*International Journal of Thermophysics, Vol. 8, No. 2, 1987*

# Simultaneous Measurement of the Thermal Conductivity and Thermal Diffusivity of Liquids

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*Received April 23, 1986*

In theory, the hot-wire technique for measuring the thermal conductivity of liquids can be used simultaneously to determine the thermal diffusivity. In practice, however, the latter property has so far been determined only with moderate accuracy because of (a) inaccurate bridge balancing due to drift problems, (b) parasitic capacities that delay the heating, and (c) poor precision in the determination of the time. A new measurement procedure has been developed which features (a) a short measuring time, (b) a reduced significance of the balancing technique, (c) a good reproducibility, and (d) a low sensitivity to most error sources. Thermal conductivity and thermal diffusivity results using this procedure, for toluene and *n*-heptane, which are the generally accepted standards for thermal conductivity, are presented and compared with results from other sources.

**KEY WORDS:** hot-wire technique; liquids; *n*-heptane; thermal conductivity; thermal diffusivity; toluene.

## 1. INTRODUCTION

The thermal conductivity of liquids is usually measured using a hot-wire technique (hot wire incorporated in a Wheatstone bridge). The theory behind this technique indicates that one should be able to determine the thermal diffusivity simultaneously. Various investigators [1–3] have attempted to measure this property, but because of practical limitations, the best reported accuracy has been 5%, with a reproducibility of only 4 to 5%.

This investigation was aimed at improving the accuracy so that the hot-wire method could seriously compete with the laser flash method and

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0195-928X/87/0200-0181$05.00/0

calorimetric techniques. The method would be particularly suitable if properties at nonambient conditions were required.

The nonreproducibility of the bridge balance and the inaccuracy of the time base were identified as the main sources for the inaccuracy of the thermal diffusivity results. The solution was first sought in an improved balancing technique. However, even when the balancing technique had been improved (see Section 3.2), the increase in accuracy was only moderate. This led to the conclusion that the zero drift of the bridge and of the DC amplifier in the system was still too large. A technique whereby the bridge could be balanced at the same time that the actual measurement was taken was needed to improve the reproducibility.

Such a method was developed (see Section 3.3) and, in combination with an accurate time determination (Section 3.4), resulted in reproducibilities of within 1%; the accuracy is estimated to be better than 2%. It is believed that even higher accuracies are possible.

## 2. BACKGROUND

The basis for the simultaneous determination is the well-known "long-time" ($t$) temperature response ($T$) of a wire (radius $a$) immersed in a liquid (thermal conductivity $\lambda$, thermal diffusivity $\kappa$), when a constant rate of heating ($Q$) is applied:

$$T=\frac{Q}{4\pi\lambda}\ln(t)-\frac{Q}{4\pi\lambda}\ln(a^2C/4\kappa)=\text{slope}\cdot\ln(t)+\text{intercept} \tag{1}$$

where $C=\exp(\gamma)$, and $\gamma=$ Euler's constant $=0.5772$.

This equation shows that the thermal conductivity can be determined from the slope of the plot of temperature versus log ($t$), and the thermal diffusivity from its intercept.

It has been suggested [1] that to measure this intercept accurately a low-speed (ca. 16-Hz) sampling device with an extremely high resolution (17-bit A/D conversion) should be employed. The reproducibility of the thermal diffusivity (4%) by that means, however, is not consistent with what would be expected. Reproducibilities of others [2, 3] are about 10%.

Much attention has been given to accurate bridge balancing techniques since a nonzero bridge diagonal voltage at a zero temperature rise of the wire will cause an error in the measured intercept (and thus in the thermal diffusivity).

Standard balancing techniques are as follows:

(a) the use of a galvanometer and a low voltage supplied to the bridge,

(b) the use of a band-filter/amplifier and a small sine-wave supply, and

(c) the use of a lock-in amplifier and a small sine-wave supply.

All these methods require the installation of expensive additional equipment but still do not improve the reproducibility.

## 3. THE NEW MEASUREMENT PROCEDURE

### 3.1. Instrumentation

The hot wire is incorporated in a Wheatstone bridge arrangement which is fed by a constant voltage source. The bridge diagonal voltage, which represents the transient temperature rise of the wire, is captured with a digital storage oscilloscope (DSO) coupled to a personal computer.

