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The Thermal Conductivity of Pure Nitrogen and of Mixtures of Nitrogen and Carbon Dioxide at Elevated Temperatures and Pressures

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The thermal conductivities of nitrogen at 470 K and six mixtures of nitrogen and carbon dioxide at various temperatures have been measured as a function of pressure up to 25 MPa. The mixtures were measured at the following temperatures: one at 302 K, three at 380 K, one at 430 K, and one at 470 K. The data were used to test three prediction methods for the thermal conductivity of gas mixtures under pressure. Surprisingly good agreement was found with predictions using the corresponding-states method of Ely and Hanley. The predictions of the more theoretically based method of Mason et al. were low throughout, due partly to its use of the Hirschfelder–Eucken equation as the low-density limit, but also because the predicted density dependence rises too slowly. The simplified version of this method proposed by Svojskij gave slightly worse predictions, particularly at higher densities. The zero-density results for nitrogen are examined by comparing the zero- and first-density coefficients with the trends shown at lower temperatures.

KEY WORDS: carbon dioxide; high pressures; mixtures; nitrogen; thermal conductivity.

1. INTRODUCTION

An accurate transient hot-wire method for measuring the thermal conductivity of gases at atmospheric pressure was developed originally by Haarman [1]. The technique has been adapted for gases under pressure by several investigators who report absolute accuracies of better than 1%. A hot-wire apparatus of this type at the National Engineering Laboratory

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(NEL) in the United Kingdom has been described previously [2, 3] and has been modified to work up to 470 K [4]. The same apparatus has been used to make the measurements reported in this paper.

In the past 5 years or so the transient hot-wire method has been used to study the thermal conductivity of a number of gas mixtures under pressure. At Brown University measurements have been made at 300.65 K on the following mixtures: He/Ar, Ne/Ar, and Ne/Ar/Kr [5]; H_2/He [6]; CH_4/He, CH_4/Ne, and CH_4/Ar [7, 8]; N_2/He, N_2/Ne, and N_2/Ar [9]; CO/He, CO/Ne, and CO/Ar [10]; CO_2/Ne and CO_2/Ar [11]; and CF_4/He and CF_4/Ne [12]. Measurements have also been made on He/Ne and Ar/Kr [13], H_2/Ne, H_2/Ar, and H_2/Kr [14], and H_2/N_2, CO/He, and CO/Ar [15] mixtures at 308 K at Imperial College and at NEL on dry air at temperatures between 312 and 373 K [16]. When measuring the thermal conductivity of gas mixtures the effect of thermal diffusion must be taken into account. This has been discussed by Khalifa et al. [17], who conclude that a transient hot-wire apparatus will always measure the thermal conductivity corresponding to the steady state with no mass transfer taking place.

Accurate data are required for testing and developing reliable prediction methods for the thermal conductivity of gas mixtures under pressure. In this paper we report measurements on mixtures of nitrogen and carbon dioxide. These data provide a severe test of such methods, because of the large effect (up to 15%) that the exchange of energy between internal and translational modes has on the thermal conductivity of carbon dioxide and its mixtures. We also report measurements on pure nitrogen at 470 K.

Three prediction methods are used in this paper. The first of these is the method of Ely and Hanley [18, 19]. It is based on the principle of corresponding states and is purported to work over the entire fluid range. The method described in Refs. 18 and 19 is a development of a previous corresponding-states method for viscosity [20]. The method requires a knowledge of the critical constants, molecular weight, Pitzer's acentric factor, and heat capacity as a function of temperature for each component of the mixture. The calculation for the thermal conductivity is broken down into two separate calculations, one for the translational energy and one for the internal energy. The internal energy part is calculated by mixing the modified Eucken values at zero density for the pure gases, which are obtained, in turn, from the Ely–Hanley corresponding-states method for viscosity. Negligible collisional relaxation of molecular internal energy is therefore assumed, and moreover, the method assumes that the internal energy contribution does not change with pressure. The prediction method is therefore somewhat simplified. It has been tested with available data and gives predictions which agree with the experimental to better than 7%. A computer program is available [19] and was used by us to produce values to compare with our measurements.

