The Thermal Conductivity of Fluid Air

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Based on available experimental data, the thermal conductivity of fluid air has been critically evaluated. A new set of recommended values is presented covering a pressure range from 1 to 1000 bar and a temperature range from 70 to 1000 K. Using the concept of residual thermal conductivity the recommended values are described by a 13-parameter equation of state in terms of temperature and density which may be applied up to a density of 900 kg/m^3. From comparisons of all data sources, the uncertainty of the recommended values was estimated to be below $\pm 4\%$. Additional experiments are needed, especially in the subcritical region of liquid air.

Key words: air; fluid region; interpolating equation; recommended values; thermal conductivity.

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1. Introduction

Air is one of the technologically most important substances. Reliable values of its thermophysical properties are therefore very often needed.

There exists a vast literature on the thermal and caloric properties of air. Based on a collection of these data, Baehr and Schwier[1] established a set of equations of state. However, Baehr and Schwier did not treat the transport properties of air, which had been measured only in a very limited range prior to 1961. The first compilation of thermal conductivity data in the fluid region of air was given in the books of Vassermann.[2,3] Touloukian[4] restricted his compilation to the thermal conductivity at atmospheric pressure. In 1975, Vargaftik[5] published a data set covering a broad range of fluid states. Unfortunately this set contained inconsistencies because, in some cases, two different thermal conductivity values were given for the same point of state. These ambiguities were eliminated in a revised version which was published in 1978.[6] However, after the first appearance of Vargaftik's work in 1971 many new experiments were published, which were not considered in the revised edition.

Recent experiments on the thermal conductivity of air give rise to a reexamination of the available data. As a result of this analysis, a new set of recommended values has been compiled which was used to establish an equation of state for the thermal conductivity of fluid air. The new data set is consistent with thermal and caloric properties with regard to the phase equilibrium curve. Its accuracy has been assessed by comparisons with all data sources.

2. Thermodynamic Key Values

Air is a mixture and not a pure fluid. Hence its vapor pressure curve consists of a bubble and a dew line (Fig. 1). In the critical region, one has to distinguish between a point of maximum pressure $p_{\max}$ and a point of maximum temperature $T_{\max}$. The point $p_{\max}$ separates the bubble line from the dew line, whereas the point $T_{\max}$ is referred to as the critical point. Its coordinates were taken from the book of Baehr and Schwier[1]

$$p_c = 37.663 \text{ bar},$$
$$T_c = 132.52 \text{ K},$$
$$\rho_c = 313 \text{ kg/m}^3. \tag{1}$$

The dew and bubble points were also calculated from the correlations established by Baehr and Schwier. The equation of the dew line reads

$$\log p_R = A_1 + A_2/T_R + A_3(1 - \sqrt{1 - T_R})e^{A_4(1 - 1/T_R)}, \tag{2}$$

with the coefficients

$$A_1 = 2.532\,93, \quad A_2 = -2.539\,01,$$
$$A_3 = 0.006\,09, \quad A_4 = 271.6.$$

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A similar relationship holds for the bubble line:

$$\log p_R = B_1 + B_2/T_R + 10^{-3} \times (3 + B_3\sqrt{B_4 + 1/T_R})\, e^{B_5(B_6 + 1/T_R)}, \quad (3)$$

with

$$B_1 = 2.2997, \quad B_2 = -2.301\,16,$$
$$B_3 = 75.0893, \quad B_4 = -1.000\,53,$$
$$B_5 = -41.503, \quad B_6 = -1.000\,755.$$

In both equations pressure and temperature are expressed in reduced form, $p_R = p/p_c$ and $T_R = T/T_c$. There is good agreement between these data and the corresponding values given by Vassermann.[2,3]

3. Thermal Conductivity

A total of 35 publications was found in the literature devoted to the thermal conductivity of air, but 15 of them had to be omitted from the analysis because they contain either less than three data points or because they report data only in small diagrams that cannot be evaluated with sufficient accuracy. Among the remaining papers which are relevant for an evaluation procedure,[2–22] 13 report original measurements while six references were previous data compilations. Naturally, these were not used for the generation of the new set of recommended values but served to estimate its tolerances by comparing it with them.

