International Journal of Thermophysics, Vol. 2, No. 3, 1981

Thermal Conductivity of Gaseous Fluorocarbon Refrigerants R 12, R 13, R 22, and R 23, Under Pressure

T. Makita, Y. Tanaka, Y. Morimoto, M. Noguchi, and H. Kubota

Received April 28, 1981

The thermal conductivity of four gaseous fluorocarbon refrigerants has been measured by a vertical coaxial cylinder apparatus on a relative basis. The fluorocarbon refrigerants used and the ranges of temperature and pressure covered are as follows:

R 12 (Dichlorodifluoromethane CCl_2F_2): 298.15–393.15 K, 0.1–4.28 MPa

R 13 (Chlorotrifluoromethane $CClF_3$): 283.15–373.15 K, 0.1–6.96 MPa

R 22 (Chlorodifluoromethane $CHClF_2$): 298.15–393.15 K, 0.1–5.76 MPa

R 23 (Trifluoromethane CHF_3): 283.15–373.15 K, 0.1–6.96 MPa

The apparatus was calibrated using Ar, N_2, and CO_2 as the standard gases. The uncertainty of the experimental data is estimated to be within 2%, except in the critical region. The behavior of the thermal conductivity for these fluorocarbons is quite similar; thermal conductivity increases with increasing pressure. The temperature coefficient of thermal conductivity at constant pressure, $(\partial\lambda/\partial T)_p$, is positive at low pressures and becomes negative at high pressures. Therefore, the thermal conductivity isotherms of each refrigerant intersect each other in a specific range of pressure. A steep enhancement of thermal conductivity is observed near the critical point. The experimental results are statistically analyzed and the thermal conductivities are expressed as functions of temperature and pressure and of temperature and density.

KEY WORDS: chlorotrifluoromethane (R 13); chlorodifluoromethane (R 22); dichlorodifluoromethane (R 12); fluorocarbon; pressure effect on thermal conductivity; thermal conductivity; trifluoromethane (R 23).

---

[1] Department of Chemical Engineering, Kobe University, Kobe 657, Japan.

1. INTRODUCTION

Fluorocarbon refrigerants are of particular importance to scientists and engineers engaged in the refrigeration technology. Recently, they have also become the working fluids in various new energy systems for the utilization of low temperature resources, such as solar, geothermal, ocean-thermal, and waste heat in chemical industries. However, there appears to be only a limited number of experimental data on the thermal conductivity of gaseous fluorocarbons under pressure. This laboratory has been measuring various thermophysical properties of several fluorocarbon refrigerants under pressure. In this paper, we report the measurements of the thermal conductivity of gaseous dichlorodifluoromethane (R 12), chlorotrifluoromethane (R 13), chlorodifluoromethane (R 22), and trifluoromethane (R 23) at temperatures between 283 and 393 K and pressures up to 7 MPa as a sequel to an earlier publication [1]. Experimental results are statistically analyzed by means of the stepwise multiple regression method. Most probable correlation formulas are obtained for each substance both in terms of temperature-pressure and temperature-density coordinates. A reduced state correlation is also attempted on the basis of the law of corresponding states.

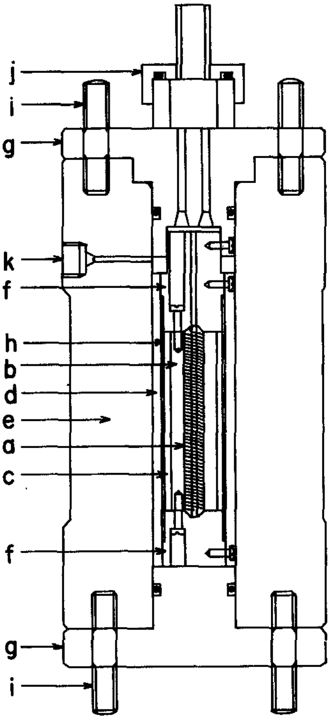

Fig. 1. Cross-sectional view of the thermal conductivity cell: a, heater (o.d. = 8 mm, L = 72 mm); b, inner cylinder, copper; c, emitter, copper (o.d. = 25 mm, L = 72 mm); d, receiver, copper (o.d. = 34 mm, i.d. = 26 mm, L = 120 mm); e, high-pressure vessel, brass (o.d. = 108 mm, i.d. = 34 mm, L = 220 mm); f, insulator, phenol resin; g, flange, brass; h, annular gap (o.d. = 26 mm, i.d. = 25 mm); i, bolt, brass; j, opening for electric leads; k, sample inlet.

2. EXPERIMENTAL

2.1. Thermal Conductivity Cell

Thermal conductivity was measured by a coaxial cylinder apparatus on a relative basis with the reference thermal conductivity values of argon [2], neon [3], and nitrogen [2]. The details of the apparatus and experimental procedures were described elsewhere [1]. A cross-sectional view of the thermal conductivity cell is shown in Fig. 1. The cell consists of three concentric copper cylinders (b, c, d) fixed vertically in a brass high-pressure vessel (e). The sample fluid is introduced into an annular gap (h) of about 0.5 mm between the emitter (c) and the receiver (d). Electrical energy is supplied to a heater (a) made of constantan wire wound on a threaded bar of polytetrafluoroethylene. The heat generated in the emitter (c) is transmitted radially outward through the sample fluid layer (h) to the receiver (d) and also axially toward both ends. To minimize axial conduction, thermal insulators (f) are provided on both ends of the emitter. The temperature difference across the fluid layer is measured with two sets of copper-constantan differential thermocouples installed in the emitter and receiver. The thermoelectromotive force is measured within $\pm 0.05\ \mu V$ by means of a digital nanovoltmeter. The temperature of the cell is maintained constant in an oil thermostat controlled within ±0.01 K. The pressure is measured with a Bourdon tube gauge calibrated against a dead-weight gauge within an uncertainty of 0.5%.

