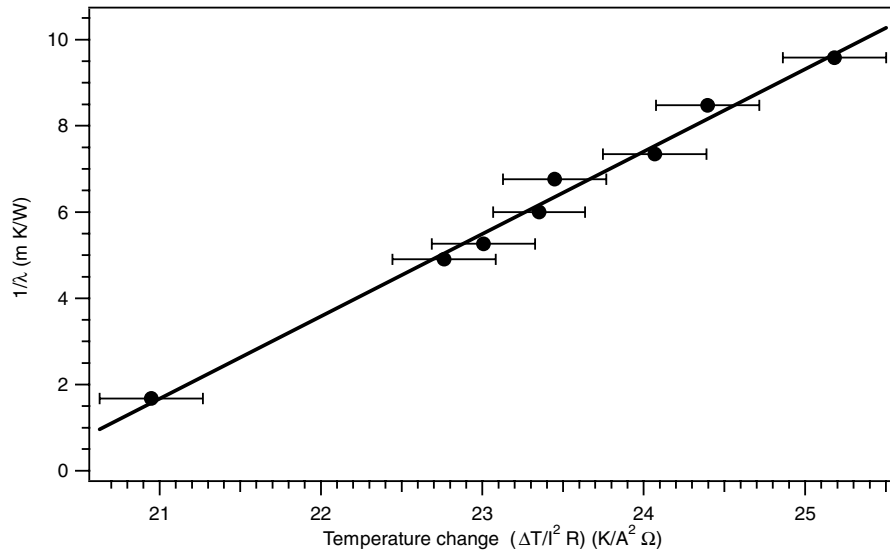


Fig. 4 Inverse of the thermal conductivity ($1/\lambda$) of the calibration liquid in the thermal conductivity cell as a function of the measured change in temperature for an applied current ($\Delta T/I^2 R$).

The heat flux is the power input divided by the area, which depends on r :

$$q = \frac{I_c^2 R}{A} = \frac{I_c^2 R}{2\pi r l} \quad (6)$$

where I_c is the current, R is the resistance, A is the surface area, r is the radius, and l is the length. Substituting Eq. (4) into Eq. (6) yields

$$\frac{\Delta T}{I_c^2 R} = \frac{-1}{\lambda} \times \frac{\partial r}{2\pi r l} \quad (7)$$

The effective last term averaged over the relevant range of r is dependent on the cell geometry and is determined by calibration. The constant α is substituted for this term. The constant β is added to account for any temperature drop across the wire insulation (the Pt wire is not exposed to hydrazine, because it catalyzes its decomposition) or across the glass walls of the tube that separates the test fluid from the constant temperature bath. The constant β is also determined by calibration. The thermal conductivity of the hydrazine tested was determined from the change in temperature for a given applied current and resistance of the Pt wire:

$$\frac{\Delta T}{I_c^2 R} = \frac{\alpha}{\lambda} + \beta \quad (8)$$

Table 2 Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) at 293.2 K of the eight liquids used to calibrate the thermal conductivity cell

Substance	λ	
	Reference [4,7]	Present study
Water	0.5973	0.635 ± 0.046
Methanol	0.2038	0.198 ± 0.015
Acetonitrile	0.1900	0.181 ± 0.014
Acetone	0.1667	0.162 ± 0.012
Dimethyl phthalate	0.1479	0.157 ± 0.012
2-propanol	0.1361	0.133 ± 0.010
Chloroform	0.1180	0.123 ± 0.009
Carbon tetrachloride	0.1044	0.103 ± 0.008

^aThermal conductivity was determined by Eq. (9) with the calibration constants $\alpha = 1.91 \pm 0.08 \text{ W} \cdot \text{m}^{-1} \cdot \text{A}^{-2} \cdot \Omega^{-1}$ and $\beta/\alpha = -38 \pm 2 \text{ W}^{-1} \cdot \text{m} \cdot \text{K}$

^bError is two standard deviations from the fit.