The distribution of the experimental points over the p,T plane is shown in Fig. 1. It should be noted that no data exist in the subcritical region, with the exception of gaseous air at atmospheric pressure. Most of these data lie in the pressure range from 100 to 500 bar and in the temperature range from 200 to 470 K. The only experiments beyond these limits were carried out by Tarzimanov,[18] up to 1000 bar and 1200 K. Except for Carmichael and Sage,[13] who used a spherical cell apparatus, all other investigators preferred either coaxial cylinder or hot wire devices under steady-state conditions. The transient hot wire method, which is considered to be very reliable, was applied to air only by Fleeter, Kestin, and Wakeham[19] and by Scott *et al.*[20]

To evaluate the experimental data, we employed the residual concept which, despite its obvious drawbacks, is still an appropriate method to represent transport coefficients over a wide range of fluid states.[23,24] The concept considers the thermal conductivity at a given temperature and density as the sum of a dilute gas contribution and a residual or excess part according to

$$\lambda(\rho,T) = \lambda_0(T) + \Delta\lambda(\rho). \quad (4)$$

The dilute gas contribution depends only on the temperature, whereas the residual part is assumed to be only a function of density. In the case of air we found this concept to be applicable up to three times the critical density. The density data were obtained from the equations of Baehr and Schwier[1] and from Vassermann[3] in the range 714 kg/m^3 $< \rho <$ 925 kg/m^3.

3.1. Dilute Gas Thermal Conductivity

The thermal conductivity $\lambda_0(T)$ of dilute air at atmospheric pressure has been investigated quite often. To generate the recommended values we selected the data sets of Tsederberg,[16] Tarzimanov,[18] and Scott *et al.*[20] Among several functional expressions that were tested to represent the experimental data, a polynomial, proposed by Hanley[25,26] to correlate gas transport coefficients from kinetic theory, turned out to give the most accurate fit. In terms of reduced quantities according to $\lambda_{0R} = \lambda_0/\Lambda$ and $T_R = T/T_c$, the temperature dependence is given by

$$\lambda_{0R}(T_R) = C_1 T_R^{-1} + C_2 T_R^{-2/3} + C_3 T_R^{-1/3} + C_4 + C_5 T_R^{1/3} + C_6 T_R^{2/3} + C_7 T_R + C_8 T_R^{4/3} + C_9 T_R^{5/3}. \quad (5)$$

The coefficients of Eq. (5) were obtained by a fit to the sum of

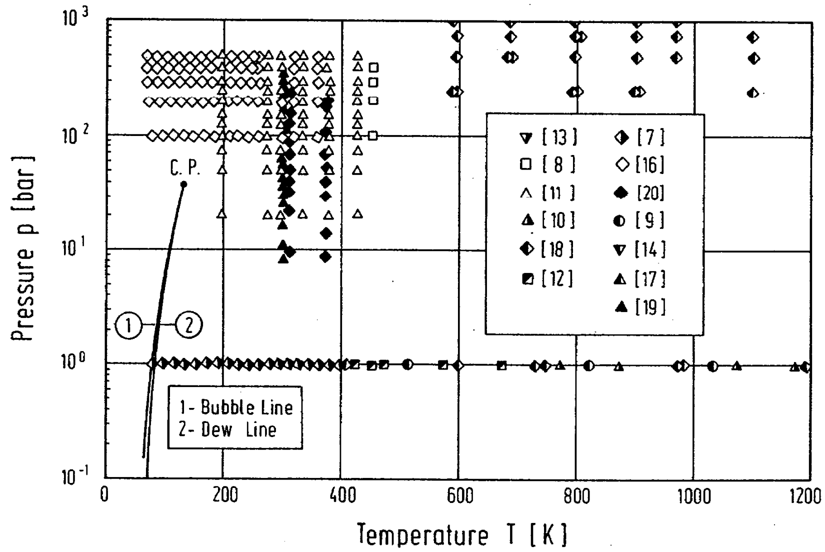

FIG. 1. Available experimental data for the thermal conductivity of air. Pressure and temperature grid.

