

Transient Hot-Wire Measurements of the Thermal Conductivity of Gases at Elevated Temperatures¹

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The paper describes a new instrument for the measurement of the thermal conductivity of gases over a wide range of thermodynamic states. The instrument operates on the transient hot-wire principle and the design of the cells that is necessary to secure an accuracy of $\pm 0.3\%$ in the thermal conductivity is considered in some detail. A selection of the results on ten pure gases is presented. The data for the monatomic gases in the limit of zero density are employed to confirm the accuracy of the measurements, whereas the results at higher densities for these and other gases are used to examine the concept of a temperature-independent excess thermal conductivity.

KEY WORDS: excess properties; gases; inelastic collisions; thermal conductivity; transient hot-wire instrument.

1. INTRODUCTION

Following the pioneering work of Haarman [1] and the developments carried out by Kestin, Wakeham, and their collaborators [2–5], the transient hot-wire instrument has become widely accepted as the most accurate technique for the measurement of the thermal conductivity of gases. Over a period of 10 years, a number of independent measurements carried out near room temperature have confirmed that an accuracy of $\pm 0.3\%$ in the thermal conductivity is possible under these conditions [6–10]. This success was first achieved in 1980, and since that time a series

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of measurements of the thermal conductivity of polyatomic gases has been carried out, almost exclusively near room temperature. The results have proved both interesting and surprising, since at the same time they cast doubt on traditional views of the evaluation of the transport properties [11] and show promise as a probe of anisotropic intermolecular pair potentials [12].

When these facts are combined with the need for high-quality data it is clear that what is required is a systematic study of the thermal conductivity over a wide range of temperatures in which the accuracy characteristic of operation near room temperature is, as nearly as possible, maintained. However, the number of measurements reported in which the transient hot-wire technique has been employed away from room temperature is very small. Roder and Nieto de Castro [13–15] have employed the technique at cryogenic temperatures, while Clifford et al. [8, 16] have operated at high temperatures, and Venart and his collaborators operated over both regions [17]. However, in none of these cases has it proved possible to maintain the high accuracy. In our own laboratory we have designed an instrument for operation over the temperature range 80–420 K but have so far reported just one set of measurements for which an accuracy of $\pm 0.3\%$ could be claimed [18]. There is therefore a considerable discrepancy between the promise of the instrument and its actual performance.

In this paper we consider the reasons for this discrepancy, which turn out to be of a practical nature rather than ones of principle. The review is conducted to provide cautionary information for those working, or intending to work, with an instrument of the transient hot-wire type and to provide a background for the design of our present instrument. The new instrument has been employed in a series of new measurements, and some of the results are presented here.

2. THERMAL CONDUCTIVITY CELLS

The principle of the transient hot-wire technique is relatively straightforward and details may be found elsewhere [2, 4, 5]. For an infinitely long thin wire of radius a , immersed in a fluid of infinite extent, the temperature rise of the wire, ΔT_{id} , following the initiation of heat generation at a rate q in it at time $t=0$ is given by [2]

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \ln \frac{4\kappa t}{a^2 C} \quad (1)$$

where λ is the thermal conductivity of the fluid, κ the thermal diffusivity, and C a numerical constant. Subject to a number of corrections [2], ren-

dered small by design [3, 7], Eq. (1) represents the working equation of the experimental method from which the thermal conductivity is derived by means of linear regression on a set of (ΔT , $\ln t$) data. In practice, the temperature rise of the wire is determined from its resistance change, which itself is measured by means of some form of automatic DC bridge [19, 20]. Because a wire of finite length must be employed in a real instrument, it is usual to employ two wires differing only in length so that a central section of one wire acts as a finite segment of an infinite wire.

Two conditions must be met if this technique is to yield accurate thermal conductivity data. First, there must be no relative motion of the fluid and the important central section of the wire, since this produces a convective contribution to the heat transfer from it. Second, there must be no contributions to the resistance change of the wire beyond those directly related to its temperature rise. It is the failure of attempts to satisfy one or other of these conditions that have made some thermal conductivity cell designs inappropriate, particularly for operation over a range of temperature. Here we consider a number of cell designs which have been proposed and used for measurements and consider their advantages and disadvantages.