Equation (8) can be rearranged to solve for the thermal conductivity if the change in temperature per change in applied current is known:

$$\frac{1}{\lambda} = \frac{(\Delta T/I_c^2 R)}{\alpha} - \frac{\beta}{\alpha} \quad (9)$$

The major assumption is that the apparatus is perfectly cylindrically symmetric and that the temperature gradient is purely radial. This ignores convection, which could potentially lead to a vertical gradient component. Also neglected were the effects of infrared radiative absorption by the liquid.

To determine the absolute values of the cell constants α and β , eight different calibration liquids were used. Figure 3 shows a plot of the temperature as a function of the applied current for water. The slope $\Delta T/I^2 R$ was determined to be $\Delta T/I^2 R = 20.95 \pm 0.16 \text{ K} \cdot \text{A}^{-2} \cdot \Omega^{-1}$. The change in temperature with applied current of eight different liquids, as listed in the experimental section, with known thermal conductivities was measured in the same experimental apparatus. The thermal conductivities used for the calibration curve are listed in Table 2. Figure 4 shows a plot of the inverse of thermal conductivity ($1/\lambda$) versus $\Delta T/I^2 R$ for the eight calibration liquids. The values are an average of five to eight measurements for each data point. The α value was found to be $\alpha = 1.91 \pm 0.08 \text{ W} \cdot \text{m}^{-1} \cdot \text{A}^{-2} \cdot \Omega^{-1}$ and the β/α value was found to be $\beta/\alpha = -38 \pm 2 \text{ W}^{-1} \cdot \text{m} \cdot \text{K}$. The best fit to the calibration curve can be used to determine the thermal conductivity of the eight calibration solutions from their measured $\Delta T/I^2 R$ by using Eq. (9). Table 2 shows the thermal conductivity predicted for the eight calibration liquids determined from the calibration curve. There is an average error of 8% from the known literature values.

Figure 5 shows a plot of the temperature as a function of the applied current for eight separate measurement runs of pure hydrazine. The slope was found to be $\Delta T/I^2 R = 21.8 \pm 0.2 \text{ K} \cdot \text{A}^{-2} \cdot \Omega^{-1}$. The thermal conductivity was found to be $\lambda = 0.32 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 293.2 K and 0.101 MPa by using the α and β coefficients and Eq. (4).

Figure 6 shows a plot of the thermal conductivity of liquid hydrazine at 293.2 K as a function of the helium pressure. The pressure regime chosen was the most relevant to spacecraft in orbit. Also shown in Fig. 6 are the values obtained from the function of thermal conductivity versus pressure from Safarov and Zaripova [3]. Safarov and Zaripova found that the pressure dependence of the thermal conductivity (in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) followed the following function:

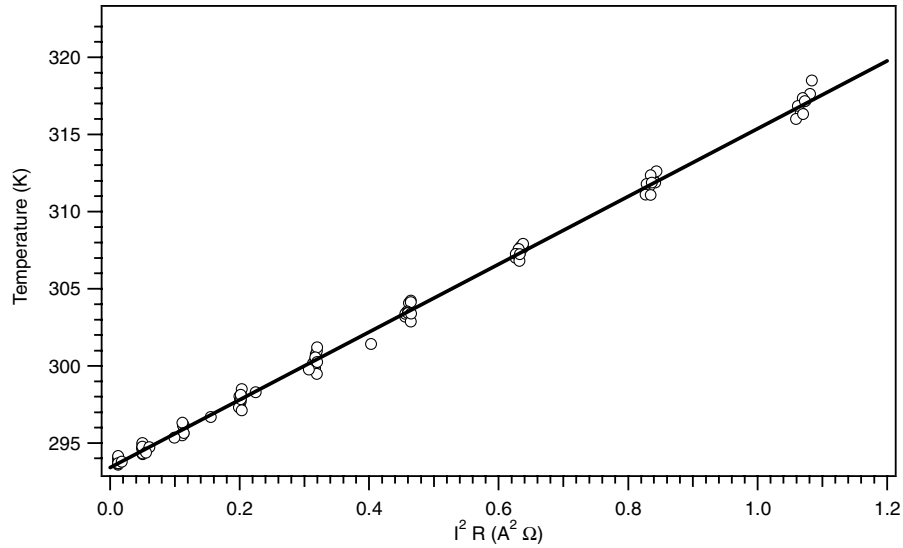


Fig. 5 Temperature as a function of applied current $I^2 R$ for hydrazine at 293.5 K. The figure is for the cumulative data for eight separate hydrazine sample runs.

$$\lambda_{P,T_1} = \left[\left(8.33 \times 10^{-2} \frac{P}{P_1} \right) + 0.917 \right] \times (-8.052 \times 10^{-5} T_x^2 + 4.943 \times 10^{-2} T_x - 6.7) \quad (10)$$

where P is the pressure of interest, P_1 is 29.43×10^6 Pa, and T_x is the boiling temperature.

The thermal conductivity for the current set of experiments was determined to be $\lambda = 0.32 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The slight pressure dependence expected from examining the results of Safarov and Zaripova [3], given the uncertainty of the current experiments, means that the thermal conductivity pressure dependence in the present experiments should be within the uncertainty of the current experiment. The scatter in Fig. 6 demonstrates this to be true. The current data show the same general trend as Safarov and Zaripova; however, given the uncertainty, the relevance is probably not significant. Given the scatter in the data from the present study, the Safarov and Zaripova pressure measurements conducted over a vastly-greater-pressure regime are clearly more reliable.

Figure 7 shows the amplitude of the frequency spectrum obtained by the receiver transducer with water or hydrazine in the 1-cm-path-length quartz cell for the speed-of-sound measurements. The measured speed of sound of several substances determined by Eq. (3) is shown in Table 3. The average speed of sound in liquid hydrazine at 293.2 K from the two containers was found to be $2092 \pm 12 \text{ m s}^{-1}$. This number is in agreement with previous experimental measurements. The low value observed by Gibek and Maisonneuve [12] was not observed in the present study.

IV. Discussion

Unfortunately, much of the previous measurements exist simply as numbers in reference material or government reports. These reports lack expanded experimental sections and/or hydrazine purities. There are only two recent peer-reviewed experimental determinations. The current measurement is in good agreement with the previous determination of Safarov and Zaripova obtained by using a different experimental technique [3]. The current measurement is also in good agreement with the value found in the *Chemical*

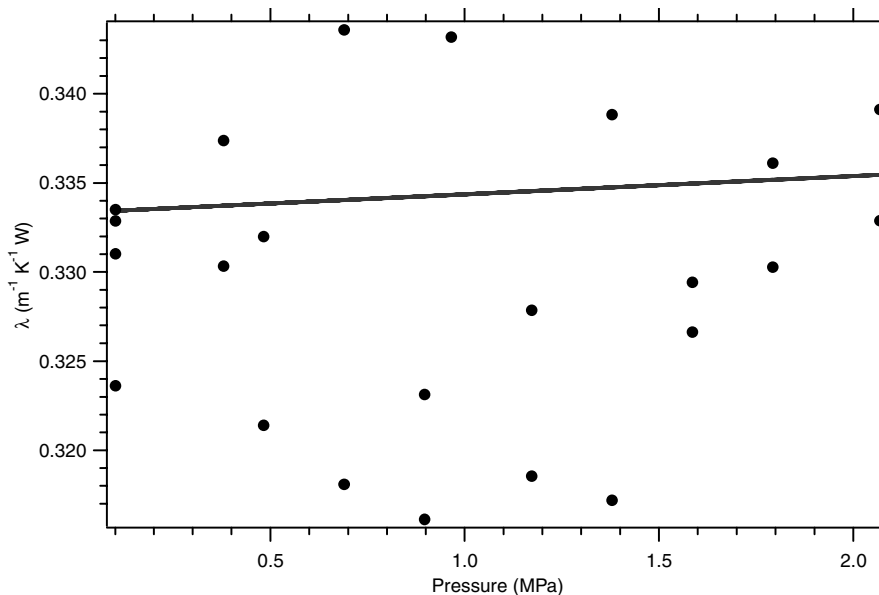


Fig. 6 Thermal conductivity λ as a function of helium pressure; current experimental measurements (circles) and predictions based on Eq. (10) (line).

