

Measurements of the Thermal Conductivity of Chlorodifluoromethane (HCFC-22) in the Temperature Range from 300 K to 515 K and at Pressures up to 55 MPa¹

Bernard Le Neindre,^{*†} Yves Garrabos,[‡] Aidar Sabirzianov,[§] and Farid Goumerov[§]

Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, CNRS, Institut Galilée, Université Paris Nord, Av. J. B. Clément, 93430 Villetaneuse, France, Institut de Chimie de la Matière Condensée de Bordeaux, CNRS-UPR 9048, Université de Bordeaux I, 87, Avenue du Dr Albert Schweitzer, F-33608 Pessac Cedex, France, and Université d'Etat de Technologie de Kazan, 68 rue K. Marx, 420015 Kazan, Russia

We report measurements of the thermal conductivity of chlorodifluoromethane (HCFC-22) with a coaxial cylinder cell operating in the steady state. The measurements of the thermal conductivity of HCFC-22 were performed along several quasi-isotherms between 300 K and 515 K, in the gas phase, the liquid phase, and the critical region. The pressure range covered varies from 0.1 MPa to 55 MPa. On the basis of the fitting of experimental data, a background equation is provided to calculate the thermal conductivity outside the critical region as a function of temperature and density. A careful analysis of the various sources of errors leads to an estimated uncertainty of the thermal conductivity, of the order of ±1.5%.

Introduction

For energy conversion processes and application in the field of chemical engineering, there was a great interest in the knowledge of thermophysical properties of chlorinated refrigerants, but most of them were restrained by the Montreal Protocol. However HCFC-22 (chlorodifluoromethane) which belongs to the series of hydrochlorofluorocarbons (HCFCs) will keep its technical importance, at least in the near future due to its lower depletion potential than those of the other fully halogenated CFCs. It is used as a temporary substitute for these compounds. On the other hand, the thermophysical properties of HCFC-22 were more widely studied than those of other HCFCs, and the thermodynamic and transport properties of this fluid are considered to become useful standards to evaluate the thermophysical properties of other refrigerants. Nevertheless the transport properties and particularly the thermal conductivity do not cover the full range of P – V – T data. Moreover, previous measurements of the thermal conductivity of HCFC-22 have revealed significant discrepancies from each other which are much larger than the respective accuracy claimed by the authors.

In a series of measurements, we have investigated the influence of temperature and pressure on the thermal conductivity of HCFC-22. The measurements were performed in order to make an analysis of the data based on the residual concept. The thermal conductivity $\lambda(T,\rho)$ as a function of temperature T and density ρ may be represented as the sum of three contributions

$$\lambda(T,\rho) = \lambda_0(T) + \delta\lambda(T,\rho) + \Delta\lambda(T,\rho) \quad (1)$$

^{*} To whom correspondence should be addressed. E-mail: leneindr@limhp.univ-paris13.fr.

[†] Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, CNRS, Institut Galilée, Université Paris Nord.

[‡] Institut de Chimie de la Matière Condensée de Bordeaux, CNRS-UPR 9048, Université de Bordeaux I.

[§] Université d'Etat de Technologie de Kazan.

The dilute gas contribution $\lambda_0(T)$ was obtained by performing measurements on the gas phase at atmospheric pressure as a function of temperature. The background term

$$\lambda_B(T,\rho) = \lambda_0 + \delta\lambda(T,\rho) \quad (2)$$

was obtained by making measurements along quasi-isotherms as a function of pressure in the liquid phase and in the gas phase far away from the critical region. The remaining contribution, $\Delta\lambda(T,\rho)$, represents the enhancement of the thermal conductivity due to critical fluctuations, in the supercritical region or in the subcritical region along the saturation curve, and was obtained by performing measurements in these two regions. In this paper we present only experimental data in the liquid phase and in the gas phase far away from the critical point in order to determine the so-called thermal conductivity background. Our measurements in the critical region and in the gas phase below the critical point will be reported later. The density was calculated with a new equation of state reported by Wagner et al.¹ where the critical parameters together with the estimated uncertainties are given as follows:

$$T_C = 369.28 \pm 0.2 \text{ K}$$

$$P_C = 4.9885 \pm 0.02 \text{ MPa}$$

$$\rho_C = 520 \pm 5 \text{ kg m}^{-3}$$

The sample was provided by ELF-ATOCHÉM, and its purity was estimated to be better than 99.8% by the manufacturer's analysis.

Experimental Apparatus

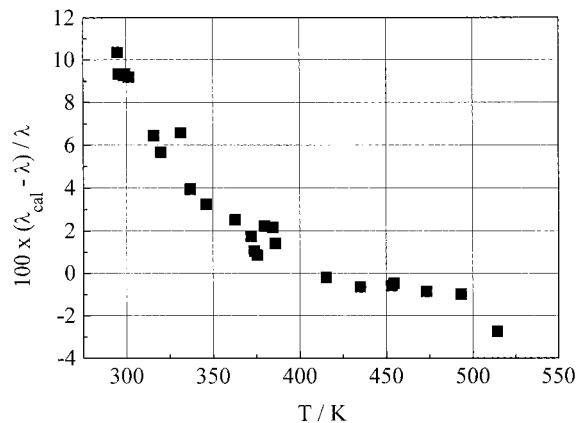
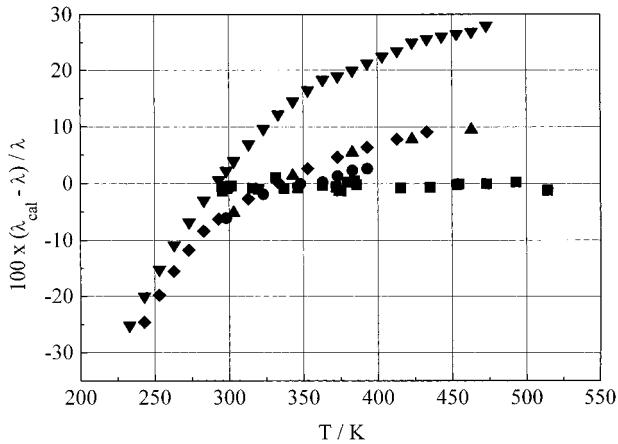
The thermal conductivity of HCFC-22 was measured in vertical coaxial cylinders, operating in the steady-state mode. The same device was already used in the measurement of the thermal conductivity of 1-chloro-1,1-difluoro-