The DSO used has an 8-bit A/D converter and a memory that can store 4000 data points. The maximum sampling frequency is 1 MHz.

The DSO and a preamplifier (differential input) are calibrated, and the error in the measurements caused by the data acquisition instrumentation is dependent solely on the resolution of the A/D converter.

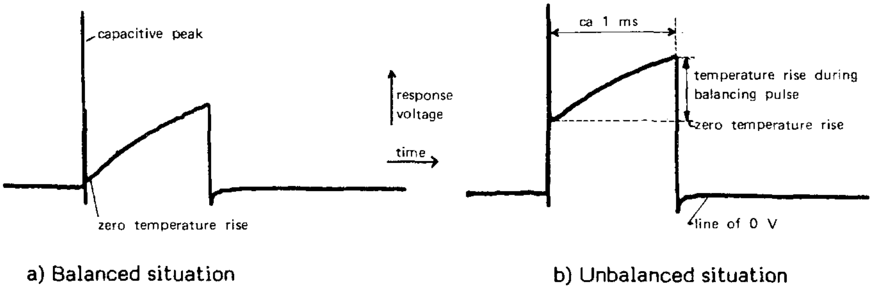
### 3.2. A New Balancing Technique

A very sensitive and convenient method (when a DSO is used) is to send short pulses (ca. 1-ms duration) to the bridge at a frequency of 1 Hz or lower and record the resulting bridge diagonal voltage. The voltage can be as high as that applied during a measurement, so a computer-controlled relay in the power-supply line of the bridge can be used to generate these pulses.

The pulses can be observed with the DSO. The pulse sent to the bridge also triggers this device.

During this short balancing pulse, the temperature of the hot wire will start rising. The initial part of the response pulse should be used as an indication of the balance of the bridge. In Figs. 1a and 1b hard-copy outputs of the DSO show a balanced and an unbalanced situation. The peak at the beginning of the pulse is caused by parasitic capacities, but careful component selection and tuning reduced these to such an extent that they influenced neither the balancing procedure nor the actual measurement.

This balancing technique, which was adopted for its convenience, is at least as sensitive as the galvanometer technique. However, drift results in measurement inaccuracies even with a perfectly balanced bridge. Compensation for drift is therefore essential and is described below.



a) Balanced situation b) Unbalanced situation

**Fig. 1.** Hard-copy outputs of the digital oscilloscope during the balancing procedure. Voltage (vertical) is plotted against time (horizontal). (a) Balanced bridge; (b) unbalanced bridge.

### 3.3. Integration of the Balancing Technique in the Measurement

The proportionality between the bridge output voltage and the temperature rise of the wire can be significantly disturbed by drift of the measuring system. In our equipment the drift indeed proved to be the factor limiting the reproducibility of the measurements. This is why the conventional balancing techniques and the technique described in Section 3.2 cannot be relied upon for purposes of determining the thermal diffusivity. These techniques serve only to balance the bridge roughly and to allow optimum use of the working range of the DSO.

To solve the balancing problem, the DSO is used at a much higher sampling frequency (50 kHz) than is normally used in the transient hot-wire method. The first measuring points then represent the bridge diagonal voltage before the temperature of the wire starts to rise. This eliminates the need to make the poor assumption, necessary in conventional balancing techniques, that the bridge diagonal voltage remains zero until the temperature starts to rise. In this way balance is achieved at the same time that the measurement is taken.

With our experimental equipment this balancing procedure resulted in a significantly improved reproducibility compared with that in previous research [1–3].

### 3.4. Importance of an Accurate Time Base

This new measuring procedure is a necessary, but not sufficient, requirement for good reproducibility. Another important requirement is an accurate time base against which the measured temperature is registered. The thermal diffusivity is found by manipulating Eq. (1):

$$\kappa = \frac{a^2 C}{4} \exp(\text{intercept/slope}) \qquad (2)$$

The physical meaning of the exponential function containing the experimental data on the right-hand side of Eq. (2) can also be deduced from Eq. (1): it is the intercept with the time axis or the time $t^*$ at which the long-time approximation predicts the start of the temperature rise of the wire:

$$t^* = \exp(-\text{intercept/slope}) = \frac{a^2 C}{4\kappa} \tag{3}$$

In other words, the thermal diffusivity is determined by the value of $t^*$, which in our case is of the order of 1 ms. A delay in the registration of the time is thus a possible source of inaccuracy. Methods of preventing such time delays have not previously been mentioned in the literature.