The second comparison that we have undertaken is with the procedure of Mason et al. [21], which is based on an extension to the Thorne–Enskog [22] theory for dense gases reported by Tuam and Gubbins [23]. The method requires a knowledge of the density dependence of the thermal conductivity of the pure gases and the zero-density thermal conductivities and viscosities of the pure components. The second virial coefficients and their temperature derivatives for each pair of components are also needed. This approach has a strong theoretical basis, although experimental data are still required for the calculations. Kestin and Wakeham [25] have empirically evaluated this scheme using data for the noble gases obtained from transient hot-wire measurements. They propose a modified combination rule for the pseudoradial distribution function of the mixture which has been used in subsequent work. Assael et al. [13] also tested the method for noble-gas mixtures. They pointed out that the first-order Chapman–Enskog value for the thermal conductivity in the low-density limit was not sufficiently accurate, especially for mixtures containing helium. They proposed multiplying the entire curve by the third-order correction factor for the low-density limit, which then gave good agreement. Assael and Wakeham [15] have also tested the method for a mixture containing polyatomic gases, namely the hydrogen/nitrogen system. Here the low-density limit, evaluated using the Hirschfelder–Eucken formula, is not expected to be well predicted because of the exchange of internal energy. However, good agreement was found for the first-density coefficients.

The third method is a simplified version of the method of Mason et al. that has been reported by Svojskij [24]. He uses the same starting equations as Mason et al. but neglects certain terms (the off-diagonal elements) to produce formulas of the Wassiljewa form. Although the formulas given are simpler, the same experimental data input is required as in the more complete theoretical approach of Mason et al. A combination rule is suggested to avoid the use of second virial coefficients and their temperature derivatives.

2. RESULTS

Table I gives the results for pure nitrogen at 470 K. Tables II–VII give the results for the six nitrogen–carbon dioxide mixtures: one at 320 K, three at 380 K, one at 470 K. Each data point in the tables is the average of at least eight runs done at usually two different bridge voltages. The techniques used have been fully described in previous papers [2–4]. The

Table I. The Thermal Conductivity of Nitrogen at 470 K

P (MPa)	T_{ref} (K)	ρ_{ref} ($kg \cdot m^{-3}$)	λ_{ref} ($mW \cdot m^{-1} \cdot K^{-1}$)	λ_{nom} ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\partial\lambda/\partial T)_\rho$ ($mW \cdot m^{-1} \cdot K^{-2}$)
1.01	471.65	7.2	37.97	37.86	0.060
1.43	474.08	10.1	38.15	37.91	0.060
2.05	474.13	14.4	38.32	38.08	0.058
2.98	473.87	20.9	38.55	38.31	0.060
3.93	473.59	27.5	38.77	38.55	0.060
6.00	473.00	41.7	39.27	39.10	0.055
8.00	472.64	55.2	39.93	39.78	0.055
9.90	472.50	67.6	40.50	40.36	0.055
14.70	474.99	97.6	42.08	41.83	0.050
19.96	475.18	128.9	43.94	43.96	0.048
24.25	473.97	153.5	45.36	45.19	0.043
27.7	473.2	172.3	46.45	46.32	0.040

Table II. The Thermal Conductivity of $(x(N_2) + (1-x)(CO_2))$ at 320 K, $x(N_2) = 0.381$

P (MPa)	T_{ref} (K)	ρ_{ref} ($kg \cdot m^{-3}$)	λ_{ref} ($mW \cdot m^{-1} \cdot K^{-1}$)	λ_{nom} ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\partial\lambda/\partial T)$ ($mW \cdot m^{-1} \cdot K^{-2}$
1.10	322.13	15.9	22.13	21.97	0.075
2.16	321.65	31.9	22.71	22.57	0.075
3.43	322.36	51.7	23.48	23.30	0.070
4.82	322.67	74.4	24.66	24.45	0.060
6.19	322.85	98.0	25.82	25.68	0.040
8.98	322.30	150.2	28.97	28.95	0.010
10.40	321.39	179.4	30.89	30.91	−0.015
11.70	321.57	206.6	33.04	33.09	−0.040
13.00	321.44	233.3	35.11	35.18	−0.040
14.60	321.33	267.1	38.13	38.23	−0.080
15.90	321.35	294.0	40.13	40.27	−0.100
17.10	320.86	319.5	42.37	42.48	−0.130

Table III. The Thermal Conductivity of $(x(N_2)+(1-x)(CO_2))$ at 380 K, $x(N_2)=0.160$