2.2. Sample Fluids

Argon, neon, and nitrogen were obtained from commercial sources with a specification of minimum purity of 99.99%. Research-grade sample fluids of R 12, R 13, R 22, and R 23 were supplied by Daikin Ind. Co. The physicochemical properties and the purities of sample fluids are summarized in Table I. These gases were used without further purification.

Table I. Physicochemical Properties of Refrigerants

Refrigerant	R 12	R 13	R 22	R 23
Chemical formula	CCl_2F_2	$CClF_3$	$CHClF_2$	CHF_3
Molecular weight	120.91	104.46	86.47	70.01
Dipole moment (D)	0.51	0.50	1.42	1.65
Critical temp. (K)	392.0	302.0	369.2	298.8
Critical press. (bar)	41.3	39.2	49.9	48.4
Critical density ($kg \cdot m^{-3}$)	558	579	513	526
Purity of sample (%)	99.99	99.9	99.99	99.91

2.3. Calibration of the Instrument

The present thermal conductivity cell is not equipped with guard heaters, which prevent the axial heat losses. The total electrical energy dissipated in the heater, Q, provides both the radial heat flux required to maintain a small temperature gradient about 0.75 K across the fluid layer, Q_r, and the axial heat loss through the insulators and the electrical leads, Q_l. The following relation should hold if the temperature difference across the fluid layer is kept constant throughout the experimental conditions:

$$Q = Q_r + Q_l = \lambda A \Delta T + B \Delta T, \tag{1}$$

where A and B are the radial and axial cell constants. To calibrate the cell, the quantity $Q/\Delta T$ is measured using argon, neon, and nitrogen:

$$Q/\Delta T = A\lambda + B \tag{2}$$

Using the selected values of thermal conductivity of these gases [2, 3], the constants A and B are determined throughout the present experimental conditions. It is found that a linear relationship between $Q/\Delta T$ and λ is almost independent of temperature and pressure as reported previously [1]. This calibration procedure enables the generation of thermal conductivity values with a mean deviation of 0.5%.

2.4. Possible Sources of Errors

The Rayleigh number Ra is usually applied to determine the possible presence of convection in fluids:

$$Ra = Gr \cdot Pr = \frac{g \cdot \rho^2 \cdot \beta \cdot \Delta T \cdot C_p \cdot d^3}{\eta \cdot \lambda} \tag{3}$$

where Gr and Pr are Grashof and Prandtl numbers, respectively, and g is the acceleration due to gravity, ρ is the density, β is the coefficient of thermal

Table II. Sources of Error and Their Contribution to Thermal Conductivity

Error source	Uncertainty in measurement	Uncertainty contributing to λ
Temperature	0.01 K	0.01%
Temperature difference	0.05 μV (= 0.001 K)	0.4%
Pressure	0.1 bar	0.04%
Power input	0.25 mW	0.07%
Calibration of the cell		0.5%

Table III. Thermal Conductivity of Dichlorodifluoromethane (R 12)[a]

P	ρ	λ	P	ρ	λ
298.15 K (25.00°C)			373.15 K (100.00°C)		
1.0	4.967	9.82	1.0	3.934	13.6
2.2	11.18	9.86	6.6	27.47	13.7
3.3	17.16	9.92	10.5	45.68	13.9
4.4	23.43	10.0	14.5	66.40	14.2
5.3	28.81	10.1	17.5	83.70	14.5
5.9	32.54	10.2	19.9	98.96	15.0
6.1	33.81	10.2	23.1	121.9	15.5
323.15 K (50.00°C)			25.8	144.5	16.2
			26.8	153.9	16.4
1.0	4.567	11.0	28.7	173.9	17.1
3.0	14.14	11.1	32.1	221.8	19.3
4.9	23.84	11.2	33.2	244.0	22.6
6.9	34.86	11.4	383.15 K (110.00°C)		
8.7	45.60	11.6			
10.0	53.98	11.8	1.0	3.828	14.2
12.3	70.42	12.2	7.8	31.79	14.4
348.15 K (75.00°C)			11.2	47.29	14.5
			15.3	67.72	14.8
1.0	4.226	12.4	18.7	86.48	15.0
3.8	16.63	12.5	22.6	110.7	15.6
6.1	27.54	12.6	25.9	134.2	16.1
9.3	44.03	12.8	30.2	171.4	17.0
12.1	60.07	13.0	33.6	209.7	18.9
14.4	74.71	13.4	37.1	268.1	22.1
18.5	105.6	14.0	39.7	364.3	32.7
20.9	128.4	15.1	393.15 K (120.00°C)		
363.15 K (90.00°C)			1.0	3.728	14.7
1.0	4.046	13.1	10.0	40.27	14.9
6.2	26.57	13.2	12.9	53.42	15.1
7.8	34.09	13.3	15.9	67.94	15.3
9.2	40.93	13.4	20.0	89.58	15.6
10.9	49.61	13.5	23.3	108.9	16.0
12.8	59.87	13.7	26.8	131.7	16.6
14.7	70.81	13.9	30.8	162.0	17.4
17.5	88.44	14.2	33.2	183.2	18.0
20.9	113.1	14.8	36.5	217.8	19.2
24.5	145.4	16.2	39.1	252.4	21.0
27.2	177.4	17.8	42.8	324.7	25.1

[a] P = pressure in bar, ρ = density in kg · m^{-3}, and λ = thermal conductivity in mW · m^{-1} · K^{-1}.