The principal advantage which accompanies the use of the transient hot-wire technique is the fact that the entire measurement can be completed in a time of 1 s or less, which is short compared with the time of onset of significant motion of the fluid with respect to the fixed cell walls. The original cell design proposed by de Groot et al. [3, 21] is shown schematically in Fig. 1a; the 7- μm -diameter platinum wire is fixed at both ends to rigid supports on the axis of the cylindrical cell. After a number of years of work it was realized that this configuration failed to satisfy the first of the conditions set out above. This is because the axial, thermal extension of the wire caused by its transient heating by 3–4 K causes it to move laterally through the gas and so a convective contribution to the heat transfer arises. This motion reveals itself as a discontinuity in the slope of the line of ΔT vs $\ln t$ which accompanies the change from a moving wire to a stationary wire in an off-axis position [6].

This defect was overcome in the cell design shown in Fig. 1b [6]. Here the wire is tensioned by a weak gold spring so that the wire extension during heating is absorbed by a contraction of the spring. The tension on the wire was chosen to be no more than 20% of the platinum yield stress, and the design has been operated successfully at room temperature [6, 7], when allowance is made for the varying tension in the wire during a measurement which affects the resistance temperature calibration [5]. For operation over a wide range of temperature the same design has proved difficult to use because the thermal characteristics of the gold springs prove unreliable over a number of cycles of temperature and because it is difficult

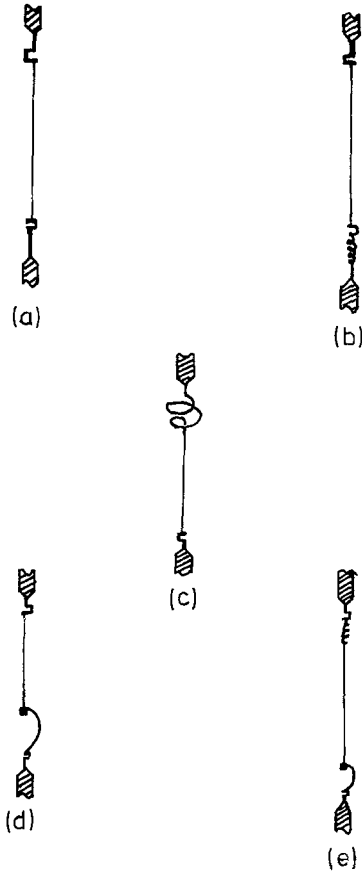


Fig. 1. Wire suspension methods for transient hot-wire cells.

to ensure that the wire is always under a tension of a known, but not excessive, amount [22]. An alternative version of this design is shown in Fig. 1c where the spring is placed above the wire and designed specifically to ensure that the wire is maintained under a tension within prescribed limits over a defined range of temperature [22]. In this case the spring was made from a beryllium-copper alloy and was designed for a specific long-term period of operation, since creep in the platinum wire limits its ultimate stability [22].

Apart from all the disadvantages of spring mechanisms mentioned above, a further difficulty has been encountered when relatively large currents flow in the helical springs, such as occur when fluids with a high thermal conductivity are measured. It has been observed that the tendency

of the spring to contract owing to magnetic forces causes an extra longitudinal tension in the wire of an oscillatory nature. This tension induces resistance oscillations in the wire of a few milliohms or less, but they are significant to the measurement since they cause oscillations in the measured wire temperature at a level of about 0.1% of the overall temperature rise. This difficulty curtailed our operation with a cell of this type to just one series of measurements.

In order to obviate some of the problems discussed above, a cell of the design shown schematically in Fig. 1d was employed. Here, the wire hangs from the top fixed support and carries a small platinum weight (70 mg) at its lower end to provide a constant tension throughout the measurement. Electrical continuity is ensured by a loop of soft gold between the weight and the bottom support. This design has been employed successfully in liquids for a number of years [23], but because of the relatively low damping in gases, special precautions are necessary elsewhere in the apparatus if the wire is not to undergo a pendulum-like oscillation driven by extraneous building vibrations. The special precautions taken in our latest equipment are described later.