P (MPa)	T_{ref} (K)	ρ_{ref} $(\text{kg}\cdot\text{m}^{-3})$	λ_{ref} $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	λ_{nom} $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$(\partial\lambda/\partial T)_\rho$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2})$
3.10	380.80	42.6	25.94	25.88	0.074
4.90	380.16	69.4	26.88	26.87	0.067
7.03	380.38	103.1	28.42	28.40	0.056
8.31	381.83	123.6	29.59	29.50	0.050
10.90	380.07	169.6	32.19	32.17	0.043
12.60	379.95	201.7	34.12	34.12	0.015
13.70	381.22	220.9	35.50	35.52	−0.011
15.80	380.90	262.1	38.35	38.37	−0.042
17.70	379.89	299.4	41.32	41.31	−0.080
19.60	379.97	334.9	44.15	44.14	−0.119
21.20	379.85	364.0	46.59	46.57	−0.140
23.10	379.47	397.7	49.57	49.47	−0.175
25.00	379.81	427.6	52.06	52.03	−0.206

Table IV. The Thermal Conductivity of $(x(N_2)+(1-x)(CO_2))$ at 380 K, $x(N_2)=0.412$

P (MPa)	T_{ref} (K)	ρ_{ref} $(\text{kg}\cdot\text{m}^{-3})$	λ_{ref} $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	λ_{nom} $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	$(\partial\lambda/\partial T)$ $(\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2})$
0.90	381.37	10.7	27.35	27.24	0.076
2.32	380.60	27.9	27.55	27.51	0.072
3.72	380.96	45.2	28.27	28.20	0.070
5.52	380.45	68.0	29.10	29.07	0.063
7.31	380.82	91.0	30.11	30.06	0.059
9.66	381.25	121.6	31.69	31.63	0.050
11.10	380.75	140.9	32.70	32.67	0.043
13.30	380.21	170.7	34.41	34.40	0.030
16.90	379.64	218.6	37.59	37.59	0.005
17.50	380.37	225.8	38.12	38.12	−0.002
18.10	380.61	233.3	38.62	38.62	−0.002
19.40	380.40	250.2	39.83	39.84	−0.016
20.88	380.17	269.0	41.29	41.29	−0.024
22.66	379.91	286.3	42.50	42.49	−0.032
23.47	380.93	299.5	43.41	43.45	−0.040
25.10	380.86	318.6	45.14	45.19	−0.056

Table V. The Thermal Conductivity of $(x(N_2)+(1-x)(CO_2))$ at 380 K, $x(N_2)=0.708$

P (MPa)	T_{ref} (K)	ρ_{ref} ($kg \cdot m^{-3}$)	λ_{ref} ($mW \cdot m^{-1} \cdot K^{-1}$)	λ_{nom} ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\partial\lambda/\partial T)$ ($mW \cdot m^{-1} \cdot K^{-2}$)
1.46	381.32	15.1	30.08	29.98	0.070
2.50	380.99	25.9	30.35	30.28	0.069
2.75	381.34	28.5	30.42	30.33	0.068
3.80	381.05	39.4	30.72	30.65	0.066
8.30	381.45	86.0	32.66	32.58	0.058
11.30	381.66	116.5	34.21	34.13	0.049
16.60	381.88	168.5	37.29	37.23	0.034
18.10	381.38	183.0	38.11	38.07	0.028
20.10	380.87	201.8	39.34	39.32	0.021
22.50	381.13	223.2	40.71	40.69	0.015
24.50	381.72	240.1	41.99	41.98	0.008

Table VI. The Thermal Conductivity of $(x(N_2)+(1-x)(CO_2))$ at 430 K, $x(N_2)=0.392$

P (MPa)	T_{ref} (K)	ρ_{ref} ($kg \cdot m^{-3}$)	λ_{ref} ($mW \cdot m^{-1} \cdot K^{-1}$)	λ_{nom} ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\partial\lambda/\partial T)_\rho$ ($mW \cdot m^{-1} \cdot K^{-2}$)
1.20	429.93	12.7	31.27	31.28	0.075
2.70	429.02	28.9	31.50	31.58	0.075
3.61	428.86	38.8	31.75	31.84	0.070
4.91	428.29	53.0	32.21	32.33	0.070
6.39	429.83	69.0	32.81	32.82	0.065
8.65	429.33	94.1	33.85	33.89	0.065
10.20	428.91	111.4	34.68	34.71	0.055
12.20	429.32	133.4	35.77	35.82	0.050
13.80	429.23	151.0	36.73	36.76	0.045
15.40	429.59	168.3	37.76	37.77	0.045
17.40	429.95	189.7	38.94	38.94	0.040
18.80	429.69	204.8	39.82	39.83	0.035
20.40	429.42	221.8	40.86	40.88	0.030
22.10	429.32	239.4	42.16	42.17	0.015
24.00	429.65	258.3	43.30	43.31	0.010
26.40	430.17	281.2	45.14	45.17	0.000