Table IV. Thermal Conductivity of Chlorotrifluoromethane (R 13)[a]

P	ρ	λ
283.15 (10.00°C)		
1.0	4.487	11.0
4.9	23.05	11.3
8.9	44.22	11.6
12.8	67.65	12.0
16.9	96.57	12.7
20.6	128.7	13.5
24.1	168.8	15.0
298.15 K (25.00°C)		
1.0	4.254	12.0
4.9	21.67	12.2
8.8	40.62	12.5
12.8	62.06	12.7
14.7	73.12	13.0
16.7	85.49	13.2
18.6	98.08	13.4
20.6	112.4	13.8
22.6	127.9	14.2
24.5	144.2	14.7
26.5	163.5	15.4
28.4	184.4	16.2
30.4	210.5	17.4
32.4	243.5	19.2
34.3	287.9	23.2
313.15 K (40.00°C)		
1.0	4.044	12.9
4.9	20.47	13.1
8.8	38.07	13.4
12.8	57.58	13.7
16.7	78.35	14.0
20.6	101.3	14.7
24.5	126.9	15.6
26.5	141.5	15.9
28.4	156.4	16.5
30.4	173.4	17.0
32.4	192.1	17.7
34.3	211.9	18.6
36.3	235.4	19.6
38.3	262.7	21.1
40.2	293.7	22.9
42.2	334.4	26.1
44.1	385.4	28.9
46.1	459.7	43.4
313.15 K (40.00°C) Continued		
52.0	702.7	58.1
53.9	748.0	53.6
55.9	783.6	50.1
57.9	811.4	49.1
59.8	833.0	48.9
61.8	852.0	48.5
65.7	882.1	48.4
69.6	905.9	48.6
323.15 K (50.00°C)		
1.0	3.915	13.6
2.9	11.51	13.7
6.9	28.25	13.8
10.8	45.64	14.1
14.7	64.30	14.4
18.6	84.46	14.8
22.6	107.0	15.2
26.5	131.3	15.8
30.4	158.4	16.6
34.3	189.4	17.7
38.3	226.5	19.0
42.2	270.3	20.8
44.1	295.4	22.1
46.1	325.4	23.9
48.1	359.8	26.4
50.0	397.3	29.4
52.0	441.9	33.4
53.9	488.0	37.8
55.9	537.5	41.8
57.9	584.9	44.9
59.8	626.0	45.8
61.8	664.4	45.7
65.7	725.4	45.3
69.6	771.9	45.1
333.15 K (60.00°C)		
1.0	3.795	14.5
2.9	11.14	14.5
6.9	27.25	14.7
10.8	43.86	15.0
14.7	61.51	15.2
18.6	80.36	15.5
22.6	101.2	15.9
26.5	123.1	16.3

[a] P = pressure in bar, ρ = density in $\mathrm{kg \cdot m^{-3}}$, and λ = thermal conductivity in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$.

Table IV. Continued

P	ρ	λ
333.15 K (60.00°C) Continued		
30.4	147.1	17.0
34.3	173.5	17.8
38.3	203.8	18.7
42.2	237.3	19.9
46.1	275.8	21.7
50.0	320.7	24.4
53.9	373.2	27.1
57.9	424.8	30.5
61.8	499.2	34.2
65.7	562.3	37.6
69.6	619.6	40.7
348.15 K (75.00°C)		
1.0	3.628	15.8
6.9	25.89	16.1
10.8	41.48	16.2
14.7	57.87	16.5
18.6	75.14	16.8
22.6	93.89	17.1
26.5	113.3	17.6
30.4	134.0	18.1
34.3	156.2	18.6
38.3	180.8	19.3
42.2	206.7	20.0
46.1	234.9	21.0
348.15 K (75.00°C) Continued		
50.0	265.6	22.3
53.9	299.2	23.7
57.9	336.8	25.4
61.8	376.4	27.2
65.7	418.3	29.3
69.6	461.4	31.3
373.15 K (100.00°C)		
1.0	3.382	17.5
10.8	38.14	17.9
14.7	52.87	18.0
18.6	68.17	18.1
22.6	84.49	18.5
26.5	101.1	18.8
30.4	118.4	19.1
34.3	136.5	19.5
38.3	155.8	19.9
42.2	175.6	20.4
46.1	196.4	21.0
50.0	218.1	21.7
53.9	240.9	22.4
57.9	265.3	23.1
61.8	290.1	23.9
65.7	315.9	24.8
69.6	342.6	25.7

expansion, C_p is the isobaric specific heat, η is the viscosity, and d is the width of the annular gap. The effect of convection could be neglected if the value of Ra is less than 1000 for a vertical coaxial cylinder apparatus [4]. In cases of the calibration gases, the influence of convection is found to be definitely negligible throughout the present experimental conditions. As for fluorocarbons, ρ, β, and C_p are calculated from the equations of state of Morsey [5] and of the Japanese Association of Refrigeration [6]. The viscosities are cited from the experimental results of Iwasaki et al. [7]. It is found that the values of Ra are less than 1000, except at the critical region, where it is almost impossible to estimate the values of Ra precisely because of the lack of reliable physical properties. Therefore, the experimental results in the critical region might be influenced by convection.

The influence of thermal radiation across the sample fluid layer is noted to be small and within the experimental error. The effect of pressure and

Table V. Thermal Conductivity of Chlorodifluoromethane (R 22)[a]