The error in $t^*$ caused by a time delay can be expressed as follows (see Appendix):

$$\frac{\Delta t^*}{t^*} = \left(\frac{t_\mathrm{b} + t_\mathrm{d}}{t_\mathrm{b}}\right)^{T_\mathrm{e}/(T_\mathrm{e} - T_\mathrm{b})} \left(\frac{t_\mathrm{e}}{t_\mathrm{e} + t_\mathrm{d}}\right)^{T_\mathrm{b}/(T_\mathrm{e} - T_\mathrm{b})} - 1 \tag{4}$$

where $t_\mathrm{b}$ and $t_\mathrm{e}$ are the times and $T_\mathrm{b}$ and $T_\mathrm{e}$ the temperatures at the beginning and at the end of a measurement and $t_\mathrm{d}$ is the time delay. The error depends on the relative error made in the absolute time and is also very sensitive to the logarithmic time span of the measurement.

To eliminate errors in $t^*$, the most practical approach is to use a high resolution for the time base.

Further, it is important to be aware of the potential inaccuracies caused by the use of digital electronic equipment. Although the time between measuring points is very accurately determined, the absolute time can be in error by a significant portion of the sampling interval. For accurate measurements, it is therefore advisable to use a sampling interval that is smaller than the maximum allowable time delay.

When slow sampling devices are used, the time delay between the triggering and the measurement will be determined by the subroutine that regulates the data capture; this time delay must be well known. Instruments without a trigger facility cannot be used for this purpose.

An error in the determination of the time is not necessarily caused by the digital equipment. The use of a filter to smooth the signal can reduce the accuracy of the determination of the thermal diffusivity, because every filter causes a time delay which depends on the rate of change of the signal. A filter for high-frequency noise, however, can be used under certain conditions. A filter to eliminate mains noise must not be used.

## 4. IMPLEMENTING THE NEW MEASUREMENT PROCEDURE

A consequence of the use of a DSO is that the storage capacity can become a limitation. If, say, the expected intercept with the time axis is approximately 1 ms, then a 0.02-ms sampling time or shorter should preferably be used. With a memory for 4000 data points, the maximum measuring time is 80 ms.

The long-time approximation is valid only after about 100 ms. This means that more terms of the exact solution have to be used. The approximation with sufficient terms can be written as follows [4]:

$$T=\frac{Q}{4\pi\lambda}\left\{\left[1-\frac{a^2}{2\kappa t}\left(\frac{\kappa}{\kappa_w}\frac{\lambda_w}{\lambda}-1\right)\right]\ln\left(\frac{4\kappa t}{a^2C}\right)+\frac{a^2}{2\kappa t}\right\} \tag{5}$$

The subscript w is used to denote a wire property.

If only the data points between 20 and 80 ms are considered, then Eq. (5) deviates only slightly from Eq. (1). The raw data are therefore corrected with the terms that constitute the difference between Eq. (1) and Eq. (3), as in the left-hand side of Eq. (6), before the regression calculation is done:

$$T-\frac{Q}{4\pi\lambda}\frac{a^2}{2\kappa t}\bigg/\left[1-\frac{a^2}{2\kappa t}\left(\frac{\kappa}{\kappa_w}\frac{\lambda_w}{\lambda}-1\right)\right]=\frac{Q}{4\pi\lambda}\left(\ln\frac{4\kappa t}{a^2C}\right) \tag{6}$$

Unfortunately these corrections are weak functions of the results of the measurement, the thermal conductivity and the thermal diffusivity. An