Table VII. The Thermal Conductivity of a Mixture of Nitrogen and Carbon Dioxide at 470 K, $x(N_2) = 0.420$

P (MPa)	T_{ref} (K)	ρ_{ref} ($kg \cdot m^{-3}$)	λ_{ref} ($mW \cdot m^{-1} \cdot K^{-1}$)	λ_{nom} ($mW \cdot m^{-1} \cdot K^{-1}$)	$(\partial\lambda/\partial T)_\rho$ ($mW \cdot m^{-1} \cdot K^{-2}$)
1.27	473.54	11.6	35.13	34.86	0.075
1.72	473.36	15.7	35.22	34.99	0.070
2.46	474.45	22.5	35.30	34.99	0.070
3.96	473.50	36.3	35.65	35.40	0.070
5.89	473.71	58.8	36.22	35.97	0.065
7.90	473.38	72.2	36.92	36.70	0.065
9.88	473.19	90.1	37.66	37.46	0.065
12.42	473.45	112.8	38.78	38.58	0.060
14.86	473.79	134.2	39.84	39.63	0.055
17.52	474.45	156.6	41.13	40.91	0.050
19.91	474.37	176.6	42.14	41.94	0.045
24.80	474.22	217.9	45.00	44.84	0.040
30.83	473.42	262.0	48.56	48.48	0.025

purities of the gases supplied were specified to be as follows: carbon dioxide (Air Products), 99.995% pure; and nitrogen (British Oxygen Company), 99.999% pure. Analyses of the mixture compositions were carried out by the British Oxygen Company using gas chromatography and were specified as accurate to 1%. Three samples were taken at various pressures along each isotherm and the result of each composition analysis agreed to within the specification.

The nitrogen densities were obtained from the IUPAC formulation [26]. Those for the mixtures were obtained using the generalized equation of state proposed by Lee and Kesler [27]. The values, λ_{ref}, correspond to

Table VIII. Coefficients of the Correlating Equation $\lambda = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3$ for the Thermal Conductivities of Mixtures of Carbon Dioxide and Nitrogen and of Pure Nitrogen

T (K)	$x(N_2)$	$10^3 a_0$ ($W \cdot m^{-1} \cdot K^{-1}$)	$10^6 a_1$ ($W \cdot m^{-2} \cdot K^{-1} \cdot kg^{-1}$)	$10^9 a_2$ ($W \cdot m^5 \cdot K^{-1} \cdot kg^{-2}$)	$10^{12} a_3$ ($W \cdot m^8 \cdot K^{-1} \cdot kg^{-3}$)
320	0.381	21.5640	24.6552	194.210	−207.824
380	0.160	24.5393	25.6496	126.399	−84.068
380	0.412	26.8866	22.6817	146.404	−120.390
380	0.708	29.5871	21.2286	177.383	−215.468
430	0.392	30.9301	19.0704	145.567	−124.119
470	0.420	34.5437	20.7240	123.211	0
470	1	37.5509	34.6146	97.4333	0

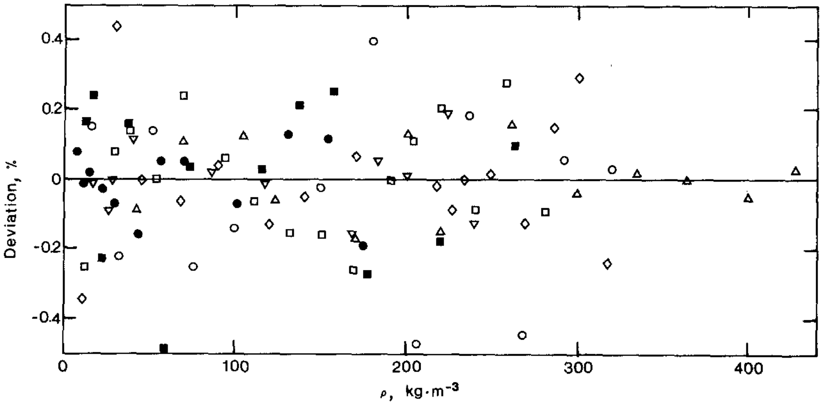

Fig. 1. Deviations of the experimental thermal conductivities of mixtures of nitrogen and carbon dioxide from the equations in Table VIII. (○) 320 K, $x(N_2) = 0.381$; (△) 380 K, $x(N_2) = 0.160$; (◇) 380 K, $x(N_2) = 0.412$; (▽) 380 K, $x(N_2) = 0.708$; (□) 430 K, $x(N_2) = 0.392$; (■) 470 K, $x(N_2) = 0.420$; (●) 470 K, $x(N_2) = 1$.

