

# **Thermal Conductivity of Nitrogen-Methane Mixtures at Temperatures Between 300 and 425 K and at Pressures up to 16 MPa**

**J. Pátek,<sup>1,2</sup> J. Klomfar,<sup>1</sup> L. Čapla,<sup>3</sup> and P. Buryan<sup>3</sup>**

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The thermal conductivities of nitrogen and three mixtures of nitrogen and methane at six nominal temperatures between 300 and 425 K have been measured as a function of pressure up to 16 MPa. The relative uncertainty of the thermal conductivity measurements at a 95% confidence level is estimated to be less than 1%. The data obtained and the results of the low-density analysis were used to test two prediction methods for the thermal conductivity of gas mixtures under pressure and for the thermal conductivity of dilute polyatomic gas mixtures. Reasonable agreement was found with expressions for predicting thermal conductivity of nonpolar mixtures in a dilute-gas limit developed by Schreiber et al. The scheme underestimates the experimental thermal conductivity with deviations not exceeding 3%. The prediction scheme for the thermal conductivity of gas mixtures under pressure suggested by Mason et al. and improved by Vesovic and Wakeham underestimates the experimental thermal conductivities throughout, likely due to its use of the Hirschfelder–Eucken equation at the low-density limit.

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**KEY WORDS:** experimental data; methane; mixtures; nitrogen; thermal conductivity; transient hot wire.

## **1. INTRODUCTION**

The gas industry is one of the fields where knowledge of thermophysical properties of gases is needed for a wide variety of applications. In particular, values of the thermal conductivity are required in energy-flow

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<sup>1</sup> Institute of Thermomechanics, Academy of Sciences of the Czech Republic, Dolejškova 5, CZ 182 00 Prague 8, Czech Republic.

<sup>2</sup> To whom correspondence should be addressed. E-mail: patek@it.cas.cz

<sup>3</sup> Institute of Chemical Technology, Technická 5, CZ 166 28 Prague 6, Czech Republic.

measurements and process simulations. It is not practicable to measure all possible compositions of natural gas, and thus accurate predictive models are required. These models must be validated with reliable data obtained on a limited number of samples that have well defined compositions.

Sufficiently accurate measurements of the thermal conductivity of binary mixtures of the main components of natural gases, i.e., methane, ethane, propane, nitrogen, and carbon dioxide, are relatively rare. The thermal conductivity of methane-ethane mixtures has been measured over a wide range of temperature and pressure with a transient hot-wire instrument by Roder and Friend [1]. Kestin et al. measured the thermal conductivity of mixtures of methane with nitrogen [2] and with carbon dioxide [3] at 27.5°C and at three mole fractions of methane. Johns et al. [4] performed a series of measurements on a nitrogen-carbon dioxide mixtures.

In the present paper, measurements on mixtures of nitrogen and methane are reported. The measurements cover the region from 300 to 425 K in temperature, and up to 16 MPa in pressures. The reported thermal conductivity measurements have been performed in a transient hot-wire apparatus described in detail elsewhere [5], including the experimental procedure and data evaluation. The pure methane was measured earlier [5] in the same apparatus.

The theory of the transient hot-wire technique for thermal conductivity measurements has been given in detail in a number of studies which provides full details: de Groot et al. [6], Healy et al. [7], and Kestin and Wakeham [8]. The principle and the working equation for the hot-wire technique have been fully discussed by Assael et al. [9].

## 2. RESULTS AND DISCUSSION

### 2.1. Thermal Conductivity Data

The sample of nitrogen employed for the thermal conductivity measurements was supplied by Messer Austria GmbH and had a stated purity of 99.999%. The samples of mixtures of nitrogen and methane obtained from Linde AG have a certified relative expanded combined uncertainty in composition at a 95% confidence level of  $\pm 0.05\%$ . The actual values of the methane mole fractions of the samples are 25.07, 50.06, and 74.94%.