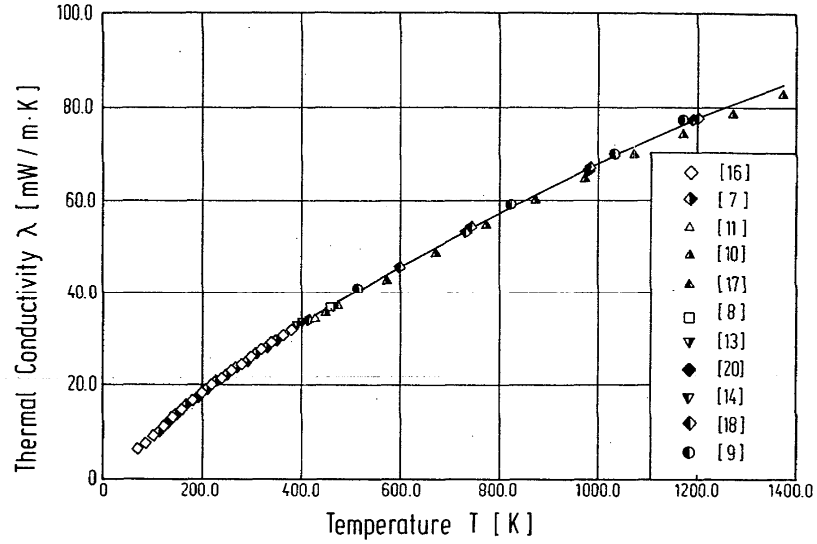

FIG. 2. Dilute gas contribution to the thermal conductivity of air as calculated from Eq. (5) and compared with experimental data.

the weighted least squares and yielded

$$C_1 = 33.972\,902\,5, \quad C_2 = -164.702\,679,$$
$$C_3 = 262.108\,546, \quad C_4 = -21.534\,695\,5,$$
$$C_5 = -443.455\,815, \quad C_6 = 607.339\,582,$$
$$C_7 = -368.790\,121, \quad C_8 = 111.296\,674,$$
$$C_9 = -13.412\,246\,5.$$

Instead of using the critical value, the thermal conductivity was expressed in reduced form by

$$\Lambda = \frac{R^{5/6} p_c^{2/3}}{(T_c M N_A^2)^{1/6}}, \qquad (6)$$

where R is the universal gas constant, N_A Avogadro's number, M the molar mass, p_c the critical pressure, and T_c the critical temperature [Eq. (1)]. This model follows from a dimensional analysis,[27] and seems to be a more appropriate corresponding states parameter than the thermal conductivity at the critical point because this is singular, whereas the parameter Λ can be determined more precisely and independently. For air, one obtains

$$\Lambda = 4.358 \cdot 10^{-3}\ \mathrm{W/m \cdot K}. \qquad (7)$$

As shown in Fig. 2, the thermal conductivity of dilute air is given by Eq. (5) in a wide temperature range from 70 to 1400 K. A comparison with the experimental data yielded a mean departure of 0.5%, with a standard deviation of ± 1.1%.

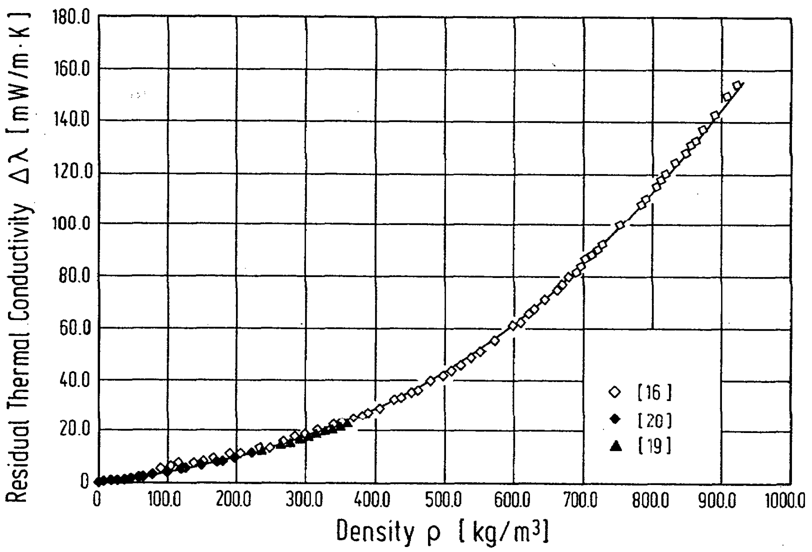

FIG. 3. Residual part of the thermal conductivity. Selected experimental data compared with Eq. (8).

