*International Journal of Thermophysics, Vol. 26, No. 3, May 2005 (© 2005)*
DOI: 10.1007/s10765-005-5566-6

# Thermal Conductivity of Carbon Dioxide–Methane Mixtures at Temperatures Between 300 and 425 K and at Pressures up to 12 MPa

**J. Pátek,[1,2] J. Klomfar,[1] L. Čapla,[3] and P. Buryan[3]**

*Received July 9, 2004*

The thermal conductivities of carbon dioxide and three mixtures of carbon dioxide and methane at six nominal temperatures between 300 and 425 K have been measured as a function of pressure up to 12 MPa. The measurements were made with a transient hot-wire apparatus. The relative uncertainty of the reported thermal conductivities at a 95% confidence level is estimated to be ±1.2%. Results of the low-density analysis of the obtained data were used to test expressions for predicting the thermal conductivity of nonpolar mixtures in a dilute-gas limit developed by Schreiber, Vesovic, and Wakeham. The scheme was found to underestimate the experimental thermal conductivity with deviations not exceeding 5%. The dependence of the thermal conductivity on density was used to test the predictive scheme for the thermal conductivity of gas mixtures under pressure suggested by Mason et al. and improved by Vesovic and Wakeham. Comparisons reveal a pronounced critical enhancement on isotherms at 300 and 325 K for mixtures with methane mole fractions of 0.25 and 0.50. For other states, comparisons of the experimental and predicted excess thermal conductivity contributions showed a smaller increase of the experimental data with deviations approaching 3% within the examined range of densities.

**KEY WORDS:** carbon dioxide; methane; mixtures; thermal conductivity; transient hot-wire.

---

[1] Institute of Thermomechanics, Academy of Sciences of the Czech Republic, Dolejškova 5, CZ 182 00 Prague 8, Czech Republic.

[2] To whom correspondence should be addressed. E-mail: patek@it.cas.cz

[3] Institute of Chemical Technology, Technická 5, CZ 166 28 Prague 6, Czech Republic.

## 1. INTRODUCTION

The thermal conductivity of gas mixtures is one of the thermophysical properties that inevitably enters into mathematical models of real systems used in the design of chemical engineering processes or in the gas industry. It is not practicable to measure the thermal conductivity of all possible compositions of all mixtures; thus, accurate predictive models are needed.

Recent developments in theory provide suitable practical expressions for prediction of the dilute-gas, residual (also called excess), and critical-enhancement contributions to the thermal conductivity of gas mixtures. As for the dilute-gas term, Schreiber et al. [1] have developed, based on formal kinetic theory results by Ross et al. [2], a practical scheme for predicting the thermal conductivity of dilute multicomponent polyatomic gas mixtures. The expressions require only properties of pure species, the interaction low-density thermal conductivities $\lambda_{ij}^{0}(\mathrm{mon})$, and the reduced collision integral ratios $A_{ij}^{*}$ and $B_{ij}^{*}$ [3] for each pair of components.

Mason et al. [3], Kestin and Wakeham [4], and Vesovic and Wakeham [5] developed a procedure for evaluation of the background thermal conductivity of dense fluid mixtures (VW procedure). The procedure is based on an extension to the Thorne–Enskog theory for dense gases developed by Tham and Gubbins [6]. In the limit of zero density, the VW scheme reduces to the Hirschfelder–Eucken formula [7], treating the transport of internal energy exclusively as a diffusive process and omitting thus the effect of inelastic collisions. Predictions for residual thermal conductivity can be obtained from the VW procedure by subtracting this zero-density value from the predicted background thermal conductivity.

Luettmer-Strathmann and Sengers [8,9] proposed a crossover model describing transport properties of fluid mixtures near the vapor–liquid critical line. The crossover functions for the transport coefficients depend on various thermodynamic properties, background transport properties, and cut-off numbers for the mode-coupling integrals. Unfortunately, not all of the required input data are available in the case of carbon dioxide–methane mixtures.

As for the other two prediction schemes mentioned above, the required input data are readily available for a number of common nonpolar molecules, but the lack of high-accuracy data covering a wide temperature range preclude extensive testing of the proposed prediction schemes. To extend the experimental knowledge base on gas mixture thermal conductivities, an experimental investigation was undertaken to establish thermal conductivity values for mixtures of nitrogen with methane [10] and in the present work for the carbon dioxide–methane system. The thermal conductivity studies of carbon dioxide–methane mixtures by other authors are limited to the measurements of Rosenbaum and Thodos [11] performed with a coaxial cylindrical cell instrument at temperatures between 333 and 433 K and at pressures to 70 MPa and the transient hot-wire results of Kestin et al. [12] at 27.5 °C obtained at three mole fractions of methane.

The present paper concerns itself with the thermal conductivity measurements of pure carbon dioxide and of carbon dioxide–methane mixtures with mole fractions near 0.25, 0.50, and 0.75 at six nominal temperatures from 300 to 425 K and at pressures up to 12 MPa. The temperature–pressure region of interest touches the critical region of the mixtures (for carbon dioxide, $T_\mathrm{c} = 304.1282\,\mathrm{K}$, $p_\mathrm{c} = 7.3773\,\mathrm{MPa}$ [14] and for methane, $T_\mathrm{c} = 190.551\,\mathrm{K}$, $p_\mathrm{c} = 4.5992\,\mathrm{MPa}$ [23]). This circumstance is the main difference compared to previous measurements on the nitrogen–methane mixtures. Most of the measurements were performed at supercritical temperatures, nevertheless it should be noted that a critical enhancement of the thermal conductivity is present over a very large range of densities and temperatures around the critical point.

The reported thermal conductivity measurements have been performed with a transient hot-wire apparatus described in detail elsewhere [13], including the experimental procedure and data evaluation. Pure methane was measured earlier [13] in the same apparatus.

## 2. RESULTS AND DISCUSSION

### 2.1. Thermal Conductivity Data

The sample of carbon dioxide employed for the thermal conductivity measurements was supplied by Messer Austria GmbH and had a stated purity of 99.98%. The samples of mixtures of methane and carbon dioxide prepared by Linde Technoplyn a.s. have a certified relative expanded combined uncertainty of ±0.05 % in composition at the 95% confidence level. The actual values of the methane mole fractions of the samples are 0.2493, 0.4994, and 0.7496.