Table 1. The Thermal Conductivity of HCFC-22 at Atmospheric Pressure

T/K	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	T/K	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	T/K	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
295.04	9.77	337.13	13.06	385.96	16.73
295.55	9.89	346.23	13.75	415.34	19.09
298.49	10.07	362.85	14.97	435.03	20.59
299.26	10.11	372.13	15.72	453.17	21.88
301.39	10.25	373.90	15.95	454.62	21.96
315.86	11.41	375.45	16.09	473.14	23.38
319.95	11.75	379.63	16.16	493.17	24.85
331.50	12.38	384.55	16.51	514.31	26.84

Table 2. Coefficients of the Ideal Gas Part of the Isobaric Heat Capacity of HCFC-22

i	a_i	θ_i
1	$0.300\ 671\ 581 \times 10^1$	
2	$0.393\ 214\ 630 \times 10^1$	$0.482\ 421\ 333 \times 10^1$
3	$0.110\ 074\ 668 \times 10^1$	$0.113\ 929\ 640 \times 10^2$
4	$0.187\ 129\ 085 \times 10^1$	$0.282\ 862\ 148 \times 10^1$
5	$0.222\ 706\ 659 \times 10^1$	$0.155\ 580\ 861 \times 10^1$

**Figure 1.** Relative deviations of theoretical values calculated by eqs 4 and 6 from our experimental data at atmospheric pressure with $\sigma = 0.4652 \text{ nm}$ and $\epsilon/k = 285.7 \text{ K}$.**Figure 2.** Relative deviations of calculated values by eq 3 from experimental data at atmospheric pressure: ■, this work; ●, Makita et al.;¹⁰ ▲, Hammerschmidt;¹¹ ▼, Watanabe et al.;⁹ ◆, Vargaftik et al.⁸

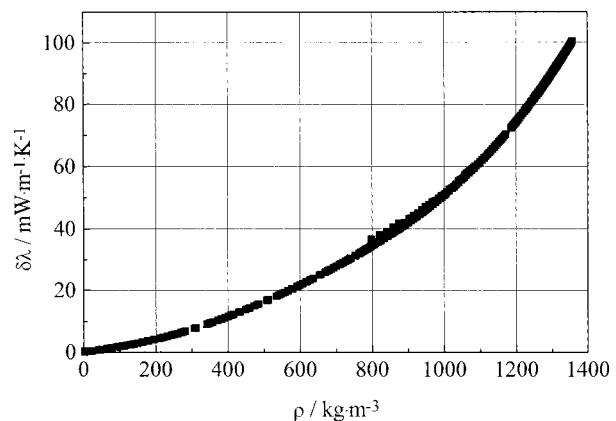
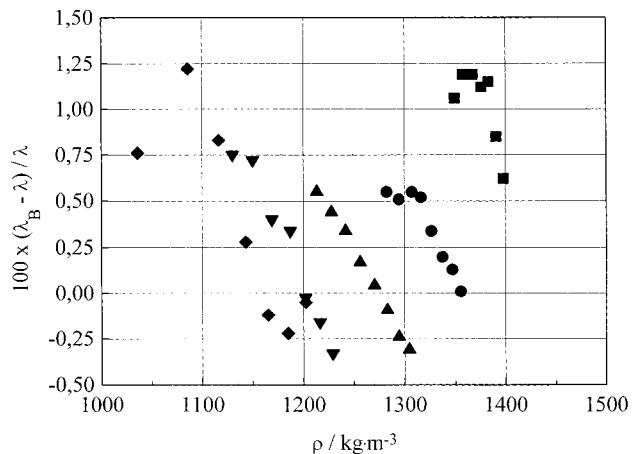
ethane (HCFC-142b),² pentafluoroethane (HFC-125),³ and 1,1,1,2-tetrafluoroethane (HFC-134a).⁴ A detailed description of the cell, the method of measurement, and corrections are available.⁵

Dilute-Gas Thermal Conductivity

The results of the measurement of the thermal conductivity at atmospheric pressure are listed as a function of

Table 3. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 299.4 \text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
299.02	1.065	1187.7	82.79
299.42	1.492	1188.8	82.33
299.42	1.982	1191.8	82.50
299.41	2.50	1194.9	82.84
299.90	3.00	1195.8	83.33
299.40	3.50	1200.7	83.69
299.40	4.00	1203.4	84.03
299.40	4.50	1206.2	84.39
299.39	5.00	1208.9	84.74
299.39	6.00	1214.1	85.27
299.38	7.00	1219.1	85.81
299.37	8.00	1223.9	86.54
299.86	8.50	1224.6	87.07
299.37	9.00	1228.6	87.10
299.36	9.30	1230.0	87.85
299.35	10.00	1233.1	88.23
299.35	11.00	1237.4	88.81
299.34	12.00	1241.7	89.40
299.33	12.00	1241.7	89.99
299.33	14.00	1249.8	90.38
299.33	15.00	1253.6	90.99
299.32	16.00	1257.4	91.40
299.31	17.00	1261.2	92.23
299.30	18.00	1264.8	92.86
299.30	19.00	1268.3	93.50
299.29	19.89	1271.4	93.93

**Figure 3.** Excess of thermal conductivity of HCFC-22.**Figure 4.** Relative deviations of calculated values by the background equation from the experimental data of Assael et al.¹² ■, $T = 252 \text{ K}$; ●, $T = 273 \text{ K}$; ▲, $T = 293 \text{ K}$; ▼, $T = 313 \text{ K}$; ◆, $T = 333 \text{ K}$.