A total of 952 data points was measured for pure nitrogen and three nitrogen-methane mixtures along six nominal isotherms 300, 325, 350, 375, 400, and 425 K with ten pressures from about 0.75 MPa to 16 MPa. Previous test measurements [5] showed that the uncertainty of the thermal conductivity data obtained on the present apparatus increases considerably

at densities below  $0.3 \text{ mol} \cdot \text{dm}^{-3}$ . Therefore, low pressure limits for all of the isotherms were chosen so that they correspond to this density limit. The operating parameters for the instrument were chosen to secure heat production in the wire from  $24 \text{ to } 40 \text{ mW} \cdot \text{m}^{-1}$  corresponding to a temperature increase of  $0.45 \text{ to } 1.3 \text{ K}$  at the end of the time interval within which the temperature rise of the hot wire is evaluated.

Table I. Thermal Conductivity of Nitrogen

$p$ (MPa)	$\rho_{\text{nom}}$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$\lambda$ ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$U_{r95}$ (%)	$p$ (MPa)	$\rho_{\text{nom}}$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$\lambda$ ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	$U_{r95}$ (%)
Nominal temperature 300 K				Nominal temperature 325 K			
0.7325	0.2940	0.02627	0.1	0.8020	0.2968	0.02795	0.1
1.505	0.6047	0.02664	0.1	1.650	0.6104	0.02835	0.3
2.300	0.9249	0.02698	0.1	2.505	0.9261	0.02870	0.1
3.100	1.247	0.02736	0.1	3.405	1.258	0.02909	0.2
3.920	1.577	0.02775	0.1	4.240	1.564	0.02942	0.1
4.740	1.907	0.02816	0.1	5.130	1.890	0.02984	0.2
5.500	2.212	0.02858	0.1	6.005	2.208	0.03024	0.2
8.599	3.442	0.03025	0.4	9.500	3.460	0.03192	0.3
11.80	4.678	0.03220	0.2	13.37	4.793	0.03405	0.8
15.07	5.890	0.03424	1.2	16.70	5.884	0.03587	1.1
Nominal temperature 350 K				Nominal temperature 375 K			
0.8850	0.3038	0.02961	0.1	0.9375	0.3001	0.03120	0.1
1.845	0.6323	0.03002	0.1	1.997	0.6377	0.03164	0.1
2.475	0.8472	0.03026	0.1	3.020	0.9614	0.03201	0.1
3.800	1.297	0.03078	0.2	3.610	1.147	0.03221	0.2
4.740	1.614	0.03108	0.2	5.200	1.644	0.03278	0.4
5.700	1.936	0.03151	0.4	6.270	1.975	0.03322	0.6
6.725	2.277	0.03194	0.3	7.425	2.329	0.03369	1.0
10.25	3.426	0.03356	0.4	10.65	3.297	0.03496	0.5
13.70	4.509	0.03519	1.7	13.61	4.154	0.03622	0.6
17.42	5.622	0.03710	1.5	16.90	5.070	0.03779	0.7
Nominal temperature 400 K				Nominal temperature 425 K			
1.000	0.2998	0.03280	0.1	1.153	0.3249	0.03437	0.1
2.193	0.6550	0.03324	0.1	2.330	0.6542	0.03480	0.2
3.300	0.9822	0.03360	0.1	3.550	0.9922	0.03516	0.1
4.460	1.322	0.03402	0.2	4.800	1.335	0.03551	0.5
5.700	1.682	0.03440	0.1	6.060	1.677	0.03597	0.3
6.965	2.045	0.03492	0.6	7.400	2.036	0.03641	0.3
8.230	2.404	0.03530	0.3	8.680	2.375	0.03664	0.2
10.83	3.127	0.03636	0.5	10.93	2.960	0.03755	1.2
13.58	3.869	0.03727	0.7	13.14	3.520	0.03847	0.5
16.29	4.576	0.03847	0.6	15.53	4.110	0.03932	0.7

The density and heat capacity of nitrogen have been calculated from the equation of state of Span et al. [10]. Those for the mixtures were obtained using the AGA8-DC92 equation of state [11, 12]. The ideal-gas isobaric heat capacity of particular components were computed according to Ref. 13. The heat capacity is required to apply a small correction in the reduction of the experimental data whereas the density is one of the primary independent variables [5].