A total of 1060 measurements are reported for pure carbon dioxide and three carbon dioxide–methane mixtures along six nominal isotherms 300, 325, 350, 375, 400, and 425 K with 10 pressures from about 0.7 to 15 MPa for carbon dioxide and to 12 MPa for the mixtures. Measurements along an additional nominal isotherm at 304 K, close to the critical temperature, were performed for carbon dioxide. The upper pressure limit for each mixture composition is determined by the maximum pressure at which the samples are supplied by Linde Technoplyn a.s. with a guaranteed composition. The low pressure limits for the isotherms were chosen so that they correspond to a density of $0.3\,\mathrm{mol{\cdot}dm^{-3}}$, as previous test measurements [13] on the present apparatus showed that the uncertainty of the measured thermal conductivities increases considerably below this limit.

The operating parameters for the instrument were chosen to secure heat production in the wire from 17 to 40 $\mathrm{mW{\cdot}m^{-1}}$ corresponding to temperature increases of 0.3–2 K at the end of the time interval within which the temperature rise of the hot-wire is evaluated. Low values of the temperature increase should be employed especially at higher densities to prevent early onset of the natural convection. To confirm that the effect of convection is not significant, multiple measurement were performed with different temperature rises. No signs indicating the onset of the natural convection were observed even at the highest pressure (6.6 MPa) on the near critical 304 K isotherm. Somewhat greater scatter of the obtained thermal conductivities occurs at higher densities almost on all isotherms and it should be ascribed to the lesser signal to noise ratio.

The density and heat capacity of carbon dioxide have been calculated from the equation of state of Span and Wagner [14]. Those for the mixtures were obtained using the AGA8-DC92 equation of state [15,16]. The ideal-gas isobaric heat capacities of particular components were computed according to Ref. 17. The density and heat capacity are required to apply small corrections (typically of the order of $10^{-1}\%$) in the reduction of the experimental data [13]. In addition, the density also plays the role of one of the primary independent variables.

For each pressure, at least four data points were taken. The results for the thermal conductivity of mixtures were adjusted at the experimental pressure to the nominal isothermal temperature using a surface fit developed for each mixture composition based on the obtained experimental data. These shifted thermal conductivities were subsequently averaged, and the averages are presented in the tables. This procedure was not used in the case of pure carbon dioxide on the isotherms at 300 and 304 K; the experimental information was not sufficient for data adjustment without loss of accuracy. Instead, the adjustment is used to the average temperature of the set of measurements performed at each nominal temperature–pressure point.

Table I gives the results for pure carbon dioxide and Tables II–IV give the results for the three carbon dioxide–methane mixtures. The tables list the thermal conductivity $\lambda$ and density $\rho_{\mathrm{nom}}$ at the nominal temperature $T_{\mathrm{nom}}$ and the experimental pressure $p$. The relative expanded uncertainty at the 95% confidence level ($U_{\mathrm{r95}}$, Ref. 18, p. 9 ) is presented in the table for each mean value. A complete tabulation of the raw thermal conductivity data is available from the authors.

**Table I.** Thermal Conductivity of Carbon Dioxide

| $T$(K) | $p$ (MPa) | $\rho_{\mathrm{nom}}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{\mathrm{r95}}$ (%) |
|---|---|---|---|---|
| 300.372 | 0.714 | 0.2964 | 0.01712 | 0.1 |
| 300.064 | 1.702 | 0.7483 | 0.01777 | 0.2 |
| 299.847 | 2.555 | 1.188 | 0.01861 | 0.3 |
| 299.728 | 3.285 | 1.615 | 0.01968 | 0.5 |
| 299.603 | 3.980 | 2.082 | 0.02109 | 0.5 |
| 299.498 | 4.555 | 2.532 | 0.02268 | 0.6 |
| 299.309 | 5.035 | 2.976 | 0.02441 | 0.4 |
| 299.192 | 5.400 | 3.374 | 0.02633 | 1.0 |
| 299.016 | 5.760 | 3.854 | 0.02896 | 0.4 |
| 298.893 | 6.100 | 4.437 | 0.03312 | 0.2 |
| 304.214 | 0.724 | 0.2964 | 0.01741 | 0.2 |
| 303.989 | 1.612 | 0.6927 | 0.01795 | 0.1 |
| 303.807 | 2.415 | 1.090 | 0.01872 | 0.4 |
| 303.512 | 3.160 | 1.503 | 0.01961 | 0.3 |
| 303.218 | 3.765 | 1.881 | 0.02053 | 0.1 |
| 303.080 | 4.340 | 2.284 | 0.02178 | 1.2 |
| 302.973 | 4.870 | 2.709 | 0.02339 | 0.5 |
| 302.920 | 5.290 | 3.097 | 0.02471 | 1.2 |
| 302.863 | 5.675 | 3.509 | 0.02694 | 0.9 |
| 302.795 | 6.025 | 3.954 | 0.02905 | 0.6 |
| 302.769 | 6.400 | 4.549 | 0.03309 | 0.3 |
| 302.672 | 6.635 | 5.047 | 0.03700 | 0.7 |
| 326.256 | 0.497 | 0.1869 | 0.01910 | 0.3 |
| 326.174 | 0.684 | 0.2588 | 0.01921 | 0.2 |
| 326.031 | 1.514 | 0.5927 | 0.01958 | 0.2 |
| 325.927 | 2.218 | 0.8957 | 0.02003 | 0.3 |
| 325.807 | 2.880 | 1.200 | 0.02052 | 0.2 |
| 325.644 | 3.500 | 1.505 | 0.02126 | 0.7 |
| 325.478 | 4.040 | 1.790 | 0.02182 | 0.3 |
| 325.416 | 4.605 | 2.109 | 0.02254 | 1.0 |
| 325.279 | 5.060 | 2.385 | 0.02323 | 0.4 |
| 325.102 | 5.575 | 2.723 | 0.02434 | 0.9 |
| 324.950 | 5.960 | 2.996 | 0.02501 | 2.0 |
| 325.115 | 6.360 | 3.292 | 0.02611 | 1.2 |
| 325.040 | 6.760 | 3.619 | 0.02716 | 0.9 |
| 325.010 | 6.900 | 3.740 | 0.02771 | 0.8 |
| 324.917 | 7.440 | 4.245 | 0.02954 | 0.3 |
| 324.896 | 7.750 | 4.567 | 0.03118 | 0.6 |
| 324.870 | 7.960 | 4.801 | 0.03214 | 0.2 |

