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ABSTRACT

The photoacoustic technique is used for thermal diffusivity measurement of gases in the region of low densities. A photoacoustic cell designed for accurate measurements in the pressure range from 0.01 to 0.15 MPa is described and experimental results with refrigerant R-22 at temperatures between 295 and 373 K are presented. Experimental thermal diffusivities were converted into thermal conductivity data with densities and isochoric specific heats calculated by an equation of state.

1. INTRODUCTION

Different experimental methods are at present available for measurement of the thermal diffusivity of fluids, e.g. the transient hot-wire method /1-3/, photon correlation spectroscopy /4-8/, or a method based upon the photoacoustic effect /9/. According to an investigation of Nieto de Castro et al. /10/, the accuracy of thermal diffusivity measurement with transient hot-wire instruments is limited to 7-9 %, whereas Kruppa and Straub /11/ estimated an overall error of about 2 % for thermal diffusivities determined by photon correlation spectroscopy. However, the application of the transient hot-wire method in dilute gases is difficult /10/, whereas thermal diffusivity measurement of gases by means of photon correlation spectroscopy is limited to reduced pressures p/p_c above 0.4 /4,5/.

In a recent article /12/, the authors presented thermal diffusivity measurement by means of the photoacoustic technique. This method delivers accurate results in the low density region, where the transient hot-wire method is less accurate and photon correlation spectroscopy is not applicable at all. Experiments with argon were carried out at atmospheric pressure and temperatures up to 423 K in order to demonstrate the applicability of the photoacoustic technique for thermal diffusivity measurement of dilute gases. A precision of less than 1 % was estimated, and deviations from best available reference data were of the order of 0.5 to 1.0 %.

In this paper, new experimental results with monochlorodifluoromethane (refrigerant R-22) in the temperature range from 295 to 373 K at a pressure of 0.01 MPa are presented. From the measured thermal diffusivities, thermal conductivity data were obtained with densities and isochoric specific heats calculated by an equation of state.

2. PRINCIPLE

In photoacoustic detectors, acoustic signals which are provoked by absorption of irradiated light in an enclosed gas volume are measured with sensitive pressure transducers, e.g. condenser microphones. In our apparatus, a continuous wave Helium-Neon-laser is used as coherent radiation source with constant wavelength 3.4 μm. This wavelength is conform to a vibrational transition line of the C-H bond, and thus corresponds to a strong absorption line of all alkanes, particularly ethane. Small amounts of ethane of the order of 500 - 2000 ppm added to the pure gas provide sufficient absorption without influencing the thermophysical properties of the pure substance. Therefore, measurements can be maintained independently from fluid-specific absorption lines.

The absorption of the infrared light causes the ethane molecules to pass into an excited state. The excited molecules return into their former state within a few μs, transferring their vibrational energy into translational energy by inelastic collisions with surrounding molecules. The energy conversion causes a slight enhancement of temperature and pressure within the enclosed gas sample. In our apparatus we use a mechanical chopper for periodical modulation of the light. This leads to pressure fluctuations as shown in Fig. 1.

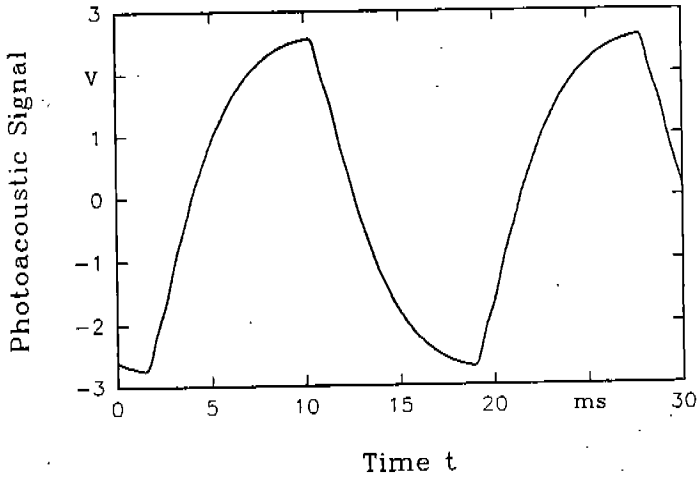

Figure 1: Photoacoustic signal.