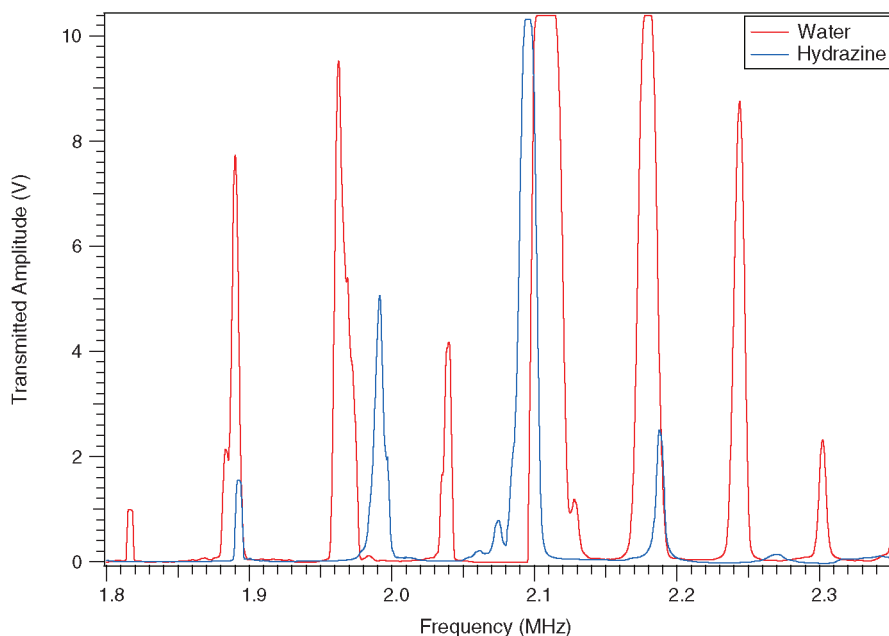


Fig. 7 Frequency resonance spectrum for water (red) and hydrazine (blue) in a quartz cell ($L = 1.0$ cm).

Properties Handbook [4]. Figure 8 shows a plot of the known measurements of pure hydrazine with the present determination included. Also shown is the thermal conductivity of several similar nitrogen based liquids (ammonia [4], MMH [9,18], UDMH [9,18], and phenylhydrazine [19] (90% in water). Figure 8 shows a general trend of decreasing thermal conductivity in these ammonialike compounds with increased substitution. Nonsubstituted ammonia (NH_3) has the highest thermal conductivity, followed by hydrazine (N_2H_4), monosubstituted hydrazine ($\text{CH}_3\text{N}_2\text{H}_3$), and disubstituted hydrazine ($\text{CH}_3\text{NHNHCH}_3$). Contamination with water in some of the samples in Fig. 8 complicates the picture somewhat. The thermal conductivity of pure phenylhydrazine is most likely lower than the measurement because the measurement was done with 10% water added, and water has a large thermal conductivity compared with most organic liquids at 293.15 K).

Safarov and Zaripova [3] observed an increase in the thermal conductivity of liquid hydrazine with increased water content (from 10–70% water; which corresponded to $\lambda = 0.395$ and $0.499 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively, at 29.43×10^6 Pa). In the current study, several samples were measured with 20% water (by volume) added to the pure hydrazine. The addition of 20% water increased the thermal conductivity of the sample to $0.41 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 0.101 MPa. This current observed value is in agreement with the previous measurements from Safarov and Zaripova. Thus, the 5% impurity of water alone is not sufficient to explain the higher values obtained by the Ralph M. Parsons Corporation [1]. The present experiment does not agree with the value of Grebenkov et al. [5]. The value obtained by Grebenkov et al. would be on the extreme low end for most organic liquids at 293 K and 0.101 MPa [8].