**Table I.** Continued

| $T$(K) | $p$ (MPa) | $\rho_{\mathrm{nom}}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{\mathrm{r}95}$ (%) |
|---|---|---|---|---|
| 352.228 | 0.572 | 0.1986 | 0.02136 | 0.1 |
| 352.100 | 0.994 | 0.3495 | 0.02141 | 0.1 |
| 351.909 | 1.420 | 0.5062 | 0.02153 | 0.1 |
| 351.867 | 1.820 | 0.6570 | 0.02181 | 0.3 |
| 351.818 | 2.214 | 0.8095 | 0.02197 | 0.3 |
| 351.436 | 4.275 | 1.681 | 0.02351 | 0.5 |
| 351.116 | 6.040 | 2.553 | 0.02551 | 0.3 |
| 350.956 | 7.540 | 3.413 | 0.02768 | 0.8 |
| 350.887 | 8.840 | 4.273 | 0.03029 | 0.6 |
| 350.827 | 9.985 | 5.142 | 0.03324 | 0.4 |
| 376.515 | 1.015 | 0.3319 | 0.02346 | 0.3 |
| 376.280 | 2.004 | 0.6713 | 0.02377 | 0.2 |
| 376.109 | 4.240 | 1.504 | 0.02504 | 0.3 |
| 376.012 | 6.260 | 2.349 | 0.02673 | 0.9 |
| 375.907 | 8.060 | 3.192 | 0.02887 | 0.4 |
| 375.854 | 9.640 | 4.011 | 0.03079 | 0.8 |
| 375.800 | 11.10 | 4.840 | 0.03322 | 0.5 |
| 375.749 | 12.56 | 5.739 | 0.03615 | 0.6 |
| 375.711 | 13.88 | 6.601 | 0.03888 | 1.7 |
| 375.684 | 14.93 | 7.314 | 0.04175 | 0.3 |
| 401.735 | 0.975 | 0.2971 | 0.02566 | 0.2 |
| 401.659 | 1.690 | 0.5218 | 0.02584 | 0.1 |
| 401.602 | 2.382 | 0.7452 | 0.02597 | 0.2 |
| 401.418 | 4.600 | 1.503 | 0.02712 | 0.2 |
| 401.300 | 6.660 | 2.268 | 0.02850 | 0.3 |
| 401.151 | 8.495 | 3.005 | 0.03004 | 0.3 |
| 401.029 | 10.34 | 3.802 | 0.03194 | 0.1 |
| 400.982 | 11.95 | 4.542 | 0.03389 | 0.6 |
| 400.930 | 13.55 | 5.315 | 0.03623 | 0.8 |
| 400.852 | 15.01 | 6.048 | 0.03843 | 0.6 |
| 428.047 | 1.040 | 0.2965 | 0.02797 | 0.7 |
| 427.952 | 2.050 | 0.5931 | 0.02812 | 0.3 |
| 427.700 | 3.020 | 0.8867 | 0.02833 | 0.5 |
| 427.665 | 3.970 | 1.182 | 0.02879 | 1.0 |
| 427.513 | 6.160 | 1.894 | 0.02966 | 0.6 |
| 427.376 | 8.240 | 2.613 | 0.03127 | 0.5 |
| 427.231 | 9.898 | 3.215 | 0.03250 | 0.9 |
| 427.125 | 12.00 | 4.015 | 0.03429 | 0.4 |

**Table II.** Thermal Conductivity of Carbon Dioxide–Methane Mixture, $x_{CH_4} = 0.2493$

| $p$ (MPa) | $\rho_{nom}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{r95}$ (%) | $p$ (MPa) | $\rho_{nom}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{r95}$ (%) |
|---|---|---|---|---|---|---|---|
| *Nominal temperature* 300 K | | | | *Nominal temperature* 325 K | | | |
| 0.724 | 0.2985 | 0.02096 | 0.1 | 0.793 | 0.3004 | 0.02340 | 0.2 |
| 1.288 | 0.5435 | 0.02125 | 0.1 | 1.420 | 0.5484 | 0.02367 | 0.1 |
| 1.835 | 0.7934 | 0.02161 | 0.2 | 2.020 | 0.7953 | 0.02398 | 0.2 |
| 2.335 | 1.033 | 0.02197 | 0.5 | 2.600 | 1.044 | 0.02439 | 0.4 |
| 2.820 | 1.277 | 0.02245 | 0.3 | 3.160 | 1.293 | 0.02478 | 0.4 |
| 3.275 | 1.517 | 0.02287 | 0.3 | 3.685 | 1.536 | 0.02519 | 0.2 |
| 3.730 | 1.770 | 0.02338 | 0.2 | 4.210 | 1.789 | 0.02561 | 0.5 |
| 4.160 | 2.021 | 0.02399 | 0.3 | 4.690 | 2.029 | 0.02615 | 0.4 |
| 4.550 | 2.262 | 0.02452 | 0.1 | 5.170 | 2.278 | 0.02675 | 0.2 |
| 4.920 | 2.502 | 0.02520 | 0.3 | 5.625 | 2.524 | 0.02733 | 0.6 |
| *Nominal temperature* 350 K | | | | *Nominal temperature* 375 K | | | |
| 0.860 | 0.3016 | 0.02600 | 0.2 | 0.919 | 0.2995 | 0.02872 | 0.3 |
| 1.310 | 0.4641 | 0.02615 | 0.1 | 1.460 | 0.4805 | 0.02883 | 0.1 |
| 1.750 | 0.6263 | 0.02631 | 0.3 | 1.986 | 0.6598 | 0.02895 | 0.3 |
| 2.180 | 0.7881 | 0.02656 | 0.2 | 2.510 | 0.8419 | 0.02913 | 0.2 |
| 2.610 | 0.9533 | 0.02669 | 0.2 | 3.015 | 1.021 | 0.02945 | 0.3 |
| 3.020 | 1.114 | 0.02694 | 0.6 | 3.510 | 1.199 | 0.02970 | 0.6 |
| 3.440 | 1.282 | 0.02718 | 0.3 | 4.005 | 1.381 | 0.02993 | 0.6 |
| 3.840 | 1.446 | 0.02747 | 0.4 | 4.500 | 1.565 | 0.03020 | 0.5 |
| 4.220 | 1.605 | 0.02766 | 0.3 | 4.975 | 1.746 | 0.03051 | 0.3 |
| 4.600 | 1.766 | 0.02799 | 0.4 | 5.440 | 1.926 | 0.03075 | 0.4 |
| *Nominal temperature* 400 K | | | | *Nominal temperature* 425 K | | | |
| 0.983 | 0.2993 | 0.03152 | 0.2 | 1.048 | 0.3000 | 0.03418 | 0.3 |
| 1.410 | 0.4319 | 0.03160 | 0.4 | 1.530 | 0.4403 | 0.03411 | 0.2 |
| 1.820 | 0.5607 | 0.03172 | 0.4 | 1.938 | 0.5598 | 0.03436 | 0.4 |
| 2.230 | 0.6911 | 0.03183 | 1.0 | 2.390 | 0.6937 | 0.03434 | 0.3 |
| 2.635 | 0.8214 | 0.03187 | 0.5 | 2.810 | 0.8189 | 0.03448 | 0.4 |
| 3.040 | 0.9531 | 0.03201 | 0.6 | 3.260 | 0.9544 | 0.03452 | 0.6 |
| 3.435 | 1.083 | 0.03228 | 0.2 | 3.690 | 1.085 | 0.03472 | 0.5 |
| 3.850 | 1.221 | 0.03241 | 0.2 | 4.120 | 1.217 | 0.03490 | 0.3 |
| 4.240 | 1.352 | 0.03258 | 0.4 | 4.540 | 1.347 | 0.03506 | 0.3 |
| 4.615 | 1.479 | 0.03271 | 0.3 | 4.960 | 1.478 | 0.03530 | 0.2 |