The thermal diffusivity of the sample gas can be derived from the time-dependent pressure rise, Fig. 2. A detailed analysis of the method has been given earlier /12/. Therefore, we shall give here only a brief summary of the analysis. The time-dependent pressure rise can be calculated from the average temperature rise as a function of time. We obtained the temperature rise from the equation of heat conduction in an infinite cylinder, because the sample chamber of the photoacoustic cell is a narrow cylindrical tube with a length-to-diameter ratio of approximately 65:

$$\lambda \frac{\partial^2 T}{\partial r^2} + \frac{\lambda}{r} \frac{\partial T}{\partial r} = \rho c_v \frac{\partial T}{\partial t} - A \quad . \tag{1}$$

Herein, λ denotes the thermal conductivity, ρ the density, c_v the isochoric specific heat, r the radius, and T the temperature of the sample gas. The heat generation A was determined from the intensity distribution of the laser beam which was measured by a sensitive beam-scanner. The solution of equ. (1) with initial temperature T_0 and constant wall temperature T_0 as boundary condition gives the local temperature rise as a function of time which after integration leads to the average temperature rise as a function of time. The pressure rise as a function of time

$$\Delta p(t) = \Delta p^{\infty} \left[1 + \sum_{m=1}^{\infty} K_m \exp\left[- \frac{\xi_m^2 \, at}{R^2} \right] \right] \tag{2}$$

can be derived from the average time-dependent temperature rise, where Δp^{∞} denotes the pressure rise for infinite time $t \rightarrow \infty$, ξ_m the roots of the Bessel function of zero order $J_0(\xi_m) = 0$, R the radius of the cylindrical sample chamber, and K_m the coefficients as given in table 1. The thermal diffusivity a, which is defined as

$$a = \lambda / \rho \, c_v \quad , \tag{3}$$

can be evaluated from the measured pressure rise, Fig. 2, by equation (2).

m	K_m
1	- 1.073299
2	+ 0.083252
3	- 0.011292
4	+ 0.001473
5	- 0.000156
6	+ 0.000013

Table 1: Values of coefficients K_m , equ. (2).

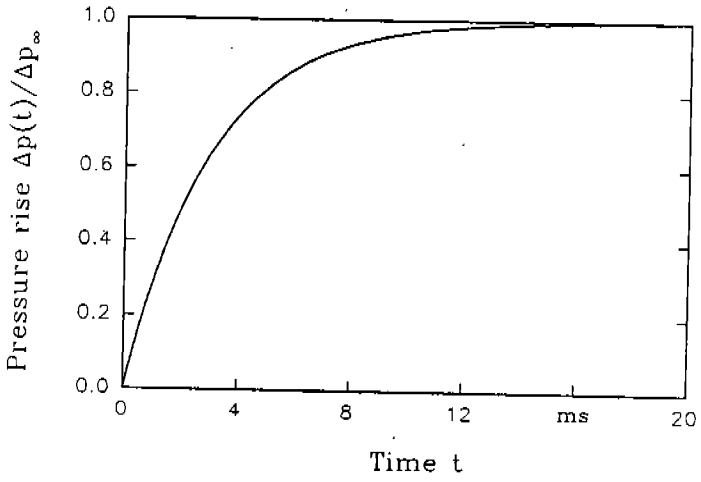

Figure 2: Reduced pressure rise vs time.