temperature in Table 1. The experimental data were fitted to a linear equation

$$\lambda_0 = -12.9 + 0.07666 T \quad (3)$$

Table 4. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 300.8\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
300.91	2.00	1185.8	84.13
300.90	3.00	1191.9	84.78
300.90	4.00	1197.8	85.44
300.89	5.00	1203.4	86.11
300.89	6.00	1208.7	86.79
300.89	7.00	1213.8	87.48
300.88	8.00	1218.7	88.19
300.88	9.00	1223.5	88.90
300.88	10.00	1228.0	89.63
300.87	11.00	1232.5	89.99
300.87	12.00	1236.8	90.74
300.86	13.00	1241.0	91.49
300.86	14.00	1245.1	92.26
300.86	15.00	1249.0	93.04
300.86	16.00	1252.8	93.44
300.85	17.00	1256.7	94.24
300.85	18.00	1260.2	94.64
300.84	19.00	1263.9	95.47
300.84	20.00	1267.4	95.88
300.84	21.00	1270.8	96.30
300.83	22.00	1274.1	97.15
300.83	23.00	1277.4	97.58
300.83	24.00	1280.6	98.02
300.83	25.00	1283.8	98.90
300.83	26.00	1286.9	99.34
300.82	27.00	1289.9	99.80
300.82	28.00	1292.8	100.25
300.82	29.00	1295.7	100.71
300.82	30.00	1298.6	101.17
300.82	31.00	1301.4	101.64
300.81	32.00	1304.1	102.11
300.81	33.00	1306.8	102.58
300.81	34.00	1309.5	103.06
300.81	35.00	1312.1	103.55
300.81	36.00	1314.8	104.04
300.80	37.00	1317.4	104.53
300.80	38.00	1319.9	105.03
300.80	39.00	1322.3	105.53
300.80	40.00	1324.8	106.04
300.80	41.00	1327.2	106.55
300.79	42.00	1329.5	107.07
300.79	43.00	1331.9	107.59
300.79	44.00	1334.2	107.59
300.79	45.00	1336.5	108.12
300.79	46.00	1338.7	108.65
300.78	47.00	1340.9	109.19
300.78	48.00	1343.1	109.73
300.78	49.00	1345.3	110.28
300.78	50.00	1347.4	110.28
300.78	51.00	1349.6	110.83
300.78	52.00	1351.7	111.39
300.78	53.00	1353.7	111.39
300.77	54.00	1355.8	111.95
300.77	55.00	1357.8	112.52

The temperature dependence of the thermal conductivity of the dilute gas can be represented by an expression derived from the kinetic theory of gases. The thermal conductivity is related to the reduced effective collision cross section Ω_λ^* , which contains all the contributions from translational, rotational, vibrational, and electronic degrees of freedom. As there is a lack of reliable experimental data on vibrational collision number, we used for the calculation of the thermal conductivity in the zero density the practical engineering form⁶

$$\lambda_0(T) = \frac{0.177568(T/M)^{0.5} C_P^0 / R}{\sigma^2 \Omega_\lambda^*} \quad (4)$$

where C_P^0 is the ideal isobaric heat capacity. The scaling factors σ and ϵ/k , which correspond to the Lennard-Jones 12-6 potential parameters, were previously determined by

Table 5. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 302.5\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
302.57	19.84	1261.9	94.95
302.57	21.00	1265.9	95.39
302.56	22.00	1269.4	95.83
302.56	23.00	1272.7	96.28
302.56	24.00	1276.0	96.74
302.55	25.00	1279.1	97.42
302.55	24.82	1278.6	97.66
302.55	26.00	1282.	98.12
302.54	27.00	1285.4	98.59
302.54	28.00	1288.3	98.83
302.54	29.00	1291.4	99.31
302.53	30.00	1294.3	99.79
302.53	32.00	1299.9	100.78
302.52	33.00	1302.6	101.02
302.51	34.00	1305.4	101.77
302.51	35.00	1308.1	102.28
302.50	36.00	1310.7	102.79
302.50	37.00	1313.3	103.31
302.50	38.00	1315.8	103.57
302.50	39.00	1318.4	104.10
302.49	40.00	1320.9	104.62
302.49	41.00	1323.3	105.16
302.49	42.00	1325.7	105.43
302.49	43.00	1328.1	105.70
302.48	44.00	1330.4	106.24
302.47	45.00	1332.7	106.79
302.48	45.70	1334.3	107.08

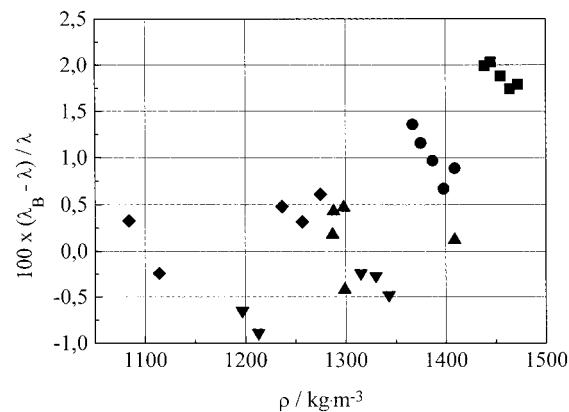


Figure 5. Relative deviations of calculated values by the background equation from the experimental data of Kim et al.¹³ ■, $T = 233\text{ K}$; ●, $T = 248\text{ K}$; ▲, $T = 273\text{ K}$; ▼, $T = 298\text{ K}$; ♦, $T = 323\text{ K}$.

Mayinger and Nabizadeh⁷ from a regression analysis of the viscosity data of HCFC-22 at atmospheric pressure ($\epsilon/k = 285.70\text{ K}$ and $\sigma = 0.4652\text{ nm}$). The ideal specific heat at constant pressure was calculated with the equation proposed by Wagner et al.¹

$$C_P^0 = R(1 + a_1 + \tau^2 [\sum_{i=2}^5 a_i(\theta_i)^2 e^{-\theta_i \tau} [1 - e^{-\theta_i \tau}]^{-2}]) \quad (5)$$

where $\tau = T_C/T$ and $R = 0.096\ 155\ 96\text{ kJ kg}^{-1}\text{ K}^{-1}$. The values of coefficients a_i and θ_i are given in Table 2.