In Fig. 1 the experimental results for pure carbon dioxide are compared with the thermal conductivity values calculated from the correlation of Vesovic et al. [19]. The deviations approach 2% for some isolated points, but the standard deviation is 0.6%, which is commensurate with the estimated uncertainty of the data. The value of the standard deviation

**Table III.** Thermal Conductivity of Carbon Dioxide–Methane Mixture, $x_{\mathrm{CH_4}} = 0.4994$

| $p$ (MPa) | $\rho_{\mathrm{nom}}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{\mathrm{r95}}$ (%) | $p$ (MPa) | $\rho_{\mathrm{nom}}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{\mathrm{r95}}$ (%) |
|---|---|---|---|---|---|---|---|
| *Nominal temperature* 300 K | | | | *Nominal temperature* 325 K | | | |
| 0.727 | 0.2980 | 0.02533 | 0.2 | 0.800 | 0.3014 | 0.02831 | 0.4 |
| 1.241 | 0.5164 | 0.02556 | 0.2 | 1.350 | 0.5150 | 0.02846 | 0.2 |
| 1.748 | 0.7392 | 0.02584 | 0.1 | 1.896 | 0.7325 | 0.02871 | 0.4 |
| 2.212 | 0.9495 | 0.02613 | 0.4 | 2.434 | 0.9523 | 0.02901 | 0.1 |
| 2.700 | 1.178 | 0.02637 | 1.0 | 2.970 | 1.177 | 0.02933 | 0.4 |
| 3.118 | 1.380 | 0.02681 | 0.3 | 3.440 | 1.379 | 0.02963 | 0.1 |
| 3.550 | 1.594 | 0.02726 | 0.3 | 3.920 | 1.590 | 0.02999 | 0.6 |
| 4.660 | 2.178 | 0.02839 | 0.4 | 5.200 | 2.176 | 0.03111 | 0.6 |
| 5.670 | 2.754 | 0.02959 | 0.2 | 6.380 | 2.750 | 0.03222 | 0.4 |
| 6.570 | 3.306 | 0.03101 | 0.8 | 7.500 | 3.325 | 0.03379 | 1.4 |
| *Nominal temperature* 350 K | | | | *Nominal temperature* 375 K | | | |
| 0.865 | 0.3016 | 0.03135 | 0.1 | 0.919 | 0.2983 | 0.03475 | 0.2 |
| 1.464 | 0.5157 | 0.03154 | 0.2 | 1.578 | 0.5166 | 0.03480 | 0.2 |
| 2.054 | 0.7310 | 0.03177 | 0.4 | 2.220 | 0.7327 | 0.03492 | 0.5 |
| 2.660 | 0.9566 | 0.03206 | 0.8 | 2.840 | 0.9447 | 0.03520 | 0.1 |
| 3.190 | 1.158 | 0.03224 | 0.3 | 3.480 | 1.167 | 0.03545 | 0.2 |
| 3.760 | 1.378 | 0.03258 | 0.2 | 4.100 | 1.386 | 0.03561 | 0.6 |
| 4.324 | 1.601 | 0.03282 | 1.0 | 4.715 | 1.606 | 0.03598 | 0.3 |
| 5.145 | 1.932 | 0.03347 | 0.3 | 5.855 | 2.022 | 0.03682 | 0.4 |
| 5.920 | 2.252 | 0.03401 | 0.5 | 6.930 | 2.425 | 0.03739 | 0.7 |
| 6.670 | 2.571 | 0.03477 | 0.6 | 8.000 | 2.833 | 0.03823 | 0.3 |
| *Nominal temperature* 400 K | | | | *Nominal temperature* 425 K | | | |
| 0.986 | 0.2994 | 0.03807 | 0.4 | 1.050 | 0.2994 | 0.04164 | 0.2 |
| 1.690 | 0.5166 | 0.03812 | 0.1 | 1.799 | 0.5159 | 0.04146 | 0.3 |
| 2.378 | 0.7318 | 0.03826 | 0.5 | 2.554 | 0.7363 | 0.04156 | 0.3 |
| 3.061 | 0.9480 | 0.03844 | 0.2 | 3.260 | 0.9444 | 0.04176 | 0.2 |
| 3.740 | 1.166 | 0.03866 | 0.2 | 4.000 | 1.165 | 0.04192 | 0.6 |
| 4.390 | 1.376 | 0.03887 | 0.3 | 4.730 | 1.384 | 0.04207 | 0.8 |
| 5.060 | 1.596 | 0.03918 | 0.5 | 5.460 | 1.605 | 0.04245 | 0.7 |
| 5.667 | 1.797 | 0.03961 | 0.3 | 6.410 | 1.895 | 0.04284 | 0.6 |
| 6.180 | 1.968 | 0.03980 | 0.6 | 7.380 | 2.194 | 0.04335 | 0.5 |
| 6.710 | 2.147 | 0.04014 | 0.6 | 8.310 | 2.483 | 0.04385 | 0.8 |

is quite comparable to the standard deviation of the primary data used for fitting of the representative equation by Vesovic et al. [19]. The present carbon dioxide results validate indirectly the results obtained in the mixture measurements that followed.