P	ρ	λ
298.15 K (25.00°C)		
1.0	3.540	10.6
4.2	15.65	10.7
5.3	20.15	10.8
6.2	23.97	10.9
7.0	27.50	11.0
7.7	30.69	11.2
8.4	33.99	11.3
9.6	39.94	11.9
323.15 K (50.00°C)		
1.0	3.254	12.1
3.8	12.78	12.2
4.4	14.91	12.2
5.3	18.16	12.3
5.8	20.00	12.3
6.7	23.39	12.4
6.9	24.15	12.4
7.6	26.86	12.5
8.5	30.43	12.6
9.3	33.69	12.7
9.6	34.93	12.7
10.5	38.75	12.8
11.8	44.48	13.0
12.8	49.09	13.2
13.6	52.92	13.3
14.5	57.40	13.5
16.0	65.31	13.8
17.5	73.89	14.2
17.7	75.10	14.2
19.4	86.03	14.7
348.15 K (75.00°C)		
1.0	3.013	13.8
4.2	13.02	14.0
5.6	17.59	14.0
7.6	24.35	14.2
8.7	28.19	14.2
9.6	31.40	14.3
11.1	36.90	14.5
11.6	38.78	14.5
13.7	46.93	14.7
16.6	58.99	15.1
19.4	71.70	15.4
21.3	81.07	15.8
21.9	84.17	15.9
348.15 K (75.00°C) Continued		
23.4	92.29	16.2
26.3	109.7	17.0
29.3	131.3	18.2
31.5	150.7	19.4
363.15 K (90.00°C)		
1.0	2.885	14.9
4.7	13.95	15.0
6.0	18.00	15.1
8.1	24.73	15.2
9.6	29.69	15.3
12.5	39.69	15.4
14.0	45.10	15.6
15.6	51.06	15.7
17.4	58.04	15.9
19.4	66.14	16.1
20.9	72.51	16.3
23.1	82.33	16.6
25.3	92.83	17.1
27.5	104.1	17.5
29.5	115.3	18.0
32.2	131.9	18.8
34.2	145.8	19.4
36.6	164.9	20.4
39.3	191.3	22.1
41.9	225.8	24.7
43.7	262.1	28.9
44.0	270.5	29.7
373.15 K (100.00°C)		
1.0	2.806	15.5
8.2	24.23	15.8
9.6	28.68	15.9
12.1	36.88	16.0
13.6	41.97	16.2
16.9	53.70	16.4
19.4	63.10	16.7
22.2	74.27	17.0
24.4	83.57	17.2
27.2	96.20	17.6
30.1	110.4	18.1
32.7	124.3	18.7
38.3	159.6	20.3
41.2	182.1	21.5
44.6	214.8	23.5

[a] P = pressure in bar, ρ = density in $kg \cdot m^{-3}$, and λ = thermal conductivity in $mW \cdot m^{-1} \cdot K^{-1}$.

Table V. Continued

P	ρ	λ	P	ρ	λ
373.15 K (100.00°C) Continued			383.15 K (110.00°C) Continued		
47.9	258.6	28.2	51.0	245.4	25.6
49.4	286.6	33.2	54.0	283.4	28.7
51.4	343.7	47.4	56.3	321.2	32.3
53.6	520.0	130.9	57.6	347.6	36.4
56.0	676.5	68.2			
383.15 K (110.00°C)			393.15 K (120.00°C)		
1.0	2.731	16.1	1.0	2.660	16.8
8.1	23.17	16.3	10.1	28.38	17.1
9.4	27.13	16.4	11.5	32.60	17.2
10.8	31.48	16.5	12.5	35.67	17.2
13.0	38.51	16.6	16.5	48.38	17.5
14.1	42.11	16.6	19.8	59.46	17.7
15.5	46.80	16.8	22.1	67.53	17.9
17.6	54.03	16.9	24.7	77.03	18.1
20.3	63.73	17.1	25.6	80.42	18.2
22.9	73.55	17.4	27.5	87.78	18.4
25.7	84.73	17.8	28.0	89.75	18.5
28.0	94.43	18.0	29.6	96.22	18.7
30.3	104.7	18.4	33.7	113.8	19.3
32.4	114.6	18.7	36.1	124.8	19.6
34.9	127.1	19.3	37.1	129.6	19.8
36.7	136.7	19.6	40.5	146.9	20.5
39.1	150.5	20.1	44.6	170.0	21.6
42.2	170.2	20.9	49.9	205.0	23.3
45.3	192.7	22.2	52.9	228.2	24.9
48.6	220.9	23.9	56.0	255.9	26.9

temperature on the dimensions of the apparatus should also be small, and it is taken into account by the above calibration.

2.5. Uncertainty in the Experimental Results

Thermal conductivity values obtained in the present measurements contain a definite uncertainty due to several sources of experimental error. The major sources of error and their contributions are estimated and are presented in Table II. Taking into account the uncertainty of the property values of the standard gases, the maximum uncertainty in the present measurements should not exceed 2%, excluding the critical region, where there are no means to estimate the uncertainty. In order to establish the reliability of the present apparatus from another point of view, measurements on methane were performed utilizing the same experimental arrangement at

Table VI. Thermal Conductivity of trifluoromethane (R 23)[a]

P	ρ	λ
283.15 K (10.00°C)		
1.0	3.002	12.0
5.0	15.59	12.3
8.8	28.57	12.7
12.8	43.57	13.3
16.2	57.67	13.9
20.3	76.91	14.8
24.5	100.2	16.2
28.2	125.7	18.5
30.2	142.7	20.2
298.15 K (25.00°C)		
1.0	2.864	13.2
2.9	8.374	13.3
6.9	20.58	13.6
10.8	33.31	13.9
14.7	47.07	14.4
18.6	62.03	15.0
22.6	78.96	15.7
26.5	97.47	16.8
30.4	118.6	18.2
34.3	143.7	20.1
38.3	175.9	23.0
42.2	219.7	27.8
313.15 K (40.00°C)		
1.0	2.705	14.4
2.9	7.941	14.5
6.9	19.40	14.7
10.8	31.21	15.1
14.7	43.73	15.5
18.6	57.10	15.9
22.6	71.82	16.5
26.5	87.35	17.2
30.4	104.3	18.1
34.3	123.1	19.0
38.3	144.7	20.3
42.2	168.8	21.9
46.1	197.3	24.5
50.0	232.3	28.4
52.0	254.1	31.0
53.9	278.4	34.8
55.9	309.4	39.2
57.9	349.5	45.9
59.8	404.0	53.3
323.15 K (50.00°C)		
1.0	2.621	15.3
2.9	7.681	15.3
6.9	18.70	15.6
10.8	29.98	15.8
14.7	41.85	16.1
18.6	54.38	16.6
22.6	68.03	17.1
26.5	82.22	17.7
30.4	97.44	18.4
34.3	113.9	19.2
38.3	132.2	20.1
42.2	152.0	21.2
46.1	173.9	22.8
50.0	198.7	24.6
53.9	227.3	27.3
57.9	261.9	30.1
61.8	303.0	34.3
65.7	354.6	39.4
69.6	422.1	47.5
333.15 K (60.00°C)		
1.0	2.540	16.2
2.9	7.437	16.3
6.9	18.06	16.4
10.8	28.87	16.6
14.7	40.17	16.9
18.6	52.00	17.3
22.6	64.78	17.7
26.5	77.92	18.3
30.4	91.82	18.9
34.3	106.6	19.7
38.3	122.8	20.4
42.2	139.9	21.2
46.1	158.2	22.2
50.0	178.3	23.5
53.9	200.2	25.2
57.9	225.2	26.9
61.8	252.4	29.2
65.7	283.1	32.1
69.6	317.9	35.0
348.15 K (75.00°C)		
1.0	2.428	17.6
2.9	7.100	17.7