an average experimental temperature T_{ref}. The thermal conductivities are corrected to a nominal temperature, T_{nom} (e.g., 320 K), by applying the equation

$$\lambda(\rho_{\text{ref}} T_{\text{nom}}) = \lambda(\rho_{\text{ref}}, T_{\text{ref}}) + (\partial\lambda/\partial T)_\rho \, (T_{\text{nom}} - T_{\text{ref}})$$

The values of $(\partial\lambda/\partial T)_\rho$ used are given in the last columns of the tables and were estimated using the method of Stiel and Thodos [28].

The data in Tables I–VII were fitted to a cubic equation in the density and the resulting coefficients are shown in Table VIII. Deviations of individual data points are given in Fig. 1. The scatter is seen to be less than 0.2%.

3. DISCUSSION

The data were also fitted to polynomials of different degrees using increasing number of points by a procedure described previously [29] to obtain coefficients for the density expansion of the thermal conductivity: $\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 + \cdots$. The optimum coefficients are given in Table IX together with their 95% confidence limits. The values of λ_0 so obtained are the best estimates of the thermal conductivity of the mixtures at zero density. These values are plotted in Fig. 2 and compared with previous data. The curves drawn are freehand and do not have any particular functional form. Positive and negative deviations from straight-line behavior are

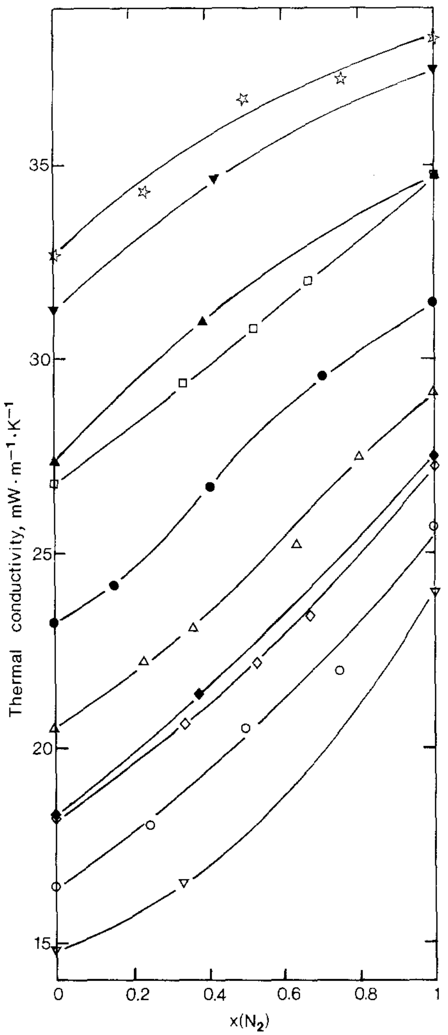

Fig. 2. The zero-density limit of the thermal conductivity of nitrogen, carbon dioxide, and their mixtures as a function of $x(N_2)$, the mole fraction of nitrogen. (☆) Westenberg and de Haas [36] at 500 K; (▼) present results at 470 K; (▲) present results at 430 K; (□) Keyes [37] at 423 K; (●) present results at 380 K; (△) Gilmore and Comings [38] at 348 K; (◆) present data at 320 K; (◇) Keyes [37] at 323 K; (○) Westenburg and de Haas [36] at 300 K; (▽) Keyes [37] at 273 K. Note that the "Present data" means data reported for the mixtures and for nitrogen at 470 K; data for the pure components have been reported previously [2, 4, 34], and for nitrogen at 320 K the values were calculated from the results of Haran et al. [40].