**Table IV.** Thermal Conductivity of Carbon Dioxide–Methane Mixture, $x_{CH_4} = 0.7496$

| $p$ (MPa) | $\rho_{nom}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{r95}$ (%) | $p$ (MPa) | $\rho_{nom}$ (mol·dm$^{-3}$) | $\lambda$ (W·m$^{-1}$·K$^{-1}$) | $U_{r95}$ (%) |
|---|---|---|---|---|---|---|---|
| *Nominal temperature* 300 K | | | | *Nominal temperature* 325 K | | | |
| 0.730 | 0.2975 | 0.03005 | 0.1 | 0.797 | 0.2991 | 0.03345 | 0.3 |
| 1.240 | 0.5112 | 0.03027 | 0.1 | 1.358 | 0.5138 | 0.03366 | 0.1 |
| 1.770 | 0.7386 | 0.03051 | 0.3 | 1.920 | 0.7336 | 0.03390 | 0.1 |
| 2.245 | 0.9472 | 0.03082 | 0.2 | 2.465 | 0.9505 | 0.03420 | 0.3 |
| 2.740 | 1.169 | 0.03109 | 1.0 | 3.020 | 1.175 | 0.03450 | 0.5 |
| 3.220 | 1.390 | 0.03153 | 0.2 | 3.520 | 1.381 | 0.03477 | 0.6 |
| 3.680 | 1.606 | 0.03188 | 0.5 | 4.040 | 1.599 | 0.03529 | 0.4 |
| 4.160 | 1.836 | 0.03236 | 0.3 | 4.555 | 1.818 | 0.03559 | 0.3 |
| 4.560 | 2.032 | 0.03271 | 0.3 | 5.040 | 2.028 | 0.03603 | 0.4 |
| 5.000 | 2.252 | 0.03324 | 0.4 | 5.560 | 2.256 | 0.03638 | 0.5 |
| *Nominal temperature* 350 K | | | | *Nominal temperature* 375 K | | | |
| 0.862 | 0.2994 | 0.03707 | 0.3 | 0.930 | 0.3009 | 0.04098 | 0.2 |
| 1.605 | 0.5626 | 0.03738 | 0.2 | 1.528 | 0.4970 | 0.04104 | 0.3 |
| 2.340 | 0.8276 | 0.03766 | 0.4 | 2.135 | 0.6982 | 0.04117 | 0.3 |
| 3.035 | 1.082 | 0.03796 | 0.4 | 2.740 | 0.9008 | 0.04129 | 0.4 |
| 3.740 | 1.345 | 0.03813 | 0.3 | 3.310 | 1.094 | 0.04145 | 0.2 |
| 4.410 | 1.599 | 0.03855 | 0.4 | 3.915 | 1.300 | 0.04181 | 1.2 |
| 5.140 | 1.879 | 0.03900 | 0.5 | 4.490 | 1.498 | 0.04204 | 0.8 |
| 5.860 | 2.159 | 0.03958 | 0.4 | 6.910 | 2.349 | 0.04355 | 1.0 |
| 6.410 | 2.376 | 0.03989 | 0.6 | 9.330 | 3.222 | 0.04538 | 0.5 |
| 7.080 | 2.643 | 0.04053 | 0.3 | 11.60 | 4.053 | 0.04722 | 0.5 |
| *Nominal temperature* 400 K | | | | *Nominal temperature* 425 K | | | |
| 0.993 | 0.3006 | 0.04503 | 0.3 | 1.050 | 0.2987 | 0.04889 | 0.4 |
| 1.700 | 0.5170 | 0.04501 | 0.1 | 1.810 | 0.5167 | 0.04908 | 0.3 |
| 2.393 | 0.7310 | 0.04519 | 0.2 | 2.558 | 0.7327 | 0.04898 | 0.5 |
| 3.115 | 0.9559 | 0.04526 | 1.0 | 3.300 | 0.9483 | 0.04919 | 0.6 |
| 3.770 | 1.162 | 0.04535 | 0.8 | 4.050 | 1.167 | 0.04919 | 0.3 |
| 4.460 | 1.379 | 0.04578 | 0.6 | 4.800 | 1.388 | 0.04980 | 0.5 |
| 5.140 | 1.596 | 0.04598 | 0.4 | 5.520 | 1.600 | 0.05001 | 0.3 |
| 6.670 | 2.087 | 0.04688 | 0.4 | 7.670 | 2.238 | 0.05089 | 0.5 |
| 8.110 | 2.555 | 0.04756 | 0.5 | 9.820 | 2.880 | 0.05188 | 0.4 |
| 9.545 | 3.024 | 0.04861 | 0.2 | 11.97 | 3.523 | 0.05348 | 1.2 |

## 2.2. Zero-Density Limit

Although there exist many studies in the literature with experimental data for the zero-density limit of the thermal conductivity of carbon dioxide, only 20 data points from five studies are of sufficient quality for fitting of the $\lambda_0(T)$ relation [19] in the temperature range from about 290 to

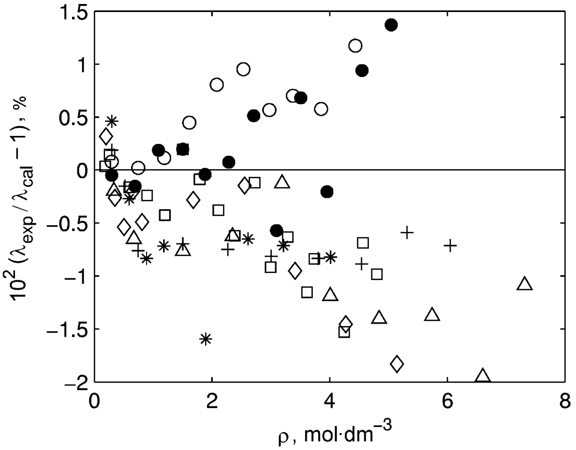

**Fig. 1.** Percentage deviations of the experimental thermal conductivity data for carbon dioxide from the correlation of Vesovic et al. [19]. Temperatures: (○) 300 K, (●) 304 K, (□) 325 K, (◇) 350 K, (△) 375 K, (+) 400 K, (∗) 425 K.