**Table II.** Thermal Conductivity of Nitrogen-Methane Mixture,  $x_{\text{CH}_4} = 0.2507$

$p$ (MPa)	$\rho_{\text{nom}}$ (mol · dm <sup>-3</sup> )	$\lambda$ (W · m <sup>-1</sup> · K <sup>-1</sup> )	$U_{r95}$ (%)	$p$ (MPa)	$\rho_{\text{nom}}$ (mol · dm <sup>-3</sup> )	$\lambda$ (W · m <sup>-1</sup> · K <sup>-1</sup> )	$U_{r95}$ (%)
Nominal temperature 300 K				Nominal temperature 325 K			
0.749	0.3013	0.02858	0.1	0.809	0.3000	0.03090	0.2
1.358	0.5478	0.02882	0.3	1.515	0.5625	0.03117	0.1
1.969	0.7962	0.02913	0.2	2.190	0.8141	0.03145	0.4
2.578	1.045	0.02941	0.2	2.880	1.072	0.03173	0.5
3.195	1.298	0.02961	0.2	3.560	1.326	0.03195	0.3
3.780	1.538	0.02995	0.1	4.240	1.580	0.03228	0.2
4.390	1.789	0.03027	0.1	4.930	1.838	0.03259	0.3
7.690	3.151	0.03219	0.2	7.310	2.724	0.03376	0.3
10.92	4.469	0.03434	0.3	9.750	3.622	0.03509	0.3
13.64	5.548	0.03630	1.0	12.25	4.524	0.03655	0.3
14.30	5.805	0.03673	0.3				
Nominal temperature 350 K				Nominal temperature 375 K			
0.871	0.2995	0.03315	0.2	0.935	0.2997	0.03557	0.1
1.638	0.5634	0.03343	0.3	1.795	0.5751	0.03589	0.3
2.390	0.8222	0.03368	0.2	2.640	0.8450	0.03617	0.4
3.184	1.095	0.03396	0.2	3.500	1.119	0.03641	0.3
3.906	1.343	0.03425	0.2	4.380	1.399	0.03666	0.3
4.720	1.622	0.03454	0.1	5.242	1.671	0.03700	0.4
5.470	1.878	0.03492	0.2	6.118	1.947	0.03721	0.4
7.300	2.500	0.03570	0.5	7.470	2.370	0.03776	0.4
9.040	3.085	0.03649	0.2	8.840	2.794	0.03823	0.3
10.93	3.711	0.03738	0.4	10.27	3.233	0.03888	0.4
Nominal temperature 400 K				Nominal temperature 425 K			
0.980	0.2943	0.03811	0.4	1.028	0.2903	0.04066	0.2
1.950	0.5846	0.03839	0.4	2.118	0.5967	0.04095	0.2
2.900	0.8679	0.03860	0.3	3.150	0.8851	0.04111	0.6
3.930	1.174	0.03878	0.2	4.200	1.177	0.04137	0.3
4.820	1.436	0.03911	0.4	5.290	1.478	0.04154	2.0
5.790	1.721	0.03938	0.6	6.360	1.770	0.04203	0.6
6.780	2.010	0.03967	0.2	7.500	2.080	0.04217	1.1
7.840	2.317	0.04005	0.7	8.480	2.343	0.04262	0.4
8.930	2.629	0.04040	0.3	9.150	2.522	0.04259	0.6
10.02	2.939	0.04089	0.4	10.04	2.758	0.04305	0.3