Table 1. Skeleton table of the recommended data set. Thermal conductivity [mW/(m·K)] of air

T [K] \ p [bar]	1.00	10.00	20.00	30.00	40.00	50.00	60.00	80.00	100.00	150.00	200.00
70.00	6.59										
80.00	7.53	143.30	144.03	144.73	145.43	146.10	146.77	148.08	149.37	152.44	155.36
90.00	8.48	128.71	129.65	130.55	131.43	132.29	133.11	134.76	136.33	140.06	143.54
100.00	9.42	113.23	114.49	115.68	116.85	117.99	119.08	121.19	123.17	127.78	131.92
120.00	11.27	12.60	14.91	81.74	84.79	87.41	89.72	93.72	97.13	104.13	110.18
130.00	12.18	13.36	15.10	18.28	61.03	67.80	72.32	78.87	83.84	93.17	100.23
140.00	13.09	14.15	15.59	17.58	21.13	32.66	48.15	61.73	69.42	81.66	90.17
160.00	14.87	15.77	16.89	18.20	19.80	21.87	24.65	33.05	42.89	60.42	71.62
180.00	16.61	17.40	18.33	19.36	20.51	21.81	23.32	27.09	31.94	45.61	57.09
200.00	18.31	19.01	19.82	20.68	21.61	22.61	23.70	26.19	29.17	38.27	47.71
220.00	19.97	20.60	21.32	22.07	22.85	23.68	24.56	26.48	28.65	35.14	42.44
240.00	21.59	22.16	22.81	23.48	24.16	24.88	25.62	27.21	28.94	33.96	39.68
260.00	23.16	23.69	24.28	24.88	25.50	26.13	26.78	28.15	29.61	33.71	38.36
280.00	24.70	25.18	25.73	26.28	26.84	27.41	27.99	29.20	30.47	33.95	37.85
300.00	26.19	26.65	27.16	27.67	28.18	28.70	29.23	30.31	31.44	34.48	37.84
320.00	27.66	28.08	28.56	29.03	29.51	29.99	30.47	31.46	32.48	35.19	38.14
340.00	29.09	29.49	29.93	30.37	30.82	31.27	31.71	32.63	33.56	36.01	38.65
360.00	30.49	30.86	31.28	31.70	32.12	32.53	32.95	33.80	34.66	36.91	39.30
380.00	31.86	32.22	32.61	33.00	33.40	33.79	34.18	34.98	35.78	37.85	40.04
400.00	33.21	33.54	33.92	34.29	34.66	35.04	35.41	36.15	36.90	38.83	40.85
450.00	36.47	36.78	37.11	37.44	37.77	38.09	38.42	39.07	39.72	41.38	43.08
500.00	39.63	39.90	40.20	40.50	40.79	41.08	41.37	41.95	42.53	43.99	45.47
550.00	42.69	42.94	43.21	43.48	43.75	44.01	44.28	44.80	45.32	46.62	47.94
600.00	45.69	45.91	46.16	46.41	46.65	46.89	47.13	47.61	48.09	49.27	50.46
650.00	48.62	48.83	49.06	49.28	49.51	49.73	49.96	50.40	50.83	51.92	53.00
700.00	51.50	51.69	51.91	52.12	52.33	52.54	52.74	53.15	53.56	54.56	55.56
750.00	54.34	54.52	54.72	54.91	55.11	55.30	55.50	55.88	56.26	57.19	58.12
800.00	57.13	57.30	57.49	57.67	57.86	58.04	58.22	58.58	58.93	59.81	60.67
900.00	62.59	62.74	62.91	63.07	63.23	63.40	63.56	63.88	64.19	64.97	65.73
1000.00	67.85	67.98	68.13	68.28	68.43	68.57	68.72	69.01	69.29	69.99	70.68