3. EXPERIMENTAL APPARATUS

The experimental apparatus is shown schematically in Fig. 3. The mechanical chopper providing periodical modulation of the infrared laser radiation is isolated by a sound-proofing box in order to protect the microphone from disturbances by sound transmission from the chopper blade and vibrations of the chopper motor. Two CaF_2-lenses are used to focus the laser beam in order to obtain maximum radiation intensity within the sample chamber. The radiation is partially absorbed by the sample gas. The photoacoustic cell has to be adjusted in order to attain coincidence of the beam axis and the axis of the cylindrical sample chamber. The adjustment is verified with a beam-scanner behind the cell by measuring the intensity distribution of the outcoming beam.

The photoacoustic cell, Fig. 4, consists of the sample chamber within a copper cylinder and the microphone chamber. The copper cylinder is designed for experiments up to maximum

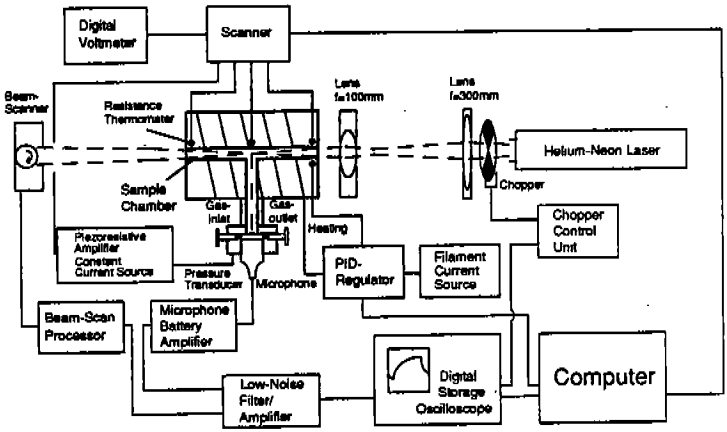

Figure 3: Experimental apparatus.

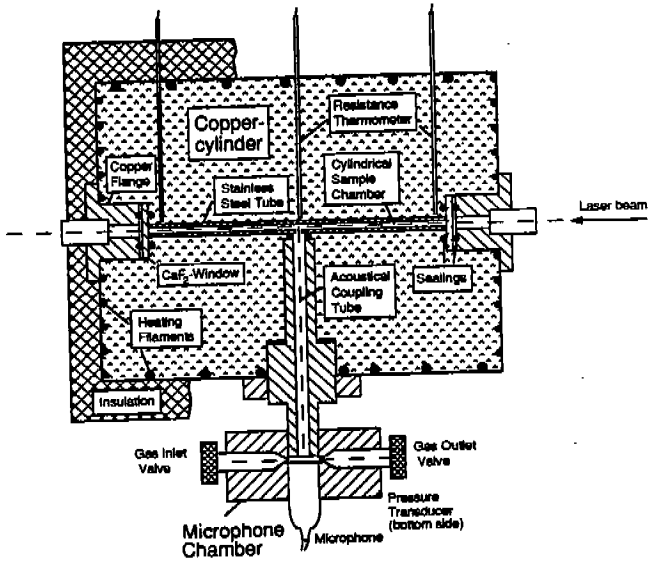

Figure 4: Photoacoustic cell.

temperatures between 373 and 423 K depending upon the system pressure. It contains heating filaments at its jacket and at the front sides so that a constant wall temperature can be maintained. The temperature is regulated by a PID-controller and a platinum resistance thermometer. The sample chamber consists of a capillary tube with an inner diameter of approximately 1.5 mm and a length of 100 mm which was shrunk into the copper block. It is enclosed at each side with a CaF_2-window allowing nearly complete transmission of the beam intensity. The microphone chamber had to be separated from the copper cylinder in order to protect the microphone from direct illumination and high temperatures. An acoustic coupling tube connects microphone and sample chamber for transmission of the photoacoustic signal.

The system pressure is detected by a piezoresistive pressure transducer mounted into the microphone compartment. The overall error of the measured pressure is 0.4 %. The wall temperature of the sample chamber is measured by platinum resistance thermometers at the center of the cell and at the front sides with an error less than 0.1 K. A condenser microphone is used for detection of the photoacoustic signal, which, after filtering and amplification, is monitored by a 12-bit storage oscilloscope. Evaluation of the measurements is carried out with a computer.