Table IX. Optimum Coefficients in the Expansion $\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 + \cdots$ for the Thermal Conductivity of Mixtures of Nitrogen and Carbon Dioxide and of Pure Nitrogen[a]

T (K)	$x(N_2)$	$10^3\lambda_0$ ($W \cdot m^{-1} \cdot K^{-1}$)	$10^6\lambda_1$ ($W \cdot m^{-2} \cdot K^{-1} \cdot kg^{-1}$)	$10^9\lambda_2$ ($W \cdot m^5 \cdot K^{-1} \cdot kg^{-2}$)
320	0.381	21.38 ± 0.12	33 ± 2	112 ± 8
380	0.160	24.15 ± 0.24	34 ± 3	75 ± 6
380	0.412	26.77 ± 0.14	28 ± 3	98 ± 9
380	0.708	29.53 ± 0.09	25 ± 3	125 ± 16
430	0.392	30.96 ± 0.12	19 ± 3	130 ± 16
470	0.420	34.56 ± 0.14	20 ± 4	133 ± 22
470	1	37.48 ± 0.07	41 ± 2	100 ± 10

[a] Errors shown are 95% confidence limits.

observed; negative at low temperatures tending to positive at higher temperatures, with an S-shaped curve exhibited by our data at 380 K.

The thermal conductivity of the mixtures as a function of density is first compared with predictions from the corresponding-states method of Ely and Hanley [18–20]. The TRAPP computer program listed in Ref. 19 was used. Deviations of our experimental points from the TRAPP predictions are given in Fig. 3. The agreement is surprisingly good in view of the

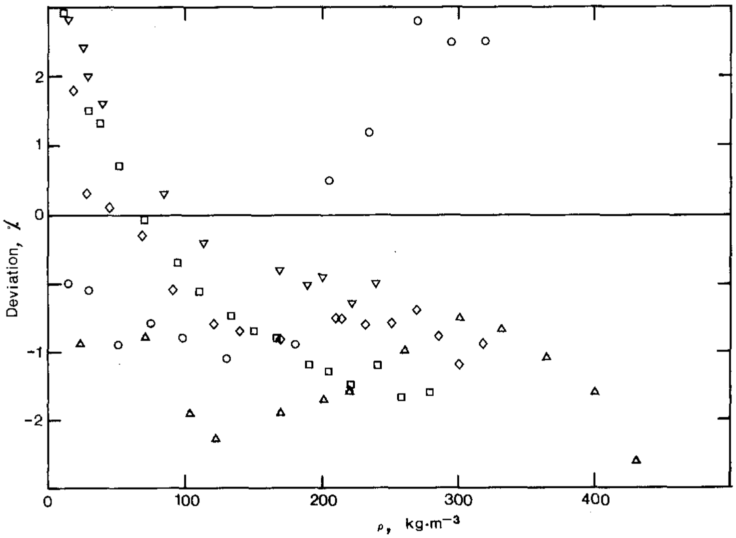

Fig. 3. Deviations of the experimental thermal conductivities from the predictions of Ely and Hanley [18]. Symbols as in the legend to Fig. 1.

Table X. Parameters Used in the Calculation of the Thermal Conductivity of Mixtures of Nitrogen and Carbon Dioxide Using the Method of Mason et al. [21]

T (K)	x_1	$10^6 B_1$ ($m^3 \cdot mol^{-1}$)	$10^6 B_2$ ($m^3 \cdot mol^{-1}$)	$10^6 B_{12}$ ($m^3 \cdot mol^{-1}$)	$A_{12}{}^a$	$B_{12}{}^a$	η_1 (μPa · s)	η_2 (μPa · s)	η_{12} (μPa · s)
320	0.381	0.938 17		−38.844	1.0931	1.1145	18.870	15.960	16.971
380	0.160	6.982 6	−70.375	−21.588	1.0935	1.1070	21.450	18.890	19.722
380	0.413	6.982 6	−70.375	−21.588	1.0935	1.1070	21.450	18.890	19.722
380	0.708	6.982 6	−70.375	−21.588	1.0935	1.1070	21.450	18.890	19.722
430	0.392	11.682	−49.324	−11.604	1.0941	1.1031	23.480	21.140	21.849
470	0.420	14.637	−35.248	−5.4173	1.0946	1.1006	25.010	22.860	23.464

[a] Subscripts: $1 = N_2$; $2 = CO_2$.