T [K] \ p [bar]	250.00	300.00	350.00	400.00	450.00	500.00	600.00	700.00	800.00	900.00	1000.00
70.00											
80.00	158.11	160.74									
90.00	146.77	149.83	152.72	155.50	158.14	160.66					
100.00	135.75	139.29	142.59	145.72	148.70	151.50					
120.00	115.36	120.02	124.21	128.09	131.74	135.12					
130.00	106.11	111.30	115.97	120.21	124.15	127.80					
140.00	96.79	102.88	107.97	112.55	116.77	120.68					
160.00	79.95	86.76	92.59	97.70	102.17	107.04					
180.00	66.17	73.61	79.95	85.51	90.49	95.02	103.04				
200.00	56.16	63.49	69.91	75.60	80.73	85.40	93.71	100.99			
220.00	49.63	56.29	62.36	67.88	72.93	77.58	85.92	93.27	99.87	105.90	
240.00	45.63	51.44	56.94	62.09	66.89	71.38	79.54	86.81	93.39	99.41	105.00
260.00	43.31	48.31	53.19	57.88	62.34	66.58	74.40	81.47	87.93	93.88	99.40
280.00	42.04	46.36	50.67	54.89	58.98	62.92	70.31	77.11	83.38	89.19	94.62
300.00	41.45	45.21	49.02	52.82	56.54	60.17	67.10	73.57	79.61	85.25	90.55
320.00	41.31	44.62	48.01	51.42	54.81	58.15	64.61	70.72	76.50	81.94	87.09
340.00	41.46	44.41	47.45	50.53	53.61	56.68	62.68	68.45	73.95	79.18	84.15
360.00	41.83	44.48	47.23	50.02	52.84	55.66	61.23	66.65	71.87	76.87	81.67
380.00	42.35	44.76	47.25	49.80	52.39	54.99	60.16	65.25	70.19	74.97	79.57
400.00	42.97	45.18	47.47	49.81	52.19	54.59	59.41	64.18	68.85	73.40	77.82
450.00	44.85	46.68	48.56	50.50	52.48	54.48	58.54	62.63	66.69	70.70	74.65
500.00	46.99	48.55	50.16	51.81	53.50	55.21	58.69	62.22	65.77	69.31	72.83
550.00	49.28	50.65	52.06	53.49	54.96	56.44	59.48	62.58	65.70	68.84	71.98
600.00	51.66	52.88	54.13	55.40	56.70	58.01	60.70	63.45	66.23	69.04	71.85
650.00	54.09	55.20	56.32	57.46	58.63	59.81	62.22	64.68	67.18	69.71	72.25
700.00	56.56	57.57	58.59	59.63	60.69	61.76	63.94	66.17	68.43	70.73	73.05
750.00	59.04	59.97	60.92	61.87	62.83	63.81	65.81	67.84	69.91	72.01	74.14
800.00	61.53	62.40	63.27	64.15	65.04	65.94	67.78	69.65	71.56	73.49	75.45
900.00	66.49	67.25	68.01	68.78	69.55	70.34	71.92	73.54	75.18	76.84	78.53
1000.00	71.36	72.04	72.72	73.40	74.08	74.77	76.17	77.59	79.03	80.49	81.97

3.2. Residual Thermal Conductivity

The pressure dependence of the thermal conductivity of air has not been investigated as much as the thermal conductivity of the dilute gas region. As the distribution of experimental data in Fig. 1 reveals, in certain pressure and temperature ranges data do not exist. However, in many cases the residual concept offers a useful tool to obtain the missing data by extrapolation, provided the concept can be applied and no splitting of the isotherms occurs at higher densities. This can easily be checked when the residual part of all data points is plotted versus density. In cases where a large scatter is observed, especially at high densities, one may deduce that the residual part is not a function of density alone. In such cases the concept is not applicable in its simple form but requires additional temperature functions.