The reduced effective thermal conductivity collision cross section Ω_λ^* was estimated using a functional expansion

$$\Omega_\lambda^* = \sum_{j=1}^3 A_j (1/T)^j \quad (6)$$

where $A_1 = 0.444\ 358$, $A_2 = 0.327\ 867$, and $A_3 = 0.193\ 683\ 5$, as a function of the reduced temperature

$$T^* = kT/\epsilon \quad (7)$$

Table 6. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 309.4\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
309.52	2.00	1149.5	78.94
309.51	3.00	1156.9	79.87
309.50	4.00	1163.9	80.81
309.49	5.00	1170.4	81.78
309.48	6.00	1176.7	82.61
309.47	7.00	1182.7	83.46
309.46	8.00	1188.3	84.14
309.45	9.00	1193.9	84.84
309.44	10.00	1199.1	85.73
309.43	11.00	1204.1	86.27
309.43	12.00	1208.9	87.00
309.42	13.00	1213.7	87.75
309.41	14.00	1218.3	88.50
309.40	15.00	1222.7	89.27
309.40	16.00	1227.0	90.06
309.39	17.00	1231.1	90.86
309.38	18.00	1235.3	91.67
309.38	19.00	1239.2	91.87
309.37	20.00	1243.0	92.50
309.36	21.00	1246.7	93.13
309.36	22.00	1250.5	93.76
309.35	23.00	1253.9	94.41
309.35	24.00	1257.5	95.07
309.34	25.00	1260.9	95.73
309.34	26.00	1264.3	96.18
309.33	27.00	1267.6	96.86
309.33	28.00	1270.7	97.32
309.32	29.00	1273.9	98.02
309.32	30.00	1276.9	98.49
309.31	31.00	1280.0	98.96
309.31	32.00	1282.9	99.44
309.31	33.00	1285.9	99.92
309.30	34.00	1288.8	100.41
309.29	35.00	1291.6	100.85
309.29	36.00	1294.3	101.40
309.29	37.00	1297.1	101.91
309.29	38.00	1299.8	102.41
309.28	39.00	1302.4	102.93
309.28	40.00	1305.0	103.44
309.27	41.00	1307.6	103.97
309.27	42.00	1310.1	104.23
309.27	43.00	1312.7	104.76
309.27	44.00	1315.0	105.03
309.26	45.00	1317.5	105.57
309.26	46.00	1319.9	105.84
309.26	47.00	1322.2	106.11
309.26	48.00	1324.5	106.39
309.25	49.00	1326.8	106.66
309.25	50.00	1329.1	107.22

Figure 1 shows a deviation plot between theoretical values calculated by eq 4 and our experimental data. The deviation was found to be less than $\pm 2\%$ from 375 K to 550 K. The agreement with the theory is very satisfactory. In fact, the theory is only valid for reduced temperatures $T^* > 1$, while 375 K corresponds to the reduced temperature $T^* = 1.3$. The comparison with other sources of data shows that the specific heat is known with an accuracy of $\pm 1\%$ and that the agreement can be improved at high temperatures if the potential parameters are obtained by a simultaneous fit of viscosity and thermal conductivity data.

Figure 2 shows the relative deviations at atmospheric pressure between the tabulated values of Vargaftik,⁸ the data reported in JAR Tables,⁹ and a set of experimental data measured by Makita et al.¹⁰ and Hammerschmidt.¹¹ Over most of the experimental range, the deviations are larger than the experimental uncertainty. However, there is always a small temperature range where the agreement is good. This temperature range is different for each author.

Table 7. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 317.7\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
317.74	2.00	1111.2	74.66
317.73	3.00	1120.4	75.68
317.72	4.00	1128.8	76.65
317.72	5.00	1136.7	77.73
317.71	6.00	1144.1	78.27
317.71	7.00	1151.0	79.09
317.70	8.00	1157.6	79.92
317.70	9.00	1164.0	81.07
317.69	10.00	1169.9	81.94
317.68	11.00	1175.7	82.88
317.68	12.00	1181.1	83.42
317.67	13.00	1186.5	84.39
317.67	14.00	1191.6	85.02
317.66	15.00	1196.5	85.65
317.65	16.00	1201.2	86.64
317.65	17.00	1205.9	87.30
317.65	18.00	1210.3	87.98
317.64	19.00	1214.7	88.70
317.64	20.00	1218.9	89.33
317.64	21.00	1222.9	90.07
317.63	22.00	1226.9	90.78
317.63	23.00	1230.9	91.51
317.63	24.00	1234.7	91.88
317.63	25.00	1238.4	92.25
317.62	26.00	1242.0	93.00
317.62	27.00	1245.5	93.42
317.62	28.00	1248.9	94.12
317.61	29.00	1252.3	94.55
317.61	30.00	1255.7	95.34
317.61	31.00	1259.0	95.74
317.61	32.00	1262.0	96.14
317.61	33.00	1265.2	96.55
317.60	34.00	1268.3	97.38
317.60	35.00	1271.3	98.25
317.60	36.00	1274.3	98.60
317.60	37.00	1277.3	99.07
317.59	38.00	1280.0	99.50
317.59	39.00	1282.9	99.93
317.59	40.00	1285.7	100.38
317.59	41.00	1288.4	100.82
317.58	42.00	1291.0	101.27
317.58	43.00	1293.7	101.75
317.58	44.00	1296.3	102.13
317.58	45.00	1298.8	102.63
317.58	46.00	1301.3	103.09

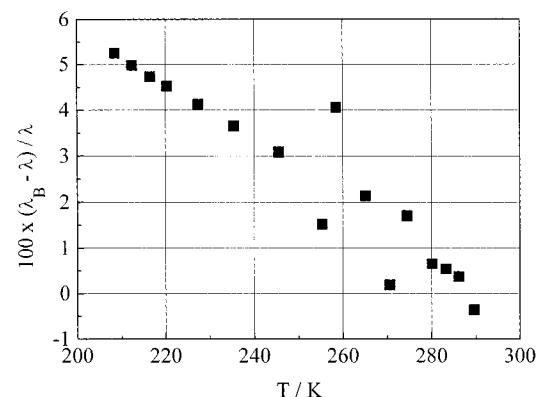


Figure 6. Relative deviations of calculated values by the background equation from the experimental data of Tsvetkov et al.¹⁴ along the saturation curve.

The best agreement was found with the measured values of Makita et al.¹⁰

Dense Fluid Thermal Conductivity

To determine the excess function or the residual term of the thermal conductivity $\delta\lambda(\rho, T)$, we have performed

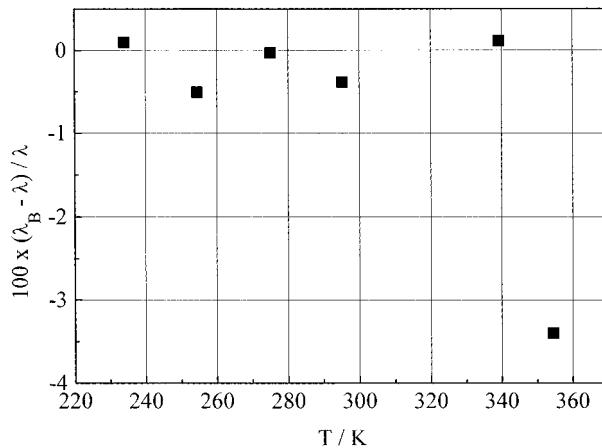


Figure 7. Relative deviations of calculated values by the background equation from the experimental data of Yata et al.¹⁵ along the saturation curve.