For thermal diffusivity measurement of refrigerant R-22, we selected a system pressure of about 0.01 MPa so that thermal diffusivities were higher than 50×10^{-6} m^2 s^{-1}. Thus modulation frequencies between 75 and 115 Hz were maintained permitting a sufficiently large part of the time-dependent pressure rise to be detected, Figs. 1 and 2. The measurements were limited to a temperature of about 373 K because the sealings of chloroprene became leaky at higher temperatures.

4. RESULTS

The experiments were conducted with gaseous refrigerant R-22 with a purity greater than 99.75 mole %. Two series of measurements were carried out in the temperature range from 295 to 373 K at a pressure of about 0.01 MPa. We arranged the oscilloscope to store about 30 periods of the photoacoustic signal at each temperature, Fig. 1, which took less than 1 s so that the system temperature and pressure remained constant within the duration of measurement. In order to improve the precision of our data, the curves of each period were evaluated individually and averaged afterwards. Table 2 contains experimental results obtained for 17 isotherms each run. The data of the two runs differ within 0.5 to 1 %. Therefore, we estimate a precision of our data of the order of 1 %.

From the measured thermal diffusivities a_{exp}, we derived thermal conductivities by

$$\lambda_{exp} = a_{exp} \rho_{ref} c_{v_{ref}} \tag{4}$$

with densities ρ_{ref} and isochoric specific heats $c_{v_{ref}}$ calculated by an equation of state of Wagner and Marx /13/. Published thermal conductivity data show deviations up to ± 6 to 7 % in the temperature range between 280 and 400 K at pressures below or close to atmospheric pressure. Fig. 5 shows deviations of thermal conductivity data of this work and other authors to a correlation of Tsvetkov /14,15/ which is based upon his own thermal conductivity measurements and data of other experimental works. Our thermal conductivities show average deviations of 1 to 2 % to the relation of Tsvetkov and his experimental data. The deviation of our data to experimental data of Hammerschmidt /16/, Makita /18/, and Gruzdev /22/ is of the order of 1 to 2 %, whereas data of the Japan Society of Mechanical Engineers /17/, Geller /19/ and Donaldson /20/ are not consistent with our data and the data of the other authors.

5. CONCLUSIONS

An experimental apparatus based upon the photoacoustic effect for thermal diffusivity measurement of gases at low pressures was presented, where other experimental techniques, e.g. the transient hot-wire method and photon correlation spectroscopy, are difficult to apply or not applicable at all. Two series of measurements were carried out with refrigerant R-22 in the temperature range from 295 to 373 K at a pressure of 0.01 MPa. From the experimental thermal

diffusivities, we derived thermal conductivity data with densities and isochoric specific heats calculated by an equation of state. Our thermal conductivity data agree within 1 to 2 % with data of Tsvetkov, Gruzdev, Makita and recent data of Hammerschmidt.

Acknowledgement

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Temperature T (K)	Pressure p (MPa)	Thermal diffusivity a_{exp} (10^{-6} $m^2 s^{-1}$)	Thermal conductivity λ_{exp} (10^{-3} W $m^{-1} K^{-1}$)
295.0	0.01047	52.85	10.74
299.0	0.01010	55.88	10.90
303.9	0.01012	57.33	11.13
308.7	0.01060	56.97	11.52
313.9	0.01034	60.11	11.79
318.5	0.01016	62.87	12.05
323.1	0.01027	63.71	12.28
328.6	0.01010	67.18	12.65
333.4	0.00995	70.07	12.93
338.4	0.01044	68.42	13.17
343.6	0.01022	71.91	13.48
348.5	0.01008	74.38	13.67
353.5	0.01052	72.93	13.92
358.1	0.01034	75.70	14.13
363.6	0.01024	78.63	14.45
368.1	0.01079	76.90	14.82
373.4	0.01063	80.10	15.13
294.9	0.01020	54.34	10.76
298.8	0.00997	56.90	10.96
303.4	0.00988	58.76	11.15
308.4	0.01021	58.83	11.47
313.8	0.01006	61.15	11.66
318.3	0.00984	64.38	11.95
323.1	0.01013	64.75	12.30
328.2	0.01002	67.60	12.63
333.3	0.00999	69.20	12.82
338.4	0.01046	67.67	13.05
343.0	0.01021	71.33	13.36
348.4	0.01013	73.69	13.62
353.2	0.01045	72.33	13.72
358.4	0.01026	76.08	14.09
363.2	0.01017	79.20	14.46
368.1	0.01073	76.62	14.69
373.4	0.01059	81.14	15.27