490 K. Therefore, additional experimental data for the dilute-gas thermal conductivity of carbon dioxide are desirable. In order to determine $\lambda_0$, the experimental data have been represented along each nominal isotherm by means of a polynomial in density,

$$\lambda = \lambda_0 + \lambda_1 \varrho + \lambda_2 \varrho^2 + \cdots \tag{1}$$

For this purpose, the results for the thermal conductivity were shifted from their experimental temperatures to the nominal temperatures by means of small (0.6% at the most) adjustments. The needed temperature derivatives of the thermal conductivity have been estimated from the experimental data.

The optimum values of the coefficients $\lambda_0$ of pure carbon dioxide and carbon dioxide–methane mixtures, together with estimates of their expanded uncertainties at the 95% confidence, level are listed in Table V. The deviations of the experimental values of $\lambda_0$ measured for carbon dioxide by various authors from the correlation by Vesovic et al. [19] are shown in Fig. 2. The deviations of the present experimental data from the correlation are consistent with our estimate that the relative expanded uncertainty (at the 95% confidence level) of the present results is about ±1.2%. In Fig. 3, the deviations of the present experimental data for $\lambda_0$ from the predictions based on the scheme by Schreiber et al. [1] are plotted together with the results obtained for carbon dioxide–methane

**Table V.** Best Estimates of the Dilute-Gas Thermal Conductivity of Carbon Dioxide and Carbon Dioxide–Methane Mixtures Using Eq. (1)

| $T$ (K) | $\lambda_0$ (mW·m$^{-1}$·K$^{-1}$) | | | |
|---|---|---|---|---|
| | $x_{CH_4} = 0.00$ | $x_{CH_4} = 0.25$ | $x_{CH_4} = 0.50$ | $x_{CH_4} = 0.75$ |
| 300 | 16.66 ± 0.04 | 20.62 ± 0.06 | 25.02 ± 0.09 | 29.74±0.05 |
| 304 | 16.98 ± 0.03 | | | |
| 325 | 18.72 ± 0.12 | 23.08 ± 0.07 | 28.11 ± 0.14 | 33.15 ± 0.08 |
| 350 | 21.09 ± 0.05 | 25.72 ± 0.11 | 31.08 ± 0.10 | 36.72 ± 0.14 |
| 375 | 23.00 ± 0.10 | 28.54 ± 0.13 | 34.67 ± 0.06 | 40.89 ± 0.15 |
| 400 | 25.25 ± 0.09 | 31.33 ± 0.09 | 38.01 ± 0.09 | 45.07 ± 0.16 |
| 425 | 27.55 ± 0.13 | 34.20 ± 0.15 | 41.25 ± 0.19 | 48.66 ± 0.19 |

mixtures by Kestin et al. [12] and by Rosenbaum and Thodos [11]. The solid lines depict the deviations of the zero-density thermal conductivities calculated using the Hirschfelder–Eucken expression from those calculated using the scheme by Schreiber et al. [1] for temperatures of 300, 375, and 425 K.

For the dilute-gas thermal conductivity of methane and carbon dioxide, the correlations of Assael et al. [20] and Vesovic et al. [19], respectively, have been used in the calculations. The ideal-gas isobaric heat capacities of pure methane and carbon dioxide have been calculated from correlations of Friend et al. [23] and Span and Wagner [14], respectively. Recently, expressions of Schreiber et al. [1] have been tested against the available experimental data by Vesovic [21,22]. In these studies, the deviations from the experimental thermal conductivity have been found to be within ±5% for most mixtures studied. The predictions underestimate the present data for the thermal conductivity of carbon dioxide–methane mixtures for all nominal temperatures. The deviations of the experimental thermal conductivities from the predictions increase with nominal temperature up to about 4% at 425 K. It seems likely that the major cause lies in the simplified description of diffusion and relaxation of the internal energy for different species used in the derivation of the prediction scheme. This explanation is supported by the fact that values calculated from the still more approximate Hirschfelder–Eucken formula [7], assuming the transport of internal energy to be entirely kinetic, exhibit still greater deviations. Much lower values of $\lambda_0$ obtained by Rosenbaum and Thodos [11] should be ascribed to the extrapolation performed from the pressure region above 3.5 MPa.

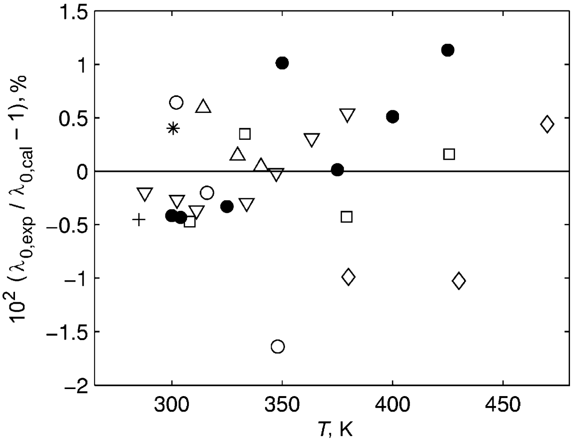

**Fig. 2.** Percentage differences between experimental values for the thermal conductivity in the zero-density limit $\lambda_0$ of carbon dioxide, measured by various authors and the values calculated from the correlation by Vesovic et al. [19]. (□) Millat et al. [20], (◇) Johns et al. [21], (○) Scott et al. [22], (✻) Clifford et al. [23], (△) Lenoir and Comings [24], (▽) Johnston and Grilly [35], (+) Dikins [36], (●) this work.