Table 8. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 337 \text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
337.14	3.00	1014.2	65.98
337.13	4.00	1030.3	67.12
337.12	5.00	1044.1	68.30
337.11	6.00	1056.4	69.53
337.10	7.00	1067.3	70.80
337.90	8.00	1077.4	71.89
337.08	9.00	1086.6	73.01
337.08	10.00	1095.3	73.70
337.70	11.00	1103.3	74.65
337.06	12.00	1110.9	75.38
337.06	13.00	1118.1	76.36
337.05	14.00	1124.9	77.11
337.05	15.00	1131.5	77.89
337.04	16.00	1137.7	78.68
337.03	17.00	1143.6	79.48
337.03	18.00	1149.4	80.30
337.02	19.00	1154.8	81.13
337.02	20.00	1160.1	81.98
337.01	21.00	1165.2	82.56
337.00	22.00	1170.2	83.44
337.00	23.00	1175.0	84.04
337.00	24.00	1179.6	84.64
337.00	25.00	1184.1	85.26
336.99	26.00	1188.6	85.88
336.99	27.00	1192.8	86.52
336.99	28.00	1197.0	87.16
336.98	29.00	1201.0	87.49
336.98	30.00	1204.9	88.15
336.98	31.00	1208.9	88.81
336.98	32.00	1212.6	89.15
336.97	33.00	1216.3	89.83
336.97	34.00	1219.9	90.53
336.96	35.00	1223.4	91.23
336.96	36.00	1226.9	91.58
336.96	37.00	1230.3	92.30
336.95	38.00	1233.6	93.03
336.95	39.00	1236.8	93.77
336.95	40.00	1240.0	94.15
336.95	41.00	1243.1	94.53
336.95	42.00	1246.2	94.91
336.94	43.00	1249.3	95.30
336.94	44.00	1252.3	95.68
336.94	45.00	1255.2	96.07
336.94	46.00	1258.1	96.46

measurements in the liquid phase and in the gas phase far away from the critical region along 14 quasi-isotherms at 299.4 K, 300.8 K, 302.5 K, 309.4 K, 317.7 K, 337 K, 356.5 K, 375.8 K, 393.8 K, 413.3 K, 453 K, 473 K, 493 K, and 514.2 K. Experimental results are listed in Tables 3–17. The excess function of the thermal conductivity, shown in

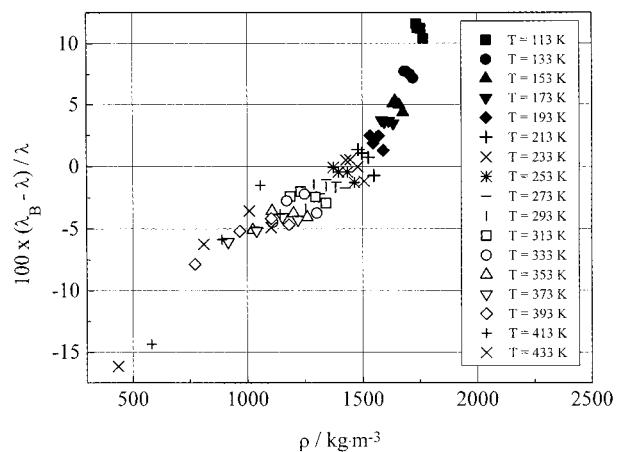


Figure 8. Relative deviations of calculated values by the background equation from the tabulated data of Vargaftik et al.⁸

Table 9. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 356.5 \text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
356.58	4.00	866.1	59.49
356.57	5.00	910.3	60.55
356.56	6.00	938.93	61.66
356.55	7.00	960.8	62.80
356.54	8.00	978.8	63.83
356.53	9.00	994.2	64.86
356.51	10.00	1007.9	66.12
356.50	11.00	1020.1	67.24
356.50	12.00	1031.3	68.40
356.48	13.00	1041.6	69.40
356.47	14.00	1051.1	70.63
356.47	15.00	1060.0	71.48
356.46	16.00	1068.4	72.36
356.45	17.00	1076.2	73.23
356.44	18.00	1083.7	74.14
356.44	19.00	1090.9	75.07
356.43	20.00	1097.7	76.03
356.42	21.00	1104.1	76.76
356.42	22.00	1110.4	77.51
356.42	23.00	1116.3	78.27
356.41	24.00	1122.1	79.04
356.41	25.00	1127.7	79.84
356.40	26.00	1133.0	80.57
356.39	27.00	1138.2	81.19
356.39	28.00	1143.2	81.74
356.39	29.00	1148.1	82.58
356.38	30.00	1152.8	83.15
356.38	31.00	1157.4	83.73
356.38	32.00	1161.9	84.33
356.37	33.00	1166.3	84.92
356.37	34.00	1170.5	85.52
356.36	35.00	1174.6	86.14
356.36	36.00	1178.6	86.76
356.36	37.00	1182.6	87.39
356.35	38.00	1186.4	88.03
356.35	39.00	1190.3	88.68
356.35	40.00	1193.9	89.34
356.34	41.00	1197.5	90.01
356.34	42.00	1201.0	90.35
356.34	43.00	1204.6	90.69
356.34	44.00	1207.9	91.03
356.34	45.00	1211.3	91.38
356.33	46.00	1214.5	91.72

Figure 3, was found to be temperature independent and was represented by a sixth-order polynomial of the form

$$\frac{\delta\lambda}{\Lambda_C} = \sum_{i=1}^6 b_i \left(\frac{\rho}{\rho_C} \right)^i \quad (8)$$

where $\rho_C = 520 \text{ kg}\cdot\text{m}^{-3}$ is the critical density, the coef-