[a] P = pressure in bar, ρ = density in $kg \cdot m^{-3}$, and λ = thermal conductivity in $mW \cdot m^{-1} \cdot K^{-1}$.

Table VI. Continued

P	ρ	λ	P	ρ	λ
348.15 K (75.00°C) Continued			373.15 K (100.00°C)		
			1.0	2.264	19.5
6.9	17.19	17.8	6.9	15.93	19.9
10.8	27.38	18.0	10.8	25.26	19.9
14.7	37.94	18.2	14.7	34.85	20.1
18.6	48.92	18.5	18.6	44.71	20.4
22.6	60.64	18.8	22.6	55.11	20.6
26.5	72.56	19.3	26.5	65.56	21.0
30.4	85.01	19.8	30.4	76.33	21.4
34.3	98.04	20.3	34.3	87.43	21.7
38.3	112.1	20.9	38.3	99.19	22.2
42.2	126.5	21.4	42.2	111.0	22.7
46.1	141.7	22.2	45.1	120.1	23.1
50.0	157.8	23.1	50.0	135.9	23.8
53.9	174.8	24.2	53.0	145.9	24.3
57.9	193.4	25.3	57.9	162.9	25.3
61.8	212.8	26.5	61.8	177.0	26.0
65.7	233.5	27.9	65.7	191.5	26.7
69.6	255.7	29.6	69.6	206.5	27.5

temperatures from 298 to 373 K under pressures up to 7 MPa. The results were compared with several literature values [1, 8–12]. It is confirmed that the present results agree with the most probable values recommended by the High Pressure Data Center of Japan [12] within 1% throughout the range of the experimental conditions.

3. EXPERIMENTAL RESULTS

The experimental data obtained are given in Tables III–VI for gaseous R 12, R 13, R 22, and R 23, respectively, where the values of density are calculated from the equations of state [5, 6]. The thermal conductivity values at atmospheric pressure are obtained by a graphical extrapolation, and are compared with the literature values for R 12 and R 22 [13–21]. The deviations of each set of experimental data from the correlated values of Touloukian et al. [13] are plotted in Fig. 2. The discrepancy of the data is serious for these gases. The present results agree with the correlated values of Touloukian et al. [13] within 2.2% for R 12 and 3.7% for R 22, respectively.

The thermal conductivities obtained for R 13 and R 22 under pressure are illustrated typically as a function of pressure in Figs. 3 and 4, respectively. As far as we know, there are no data available on the thermal conductivity of

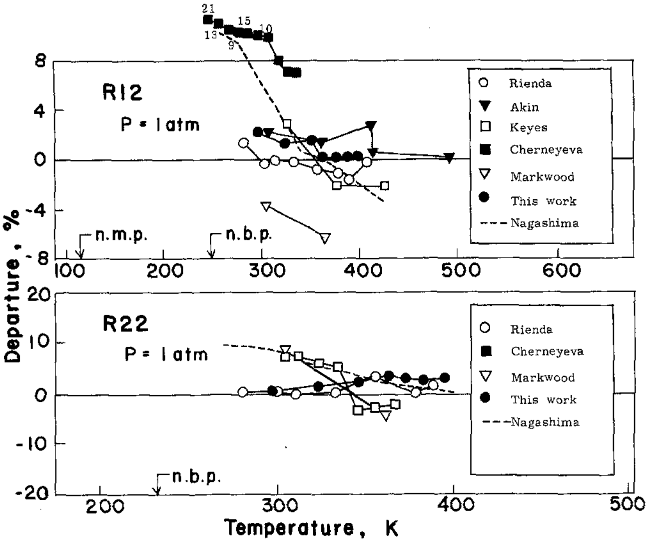

Fig. 2. Deviation plot for thermal conductivity of R 12 and R 22 at atmospheric pressure.

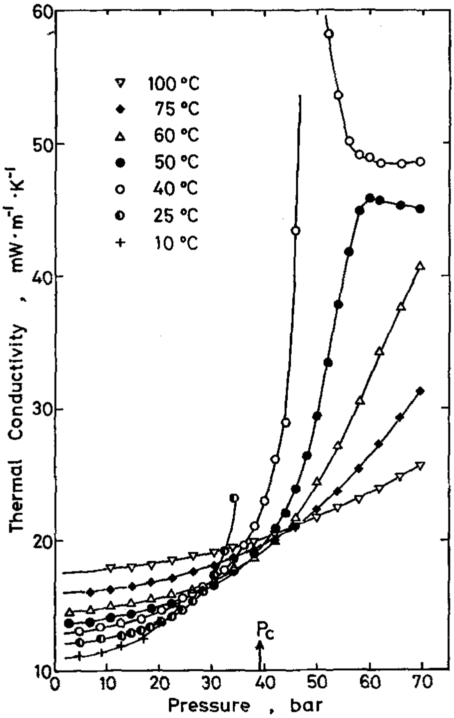

Fig. 3. Thermal conductivity of R 13 as a function of pressure.