For each pressure, four to six data points were taken. The results for the thermal conductivity were adjusted at the experimental pressure to the nominal isothermal temperature using a surface fit developed in this work. These shifted thermal conductivities were subsequently averaged, and the averages are presented in the tables. Table I gives the results for pure nitrogen and Tables II to IV give the results for the three nitrogen-methane mixtures. The tables list the thermal conductivity and density  $\rho_{\text{nom}}$  at the

**Table III.** Thermal Conductivity of Nitrogen-Methane Mixture,  $x_{\text{CH}_4} = 0.5006$

$p$ (MPa)	$\rho_{\text{nom}}$ (mol·dm <sup>-3</sup> )	$\lambda$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )	$U_{r95}$ (%)	$p$ (MPa)	$\rho_{\text{nom}}$ (mol·dm <sup>-3</sup> )	$\lambda$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )	$U_{r95}$ (%)
Nominal temperature 300 K				Nominal temperature 325 K			
0.730	0.2944	0.03081	0.1	0.808	0.3003	0.03372	0.3
1.194	0.4833	0.03101	0.1	1.324	0.4933	0.03388	0.5
1.655	0.6723	0.03118	0.8	1.833	0.6844	0.03408	1.6
2.082	0.8483	0.03142	0.4	2.334	0.8737	0.03425	0.6
2.560	1.047	0.03164	0.1	2.815	1.056	0.03434	0.5
2.980	1.222	0.03180	0.1	3.360	1.263	0.03465	0.5
3.420	1.407	0.03205	0.3	3.800	1.431	0.03480	0.7
4.060	1.677	0.03243	0.4	7.460	2.838	0.03694	0.7
4.802	1.993	0.03290	0.2	11.24	4.286	0.03929	0.5
5.522	2.301	0.03325	0.6	14.93	5.659	0.04200	0.3
Nominal temperature 350 K				Nominal temperature 375 K			
0.845	0.2911	0.03661	0.2	0.905	0.2907	0.03975	0.3
1.438	0.4963	0.03679	0.2	1.594	0.5124	0.03998	0.4
2.015	0.6964	0.03692	0.4	2.208	0.7102	0.04017	0.3
2.580	0.8929	0.03718	0.3	2.825	0.9091	0.04035	0.6
3.160	1.095	0.03739	0.6	3.520	1.133	0.04045	0.4
3.725	1.292	0.03771	0.6	4.220	1.359	0.04064	0.2
4.370	1.518	0.03793	0.3	4.870	1.568	0.04095	0.4
7.650	2.664	0.03943	0.5	7.990	2.569	0.04224	0.6
11.00	3.823	0.04139	0.2	11.13	3.560	0.04376	0.5
15.45	5.314	0.04422	0.6				
Nominal temperature 400 K							
1.022	0.3074	0.04307	0.5				
1.712	0.5150	0.04318	0.4				
2.354	0.7080	0.04325	0.1				
3.300	0.9922	0.04353	0.3				
3.875	1.165	0.04360	0.4				
4.510	1.355	0.04378	0.5				
5.140	1.543	0.04401	0.4				
7.720	2.310	0.04489	0.4				
10.80	3.210	0.04615	0.3				
13.50	3.980	0.04745	0.9				

nominal temperature  $T_{\text{nom}}$  and the experimental pressure  $p$ . The relative expanded uncertainty at a 95% confidence level ( $U_{195}$ ) is presented in the table for each mean value. The uncertainties were evaluated according to the procedure recommended in Ref. 38 (p. 9) as follows: The estimate of the standard deviation of the mean was multiplied by the coverage factor  $k_{95}$  dependent on the degrees of freedom  $\nu$  of the uncertainty. A complete

