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Thermal Conductivity of Refrigerants R123, R134a, and R125 at Low Temperatures

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Using a transient coaxial cylinder technique, thermal conductivities were measured for liquid 1,1,1-trifluoro-2,2-dichloroethane (refrigerant R123), 1,1,1,2-tetrafluoroethane (refrigerant R134a), and pentafluoroethane (refrigerant R125). The uncertainty of the experimental data is estimated to be within 2–3%. Thermal conductivities of refrigerants were measured at temperatures ranging from −114 to 20°C under pressures up to 10 MPa. The apparatus was calibrated with four kinds of liquids and gases. The features of the density dependence of thermal conductivity are indicated. Existing equations for calculating the coefficient are analyzed in cases where development has been sufficient to enable comparisons to be made with experiment. Saturated-liquid thermal conductivities for R134a and R123 are compared with corresponding experimental values.

KEY WORDS: chlorofluorocarbons; fluorocarbons; isobaric heat capacity; refrigerants; R123; R125; R134a; saturated liquid; thermal conductivity; transient method.

1. INTRODUCTION

The variation of thermal conductivity as a function of the thermodynamic state of liquid refrigerants is of engineering importance. Only limited experimental transport-property data over a wide range of temperatures and pressures are available in the literature and therefore experimental and correlation techniques must be developed.

In this investigation, a coaxial cylinder cell was constructed for measuring the thermal conductivity of refrigerants in the liquid state at low

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temperatures at pressures ranging from 0.1 to 10 MPa. The purpose of the present study is also to verify the Predvoditelev-Vargaftik correlation technique by comparing our experimental data with those in the literature.

2. EXPERIMENTS

The main component of the experimental facility consisted of the coaxial cylindrical cell presented in Fig. 1. This cell has been used earlier to measure the thermal conductivity of carbon dioxide, dichlorodifluoromethane (refrigerant R12), chlorodifluoromethane (refrigerant R22), refrigerant R502, and refrigerant R503 in the liquid state [1]. In the present study measurements were carried out at pressures up to 10 MPa and temperatures ranging from 140 to 290 K.

The coaxial cell consisted of an inner cylinder with an outer diameter of 13.793 mm and an outer cylinder with an inner diameter of 14.323 mm, thus providing an annular gap of 0.265×10^{-3} m. The inner cylinder was 95.01 mm in length, with the main heater within it. The outer cylinder was

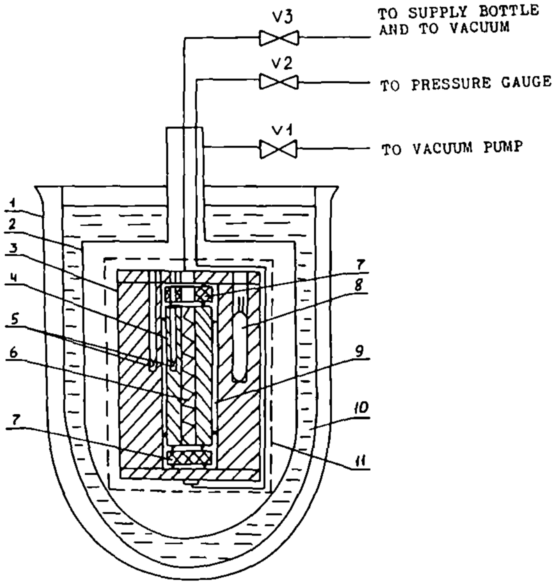

Fig. 1. Schematic diagram of the thermal-conductivity apparatus: (1) Dewar vessel; (2) vacuum chamber; (3) outer cylinder, copper; (4) inner cylinder, copper; (5) copper-constantan thermocouples; (6) heater; (7) guard rings; (8) platinum resistance thermometer; (9) annular gap; (10) liquid nitrogen; (11) passive shielding system, *V* valve.

20.340 mm in thickness and 130.0 mm in length. The assembled unit measured 55.0 mm in diameter and 156.0 mm in length. The inner and outer cylinders had openings with thermocouple wells located in them. Copper–constantan thermocouples were inserted into these wells and were used to measure temperature differences across the annular gap.

The thermal conductivity cell was located within a vacuum chamber. The relatively small copper vacuum chamber was immersed in a Dewar filled with liquid nitrogen. The vacuum chamber was provided with strip heaters and a metal heat shield. Heat was supplied automatically in response to the signal from the copper–constantan thermocouple, from which the signal was chopped and amplified.

A two-layer passive shielding system was designed to minimize heat losses from the calorimeter to the environment. Conductive heat transfer is eliminated by maintaining a vacuum around the cell in a vacuum chamber maintained at liquid nitrogen temperature. Radiation heat transfer in the vacuum chamber is minimized by the use of passive shields.