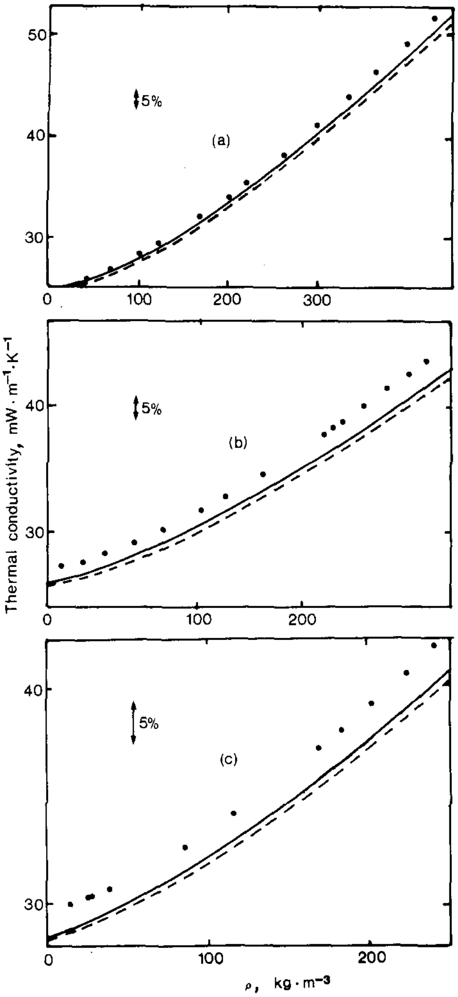

Fig. 4. Comparison of experimental data with predictions for mixtures of nitrogen and carbon dioxide at 320 K. (●) Experimental; (——) predictions from Mason et al. [21]; (– – –) predictions from Svojskij [24]. (a) $x(N_2) = 0.160$; (b) $x(N_2) = 0.412$; (c) $x(N_2) = 0.708$.

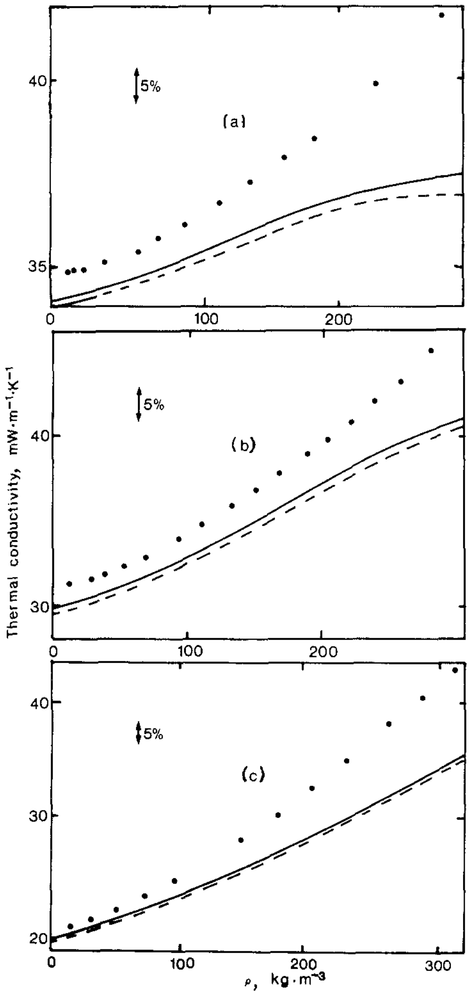

Fig. 5. Comparison of experimental data with predictions for the thermal conductivity of mixtures of nitrogen and carbon dioxide. (●) Experimental; (——) predictions from Mason et al. [21]; (– – –) predictions from Svojskij [24]. (a) 470 K, $x(N_2) = 0.420$; (b) 430 K, $x(N_2) = 0.392$; (c) 320 K, $x(N_2) = 0.381$.

approximations that are made in the method. For most of the isotherms there is a trend from negative deviations at low density to positive at high density, but the isotherm at 380 K goes against this trend.