**Table IV.** Thermal Conductivity of Nitrogen-Methane Mixture,  $x_{\text{CH}_4} = 0.7494$

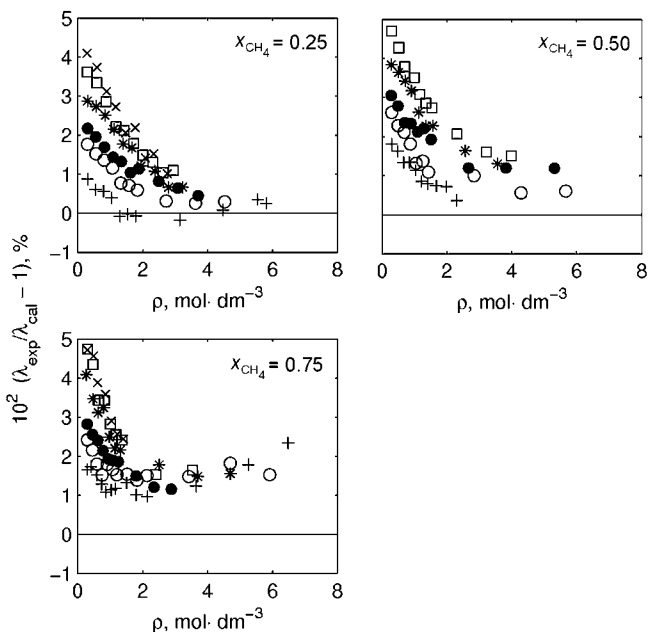
$p$ (MPa)	$\rho_{\text{nom}}$ (mol·dm <sup>-3</sup> )	$\lambda$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )	$U_{195}$ (%)	$p$ (MPa)	$\rho_{\text{nom}}$ (mol·dm <sup>-3</sup> )	$\lambda$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )	$U_{195}$ (%)
Nominal temperature 300 K				Nominal temperature 325 K			
0.735	0.2973	0.03298	0.2	0.800	0.2981	0.03639	0.2
1.004	0.4074	0.03316	0.2	1.218	0.4554	0.03653	0.3
1.454	0.5932	0.03336	0.4	1.585	0.5944	0.03660	0.5
1.800	0.7374	0.03350	0.2	1.998	0.7518	0.03673	0.2
2.135	0.8781	0.03364	0.2	2.400	0.9059	0.03707	0.3
2.495	1.031	0.03389	0.4	2.835	1.074	0.03728	0.3
2.820	1.169	0.03412	0.2	3.170	1.204	0.03743	0.8
3.600	1.506	0.03470	0.3	3.975	1.518	0.03793	0.4
4.280	1.803	0.03508	0.1	4.750	1.824	0.03838	0.2
5.030	2.136	0.03563	0.3	5.525	2.132	0.03895	0.3
8.340	3.649	0.03854	0.4	8.720	3.422	0.04132	0.2
11.78	5.260	0.04225	0.4	11.85	4.695	0.04413	0.3
14.41	6.475	0.04549	0.4	14.90	5.914	0.04685	0.5
Nominal temperature 350 K				Nominal temperature 375 K			
0.860	0.2970	0.03986	0.2	0.822	0.2645	0.04381	0.3
1.324	0.4584	0.03999	0.6	1.454	0.4689	0.04385	0.2
1.790	0.6214	0.04017	0.2	1.950	0.6299	0.04394	0.5
2.235	0.7777	0.04030	0.3	2.462	0.7966	0.04425	0.3
2.700	0.9417	0.04047	0.2	2.980	0.9657	0.04418	0.3
3.140	1.097	0.04069	0.4	3.520	1.142	0.04433	0.3
3.590	1.257	0.04093	0.6	4.040	1.313	0.04458	0.2
5.100	1.798	0.04166	0.2	7.670	2.510	0.04645	0.1
6.630	2.350	0.04249	0.3	11.27	3.692	0.04857	0.5
8.100	2.883	0.04344	0.5				
Nominal temperature 400 K				Nominal temperature 425 K			
0.993	0.2992	0.04782	0.1	1.058	0.2996	0.05161	0.2
1.570	0.4737	0.04789	0.3	1.687	0.4782	0.05180	0.3
2.156	0.6512	0.04774	0.2	2.150	0.6097	0.05166	0.4
2.740	0.8284	0.04801	0.4	3.020	0.8568	0.05189	0.8
3.340	1.011	0.04801	0.3	3.640	1.033	0.05181	0.4
3.880	1.175	0.04814	0.2	4.295	1.219	0.05194	0.3
4.490	1.361	0.04837	0.7	4.940	1.402	0.05217	0.2
7.920	2.404	0.04971	0.8				
11.65	3.526	0.05188	0.3				

tabulation of the raw thermal conductivity data is available in electronic form from the authors.