After careful analysis of the experimental data, the measurements of Tsederberg and Ivanova,[16] Fleeter, Kestin, and Wakeham,[19] and Scott *et al.*[20] were selected. For the representation of the residual thermal conductivity of these data, a polynomial of 4th degree turned out to be sufficient,

$$\Delta\lambda_R = D_1\rho_R + D_2\rho_R^2 + D_3\rho_R^3 + D_4\rho_R^4, \qquad (8)$$

with the coefficients listed below:

$$D_1 = 3.120\,131\,25, \quad D_2 = -2.307\,624\,00\cdot 10^1,$$

$$D_3 = 1.650\,494\,30, \quad D_4 = -1.911\,481\,75\cdot 10^{-1}.$$

Again, the residual thermal conductivity is reduced by the factor Λ from Eq. (6). We have $\Delta\lambda_R = \Delta\lambda/\Lambda$, whereas the density was reduced by its critical value $\rho_R = \rho/\rho_c$. Figure 3 presents the residual thermal conductivity according to Eq. (8) and compares calculated values with the selected experimental data.

By means of Eqs. (5) and (8) representing the new set of recommended values, we calculated a skeleton table for the thermal conductivity of air for given pressures and temperatures (Table 1). The spacing of temperatures and pressures was chosen in different steps in order to permit a safe interpolation of the values. However, in process design systems, the use of Eqs. (5) and (8) is recommended for easier computation.

In order to give an illustrative representation and a clear view of the influence of pressure and temperature on the thermal conductivity, we plotted a perspective view of the surface (Fig. 4).

The fact that air is a mixture requires that the shape of the surface differs from that of a pure substance only in the nature of the bubble line and the dew line properties. The difference is not visible in Fig. 4. As a typical feature a predominant influence of temperature on thermal conductivity is observed, showing two main characteristics. At low temperatures one notes a steep decrease of thermal conductivity with increasing temperature, as is typical for liquids. As can be seen from Fig. 4, this effect is still noteworthy at pressures far above the critical point, where a distinction between the liquid and gaseous phase cannot be made. Thus in this region, the thermal conductivity exhibits a liquidlike behavior. At higher temperatures thermal conductivity passes through a minimum along the isobars and then increases. Its behavior is then comparable to that of a gas. The liquid- and the gaslike behaviors reflect the different mechanisms of microscopic energy transfer. The boundary between the liquid- and the gaslike behavior is the locus of all minima of the isobars.

4. Estimation of Uncertainty

To assess the uncertainty of the recommended values, all the experimental data and also the data from previous compilations were compared with the recommended values. The results of these calculations are summarized in detail in Table 2. The mean departures and their standard deviations suggest moderate discrepancies among the results of the different authors. The data of Stolyarov, Ipatiev, and Teodorovich,[8] and Geier and Schäfer[10] seem to be systematically too low; this holds also for tables given in the Landolt–Börnstein series.[22] The earlier compilation of Tsederberg[21] and also the

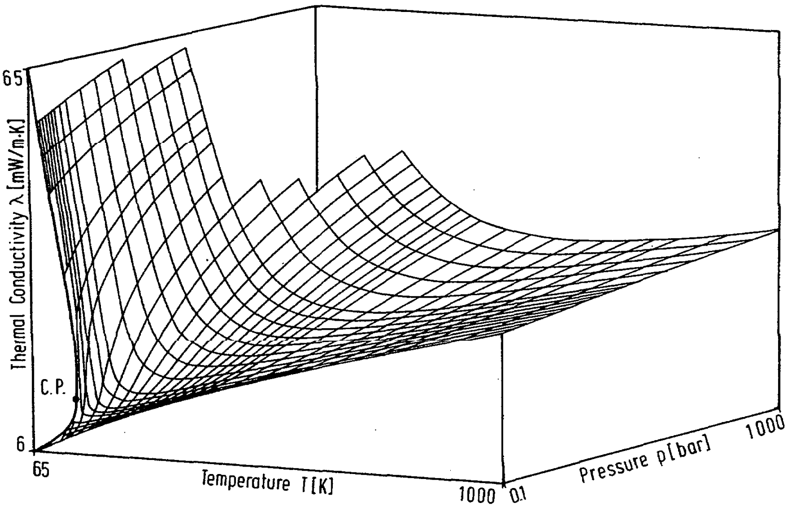

FIG. 4. Thermal conductivity surface of fluid air vs pressure and temperature.