While the type of design shown in Fig. 1d solves many of the problems associated with other cells, it introduces a further difficulty. Most of the temperature rise of the wire takes place in the first few hundredths of seconds of heating, as does the inevitable axial wire extension. The effect, therefore, is essentially the same as dropping the weight on the end of the elastic wire. Consequently, the thermal extension induces axial oscillations of the wire/weight assembly, which again cause resistostrictive oscillations of the wire resistance at the level of a few milliohms. These oscillations have been observed directly on the output of a fast recovery storage oscilloscope and are significant since, as before, they contribute to apparent oscillations of the wire temperature superimposed on its steady increase.

To overcome this final problem the scheme shown in Fig. 1e has been adopted. Here the wire/weight assembly is suspended from a very weak gold spring designed so that its spring constant is a factor of 10 less than that of the wire itself. In this way the inertia of the falling weight is transmitted to the gold spring rather than the wire, which itself is not then subjected to a significant, oscillating stress. The small vertical motion of the entire wire (at most a few microns) that results from this arrangement makes no significant contribution to the heat transfer from it.

All of the effects outlined above are very small. Even in the worst case they contribute no more than $\pm 0.1\%$ to the measured temperature rise of the wire, which is comparable with the resolution of many instruments. It was originally thought that errors of this magnitude could be tolerated in reporting a thermal conductivity with an error of $\pm 0.3\%$. This remains

true if the errors are random, but as has been explained, the errors discussed here are systematic, although oscillatory, and usually very reproducible. In this case the effects on the measured thermal conductivity can be substantial. For example, the change from cells of type 1d to cells of type 1e in a measurement in argon reduces the maximum deviation from a linear fit of ΔT vs $\ln t$ from ± 0.12 to $\pm 0.07\%$. At the same time the loss of the systematic character of the deviations causes a change in the derived thermal conductivity of about 2%.

The observations set out above should be regarded as a warning to users of the transient hot-wire technique that at the highest level of precision, great care must be exercised to search for and rectify sources of systematic error which can arise from relatively subtle origins. It is also worthwhile pointing out that in instruments with a poorer resolution than $\pm 0.1\%$ in the temperature rise, these effects could not be observed, but this does not mean that their consequences are not significant.

3. EXPERIMENTAL

3.1. The Present Instrument

Guided by the experience described above a new set of thermal conductivity cells using the design of Fig. 1e has been constructed. With the exception of the wire mounting itself the cell is identical to that described elsewhere [22]. For operation over a wide range of temperature from 80 to 420 K, the cell is housed in the thermostat assembly shown in Fig. 2. Space limitations preclude a detailed description of the system here, but it is worthwhile mentioning its major features.

The thermal conductivity cells (1 and 2) are contained in the high-pressure vessel (16). The electrical connections are led from the pressure vessel through the gas feed tube (28), which is terminated at room temperature with an electrical feedthrough. The temperature of the vessel is measured by means of two platinum resistance thermometers inserted in the walls (11 and 18). The pressure vessel is suspended by thin steel struts (19) from the upper section of a thick-walled copper cylinder (23). This section, together with the lower part (20), forms a constant temperature enclosure around the pressure vessel. The space between the pressure vessel and the enclosure may be filled with an exchange gas through the port (34). The enclosure is fitted with bifilar windings of heating cable, comprising two separate heaters for the top and bottom sections (25) and cooling coils (26). Liquid nitrogen, or cold nitrogen vapor, can be circulated through the latter from a dewar supply. The temperature of the enclosure is monitored by two thermocouples embedded in the wall (12) and controlled