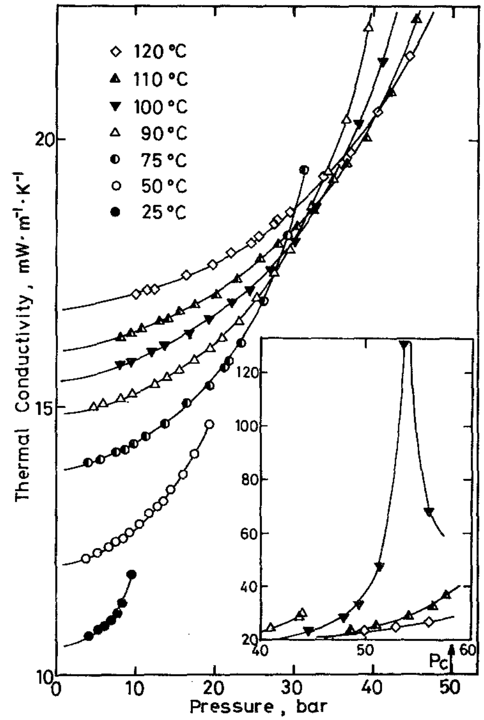

Fig. 4. Thermal conductivity of R 22 as a function of pressure.

R 12, R 22, and R 23 covering the range of temperatures and pressures reported here. Venart et al. [22] measured the thermal conductivity of R 13 by the transient hot wire method. Since they did not report their results in tabular form, it is not possible to compare the results numerically. However, it seems that our results at 373 K agree well with those of Venart et al., although considerable inconsistencies are found at lower temperatures.

As seen in Figs. 3 and 4, although the absolute values of the thermal conductivity of four gaseous fluorocarbons are different from each other, the relative behavior concerning the effects of temperature and pressure is quite similar. The general characteristics of the behavior may be summarized qualitatively as follows:

1. Thermal conductivity increases with increasing pressure at each temperature. The effect of pressure is more marked at lower temperatures. Although a negative pressure effect is reported for the viscosity of gaseous R 12 and R 22 [7] below 25°C, that is, $(\partial\eta/\partial p)_T < 0$,

thermal conductivity always increases with pressure throughout the present experimental conditions.

2. The temperature coefficient of thermal conductivity, $(\partial\lambda/\partial T)_p$, is positive at low pressures. The value decreases gradually with increasing pressure and becomes negative at higher pressures.
3. At lower temperatures below the critical point, thermal conductivity increases with pressure and varies discontinuously at the saturation pressure due to the liquefaction. The isotherms slightly above the critical temperature show a steep enhancement in the vicinity of the critical pressure. On the other hand, the isotherms at higher temperatures, far from the critical point, increase gradually and continuously with pressure.
4. The absolute values of thermal conductivity λ and its pressure coefficient $(\partial\lambda/\partial p)_T$ are found to increase in the following order.

$$\text{R }12 < \text{R }22 \approx \text{R }13 < \text{R }23$$

Another way of plotting data is to treat the thermal conductivity as a function of temperature and density. Both the thermal conductivity and the residual thermal conductivity, $\lambda - \lambda_0$, of R 13 are plotted in Figs. 5 and 6,

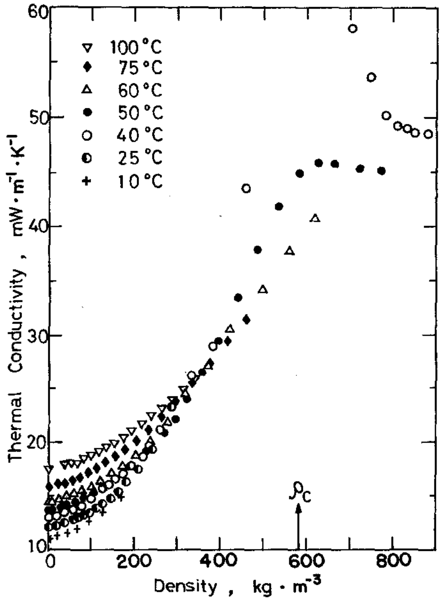

Fig. 5. Thermal conductivity of R 13 as a function of density.

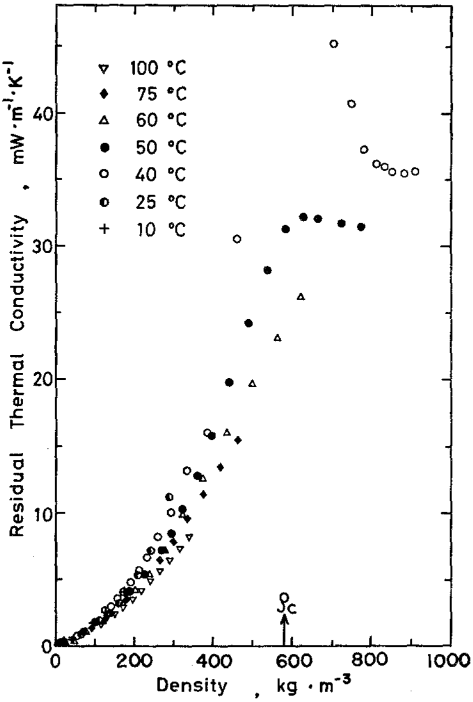

Fig. 6. Residual thermal conductivity of R 13 as a function of density.

respectively. Although the residual thermal conductivity at all temperatures may be approximated by a single function of density below $\rho = 150\ \mathrm{kg \cdot m^{-3}}$, it becomes remarkably dependent on temperature as the density approaches the critical value. The critical anomaly of thermal conductivity is observed definitely in Fig. 6. Anomalous behavior of a similar nature was also observed in the previous work on SF_6 [1].