Table 2. Comparison of the recommended data set with other sources and compilations

Author/ Year	Temperature Range K	Pressure Range bar	Method	Mean departures ± Stand. dev.	Number of Points	Ref.
Taylor 1946	80-380	1	Hot wire	1.7±0.9 %	18	7
Stolyarov 1950	293-435	1-500	Coaxial cylinder	-5.2±3.9 %	35	8
Vines 1960	514-1173	1	Coaxial cylinder	0.8±0.2 %	8	9
Geier 1961	273-1373	1	Hot wire	-2.1±0.5 %	17	10
Golubev 1963	196-426	1-500	Coaxial cylinder	1.4±3.6 %	110	11
Senftleben 1964	273-673	1	Hot wire	1.4±3.6 %	12	12
Carmichael 1966	244-377	1	Spherical cell	0.7±0.5 %	5	13
Ghambir 1967	308-363	1	Hot wire	0.2±2.2 %	3	14
Tsederberg 1971	70-380	1 98-490	Hot wire	-0.9±1.0 % 0.2±2.0 %	19 88	16
Irving 1973	273-448	1	Hot wire	-1.9±0.2 %	8	17
Tarzimanov 1977	406-1199	1-500	Hot wire	+1.3±1.3 %	30	18
Fleeter 1980	300	1-36	Hot wire	-1±0.5 %	13	19
Scott 1981	300-400 312-373	1 9-928	Hot wire	0.2±0.1 %	6	20
Vassermann 1965/68	75-160	1-500	Compilation	0.7±2.4 %	106	2,3
Tsederberg 1965	273-1273	1-200	Compilation	3.5±1.3 %	68	21
Landolt-Börnstein 1968	273-473	1-400	Compilation	-2.9±2.9 %	51	22
Carroll 1968	160-800	1-1013	Compilation	-0.7±3.0 %	302	15
Touloukian 1970	50-1500	1	Compilation	-0.8±0.7 %	28	4
Vargaftik 1978	85-800	1-1000	Compilation	1.2±1.6 %	183	6

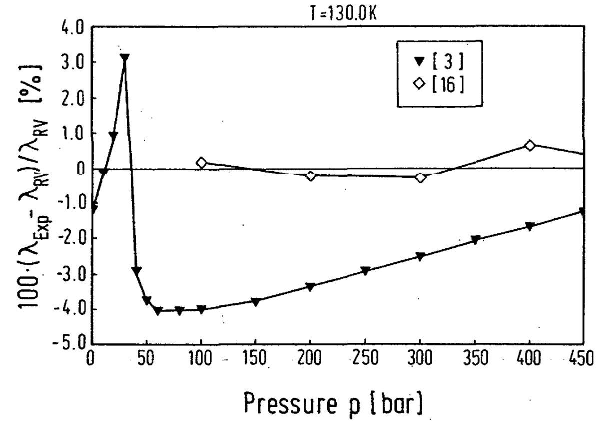

FIG. 5. Comparison of data from other literature sources with values calculated from the equation of state proposed in this work at $T = 130$ K.

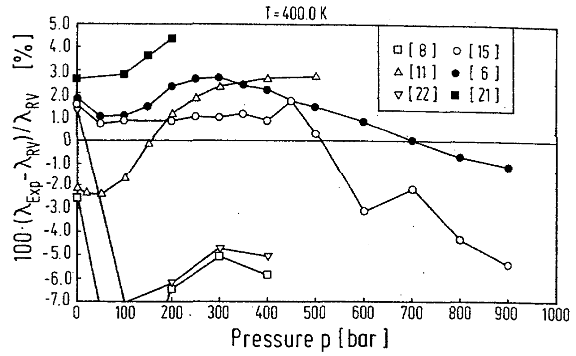

FIG. 7. Comparison of data from other literature sources with values calculated from the equation of state proposed in this work at $T = 400$ K.

recent set of Vargaftik *et al.*[6] seem to be too high.