The effect of pressure on thermal properties is very low in condensed substances. Pressure is shown to have little effect on the

thermal conductivity of water, ammonia, and hydrazine over the pressure ranges of the current experiment. In general, thermal conductivity is increased slightly with increased pressure [7,20–22]. The results of the current experiment were consistent with this observation. As shown in Fig. 6, there is good agreement between the observed pressure dependence and the previously observed pressure dependence by Safarov and Zaripova [3]. The pressure dependence observed in the current experiment is also similar to that observed by Grebenkov et al. [5], but their experimental values are almost an order of magnitude less than accepted values for the thermal conductivity of liquid hydrazine. Under normal in-orbit hydrazine pressure conditions, the uncertainty in the hydrazine thermal conductivity is greater than the known pressure dependence, which is negligible for practical purposes in these pressure regimes.

Table 4 shows the calculated thermal conductivity of several pure liquids used in this study, for which the speed of sound in the medium is well known [8,9,11,15–17]. The speeds of sound in hydrazine, MMH, and UDMH were previously measured by Kretschmar [10,11] [$c_N = 2093 \text{ m} \cdot \text{s}^{-1}$ (N_2H_4), $1548 \text{ m} \cdot \text{s}^{-1}$ (MMH), and $1247 \text{ m} \cdot \text{s}^{-1}$ (UDMH)] at 293.2 K. As shown in Table 4, the modified Bridgman equation yields reasonable estimates of the thermal conductivity for all liquids studied in this experiment (an average of 20% error) except hydrazine. Hydrazine has an estimated value of nearly double the measured value. The modified Bridgman equation suggests that the older measurements of thermal conductivity are correct, even though these older measurements have $\sim 5\%$ water added. The addition of water to hydrazine most likely increased the thermal conductivity measured in these older measurements. The current results suggest that the Bridgman equation does a particularly poor job at determining the thermal conductivity of hydrazine. Equations that estimate the

Table 3 Speed of sound at 293 K determined by Eq. (3) for several different liquids and the two different sample cells

Substance	Speed of sound, $\text{m} \cdot \text{s}^{-1}$		
	1 cm cell	3.5 cm cell	Reference
Water	1483	1483	1483 [8]
Methanol	1109	1103	1121 [8]
2-Propanol	1181	—	1156 [15,16]
Acetone	1208	1136	1203 [8]
Tetrachloromethane	938	—	937 [17]
Hydrazine	2083	2102	2093 [9]