Table 10. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 375.8\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
375.88	7.00	792.4	54.25
375.86	8.00	841.5	55.89
375.83	9.00	874.6	57.49
375.81	10.00	900.0	58.89
375.80	11.00	920.9	60.07
375.78	12.00	938.7	61.43
375.78	13.00	954.4	62.54
375.76	14.00	968.4	63.69
375.75	15.00	981.1	64.89
375.74	16.00	992.7	65.94
375.73	17.00	1003.4	67.03
375.72	18.00	1013.4	68.16
375.71	19.00	1022.7	69.13
375.70	20.00	1031.5	70.12
375.70	21.00	1039.8	70.94
375.70	22.00	1047.7	71.78
375.68	23.00	1055.2	72.63
375.68	24.00	1062.4	73.50
375.67	25.00	1069.2	74.40
375.67	26.00	1075.8	75.09
375.66	27.00	1082.1	75.79
375.66	28.00	1088.1	76.50
375.65	29.00	1094.0	77.23
375.65	30.00	1099.6	77.97
375.65	31.00	1105.1	78.46
375.64	32.00	1110.4	79.23
375.63	33.00	1115.5	80.00
375.63	34.00	1120.5	80.53
375.62	35.00	1125.3	81.33
375.62	36.00	1130.0	81.88
375.62	37.00	1134.6	82.43
375.61	38.00	1139.1	82.99
375.61	39.00	1143.4	83.55
375.61	40.00	1147.7	84.12
375.60	41.00	1151.8	84.71
375.60	42.00	1155.9	85.30
375.60	43.00	1159.8	85.60
375.60	44.00	1163.7	86.20
375.59	45.00	1167.5	86.81
375.59	46.00	1171.2	87.43

ficients b_i in eq 8 are $b_1 = 0.533\,878$, $b_2 = -0.103\,528\,74$, $b_3 = 1.328\,889\,7$, $b_4 = -1.100\,191$, $b_5 = 0.387\,148\,1$, and $b_6 = -0.045\,501\,816$, and $\Delta_C = 17.4\text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

In the liquid range, we have compared, as a function of density, the values calculated by our background equation (λ_B) with the experimental data measured by Assael et al.¹² (Figure 4) and Kim et al.¹³ (Figure 5). The agreement is very good since the mean deviations are within the experimental uncertainties ($\pm 1.5\%$). This good agreement shows that our background equation can be used to calculate the thermal conductivities of HCFC-22 at lower temperatures. Along the saturation curve, similar comparisons, as a function of temperature, are shown with the experimental data of Tsvetkov et al.¹⁴ (Figure 6) and those of Yata et al.¹⁵ (Figure 7). The mean deviations with the data of Yata et al.¹⁵ are within the experimental uncertainties ($\pm 1.5\%$). The deviations are slightly larger with the data of Tsvetkov et al.¹⁴ The relative deviations with the tabulated data of Vargaftik et al.⁸ are displayed in Figure 8. The agreement is poor except in a limited temperature range around 300 K.

Thermal Conductivity in the Critical Region

Around the critical density the well-known enhancement of the thermal conductivity was observed. This critical enhancement of the thermal conductivity $\Delta\lambda(T,\rho)$ was carefully measured along several quasi-isotherms. Some preliminary results are reported along the critical isochore

Table 11. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 393.8\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
393.90	15.00	897.6	61.12
393.89	16.00	913.8	62.49
393.88	17.00	928.3	63.64
393.87	18.00	941.6	64.82
393.87	19.00	953.8	66.05
393.86	20.00	965.1	67.00
383.86	21.00	975.6	67.98
393.85	22.00	985.5	68.99
393.85	23.00	994.8	69.67
393.84	24.00	1003.6	70.38
393.84	25.00	1011.9	71.09
393.83	26.00	1019.8	71.82
393.83	27.00	1027.4	72.56
393.83	28.00	1034.6	73.32
393.83	29.00	1041.6	73.71
393.83	30.00	1048.2	74.09
393.82	31.00	1054.7	74.89
393.82	32.00	1060.9	75.69
393.82	33.00	1066.8	76.10
393.82	34.00	1072.6	76.52
393.82	35.00	1078.2	77.36
393.82	36.00	1083.6	77.36
393.82	37.00	1086.8	78.22
393.81	38.00	1094.0	79.10
393.81	39.00	1098.9	79.10
393.81	40.00	1103.7	79.55
393.81	41.00	1108.4	80.00
393.81	42.00	1113.0	80.46
393.80	43.00	1117.5	81.40
393.80	44.00	1121.8	81.39
393.80	45.00	1126.1	81.86
393.79	46.00	1130.3	82.34

Table 12. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 413.3\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
413.35	15.00	797.5	55.51
413.34	16.00	820.6	56.84
413.34	17.00	840.8	57.95
413.33	18.00	858.8	59.40
413.32	19.00	875.0	60.61
413.31	20.00	889.7	60.92
413.31	21.00	903.2	62.19
413.32	22.00	915.7	63.18
413.31	23.00	927.4	63.86
413.30	24.00	938.3	64.90
413.30	25.00	948.5	65.97
413.29	26.00	958.2	66.71
413.29	27.00	967.4	67.46
413.29	28.00	976.1	67.85
413.29	29.00	984.3	68.62
413.28	30.00	992.3	69.42
413.28	31.00	999.8	69.83
413.28	32.00	1007.1	70.65
413.28	33.00	1014.1	71.49
413.27	34.00	1020.8	71.92
413.27	35.00	1027.3	72.35
413.36	36.00	1033.6	73.24
413.27	37.00	1039.6	74.14
413.26	38.00	1045.5	74.60
413.26	39.00	1051.1	75.08
413.26	40.00	1056.7	76.02
413.26	41.00	1062.0	76.51
413.26	42.00	1067.2	77.00
413.25	43.00	1072.3	77.49
413.25	44.00	1077.2	78.00
413.25	45.00	1082.0	78.51
413.25	46.00	1086.7	79.02

(Table 18) and compared to an equation assuming the classical divergence with the critical exponent equal to -0.65

$$\Delta T = 1.7 \Delta T^{-0.65} \quad (9)$$

Table 13. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 433.8\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
432.80	15.00	691.9	50.71
432.80	16.00	722.4	52.03
432.79	17.00	748.9	53.41
432.78	18.00	772.1	54.87
432.77	19.00	792.9	56.14
432.77	20.00	811.5	57.21
432.76	21.00	828.4	58.31
432.75	22.00	843.9	59.45
432.74	23.00	858.2	60.64
432.74	24.00	871.5	61.57
432.74	25.00	883.9	62.52
432.74	26.00	895.5	63.16
432.73	27.00	906.4	64.16
432.73	28.00	916.70	64.84
432.72	29.00	926.49	65.90
432.72	30.00	935.79	66.62
432.72	31.00	944.59	66.99
432.72	32.00	953.10	67.35
432.71	33.00	961.09	68.10
432.71	34.00	968.89	68.49
432.71	35.00	976.29	69.27
432.70	36.00	983.49	70.06
432.70	37.00	990.4	70.46
432.70	38.00	997.1	71.29
432.70	39.00	1003.5	71.70
432.70	40.00	1009.7	72.12