A more detailed assessment, however, can be read from departure plots along selected isotherms, as given in Figs. 5–8 for the widely spaced isotherms 130, 300, 400, and 800 K. In these diagrams, the deviation of each literature data point denoted by $\lambda_{\rm Exp}$ is defined according to

$$100(\lambda_{\rm Exp} - \lambda_{\rm RV})/\lambda_{\rm RV}\,\%$$

with $\lambda_{\rm RV}$ being the recommended value. The maximum deviation among different sources at temperatures of 300 and 400 K is as high as 12%. It reduces considerably, if those data were omitted that appear systematically too low; then the maximum uncertainty would be estimated to be at most ± 4%, and ± 2.5% at higher temperatures above 400 K. These uncertainties clearly exceed the values claimed by the authors themselves. In order to reduce these uncertainties, further experiments are necessary at subcritical pressures and temperatures, especially in the liquid region.

Likewise, it is highly desirable to explore by new experiments the thermal conductivity of air in the critical region and to examine a possible critical enhancement. As can be seen from Fig. 3, present data do not support a divergence of the thermal conductivity of air in the critical region. However, it must be expected that the overlapping enhancements of the thermal conductivities of the most important constituents of air, nitrogen, and oxygen will result in an enhancement in the thermal conductivity of air, too. It therefore has to be assumed that values calculated from Eqs. (5) and (8) will be considerably too small at densities from 200 to 450 kg/m^3, pressures from 30 to 80 bar, and temperatures from 120 to 160 K.

During preparation of this paper, the authors were informed about a similar evaluation carried out by Kadoya, Matsunaga, and Nagashima.[28] A comparison[29] to the results reported here revealed almost perfect agreement in the selection of the most reliable data sets. To represent them, Kadoya *et al.* adopted an equation of state, with 12 adjustable parameters, which agrees with Eqs. (5) and (8) proposed here in seven structural terms. Values that were calculated from both equations in the range of available experimental data agree well within the tolerances ascribed to the recommended data set.

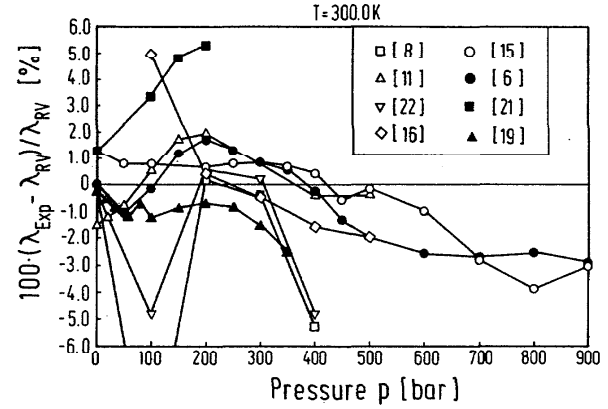

FIG. 6. Comparison of data from other literature sources with values calculated from the equation of state proposed in this work at $T = 300$ K.

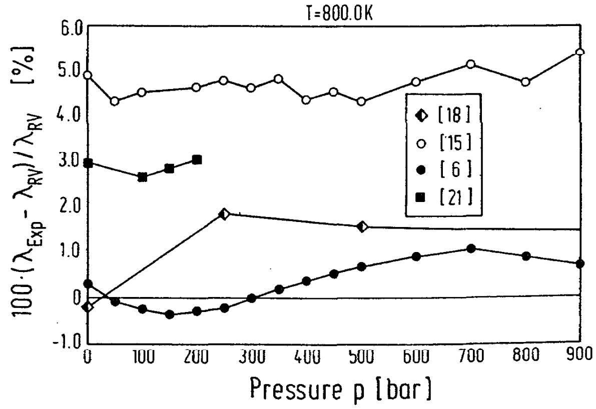

FIG. 8. Comparison of data from other literature sources with values calculated from the equation of state proposed in this work at $T = 800$ K.

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