4. ANALYSIS AND CORRELATION OF RESULTS

The experimental results are statistically analyzed by the stepwise multiple regression method of Efroymson [23, 24]. The thermal conductivity λ for each substance is correlated with temperature T and pressure P. The correlation equations thus obtained are as follows:

R 12

$$\lambda(T, P) = (a_1 + a_2/T^2 + a_3 \cdot T^3) + a_4 \cdot T^3 \cdot P + (a_5 + a_6/T^2)P^3 + (a_7/T^2)P^4 + a_8 \cdot P^9 \quad (4)$$

R 13

$$\lambda(T, P) = (a_1 + a_2/T + a_3/T^2) + a_4 \cdot T^3 \cdot P + (a_5/T + a_6/T^2)P^2 + (a_7/T^2)P^3 + a_8 \cdot T^2 \cdot P^5 \quad (5)$$

R 22

$$\lambda(T, P) = (a_1 + a_2/T^2 + a_3 \cdot T^3) + (a_4 + a_5/T^2)P + (a_6 \cdot T + a_7 \cdot T^3)P^2 + (a_8/T)P^6 + a_9 \cdot T \cdot P^8 + a_{10} \cdot P^{10} \quad (6)$$

R 23

$$\lambda(T, P) = (a_1 + a_2 \cdot T) + a_3 \cdot T \cdot P + (a_4/T + a_5/T^2 + a_6 \cdot T^3)P^2 + (a_7/T^2 + a_8 \cdot T^2)P^3 + a_9 \cdot P^{10} \quad (7)$$

where λ is represented in $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, T in K, and P in bar (10^5 Pa), respectively. These correlation formulas are the most probable ones among the simple polynomial equations consisting of T and P. The empirical coefficients and the available ranges of parameters for the four substances are summarized in Table VII. The mean and maximum deviations of the data from the equations are also included. The maximum deviation appears near the critical point for each substance. These equations are reliable interpolation formulas within the limited ranges of parameters. As emphasized by Hanley et al. [2, 25] an extensive and consistent correlation of the transport coefficients appears possible only in terms of temperature-density coordinates. However, a $\lambda = \lambda\ (T, P)$ type correlation is still attractive for correlations of limited ranges in view of the fact that the practical variables are temperature and pressure and that the valid equations of state are not always available.

The correlations in terms of temperature T and density ρ are also made by the same procedures mentioned above. The best correlation equations selected are as follows:

R12

$$\lambda(T, \rho) = (b_1 + b_2/T + b_3 \cdot T^3) + (b_4/T^2)\rho + (b_5 + b_6/T^2)\rho^2 + b_7 \cdot T \cdot \rho^7 + b_8 \cdot \rho^{10} \quad (8)$$

R13

$$\lambda(T, \rho) = (b_1 + b_2/T + b_3/T^2) + (b_4/T + b_5 \cdot T^2 + b_6 \cdot T^3)\rho + (b_7/T^2)\rho^2 \quad (9)$$

Table VII. Empirical Coefficients in Eqs. (4–7).

Refrigerant	R 12 (CCl_2F_2)	R 13 ($CClF_3$)	R 22 ($CHClF_2$)	R 23 (CHF_3)
Temp. range (K)	298.15–393.15	283.15–373.15	298.15–393.15	283.15–373.15
Press. range (bar)	1–42.8	1–69.6	1–57.6	1–69.6
Upper limit of λ ($mW \cdot m^{-1} \cdot K^{-1}$)	25.1	25.7	36.4	30.1
a_1	0.9922031E 01	0.7297197E 02	0.1109092E 02	−0.1241396E 02
a_2	−0.2461125E 06	−0.3059090E 05	−0.3919324E 06	0.8564529E−01
a_3	0.1036690E−06	0.3691068E 07	0.1368698E−06	0.2022645E−03
a_4	0.8194003E−09	0.1350635E−08	−0.5590635E−01	−0.1923572E 02
a_5	−0.8455477E−03	−0.5706102E 01	0.1290847E 05	0.5102112E 04
a_6	0.1140144E 03	0.1810817E 04	0.2354174E−04	0.2806757E−09
a_7	0.6710998E 00	0.8215063E 01	−0.1470359E−09	0.1499435E 02
a_8	0.4555342E−14	−0.2428380E−13	0.5595371E−06	−0.6607680E−09
a_9			−0.2438776E−14	−0.3799550E−18
a_{10}			0.1776880E−15	
Number of data points	73	93	126	108
Mean dev. (%)	0.77	0.76	0.64	0.66
Max. dev. (%)	2.70	2.38	2.70	2.54

Table VIII. Empirical Coefficients in Eqs. (8–11).

Refrigerant	R 12 (CCl_2F_2)	R 13 ($CClF_3$)	R 22 ($CHClF_2$)	R 23 (CHF_3)
Temp. range (K)	298.15–393.15	283.15–373.15	298.15–393.15	283.15–373.15
Density range ($kg \cdot m^{-3}$)	0–342.7	0–342.6	0–347.6	0–261.9
Upper limit of λ ($mW \cdot m^{-1} \cdot K^{-1}$)	25.1	25.7	36.4	30.1
b_1	0.1530346E 02	0.7720752E 02	0.6075040E 02	0.1141964E 02
b_2	−0.2340805E 04	−0.3329958E 05	−0.2438142E 05	−0.3270401E 06
b_3	0.8802593E−07	0.4121889E 07	0.2787347E 07	0.2053325E−06
b_4	0.4405561E 06	−0.4538773E 04	0.2079939E 07	0.6322657E 06
b_5	−0.1330921E 03	0.7942704E−03	−0.7016379E−07	0.3220489E−06
b_6	0.3258185E 08	−0.1745451E−05	0.1618377E 08	−0.2580962E 06
b_7	0.3255683E 02	0.6791243E 07	0.8771901E−02	0.9073068E 08
b_8	−0.2741264E 06		−0.8180258E 05	0.2499338E−05
b_9			0.5538115E 06	
Number of data points	73	93	126	108
Mean dev. (%)	0.39	0.77	0.35	0.40
Max. dev. (%)	2.61	2.31	1.93	1.52