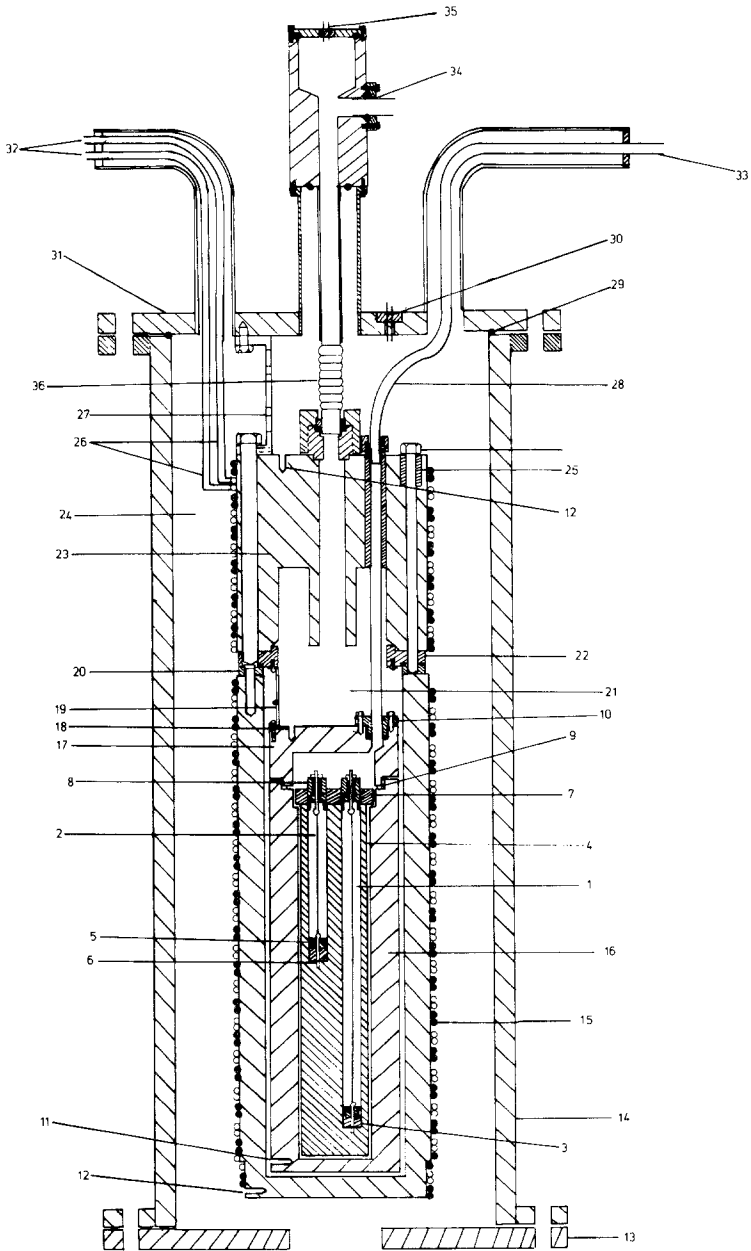


Fig. 2. The present thermal conductivity instrument.

by two PID controllers. The massive constant-temperature enclosure itself is suspended by further thin struts (27) from the top plate (31) of a vacuum vessel (14) which is mounted directly above the orifice of a vacuum system (13). The vacuum provides thermal insulation at the extremes of the operating range of the instrument. The method of mounting of the pressure vessel by means of massive components on thin struts ensures insulation from building vibration, while the massive copper block ensures a temperature stability of ± 1 mK over the 10 min which an entire measurements cycle requires for completion.

3.2. The Measurements

Measurements of the thermal conductivity of 10 pure gases have been carried out at four isotherms over the temperature range 300–425 K and at pressures up to 10 MPa. The gases studied are hydrogen, helium, methane, neon, ethylene, ethane, argon, carbon dioxide, nitrous oxide, and carbon tetrafluoride. Here we have space to give only a selection of the results which serve to illustrate what it is possible to achieve with the transient hot-wire instrument. For each gas the density data have been taken from the most reliable sources [24–34], and the heat capacity has been obtained either from the full equation of state or via the virial expansion corrections to the ideal gas value [35].