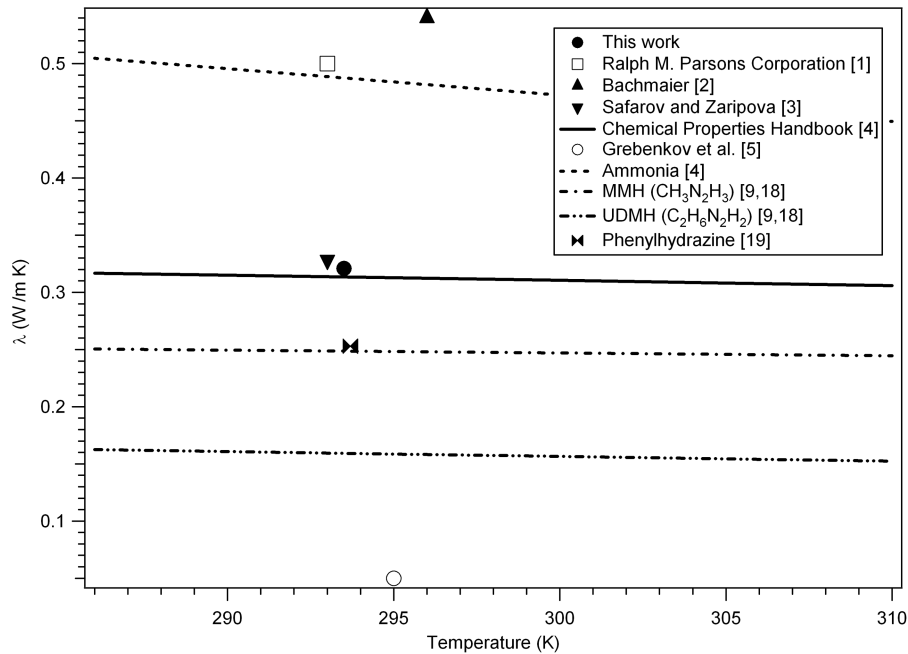


Fig. 8 Thermal conductivity of hydrazine compared with other similar nitrogen compounds.

speed of sound based on thermochemical properties of the liquid often have higher errors when the liquid has strong intermolecular bonding [7].

The speed of sound c_N in a fluid can be calculated by using the parameters from the equation of state [23–25]:

$$c_N = \left(-v^2 \left(\frac{\partial P}{\partial T} \right)_T \right)^{0.5} \tag{11}$$

An accurate value for the compressibility factor Pv/R_cT of hydrazine is needed to determine correct speed-of-sound values from the equations of state. The critical temperature and critical pressure of hydrazine are 653.15 K and 14.69 MPa. The critical volume is less well known, with $v_c = 3.155 \text{ m}^3 \cdot \text{kg}^{-1}$, $v_c = 3.740 \text{ m}^3 \cdot \text{kg}^{-1}$, and $v_c = 4.323 \text{ m}^3 \cdot \text{kg}^{-1}$ previously used [24–28]. Using the value given by Giordano and De Serio [24] ($v_c = 3.740 \text{ m}^3 \cdot \text{kg}^{-1}$), a speed of sound of $c_N = 1830 \text{ m} \cdot \text{s}^{-1}$ was obtained from the Giordano and Serio equation of state. Using the value given by Barragan et al. [25] ($v_c = 3.710 \text{ m}^3 \cdot \text{kg}^{-1}$), a speed of sound of $c_N = 1430 \text{ m} \cdot \text{s}^{-1}$ was obtained from the Giordano and Serio [24] equation of state. This value is slightly lower than the speed of sound obtained from the Barragan et al. [25] equation of state $c_N = 1495 \text{ m} \cdot \text{s}^{-1}$. The critical volume value of Giordano and Serio [24] only has to be changed by 0.4% ($v_c = 3.755 \text{ m}^3 \cdot \text{kg}^{-1}$) to match the experimental values of $c_N = 2090 \text{ m} \cdot \text{s}^{-1}$ at 293.2 K from the Giordano and Serio equation of state. This demonstrates how sensitive the equations of states are to the critical volume value when

determining accurate speed-of-sound numbers. In processes in which the speed of sound is a critical value, such as modeling the waterhammer effect, this dependence should be noted.

V. Conclusions

The thermal conductivity of hydrazine was measured by using the steady-state hot-wire method. The current measurement is consistent with one previous measurement as well as the recommended value in the *Chemical Properties Handbook* [4]. Older measurements that contained 5% water are consistent with the estimated thermal conductivity estimated by using the speed of sound in hydrazine. The modified Bridgman equation was found to be inappropriate for estimating the thermal conductivity of hydrazine. Given the importance of the thermal conductivity, a more modern measurement by transient hot-wire method that included temperature dependence would be appropriate. A measurement of the thermal conductivity of hydrazine as a function pressure by the transient hot-wire method demonstrates that pressures normal to on-orbit storage do not change the thermal conductivity much.

Acknowledgments

This work was supported under The Aerospace Corporation’s Mission Oriented Investigation and Experimentation program, funded by the U.S. Air Force Space and Missile Systems Center under contract no. FA8802-04-C-0001.