Table 2: Thermal diffusivities of refrigerant R-22, two runs. Thermal conductivities have been derived from measured thermal diffusivities by equ. (4) with densities and isochoric specific heats calculated by an equation of state of Wagner and Marx /13/.

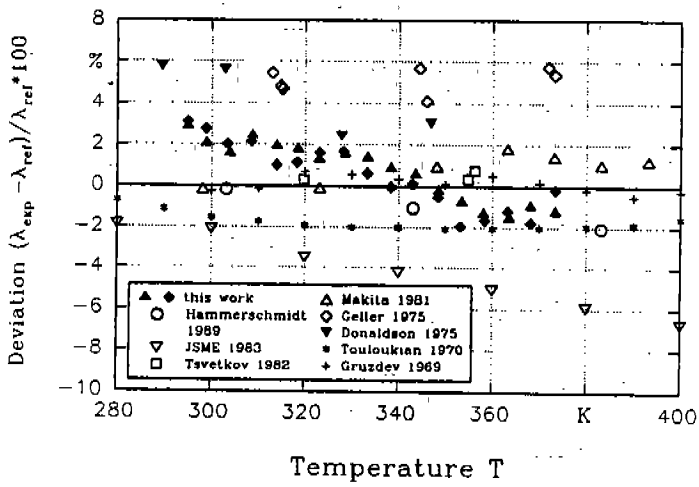

Figure 5: Deviation of thermal conductivity data from this work (two runs) and other authors to a correlation of Tsvetkov /14,15/, Hammerschmidt 1989 /16/, JSME 1983 /17/, Tsvetkov 1982 /15/, Makita 1981 /18/, Geller 1975 /19/, Donaldson 1975 /20/, Touloukian 1970 /21/, Gruzdev 1969 /22/.

REFERENCES

/1/ Knibbe, P.G.; Raal, J.D.: *Simultaneous Measurement of the Thermal Conductivity and Thermal Diffusivity of Liquids.* Int. J. Thermophys. 8, 181 - 191 (1987).

/2/ Nilsson, O.; Sandberg, O.; Bäckström, G.: *dc-ac hot-wire procedure for determining thermophysical properties under pressure.* Rev. Sci. Instrum. 57, 2303 - 2309 (1986).

/3/ Nagasaka, Y.; Nagashima, A.: *Simultaneous measurement of the thermal conductivity and the thermal diffusivity of liquids by the transient hot-wire method.* Rev. Sci. Instrum. 52, 229 - 232 (1981).

/4/ Kruppa, B.; Straub, J.: *Thermal Diffusivity of Refrigerants.* Proceedings of the International Institute of Refrigeration (IIR), Herzlia, Israel, March 5 - 7 (1990).

/5/ Kruppa, B.; Jany, P.; Straub, J.: *Experimental Apparatus for Measuring the Thermal Diffusivity of Pure Fluids at High Temperatures.* Int. J. Thermophys. 9, 911 - 921 (1988).

/6/ Jany, P.; Straub, J.: *Thermal Diffusivity of Fluids in a Broad Region Around the Critical Point.* Int. J. Thermophys. 8, 165 - 180 (1987).