## 2.3. Density Dependence of the Mixture Thermal Conductivity

As follows from the comparisons presented in Fig. 3, the Hirschfelder–Eucken zero-density limit $\lambda_{0,\mathrm{VW}}$ contributes substantially to the total deviation of the experimental thermal conductivity from the calculated VW value $\lambda_{\mathrm{VW}}$. Therefore, comparisons of the density dependence $\Delta\lambda_{\mathrm{exp}}$ of the experimental thermal conductivity $\lambda_{\mathrm{exp}}$ defined as

$$\Delta\lambda_{\mathrm{exp}} = \lambda_{\mathrm{exp}} - \lambda_{0,\mathrm{exp}} \tag{2}$$

with the VW predicted residual contribution $\Delta\lambda_{\mathrm{r,VW}}$

$$\Delta\lambda_{\mathrm{r,VW}} = \lambda_{\mathrm{VW}} - \lambda_{0,\mathrm{VW}} \tag{3}$$

seems to be more informative as concerns the thermal conductivity density dependence. Here, $\lambda_{0,\mathrm{exp}}$ and $\lambda_{0,\mathrm{VW}}$ denote the experimental and calculated zero-density limits, respectively. Deviations $\Delta$ of $\Delta\lambda_{\mathrm{exp}}$ from $\Delta\lambda_{\mathrm{r,VW}}$ in percent of the total VW thermal conductivity $\lambda_{\mathrm{VW}}$,

$$\Delta = 100(\Delta\lambda_{\mathrm{exp}} - \Delta\lambda_{\mathrm{r,VW}})/\lambda_{\mathrm{VW}}, \tag{4}$$

are presented in Fig. 4 for the present experimental data and data obtained by Kestin et al. [12]. The transport properties of pure methane

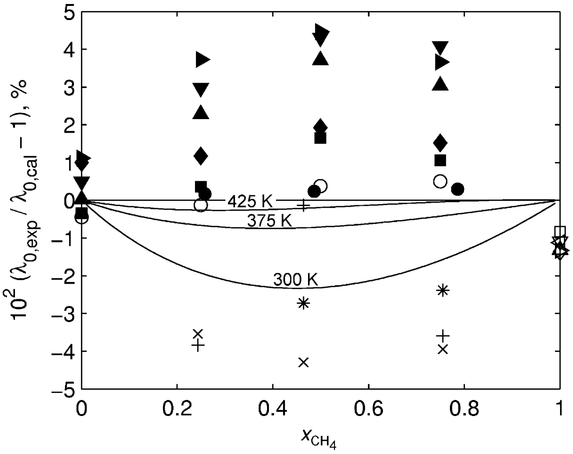

**Fig. 3.** Percentage deviations of the experimental thermal conductivities in the limit of zero density of carbon dioxide–methane mixtures from predicted values as a function of $x_{\mathrm{CH_4}}$, the mole fraction of methane. Nominal temperatures: (□) 290 K, (◇) 310 K, (△) 320 K, (▽) 330 K, (▷) 340 K, (◁) 360 K, (○) 300 K, (■) 325 K, (♦) 350 K, (▲) 375 K, (▼) 400 K, (▶) 425 K, (●) results of Kestin et al. [12] for 300.65 K, results of Rosenbaum and Thodos [11]: (+) 335 K, (×) 370 K, (✻) 404 K, solid lines: Hirschfelder–Eucken expression for 300, 375, and 425 K.

and carbon dioxide used in this calculation were obtained from the formulation developed by Friend et al. [23] and Vesovic et al. [19], respectively. The interaction thermal conductivities have been taken from the correlation of the extended law of corresponding states (Maitland et al. [24]). The critical enhancement is apparent at the highest densities for experimental data points along the 300 K isotherm and to a lesser degree along the 325 K one. The deviations approach 3%, increasing both with increasing density and with increasing temperature. Increased deviations at high densities indicate that the experimental thermal conductivities increase slower with density than those calculated by the VW scheme. This behavior of the VW scheme seems to be rather general, as it was also observed for binary mixtures of noble gases and for mixtures of noble gases with hydrogen and nitrogen by Kestin and Wakeham [4], and for mixtures of methane and nitrogen by Kestin et al. [32].

In Fig. 5 the same deviations $\Delta$ as in Fig. 4 defined by Eq. (4) are depicted for experimental data obtained at temperatures near the carbon dioxide critical temperature of 304.1282 K. The aim is to demonstrate that

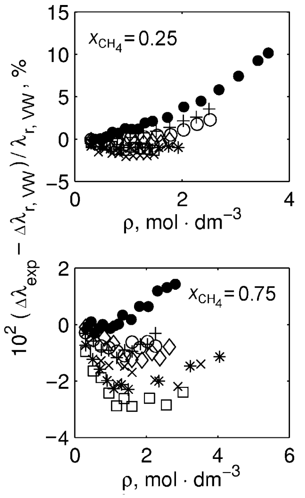

**Fig. 4.** Deviations of $\Delta\lambda_{\mathrm{exp}}$ from $\Delta\lambda_{\mathrm{r,VW}}$ in percent of the total VW thermal conductivity $\lambda_{\mathrm{VW}}$ for carbon dioxide-methane mixtures. Temperatures: (+) 300 K, (○) 325 K, (◇) 350 K, (✳) 375 K, (□) 400 K, (×) 425 K; (●) results of Kestin [12] for 300.65 K.

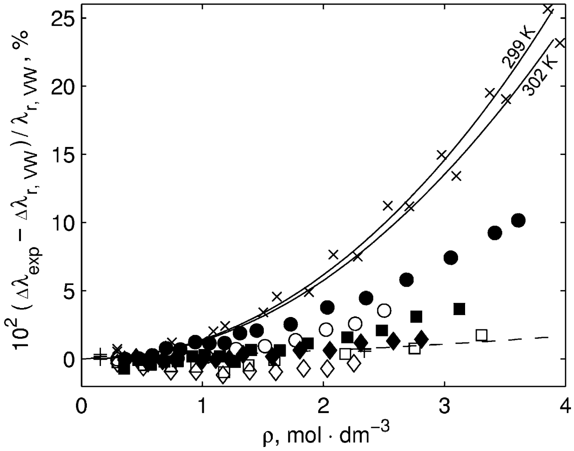

**Fig. 5.** Deviations of $\Delta\lambda_{\mathrm{exp}}$ from $\Delta\lambda_{\mathrm{r,VW}}$ in percent of the total VW thermal conductivity $\lambda_{\mathrm{VW}}$ for carbon dioxide-methane mixtures at temperatures near 300 K. Compositions $x_{\mathrm{CH_4}}$: (×) 0.0, (○) 0.25, (□) 0.50, (◇) 0.75, (△) 1.0; solid line, $CO_2$ critical enhancement at 299 and 302 K; dashed line, $CH_4$ critical enhancement at 300 K; results of Kestin et al. [12] for 300.65 K: (●) 0.2577, (■) 0.4863, (◆) 0.7861.

the observed deviations $\Delta$ of the experimental mixture thermal conductivities, interpreted here as the critical enhancement, are consistent with the critical enhancement of pure components computed from formulations [19,23]. It should be noted here, that the increase in the carbon dioxide thermal conductivity is steeper along the 299 K isotherm than on the 302 K isotherm up to pressures of 7 MPa. The peak in the thermal conductivity occurs only in very close vicinity of the critical point, expressed in terms of pressure in tenths of MPa.