The experimental data were used to test the procedure for evaluation of the background thermal conductivity of dense fluid mixtures proposed by Mason et al. [14]. The procedure is based on an extension to the Thorne-Enskog theory for dense gases developed by Tuam and Gubbins [15]. The most recent version of the procedure has been developed by Kestin and Wakeham [16] and Vesovic and Wakeham [17].

The method requires a knowledge of the density dependence of the thermal conductivity of the pure components, the zero-density thermal conductivities and viscosities of the pure gases, and their second virial coefficients. The interaction low-density thermal conductivities  $\lambda_{ij}^0(\text{mon})$  and the reduced collision integral ratios  $A_{ij}^*$  and  $B_{ij}^*$  [14] for each pair of components are also needed.

The transport properties of pure methane and nitrogen were obtained from the formulations of their thermal conductivity by Friend et al. [18] and Stephan et al. [19], respectively. The interaction properties have been



**Fig. 1.** Deviations of the experimental thermal conductivities of nitrogen-methane mixtures from the predictions of Vesovic and Wakeham [17]. Temperatures: (+) 300 K, (O) 325 K, (●) 350 K, (\*) 375 K, (□) 400 K, (x) 425 K.

taken from the correlations of the extended law of corresponding states (Maitland et al. [20]). Figure 1 shows the deviations of the experimental data from those predicted by the scheme. The predictions underestimate the experimental values for all compositions and nominal temperatures. The deviations do not exceed 5%, being worst at low densities, decreasing progressively as the density increases, and increasing with temperature. Increased deviations at low densities likely stem from the fact that the procedure reduces to the Hirschfelder–Eucken diffusional formula [21] in the limit of zero density, assuming the transport of internal energy to be entirely kinetic.

## 2.2. Zero-Density Limit

Although there exist many studies in the literature with experimental data on the zero-density limit of the thermal conductivity of nitrogen, only 23 data points from nine studies covering the temperature range from about 275 to 460 K are of sufficient quality for fitting the  $\lambda_0(T)$  relation [22]. Therefore, further experimental data for the dilute-gas thermal conductivity of nitrogen are desirable. In order to determine  $\lambda_0$  and the initial slope with respect to density  $\lambda_1(T)$ , the experimental data have been represented along each nominal isotherm by means of a polynomial in density

$$\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 + \dots \quad (1)$$

For this purpose, the results for the thermal conductivity were shifted from their experimental temperatures to the nominal temperature by means of small (0.2%) corrections. The needed temperature derivatives of the thermal conductivity have been estimated from the experimental data themselves.

The presence of terms of higher order in the polynomial least-squares fit to a limited number of experimental points results in a systematic shift in the resultant coefficients  $\lambda_0$  and  $\lambda_1$ . Therefore, the lowest seven experimental pressures on each isotherm were selected so that the terms  $\lambda_0$  and  $\lambda_1 \rho$  were the only statistically significant terms in the polynomial fit.