**Table I.** Thermal Conductivity and Thermal Diffusivity Results for Toluene and *n*-Heptane

| Toluene | | | *n*-Heptane | | |
|---|---|---|---|---|---|
| Temp. (°C) | Th. cond. ($W \cdot m^{-1} \cdot K^{-1}$) | Th. diff. ($10^{-8}\,m^2 \cdot s^{-1}$) | Temp. (°C) | Th. cond. ($W \cdot m^{-1} \cdot K^{-1}$) | Th. diff. ($10^{-8}\,m^2 \cdot s^{-1}$) |
| 14.4 | 0.1349 | 9.03 | 13.8 | 0.1262 | 8.18 |
| 32.6 | 0.1294 | 8.55 | 33.1 | 0.1195 | 7.67 |
| 54.8 | 0.1235 | 7.99 | 55 | 0.1124 | 7.22 |
| 74.6 | 0.1180 | 7.56 | 74.6 | 0.1059 | 6.83 |
| 94.4 | 0.1134 | 7.21 | 94.4 | 0.1007 | 6.5 |
| 113.6 | 0.1081 | 6.65 | 113.6 | 0.0961 | 6.23 |
| 133.2 | 0.1045 | 6.4 | 133.1 | 0.0917 | 5.85 |
| 152.8 | 0.0996 | 6.12 | 152.2 | 0.0870 | 5.54 |
| 171.2 | 0.0959 | 5.76 | 170.6 | 0.0831 | 5.2 |

iterative procedure must therefore be used, but the solution converges rapidly.

The recent development of the plug-in oscilloscope for personal computers may result in systems with sufficient memory to overcome this problem.

## 5. REVIEW OF ERROR SOURCES

Traditional error sources such as convection, the end-effect [5], radiation [6], change in the heat production rate, and wall effects contributed together less than 0.4% to the total error of the measurement. Time delays which could be caused by

(a) bouncing of the switch that initiates the measurement and

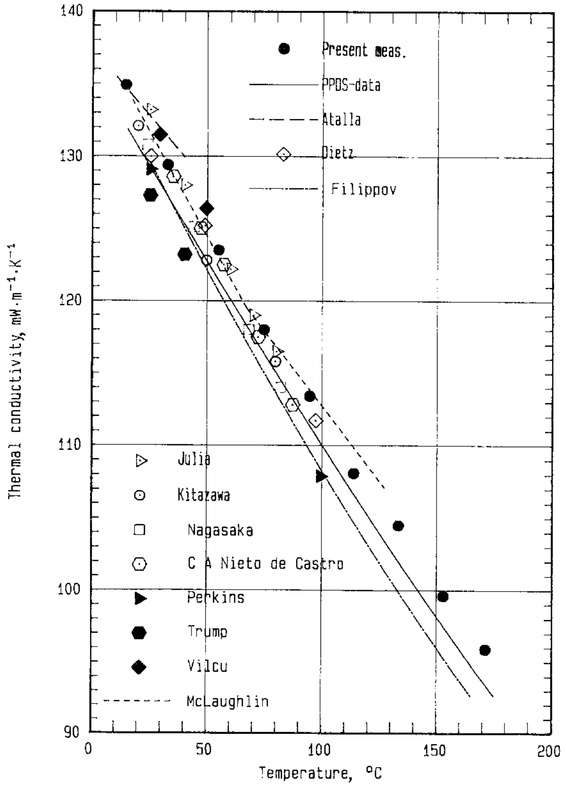


Fig. 2. Thermal conductivity of toluene.

(b) parasitic capacities that store a part of the energy that was meant to heat the wire

were minimized by choosing appropriate electronic components and resulted in a negligible error.

## 6. RESULTS

Table I gives the data obtained by applying the new measurement procedure in a hot-wire apparatus that is described elsewhere [7]. For all the measurements, a platinum wire 24.4 $\mu$m in diameter and 217 mm long and a heat input of 0.35 $W \cdot m^{-1}$ were used.

In Figures 2 to 5 the thermal conductivities and thermal diffusivities of toluene and *n*-heptane are presented as a function of the temperature. Each indicated point is the average of 10 separate measurements and has a