Table 14. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 453\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
453.18	0.10	2.40	21.88
453.16	1.00	23.8	22.14
453.15	2.00	49.4	22.52
453.13	3.00	77.1	23.04
453.10	4.00	107.3	23.70
453.09	5.00	140.2	24.45
453.04	6.00	176.5	25.89
452.99	7.00	216.4	27.49
452.95	8.00	260.1	29.29
452.90	9.00	307.6	31.33
452.85	10.00	358.0	33.73
452.82	11.00	409.6	35.77
452.77	12.00	460.5	38.36
452.75	13.00	508.6	40.49
452.72	14.00	552.6	42.61
452.70	15.00	591.9	44.52
452.68	16.00	626.9	46.29
452.66	17.00	657.8	48.04
452.65	18.00	685.4	49.57
452.64	19.00	710.0	51.00
452.63	20.00	732.3	52.33
452.62	21.00	752.4	53.52
452.61	22.00	770.9	54.56
452.61	23.00	787.8	55.41
452.60	24.00	803.5	56.52
452.60	25.00	818.0	57.44
452.59	26.00	831.6	58.63
452.58	27.00	844.4	59.62
452.56	28.00	856.3	60.63
452.57	29.00	867.7	61.43
452.57	30.00	878.4	62.23
452.56	31.00	888.5	63.34
452.56	32.00	898.2	64.19
452.55	33.00	907.4	65.08
452.55	34.00	916.3	65.68
452.54	35.00	924.7	66.60
452.54	36.00	932.8	67.22
452.54	37.00	940.6	67.54
452.53	38.00	948.2	68.85
452.53	39.00	955.4	69.52
452.53	40.00	962.4	70.55
452.52	41.00	969.1	71.25
452.52	42.00	975.7	71.97
452.52	43.00	982.0	72.33
452.52	44.00	988.2	72.70
452.51	45.00	994.1	73.44
452.51	46.00	999.9	74.21

Table 15. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 473\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
473.14	0.10	2.29	23.39
473.13	1.00	22.7	23.64
473.12	2.00	46.8	24.02
473.10	3.00	72.5	24.56
473.08	4.00	100.0	25.09
473.06	5.00	129.5	25.86
473.03	6.00	161.1	26.91
473.00	7.00	195.0	28.10
472.97	8.00	231.2	29.52
472.93	9.00	269.5	31.09
472.90	10.00	309.8	32.73
472.87	11.00	351.2	34.56
472.83	12.00	393.0	36.70
472.81	13.00	434.1	38.54
472.78	14.00	473.7	40.35
472.76	15.00	511.0	42.19
472.74	16.00	545.7	44.06
472.72	17.00	577.6	45.80
472.71	18.00	606.8	47.20
472.70	19.00	633.5	48.67
472.69	20.00	657.9	49.88
472.68	21.00	680.2	51.16
472.67	22.00	700.8	52.10
472.66	23.00	719.8	53.08
472.65	24.00	737.5	54.10
472.64	25.00	753.9	55.17
472.64	26.00	769.2	56.26
472.63	27.00	783.5	57.17
472.63	28.00	797.0	58.11
472.63	29.00	809.7	59.08
472.62	30.00	821.8	60.09
472.61	31.00	833.2	60.86
472.61	32.00	844.0	61.65
472.60	33.00	854.4	62.47
472.60	34.00	864.2	63.30
472.60	35.00	873.7	63.87
472.59	36.00	882.7	64.74
472.59	37.00	891.4	65.36
472.58	38.00	899.7	66.24
472.58	39.00	907.8	67.18
472.58	40.00	915.5	67.82
472.57	41.00	923.0	68.48
472.57	42.00	930.2	69.14
472.57	43.00	937.2	69.81
472.57	44.00	943.9	70.16
472.56	45.00	950.5	70.51
472.56	46.00	956.8	70.86

where $\Delta T = (T - T_c)/T_c$. The agreement is very satisfactory except for the first point near the critical temperature, which is much lower than the calculated one. The same discrepancy was already observed for other refrigerants. This indicates that in a temperature range within one degree above the critical temperature, the measured thermal conductivity values which are integrated over a small temperature gradient are always lower than those predicted by scaling theory. Due to the lack of a scaled equation of state near the critical point, it was not possible to follow the elaborated methodology proposed by Olchowy and Sengers¹⁶ to calculate crossover functions and analyze the critical enhancement in the crossover region.

Conclusion

New measurements of the thermal conductivity of HCFC-22 have been presented in the temperature range from 300 K to 515 K along 14 quasi-isotherms and at pressures up to 55 MPa, with an estimated uncertainty of $\pm 1.5\%$. A background equation was determined which can be used to calculate the thermal conductivity from 220 K

Table 16. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 493\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
493.17	0.10	2.17	24.85
493.17	1.00	21.7	25.13
493.16	2.00	44.5	25.52
493.14	3.00	68.6	25.93
493.13	4.00	93.9	26.44
493.11	5.00	120.8	27.09
493.10	6.00	149.1	27.94
493.07	7.00	178.9	28.85
493.04	8.00	210.2	29.94
493.02	9.00	242.9	30.98
492.99	10.00	276.8	32.24
492.97	11.00	311.6	33.59
492.94	12.00	346.8	35.07
492.92	13.00	381.9	36.77
492.90	14.00	416.5	38.20
492.87	15.00	450.0	40.10
492.86	16.00	482.0	41.55
492.84	17.00	512.4	42.97
492.83	18.00	540.9	44.34
492.82	19.00	567.6	45.66
492.80	20.00	592.5	46.89
492.79	21.00	615.7	48.35
492.78	22.00	637.3	49.55
492.77	23.00	657.5	50.62
492.77	24.00	676.3	51.56
492.76	25.00	693.9	52.52
492.75	26.00	710.5	53.53
492.75	27.00	726.0	54.35
492.74	28.00	740.7	55.42
492.73	29.00	754.5	56.31
492.73	30.00	767.6	57.23
492.72	31.00	780.1	58.17
492.72	32.00	791.9	58.90
492.71	33.00	803.2	59.64
492.71	34.00	814.0	60.41
492.70	35.00	824.3	61.19
492.70	36.00	834.2	62.00
492.70	37.00	843.6	62.82
492.69	38.00	852.7	63.39
492.69	39.00	861.5	64.25
492.68	40.00	869.9	64.84
492.68	41.00	878.0	65.43
492.68	42.00	885.9	66.04
492.68	43.00	893.4	66.66
492.67	44.00	900.8	67.29
492.67	45.00	907.9	67.94
492.67	46.00	914.8	68.26

to 600 K with an accuracy of $\pm 2\%$. It is obvious that in the critical region a supplementary functional form must be added to account for the critical enhancement.¹⁶