For some of the gases studied here, specifically ethylene and carbon dioxide, the conditions employed approach those of the critical state. The transient hot-wire technique is not the best type of instrument for operation in this region because, for the temperature rises normally used in such experiments (3–4 K), the temperature dependence of the thermal conductivity is often too rapid and the onset of convection is often too early to permit useful measurements. In the present work these difficulties have been obviated by employing a smaller temperature rise, but this inevitably leads to a loss of precision. Thus, whereas the majority of the measurements has an estimated uncertainty of $\pm 0.3\%$, this is degraded to one of $\pm 2.0\%$ in the critical region.

4. RESULTS

4.1. The Monatomic Gases

The monatomic gases helium, neon, and argon are included in the study to provide a running check on the operation of the instrument. This is made possible by the fact that the zero-density limit of the thermal con-

ductivity of such a gas, λ_0 , is related to its viscosity in the same limit, η_0 , by the kinetic theory result

$$\frac{4\lambda_0 M}{15R\eta_0 F} = 1.000 = Eu^* \tag{2}$$

In this expression, R denotes the universal gas constant and F a correction factor of the kinetic theory readily estimated [10].

As an example of the results the thermal conductivity data for argon along three nominal isotherms are shown graphically in Fig. 3. The data have been subjected to statistical analysis in order to provide the optimum values of the zero-density coefficients in the density expansion of the thermal conductivity, λ_0 .

The derived values of λ_0 for helium, neon, and argon are listed in Table I. These results have been combined with the best available viscosity

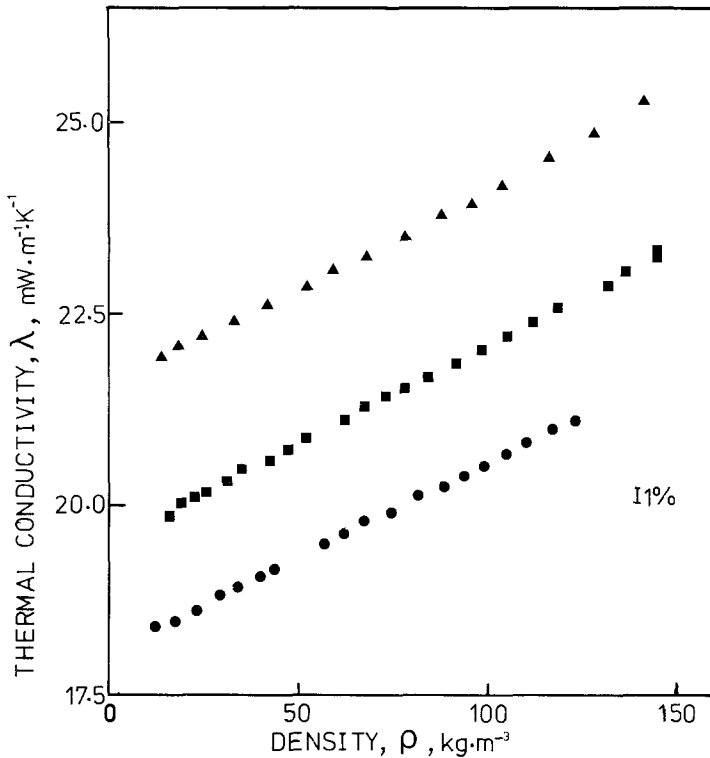


Fig. 3. The thermal conductivity of argon. (●) 308.15 K; (■) 338.15 K; (▲) 378.15 K.