R22

$$\lambda(T, \rho) = (b_1 + b_2/T + b_3/T^2) + (b_4/T^2 + b_5 \cdot T^3)\,\rho + (b_6/T^2)\,\rho^2 + b_7 \cdot T^2 \cdot \rho^5 + b_8 \cdot \rho^8 + b_9 \cdot \rho^{10} \quad (10)$$

R23

$$\lambda(T, \rho) = (b_1 + b_2/T^2 + b_3 \cdot T^3) + (b_4/T^2 + b_5 \cdot T^3)\rho + (b_6/T + b_7/T^2 + b_8 \cdot T^3)\,\rho^2 \quad (11)$$

where the units of λ, T, and ρ are $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, K, and $\text{kg} \cdot \text{dm}^{-3}$, respectively. The empirical coefficients and the statistical data are given in Table VIII. The correlation of the data is considerably improved as compared to the case of the $\lambda(T, P)$ correlation.

Another attempt has been made to develop a reduced state correlation on the basis of the law of corresponding states. Comparison and superposition of data among four gases is quite limited in the present work because the critical temperatures of these gases are dispersed. The reduced thermal conductivity $\lambda_r = \lambda/\ \lambda_c$ is calculated for each substance along five isotherms between $T_r = 0.94$–1.02 by use of the correlation formulas (4)–(7), and the critical thermal conductivity λ_c is estimated empirically by the following expression [26]:

$$\lambda_c = 2.60\ (\lambda^0)_{T_c} \quad (12)$$

where $(\lambda^0)_{T_c}$ is the thermal conductivity at the atmospheric pressure and the critical temperature. Consequently, it is found that the reduced state correlations of R 13 and R 22 are in excellent agreement, with a mean deviation of 0.57%. On the other hand, the effects of temperature and pressure on the thermal conductivity of R 12 and R 23 are different from those of R 13 and R 22. An $\lambda/\lambda^0 = f(T_r, P_r)$ type correlation was also attempted, but a similar relation was obtained. Although a third parameter has been sought for the generalized correlation for these gases, no adequate single parameter has been found so far. An ingeneous combination of several parameters by dimensional analysis may be required for this purpose. It may be added that accurate experimental data are needed for similar fluorocarbons under pressure.

ACKNOWLEDGMENTS

This investigation has been partly supported by a Scientific Research Grant from the Ministry of Education, Japan. The statistical analysis of data

was performed by means of the computer ACOS series 77 NEAC System 700S at the Kobe University Computation Center.

REFERENCES

1. Y. Tanaka, M. Noguchi, H. Kubota, and T. Makita, *J. Chem. Eng. Japan* **12**:171 (1979).
2. H. J. M. Hanley, R. D. McCarty, and W. H. Haynes, *J. Phys. Chem. Ref. Data* **3**:979 (1974).
3. J. V. Sengers, W. T. Bolk, and C. J. Stigter, *Physica* **30**:1018 (1964).
4. H. Kraussold, *Forsch. Geb. Ing. Wes.* **5**:186 (1934).
5. T. E. Morsey, *J. Chem. Eng. Data* **15**:256 (1970).
6. Japanese Association of Refrigeration, *Thermophysical Properties of Refrigerants (R22, Chlorodifluoromethane)* (Nihon Reito Kyokai, Tokyo, Japan, 1975).
7. H. Iwasaki et al., private communications.
8. L. F. Carmichael, H. H. Reamer, and B. H. Sage, *J. Chem. Eng. Data* **11**:52 (1966).
9. B. Le Neindre, R. Tufeu, P. Bury, P. Johanin, and B. Vodar, in *Proceedings of the Eighth International Conference on Thermal Conductivity* (Plenum Press, New York, 1969), p. 229.
10. D. Misic and G. Thodos, *Physica* **32**:885 (1966).
11. B. M. Rosenbaum and G. Thodos, *Physica* **37**:442 (1967).
12. Promotion Bureau, Science and Technology Agency (Japan), Report of the Physical and Chemical Property Data, *High Press. Data* **4** (1976); **5** (1977).
13. Y. S. Touloukian, P. E. Liley, and S. C. Saxena, *Thermophysical Properties of Matter (TPRC Data Series) Vol. 3. Thermal Conductivity-Nonmetallic Liquids and Gases* (IFI/Plenum Data Corp., New York, 1970).
14. J. M. B. Rienda, Ph.D. thesis, Madrid University, Madrid, Spain (1963).
15. S. W. Akin, *Trans. ASME* **72**:751 (1950).
16. A. K. Abas-Zade, *Doklady Akad. Nauk* **99**:227 (1954).
17. L. A. Bromley, USAEC Rept. UCRL-1852 (1952), p. 1.
18. F. G. Keyes, *Trans. ASME* **76**:809 (1954).
19. L. Cherneyeva, *Kholodil'naya Tekh.* **29**:55 (1952); **30**:60 (1953).
20. W. H. Markwood, Jr., and A. F. Benning, *Refrig. Eng.* **45**:95 (1943).
21. A. Nagashima, *Refrigeration* **52**:42 (1977).
22. J. E. S. Venart, N. Mani, and R. V. Paul, in *Proceedings of the Fourteenth International Conference on Thermal Conductivity* (Plenum Press, New York, 1976), p. 287.
23. N. R. Draper and H. Smith, *Applied Regression Analysis* (John Wiley & Sons, New York, 1966).
24. A. Ralston and H. S. Wilf, *Mathematical Methods for Digital Computers* (John Wiley & Sons, New York, 1952).
25. H. J. M. Hanley, R. D. McCarty, and W. M. Haynes, *Cryogenics* **15**:413 (1975).
26. B. W. Gamson, *Chem. Eng. Prog.* **45**:154 (1949).