/7/ Leipertz, A.; Wu, G.; Fiebig, M.: *Spectroscopic Determination of the Thermal Diffusivity of Organic Mixtures and Refrigerants.* Proceedings of the International Centre for Heat and Mass Transfer 24, 393 - 403, Belgrade (1987).

/8/ Hatakeyama, T.; Nagasaka, Y.; Nagashima, A.: *Measurement of the Thermal Diffusivity of Liquids by the Forced Rayleigh Scattering Method.* ASME/JSME Thermal Engineering Joint Conference, Honolulu, Hawaii, March 22 - 27 (1987).

/9/ Stephan, K.; Rothacker, V.; Hurdelbrink, W.: *Thermal Diffusivities Determined by Photoacoustic Spectroscopy.* Chem. Eng. Process. 26, 257 - 261 (1989).

/10/ Nieto de Castro, C.A.; Taxis, B.; Roder, H.M.; Wakeham, W.A.: *Thermal Diffusivity Measurement by the Transient Hot-Wire Technique: A Reappraisal.* Int. J. Thermophys. 9, 293 - 316 (1988).

/11/ Kruppa, B.; Straub, J.: *Measurement of Thermal Diffusivity of the Refrigerants R22 and R134a by means of Dynamic Light Scattering.* 11th Symp. on Thermophysical Properties, Boulder, Colorado, USA, June 23 - 27 (1991).

/12/ Stephan, K.; Biermann, J.: *The photoacoustic technique as a convenient instrument to determine thermal diffusivities of gases.* Int. J. Heat Mass Transfer 35, Vol. 3 (1992).

/13/ Marx, V.: *Fundamentalgleichungen zur Beschreibung des thermodynamischen Zustandsverhaltens der Substanzen Dichlordifluormethan (R12), Monochlordifluormethan (R22), Trichlormonofluormethan (R11) und Trichlortrifluorethan (R113).* Dissertation Ruhr-Universität Bochum 1989.

/14/ Tsvetkov, O.B.; Laptyev, Y.A.: *Thermal Conductivity of Difluoromonochloromethane in the Critical Region.* Int. J. Thermophys. 12, 53 - 65 (1991).

/15/ Tsvetkov, O.B.: *Transfer Properties of Freon-22 Vapor.* Inzh.-Fiz. Zh. 42, 955 - 961, Leningrad, USSR (1982).

/16/ Hammerschmidt, J.; Hemminger, W.: *Die Wärmeleitfähigkeit von Monochlordifluormethan (R22) und von Dichlortrifluorethan (R123) im Temperaturbereich von 30 bis 190 °C bei Atmosphärendruck.* Deutscher Kältetechnischer Verein, DKV-Tagungsbericht 16. Jahrg., Band 2, Hannover F.R.G. (1989).

/17/ JSME Data Book: *Thermophysical Properties of Fluids.* Japan Society of Mechanical Engineers, Tokyo (1983).

/18/ Makita, T.; Tanaka, Y.; Morimoto, Y.; Noguchi, M.; Kubota, H.: *Thermal Conductivity of Gaseous Fluorocarbon Refrigerants R 12, R 13, R 22, and R 23, Under Pressure.* Int. J. Thermophys. 2, 249 - 268 (1981).

/19/ Geller, V.Z.: *Thermal conductivities of some Freons of the methane series.* Teplofiz. Svoistva Veshchestv Mater., No. 8, 162 -176 (1975).

/20/ Donaldson, A.B.: *On the Estimation of Thermal Conductivity of Organic Vapors. Data for some Freons.* Ind. Eng. Chem. Fundam. 14, 325 - 328 (1975).

/21/ Touloukian, Y.S.; Liley, P.E.; Saxena, S.C.: *Thermophysical Properties of Matter,* Vol.3. IFI/Plenum Press, New York, Washington (1970).

/22/ Gruzdev, V.A.; Shestova, A.I.; Selin, V.V.: *Thermal conductivity of Freons,* in: *Thermophysical Properties of Freons* (in Russian). 62 - 74, Novosibirsk (1969).