Table I. Experimental Eucken Factors for the Monatomic Gases

Gas	Temperature (K)	λ_0 ($\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	η_0 ($\mu\text{Pa}\cdot\text{s}$)	$F(T)$	Eu*
He	308.15	159.6	20.31	1.0043	1.004 ± 0.005
	338.15	170.4	21.65	1.0042	1.0058 ± 0.005
	379.65	183.6	23.44	1.0042	1.0011 ± 0.005
Ne	308.15	50.02	32.47	1.0035	0.9935 ± 0.005
	337.65	53.34	34.57	1.0038	0.9948 ± 0.005
	379.65	57.70	37.49	1.0039	0.9922 ± 0.005
Ar	308.15	18.11	23.24	1.0012	0.9973 ± 0.005
	338.15	19.57	25.14	1.0015	0.9959 ± 0.005
	378.15	21.61	27.68	1.0018	0.9985 ± 0.005

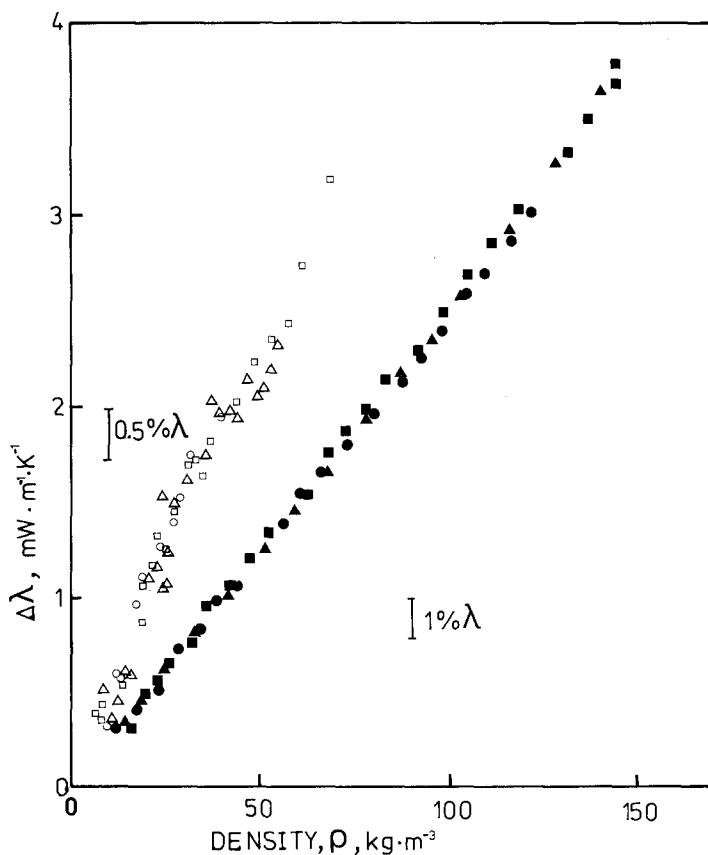


Fig. 4. The excess thermal conductivity of neon and argon. Neon: (○) 308.15 K; (□) 337.65 K; (△) 379.65 K. Argon: (●) 308.15 K; (■) 338.15 K; (▲) 378.15 K.

data [36] to yield experimental values of the Eucken factor, Eu^* , which are included in Table I. It can be seen that the experimental values of Eu^* essentially include within their range of uncertainty the theoretical value of unity. This result confirms the accuracy of the thermal conductivity measurements.

Figure 4 displays the excess thermal conductivity

$$\Delta\lambda = \lambda(\rho, T) - \lambda_0(T) \tag{3}$$

for neon and argon for the three isotherms studied. The figure amply confirms the essential independence of temperature displayed by the excess thermal conductivity far from the critical point at a level of precision not reported hitherto. This result is of considerable importance for the purposes of predicting the thermal conductivity of gases but awaits a satisfactory explanation founded on theory.

4.2. The Polyatomic Gases

The density dependence of the thermal conductivity of carbon dioxide is shown in Fig. 5 as an example of the behavior of polyatomic gases. As