Acknowledgment

We are indebted to ATOCHEM for providing us HCFC-22 samples.

List of Symbols

a_i	constants in eq 5
A_i	constants in eq 6
b_i	constants in eq 8
C_P^0	ideal isobaric heat capacity, $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
k	Boltzmann constant, $\text{J}\cdot\text{K}^{-1}$
M	molar mass, $\text{g}\cdot\text{mol}^{-1}$
P	pressure, MPa
R	universal gas constant, $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
T	temperature, K
$T^* = kT/\epsilon$	reduced temperature

Table 17. Thermal Conductivity of HCFC-22 along the Quasi-Isotherm $T = 514.2\text{ K}$

T/K	P/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\lambda/\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
514.32	0.10	2.07	26.63
514.32	1.00	20.7	26.84
514.31	2.00	42.3	27.17
514.30	3.00	64.9	27.62
514.29	4.00	88.5	28.03
514.27	5.00	113.1	28.52
514.26	6.00	138.8	29.01
514.24	7.00	165.5	29.72
514.23	8.00	193.2	30.40
514.21	9.00	221.9	31.18
514.19	10.00	251.3	32.23
514.18	11.00	281.3	33.34
514.16	12.00	311.6	34.54
514.14	13.00	342.0	35.72
514.12	14.00	372.1	36.99
514.10	15.00	401.8	38.23
514.08	16.00	430.6	39.67
514.06	17.00	458.5	41.22
514.05	18.00	485.2	42.63
514.04	19.00	510.7	43.99
514.03	20.00	534.8	45.14
514.01	21.00	557.7	46.51
514.00	22.00	579.3	47.63
513.99	23.00	599.7	48.80
513.98	24.00	619.0	49.84
513.97	25.00	637.2	50.94
513.97	26.00	654.3	51.89
513.96	27.00	670.6	52.87
513.96	28.00	686.0	53.67
513.96	29.00	700.6	54.52
513.95	30.00	714.5	55.60
513.94	31.00	727.8	56.27
513.94	32.00	740.4	56.96
513.93	33.00	752.4	57.90
513.93	34.00	763.9	58.62
513.92	35.00	775.0	59.37
513.92	36.00	785.5	60.13
513.91	37.00	795.7	60.65
513.91	38.00	805.4	61.44
513.91	39.00	814.8	61.99
513.90	40.00	823.9	62.53
513.90	41.00	832.6	63.09
513.89	42.00	841.0	63.66
513.89	43.00	849.2	64.24
513.89	44.00	857.1	64.84
513.89	45.00	864.7	65.44
513.89	46.00	872.1	66.05

$$\Delta T = (T - T_C)/T_C \quad \text{reduced temperature}$$

Greek Letters

ϵ	energy scaling factor, J
λ_0	thermal conductivity at atmospheric pressure, $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
λ_B	background thermal conductivity, $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Λ_C	excess thermal conductivity at T_C , $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
$\delta\lambda$	excess function of thermal conductivity, $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
$\Delta\lambda$	thermal conductivity enhancement, $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
θ_i	constants in eq 5
ρ	density, $\text{kg}\cdot\text{m}^{-3}$
σ	length scaling factor, nm
$\tau = T_C/T$	reduced temperature
Ω_λ^*	reduced collision integral
<i>Subscripts</i>	
c	critical

Table 18. Thermal Conductivity of HCFC-22 along the Critical Isochore

T/K	$\Delta T/K$	$\rho/kg\cdot m^{-3}$	$\lambda/mW\cdot m^{-1}\cdot K^{-1}$	$\Delta\lambda_{exp}/mW\cdot m^{-1}\cdot K^{-1}$	$\Delta\lambda_{cal}/mW\cdot m^{-1}\cdot K^{-1}$	$100(\lambda_{cal} - \lambda_{exp})/\lambda_{exp}$
369.61	8.94×10^{-4}	540.0	118.97	85.06	163.0	65.5
369.62	9.21×10^{-4}	505.4	117.96	85.88	159.9	62.7
370.91	4.41×10^{-3}	523.6	86.41	53.28	57.71	5.1
370.91	4.41×10^{-3}	516.9	86.41	53.63	57.71	4.7
371.91	7.12×10^{-3}	525.9	74.12	40.79	42.29	2.0
371.91	7.12×10^{-3}	515.3	73.72	40.94	42.29	1.8
372.75	9.40×10^{-3}	522.5	68.41	35.2	35.31	0.2
372.75	9.40×10^{-3}	514.5	68.07	35.28	35.31	0.0
373.86	1.24×10^{-2}	530.5	63.59	29.86	29.49	-0.6
373.86	1.24×10^{-2}	519.1	63.59	30.46	29.49	-1.5
375.65	1.72×10^{-2}	524.1	57.27	23.75	23.79	0.1
375.65	1.72×10^{-2}	515.9	57.04	23.94	23.79	-0.3
378.78	2.57×10^{-2}	520.1	51.67	18.11	18.35	0.5
383.62	3.88×10^{-2}	526.0	48.18	13.95	14.04	0.2
383.62	3.88×10^{-2}	519.2	47.85	13.97	14.04	0.1
388.67	5.25×10^{-2}	525.2	44.66	10.08	11.54	3.3
388.67	5.25×10^{-2}	500.6	43.65	10.36	11.54	2.7
394.0	6.69×10^{-2}	518.7	44.39	9.74	9.85	0.2
413.4	1.19×10^{-1}	536.0	43.49	6.43	6.78	0.8

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