The more theoretically based method of Mason et al. [21] is then used to predict the thermal conductivity of the mixtures. The method was used as prescribed in their paper except that the combination rule for the pseudoradial distribution function was replaced by that proposed by Kestin and Wakeham [25]. Second virial coefficients were obtained from the compilation of Dymond and Smith [30], whose data were fitted to a cubic polynomial in reciprocal temperature from which smoothed virial coefficients and their temperature derivatives were obtained. For the mixture, virial coefficients values were obtained using the method of Tsonopoulos [39] and fitted to the same cubic polynomial. $A^*_{12}(T)$ and $B^*_{12}(T)$, the ratios of collision integrals, were obtained using the correlation of Neufield et al. [32] and the Lennard-Jones parameters of Hirschfelder et al. [33]. The density dependence of the thermal conductivity of the pure components was obtained from published correlation equations [2, 4, 35] and the present correlation for nitrogen at 470 K. Low-density viscosity coefficients were obtained from the correlation of Watson [35] and the values for the mixture viscosity parameter, η_{12}, were obtained from Refs. 33 and 35. For the calculation at 320 K complex results were obtained by using Eq. (7) of Ref. 21. As forseen in this reference alternative methods need to be sought, and in this case we used a value of the hard-sphere diameter of CO_2 calculated from the viscosity of the pure gas [35] at 320 K. The parameters used in the equation are given in Table X.

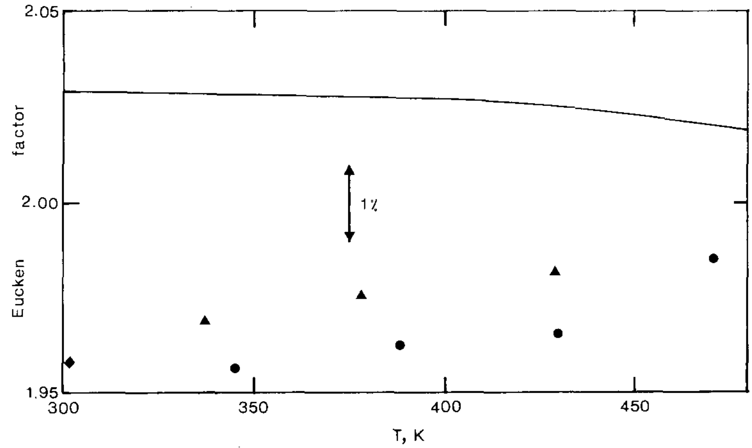

Fig. 6. Eucken factors for N_2 as a function of temperature. (●) National Engineering Laboratory (present and earlier data) [2, 4]; (▲) Imperial College [40]; (◆) Brown University [41]; (——) modified Eucken equation.

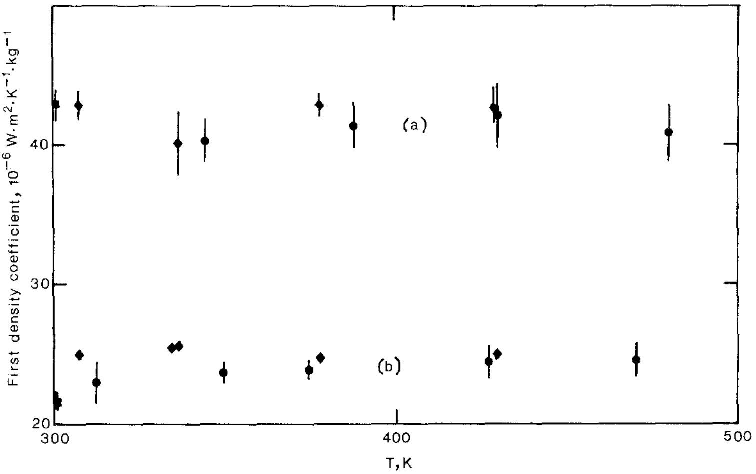

Fig. 7. First-density coefficients for (a) nitrogen and (b) argon from experimental data, shown with error bars. (●) National Engineering Laboratory (present and earlier data) [2, 4]; (◆) Imperial College [40]; (■) Brown University [41].

Obviously the system N_2/CO_2 is a severe test of the theory. Rotational relaxation has a large effect on the thermal conductivity of pure CO_2 and the Hirschfelder–Eucken equation is known not to work well in such cases. Figures 4 and 5, which give the results of the calculation, show that the disagreement increases with density. It also can be seen that it does not improve at higher temperatures. The simplified method of Svojskij gives similar, although slightly worse results. In these days of computer calculation, the advantages of a simpler cheme of equations do not seem to be sufficient to compensate even for a small loss of precision.

Finally, some remarks about the results for pure nitrogen at 470 K. The Eucken factor follows the same general trend seen for lower-temperature data, as shown in Fig. 6. The first density coefficient of the thermal conductivity (λ_1, in Table IX) is shown in Fig. 7 to be equal, within experimental error, to values at low temperatures. (A similar figure, for the lower-temperature data, is incorrectly reproduced in Ref. 4.)

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