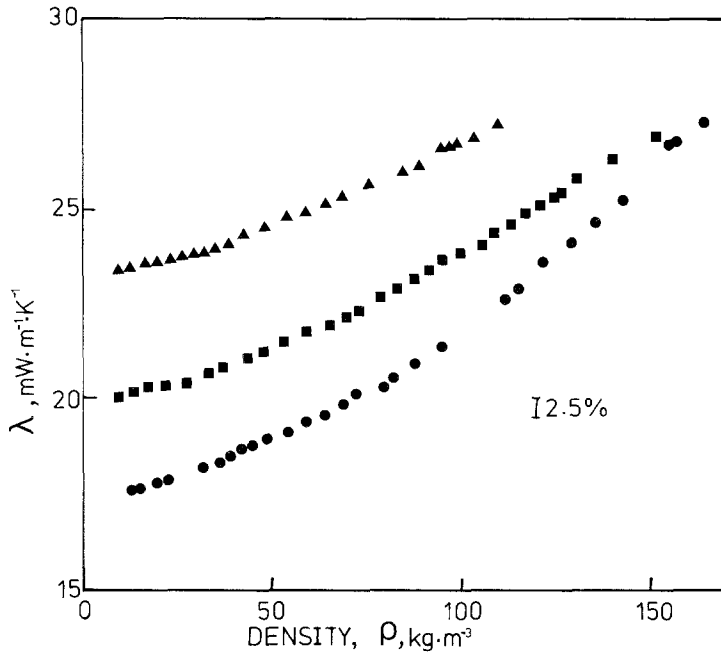


Fig. 5. The thermal conductivity of carbon dioxide. (●) 308 K; (■) 337.65 K; (▲) 379.15 K.

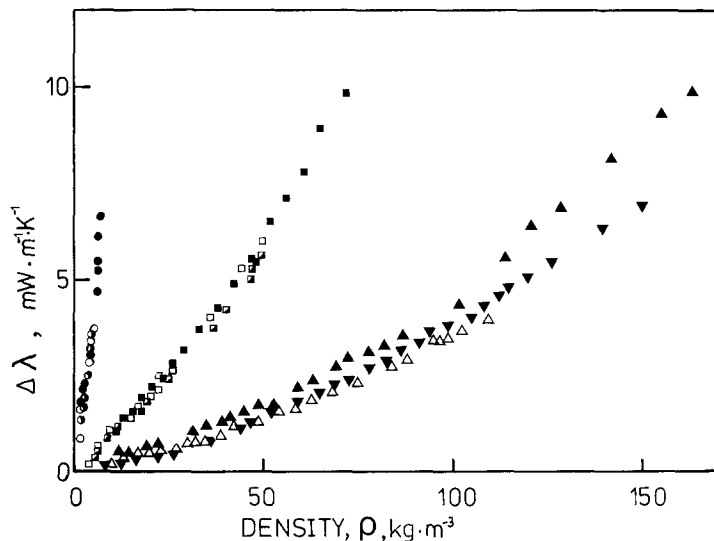


Fig. 6. The excess thermal conductivity of hydrogen, methane, and carbon dioxide. Hydrogen: (●) 308 K; (○) 337.65 K; (◐) 379.65 K. Methane: (■) 308 K; (□) 337.65 K; (◑) 379.15 K. Carbon dioxide: (▲) 308 K; (▼) 337.65 K; (△) 379.15 K.

before, a statistical analysis yields zero-density thermal conductivities, but in this case their interpretation is complicated by the contribution of internal energy and inelastic collisions. An analysis of these data is again beyond the scope of this paper so that we confine ourselves to a presentation of the results for the excess thermal conductivity of hydrogen, methane, and carbon dioxide, a plot of which is contained in Fig. 6. For hydrogen and methane the essential freedom from a temperature dependence in the excess thermal conductivity is again confirmed. On the other hand, for carbon dioxide, which is near the critical temperature along the lowest isotherms studied, there is a clear departure from this behavior. The predominant contribution to this effect arises undoubtedly from the enhancement of the thermal conductivity in the critical region.

5. CONCLUSION

The instrument described in the paper satisfies all of the constraints imposed for the performance of measurements of the thermal conductivity of gases with an accuracy of $\pm 0.3\%$ over a wide range of temperature. The accuracy has been confirmed by measurements of the thermal conductivity

of three monatomic gases in the temperature range 300–425 K. A detailed analysis of these results and those for polyatomic gases will be reported in later publications.

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