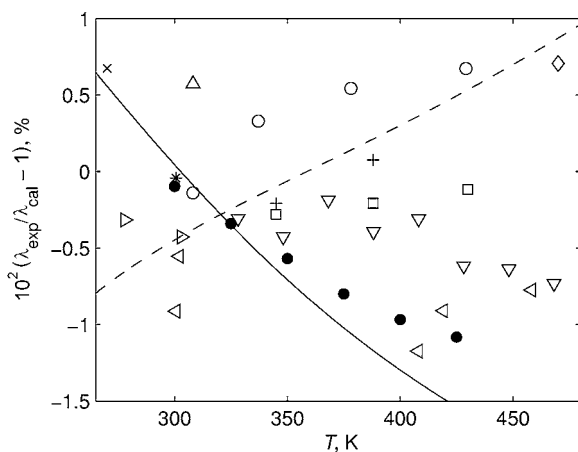
The optimum values of the coefficients  $\lambda_0$  and  $\lambda_1$  together with estimates of their expanded uncertainties at a 95% confidence level are listed in Table V. The deviations of the experimental values of  $\lambda_0$  measured for nitrogen by various authors and of the correlations by Stephan et al. [19] and Uribe et al. [23], from the correlation by Millat and Wakeham [22] 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 (95% confidence level,  $k = 2$ ) of the present results is less than  $\pm 1.0\%$ .



**Table V.** Best Estimates of the Density Coefficients in the Expansion of the Thermal Conductivity of Nitrogen

$T$ (K)	$\lambda_0$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )	$\lambda_1$ (μW · m <sup>2</sup> · K <sup>-1</sup> · kg <sup>-1</sup> )
300	25.97 ± 0.04	41.1 ± 0.8
325	27.66 ± 0.04	42.0 ± 1.0
350	29.30 ± 0.04	41.3 ± 0.7
375	30.89 ± 0.05	42.5 ± 1.0
400	32.46 ± 0.04	42.2 ± 0.8
425	34.01 ± 0.04	41.4 ± 1.2

The optimum values of the coefficients  $\lambda_0$  of the nitrogen-methane mixtures together with their uncertainty estimates are listed in Table VI. Recently Schreiber et al. [24] have developed a practical scheme for predicting the thermal conductivity of a dilute multicomponent polyatomic gas mixtures. The scheme is based on formal kinetic theory results by Ross et al. [25]. The expressions contain no adjustable parameters and require only thermal conductivity and isobaric heat capacity of pure species and a



**Fig. 2.** Percentage differences between experimental values for the thermal conductivity in the zero-density limit  $\lambda_0$  of nitrogen, measured by various authors and the values calculated from the correlation by Millat and Wakeham [22]. Solid line: Stephan et al. [19], dashed line: Uribe et al. [23], ( $\diamond$ ) Johns et al. [4], ( $\triangleleft$ ) Le Neindre [28], ( $\nabla$ ) Haarman [29], ( $*$ ) Clifford et al. [30], ( $+$ ) Clifford et al. [31], ( $\circ$ ) Haran et al. [32], ( $\square$ ) Johns et al. [33], ( $\times$ ) Millat et al. [34], ( $\triangle$ ) Mostert et al. [35], ( $\triangleright$ ) Perkins et al. [36], ( $\bullet$ ) this work.

Table VI. Zero-Density Thermal Conductivities of Nitrogen-Methane Mixtures

$T$ (K)	$\lambda_0$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )		
	$x=0.25$	$x=0.50$	$x=0.75$
300	28.25 ± 0.09	30.50 ± 0.07	32.65 ± 0.09
325	30.60 ± 0.08	33.45 ± 0.10	36.08 ± 0.17
350	32.84 ± 0.06	36.34 ± 0.16	39.57 ± 0.10
375	35.29 ± 0.10	39.50 ± 0.08	43.63 ± 0.13
400	37.85 ± 0.12	42.86 ± 0.11	47.71 ± 0.15
425	40.46 ± 0.11		51.55 ± 0.14

set of interaction parameters that are readily available for a number of binary interactions between common nonpolar molecules [20]. The expressions have been tested against available experimental data by Vesovic [26]. For most mixtures studied, the deviations from the experimental thermal conductivity have been found to be within  $\pm 2.5\%$ .