## 3. CONCLUSIONS

The thermal conductivity has been measured for pure carbon dioxide and three carbon dioxide–methane mixtures in the temperature region from 300 to 450 K and up to 12 MPa in pressure. The experimental data have been analyzed to obtain coefficients of the density expansion of the thermal conductivity both for carbon dioxide and carbon dioxide–methane mixtures. It has been demonstrated that the thermal conductivity of carbon dioxide can be measured with the present apparatus with a relative expanded uncertainty (at 95% confidence level) of ±1.2%.

Expressions for prediction of the thermal conductivity of nonpolar mixtures in a dilute-gas limit, developed by Schreiber et al. [1], have been tested against the reported experimental data. The scheme underestimates the experimental thermal conductivities, and deviations do not exceed 5%. This result is consistent with that obtained by Vesovic [22] for thermal conductivities of various mixtures available in the literature. Comparisons with predictions given by the Hirschfelder–Eucken formula indicate that the approximation used for development of the zero-density limit of the VW scheme introduces errors into the VW predictions that are largest for near-equimolar mixtures.

To minimize this effect, the experimental and VW predicted thermal conductivities were compared only after subtraction of their zero-density limits. In these tests, a pronounced critical enhancement was observed on isotherms at 300 and 325 K for mixtures with methane mole fractions of 0.25 and 0.50. For other states, the density dependence of the calculated residual thermal conductivity was found steeper than that of the experimental thermal conductivities. The tested predictive procedure thus seems to introduce some additional error when applied at elevated densities.

The systematic trend in deviations cannot be ascribed only to the way of accounting for the transport of the internal energy of molecules in the derivation of the tested prediction scheme, as a similar effect was observed also in binary mixtures of noble gases.

## ACKNOWLEDGMENT

The work described in this paper has been performed under Grant No. 101/01/0434 awarded by the Grant Agency of the Czech Republic.

## REFERENCES

1. M. Schreiber, V. Vesovic, and W. A. Wakeham, *Int. J. Thermophys.* **18**:925 (1997).
2. M. J. Ross, V. Vesovic, and W. A. Wakeham, *Physica A* **183**:519 (1992).
3. E. A. Mason, H. E. Khalifa, J. Kestin, R. DiPippo, and J. R. Dorfman, *Physica A* **91**:377 (1978).
4. J. Kestin and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **84**:762 (1980).
5. V. Vesovic and W. A. Wakeham, *High Temp. High Press.* **23**:179 (1991).
6. M. K. Tham and K. E. Gubbins, *J. Chem. Phys.* **55**:268 (1971).
7. J. O. Hirschfelder, *J. Chem. Phys.* **26** 282 (1957).
8. J. Luettmer-Strathmann and J. V. Sengers, *Int. J. Thermophys.* **15**:1421 (1994).
9. J. Luettmer-Strathmann and J. V. Sengers, *J. Chem. Phys.* **104**:3026 (1996).
10. J. Pátek, J. Klomfar, L. Čapla, and P. Buryan, *Int. J. Thermophys.* **24**:923 (2003).
11. B. M. Rosenbaum and G. Thodos, *J. Chem. Phys.* **51**:1361 (1969).
12. J. Kestin, S. T. Ro, and Y. Nagasaka, *Ber. Bunsenges. Phys. Chem.* **86**:945 (1982).
13. J. Pátek and J. Klomfar, *Fluid Phase Equilib.* **198**:147 (2002).
14. R. Span and W. Wagner, *J. Phys. Chem. Ref. Data* **15**:1509 (1996).
15. *Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases*, A.G.A. Report No. 8, Second Ed. (Arlington, Virginia, 1992).
16. *ISO 12 213, Natural Gas–Calculation of Compression Factor: Calculation using Molar–Composition Analysis.* First Ed., (Geneva, 1997).
17. M. Bureš, R. Holub, J. Leitner, and P. Vonka, *The Thermochemical Quantities of Organic Compounds* (Institute of Chemical Technology Editing Center, Prague, 1992).
18. B. N. Taylor and Ch. E. Kyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Tech. Note 1297 (1994).
19. V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, *J. Phys. Chem. Ref. Data* **19**:763 (1990).
20. M. J. Assael, J. Millat, V. Vesovic, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **19**:1137 (1990).
21. V. Vesovic, *High Temp. High Press.* **32**:163 (2000).
22. V. Vesovic, *Int. J. Thermophys*. **22**:801 (2001).
23. D. G. Friend, J. F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **18**:583 (1989).
24. G. C. Maitland, E. B. Smith, M. Rigby, and W. A. Wakeham, *Intermolecular Forces* (Claredon Press, Oxford, 1981).
25. J. Millat, M. Mustafa, M. Ross, W. A. Wakeham, and M. Zalaf, *Physica A* **145**:461 (1987).
26. A. I. Johns, S. Rashid, J. T. R. Watson, and A. A. Clifford, *J. Chem. Soc. Faraday Trans. 1* **82**:2235 (1986).
27. A. Scott, A. I. Johns, J. T. R. Watson, and A. A. Clifford, *J. Chem. Soc. Faraday Trans. 1* **79**:733 (1983).
28. A. A. Clifford, J. Kestin, and W. A. Wakeham, *Physica A* **97**:287 (1979).
29. J. M. Lenoir and E. W. Comings, *Chem. Eng. Prog.* **47**:223 (1951).
30. H. L. Johnston and E. R. Grilly, *J. Chem. Phys.* **14**:233 (1946).
31. B. G. Dikins, *Proc. Roy. Soc. Lond. A***143**: 517 (1934).
32. J. Kestin, Y. Nagasaka, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **86**:632 (1982).