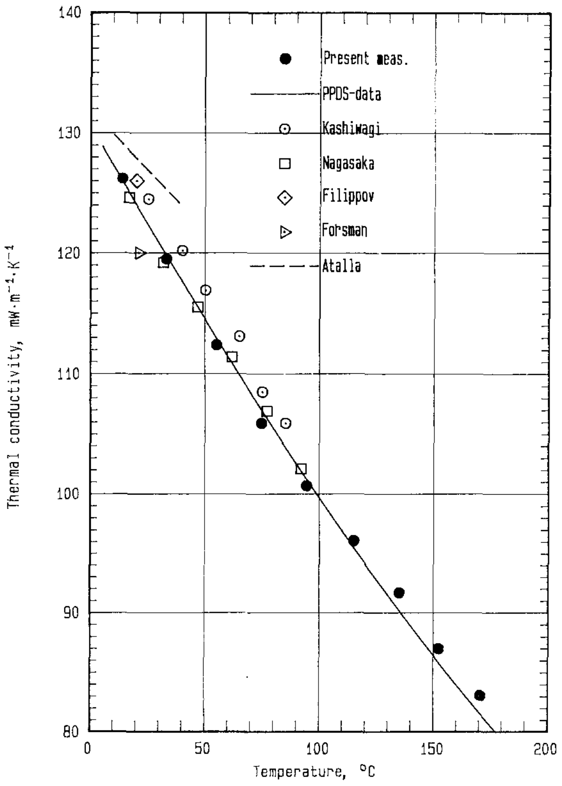


**Fig. 3.** Thermal conductivity of *n*-heptane.

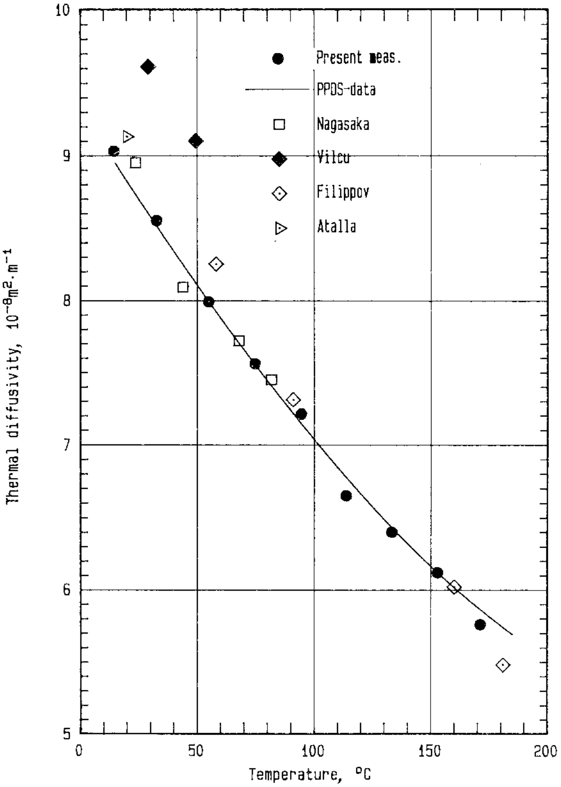


Fig. 4. Thermal diffusivity of toluene.

reproducibility usually well within 1%. Data from other sources [1, 6, 9–23] are included in the figures and show a good agreement with the data obtained here.

## APPENDIX: ERROR DUE TO AN INACCURATE TIME BASE

The values of $A$ and $t^*$ in Eq. (A.1), determined by a least-squares analysis on a series of measuring points, are the constants from which the thermal conductivity and the thermal diffusivity are calculated.

$$T = A \ln(t) - A \ln(t^*) \tag{A.1}$$

The beginning and the end of the measurement can be represented by the

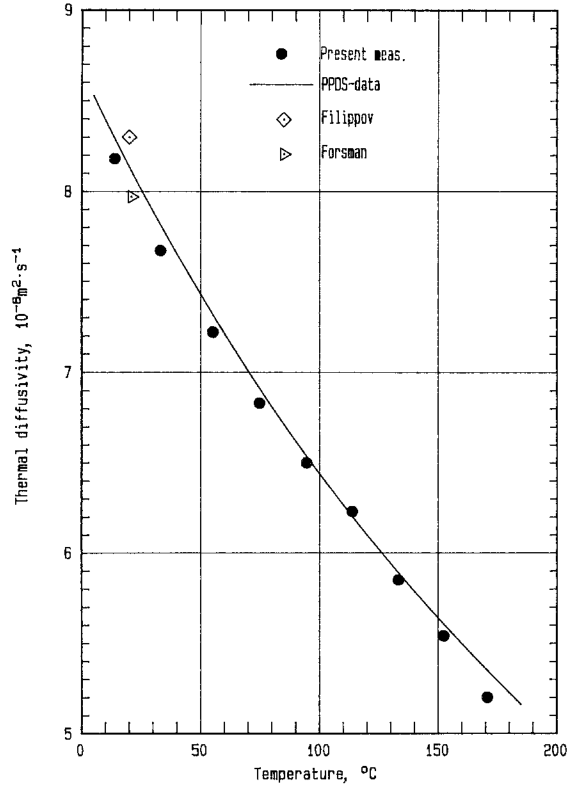


Fig. 5. Thermal diffusivity of *n*-heptane.