The deviations of the present experimental data for  $\lambda_0$  from the predictions based on the scheme by Schreiber et al. [24] are plotted in Fig. 3,

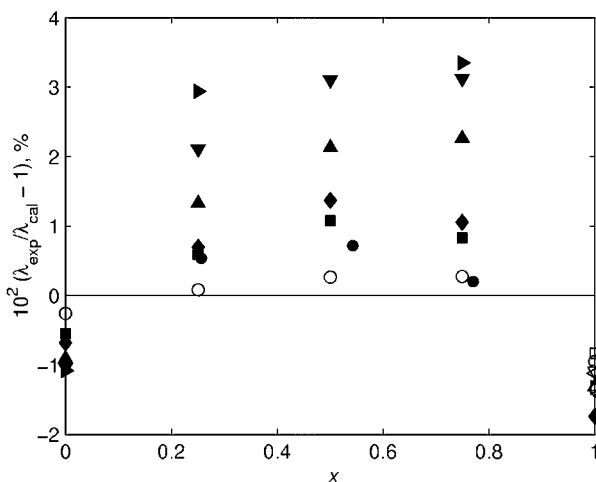


Fig. 3. Percentage deviations of the experimental thermal conductivities in the limit of zero-density of nitrogen-methane mixtures from predicted values as a function of  $x_{\text{CH}_4}$ , the mole fraction of methane. Nominal temperatures: ( $\square$ ) 290 K, ( $\diamond$ ) 310 K, ( $\triangle$ ) 320 K, ( $\nabla$ ) 330 K, ( $\triangleright$ ) 340 K, ( $\triangleleft$ ) 360 K, ( $\circ$ ) 300 K, ( $\blacksquare$ ) 325 K, ( $\blacklozenge$ ) 350 K, ( $\blacktriangle$ ) 375 K, ( $\blacktriangledown$ ) 400 K, ( $\blacktriangleright$ ) 425 K, ( $\bullet$ ) results of Kestin et al. [2] for 300.65 K.

together with the results obtained for nitrogen-methane mixtures by Kestin et al. [2]. For the dilute-gas thermal conductivity of methane and nitrogen, the correlations of Assael et al. [27] and Millat and Wakeham [22], respectively, have been used in the calculations, while the ideal-gas isobaric heat capacity of pure methane and nitrogen have been calculated from the correlations of Friend et al. [18] and Span et al. [10], respectively. The predictions underestimate the the present data for the thermal conductivity of methane-nitrogen mixtures for all nominal temperatures. The deviations of the experimental thermal conductivities from the predictions increase with the nominal temperature up to about 3% 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.

### 3. CONCLUSION

The thermal conductivity of pure nitrogen and three nitrogen-methane mixtures have been measured in the temperature region from 300 to 450 K and at pressures up to 16 MPa. The experimental data obtained have been analyzed to obtain coefficients of the density expansion of the thermal conductivity both for nitrogen and nitrogen-methane mixtures. It has been demonstrated that the thermal conductivity of nitrogen can be measured with the present apparatus with a relative expanded uncertainty (95% confidence level,  $k = 2$ ) of 1%.

Expressions for prediction of the thermal conductivity of nonpolar mixtures in a dilute gas limit developed by Schreiber et al. [24] have been tested against the reported experimental data. The scheme underestimates the experimental thermal conductivities, and deviations do not exceed 3%. This result is consistent with those obtained by Vesovic [26] for thermal conductivities of various mixtures available in the literature.

In the test of the Vesovic-Wakeham version of the expressions for the background thermal conductivity of dense fluid mixtures developed by Mason et al. [14], reasonable agreement was found for densities above  $2 \text{ mol} \cdot \text{dm}^{-3}$ , but for the lower densities, the deviations increase to 5%.

The available kinetic theory for the density dependence of the thermal conductivity of gas mixtures seems to be not sufficiently accurate to describe experimental data within their uncertainty at the limit of zero density. Better agreement of the theory should be expected if the inelastic effects are included in dense fluid transport theory, at least, in the form suggested by Monchick [37].

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