Table 4 Thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) calculated by Eq. (1) at 293.15 K

Substance	λ		
	Calculated	Reference	% difference
Water	0.601	0.597	0.7
Methanol	0.262	0.204	28.4
Acetone	0.189	0.167	13.2
Chloroform	0.151	0.118	28.0
Carbon tetrachloride	0.123	0.104	18.3
2-propanol	0.177	0.136	30.1
Hydrazine	0.575	0.32	79.7
MMH	0.298	0.249	19.7
UDMH	0.189	0.159	18.9

References

- [1] "Hydrazine Study" Ralph M. Parsons Corp., Rept. NOa-10118, Pasadena, CA, Oct. 1950.
- [2] Bachmaier, F., "Researches About the System Hydrazine-Methylalcohol," DLR, German Aerospace Center, Rept. FB-68-05, N68-20247, Köln-Porz, Germany, Jan. 1968.
- [3] Safarov, M. M., and Zaripova, M. A., "Density Dependence of Heat Conductivity of Aqueous Hydrazine Solutions within Wide Ranges of Temperatures and Pressure," *Journal of Engineering Physics and Thermophysics*, Vol. 68, No. 3, 1995, pp. 390–394.
doi:10.1007/BF00859054
- [4] Yaws, C. L. (ed.), *Chemical Properties Handbook*, McGraw-Hill, New York, 1999; also available online at http://www.knovel.com/webportal/basic_search/display?_EXT_KNOVEL_DISPLAY_bookid=49 [retrieved July 2009].
- [5] Grebenkov, J. A., Kotelevsky, G. Y., and Sapitsa, V. V., "Heat Transfer Measurements of Some Technically Important Nitrogen Containing Liquids," *Doklady of the National Academy of Sciences of Belarus*, Vol. 3, 2003, pp. 109–115.
- [6] Bridgman, P. W., "A Complete Collection of Thermodynamic Formulas," *Physical Review*, Vol. [3], No. 4, 1914, 273–281.
- [7] Tseederberg, V. N., and Cess, R. D., "Thermal Conductivity of Gases and Liquids," MIT Press, Cambridge, MA, 1965.
- [8] Lide, D. R. (ed.), *CRC Handbook of Chemistry and Physics* [online book], 89th ed., CRC Press, Boca Raton, FL, 2009, <http://www.hbcpnetbase.com> [retrieved July 2009].
- [9] Eckart, W. S., *Hydrazine and Its Derivatives Preparation, Properties, Applications*, 2nd ed., Wiley, New York, 2001.
- [10] Kretschmar, G. G., "The Velocity of Sound in Some Rocket Propellant Liquids," *ARS Journal*, Vol. 23, 1953, pp. 82–84.
- [11] Kretschmar, G. G., "The Isothermal Compressibilities of Some Rocket Propellant Liquids, and the Ratio of the Two Specific Heats," *Jet Propulsion*, Vol. 24, 1954, pp. 379–381.
- [12] Gibek, I., and Maisonneuve, Y., "Waterhammer Tests with Real Propellants," 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Tucson, AZ, AIAA Paper 2005-4081, 10–13 July 2005.
- [13] "Standard Test Method for Thermal Conductivity of Liquids" ASTM International, Standard ASTM D2717-95 West Conshohocken, PA, Aug. 1995, p. 1071.
- [14] Han, W., Sinha, N. D., Springer, N. K., and Lizon, D. C., "Noninvasive Measurement of Acoustic Properties of Fluids Using Ultrasonic Interferometry Technique," 8th International Symposium on Non-Destructive Characterization of Materials, Boulder, CO, Los Alamos National Labs., Paper LA-UR-97-2018, 15–20 June 1997.