points $t_b$, $T_b$ and $t_e$, $T_e$. The regression constants then follow from these points by the relations

$$A=\frac{T_e-T_b}{\ln(t_e/t_b)}, \qquad t^*=t_b e^{-T_b/A} \tag{A.2}$$

A delay in the registration of the time would change Eq. (A.1) as follows:

$$T=A'\ln(t+t_d)-A'\ln(t^{*\prime}) \tag{A.3}$$

The new regression constants $A'$ and $t^{*\prime}$ then follow from Eq. (A.2) by substituting $t_d-t_d$ for $t_b$ and $t_e-t_d$ for $t_e$.

It is easy to deduce that the error in $t^*$ is then determined by

$$\frac{t^{*\prime}-t^*}{t^*}=\left(\frac{t_b+t_d}{t_b}\right)^{T_e/(T_e-T_b)}\left(\frac{t_e}{t_e+t_d}\right)^{T_b/(T_e-T_b)}-1 \tag{A.4}$$

## ACKNOWLEDGMENT

The author wishes to thank Dr. R. E. Hicks for his contribution to this paper.

## REFERENCES

1. Y. Nagasaka and A. Nagashima, *Rev. Sci. Instrum.* **52**:229 (1981).
2. R. Vilcu and A. Ciochina, *Rev. Roum. Chim.* **26**:527 (1981).
3. R. G. Ross, P. Anderson, and G. Bäckström, *Mol. Phys.* **38**:377 (1979).
4. J. J. Healy, J. J. de Groot, and J. Kestin, *Physica* **82C**:392 (1975).
5. P. G. Knibbe, *Int. J. Heat Mass Transfer* **29**:463 (1986).
6. E. McLaughlin and J. F. T. Pittman, *Phil. Trans. R. Soc. Lond. A.* **270**:557 (1971).
7. P. G. Knibbe, Ph. D. thesis, University of Natal (1986).
8. Y. Nagasaka and A. Nagashima, *Ind. Eng. Chem. Fund.* **20**:216 (1981).
9. *Physical Property Data Service* (The Institution of Chemical Engineers, Rugby, England).
10. S. R. Atalla, A. A. El-Sharkawy, and F. A. Gasser. *Int. J. Thermophys.* **2**:155 (1981).
11. F. J. Dietz, J. J. de Groot, and E. U. Franck, *Proc. Int. Conf. Prop. Steam* **9**:425 (1979).
12. L. P. Filippov, S. N. Nefedov, S. N. Kravchun, and E. A. Kolykhalova, *Inzhenerno-Fiz. Zh.* **38**:644 (1980).
13. Y. H. Julia, J. F. Renaud, D. J. Ferrand, and P. F. Malbrunot, *Rev. Sci. Instrum.* **48**:1654 (1977).
14. N. Kitazawa and A. Nagashima, *Bull JSME* **24**:374 (1981).
15. C. A. N. deCastro, S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *Int. J. Thermophys.* **4**:311 (1983).
16. R. A. Perkins, S. S. Mohammadi, R. C. McAllister, M. S. Graboski, and E. D. Sloan, *J. Phys. E. Sci. Instrum.* **14**:1279 (1981).
17. W. N. Trump, H. W. Luebke, L. Fowler, and E. M. Emery, *Rev. Sci. Instrum.* **48**:47 (1977).
18. H. Kashiwagi, M. Oishi, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:101 (1982).
19. L. P. Filippov and S. N. Nefedov, *Zavodskaya Lab.* **45**:1126 (1979).
20. H. Forsman, P. Anderson, and G. Bäckström, *Physica* **114B**:287 (1982).
21. R. Vilcu, A. Ciochina, and G. Vasu, *Rev. Roum. Chim.* **27**:313 (1982).
22. L. P. Filippov, S. N. Nevedov, and S. N. Kravchun, *Int. J. Thermophys.* **1**:141 (1980).
23. Y. Nagasaka and A. Nagashima, *Rev. Sci. Instrum.* **52**:229 (1981).