- [15] Oakley, B., Hanna, D., Shillor, M., and Barber, G., "Ultrasonic Parameters as a Function of Absolute Hydrostatic Pressure. 2: Mathematical Models of the Speed of Sound in Organic Liquids," *Journal of Physical and Chemical Reference Data*, Vol. 32, No. 4, 2003, pp. 1535–1544.
doi:10.1063/1.1555589
- [16] González, B., Domínguez, Á., and Tojo, J., "Viscosities, Densities, and the Speed of Sound of the Cycloalkanes with Secondary Alcohols at $T=(293.15, 298.15 \text{ and } 303.15) \text{ K}$: New UNIFAC-VISCO Interaction Parameters," *Journal of Chemical and Engineering Data*, Vol. 51, No. 3, 2006, pp. 1076–1087.
doi:10.1021/je050540h
- [17] Takagi, T., Sawada, K., "Speed of Sound in Liquid Tetrachloromethane and Benzene at Temperatures from 283.15 K to 333.15 K and Pressures Up to 30 MPa," Urakawa, H., Ueda, M., and Cibulka, I., *Journal of Chemical Thermodynamics*, Vol. 36, No. 8, 2004, pp. 659–664.
doi:10.1016/j.jct.2004.04.013
- [18] "Engineering Properties Data on Rocket Propellants (U)," U.S. Air Force Rocket Propulsion Lab., Rept. AFRPL-TR-66-122, July 1966.
- [19] Safarov, M. M., Zarpova, A. M., Radjobov, S. F., and Davlatova, V. S., "Thermophysical Properties of Hydrazine-Substituted Aqueous Solutions Under Various Temperatures and Pressures," *High Temperatures—High Pressures*, Vol. 31, No. 1, 1999, pp. 37–42.
doi:10.1068/htec431
- [20] *Thermophysical Properties of Fluid Systems* [online database], <http://webbook.nist.gov/chemistry/fluid/> [retrieved July 2009].
- [21] Perkins, R., Ramires, M. L. V., de Castro, C. N., and Cusco, L., *Journal of Chemical and Engineering Data*, Vol. 47, No. 5, 2002, pp. 1263–1271.
doi:10.1021/je0101202
- [22] Bruno, T. J., Huber, M. L., Laesecke, A., Lemmon, E. W., and Perkins, R. A., "Thermochemical and Thermophysical Properties of JP-10," National Inst. of Standards and Technology Rept. 6640, Gaithersburg, MD, 2006.
- [23] Mitchell, C. M., Rakoff, W. R., Jobe, O. T., and Sanchez, D. L., "Thermodynamic Analysis of Equations of State for Monopropellant Hydrazine," *Journal of Thermophysics and Heat Transfer*, Vol. 21, No. 1, 2007, pp. 243–246.
doi:10.2514/1.22798
- [24] Giordano, D., and De Serio, M., "Thermodynamic Model of Hydrazine that Accounts for Liquid-Vapor Phase Change," *Journal of Thermophysics and Heat Transfer*, Vol. 16, No. 2, 2002, pp. 261–272.
doi:10.2514/2.6676
- [25] Barragan, M., Woods, S., Julian, L. H., Wilson, B. D., and Saulsberry, R., "Thermodynamic Equations of State for Hydrazine and Monomethylhydrazine," *Combustion and Flame*, Vol. 131, No. 3, 2002, pp. 316–328.
doi:10.1016/S0010-2180(02)00410-8
- [26] Giordano, D., "Survey of Thermodynamic Properties of Hydrazine," *Journal of Chemical and Engineering Data*, Vol. 46, No. 3, 2001, pp. 486–505.
doi:10.1021/je000301o
- [27] Yaws, C. L., Hopper, J. R., and Rojas, M. G., "Ammonia and Hydrazine," *Chemical Engineering Journal (Lausanne)*, Vol. 81, No. 25, 1974, pp. 91–100.
- [28] Hannum, J. A., "Hazards of Chemical Rockets and Propellants. Volume 3: Liquid Propellants Manual," Chemical Propulsion Information Agency, Rept. AD-A158115, Laurel, MD, 1985.