The supporting equipment included a pressure gauge, an intermediate pressure vessel, and an evacuation system consisting of a mechanical forepump and an oil diffusion pump. More detailed information concerning the thermal-conductivity cell can be found elsewhere [2]. The working equation of the method, based on the solution of the Fourier heat conduction equation, is given by

$$\lambda = \frac{Q \ln(R/R_0)}{2\pi \, \Delta T L} (1 - \Delta\sigma - \Delta\sigma_0) \tag{1}$$

with

$$\Delta\sigma = \frac{mcb}{Q} \tag{2}$$

and

$$\Delta\sigma_0 = \frac{m_0 c_0 b}{2Q} \left[\frac{1}{\ln(R/R_0)} - \frac{2R_0^2}{R^2 - R_0^2} \right] \tag{3}$$

where ΔT is the temperature difference across the fluid layer, Q is the power input, λ is the thermal conductivity, R and R_0 are the radii of external and internal cylinders, m and m_0 are the mass of the inner cylinder and of a test liquid, b is the monotonous heating rate $b = \partial T/\partial \tau$, c and c_0 are the heat capacities of the inner cylinder and the fluid layer, and L is the length of the inner cylinder.

The fluid surrounds the inner cylinder and fills the gaps between the inner and the outer cylinders and between the guard rings at the upper end of the inner cylinder. Heat supplied by the inner cylinder heater is transported across the gap of thickness δ through the sample fluid. The power emitted by the heater and the temperature difference between the two cylinders must be measured.

The power input Q was obtained from measurements of voltage and current. The current was determined from the measurement of a voltage at terminals of a standard resistor, 0.01 Ω.

The temperatures were measured with a small 10-Ω ceramic-encapsulated platinum resistance thermometer (TSPN-5) to within 1 mK on the IPTS-68.

The temperature difference measured with copper–constantan thermocouples in series was amplified with a nanovoltmeter amplifier. The temperature difference ΔT was always kept to a minimum to avoid convection yet sufficiently large to ensure reasonable accuracy of measurement. During these measurements the temperature differences across the liquid gap ranged from 1 to 3 K or less. For the experimental conditions of this study the correction for convection using the Rayleigh number relations [1] was shown to be negligible. The correction for radiation was given by the Stefan–Boltzmann law of radiation assuming that liquid refrigerants are transparent fluids. In practice the values $\Delta\sigma$ and $\Delta\sigma_0$ in Eqs. (2) and (3) have to take into account the heat adsorbed by the inner cylinder and by the liquid fluid layer. These corrections can be determined quite accurately, and for the temperature rise of the order $(8\text{–}10) \times 10^{-3}\ \mathrm{K \cdot s^{-1}}$ they never exceed 2–3%. The overall precision in the determination of the thermal conductivity was of the order 2–3% or better.

The experimental procedure for a typical set of isobaric measurements consisted in, first, introducing the liquid charge into the intermediate pressure vessel, which was directly connected to the calorimeter. After reaching thermal equilibrium the inner cylinder heater was switched on. Measurements were made for increasing temperatures in the monotonous heating regime. The following measurements were taken: heat input, temperature difference between the cylinders, heating rate, pressure, and absolute temperature. During these runs the temperature rise ranged from 6×10^{-3} to $9 \times 10^{-3}\ \mathrm{K \cdot s^{-1}}$, the power input being nearly 8–10 W.

To establish the reliability of the present apparatus, a few thermal-conductivity measurements were made with toluene, argon, helium, and difluoromonochloromethane (refrigerant R22) at temperatures from 140 to 290 K under pressures up to 10 MPa. Helium, toluene, argon, and R22 were chosen because a large number of accurate experimental data are available [3] and toluene has been proposed as a possible standard [3]. The measured values are in agreement with previously published data and we can conclude that the present instrument operates within the combined experimental error.

The refrigerants used were research-grade substances supplied by the State Institute of Applied Chemistry (St. Petersburg, Russia) which had a purity of at least 99.83 wt%. The sample R123 was stated to be an isomeric blend of 95% R123 ($CHCl_2$-CF_3) and 5% R123a ($CHClF$-$CClF_2$). The thermal conductivity measurements of R123 in Section 3 are consistent with this level of purity. The purity was checked by gas chromatographic analysis in the thermophysical laboratory at the Technological Institute of Refrigeration, St. Petersburg.

3. RESULTS

The sets of experimental conductivity values obtained in this study for 1,1,1,2-tetrafluoroethane (refrigerant R134a), 1,1,1-trifluoro-2,2-dichloroethane (refrigerant R123), and pentafluoroethane (refrigerant R125) are presented in Table I. The thermal conductivity was measured at the quasi-isobars, with a total of about 54 experimental points.

Table I. Experimental Results for the Thermal Conductivity of Refrigerants Near the Liquid Saturation Line

Refrigerant R134a		Refrigerant R123		Refrigerant R125	
T (K)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)	T (K)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)	T (K)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)
169.87	1430	159.34	1154	172.74	1116
170.84	1428	163.61	1142	178.72	1094
172.85	1420	173.28	1120	195.03	1030
175.60	1416	176.04	1111	206.87	987
180.46	1388	180.10	1099	215.88	953
189.61	1340	187.27	1083	226.08	912
198.82	1286	199.73	1047	235.69	882
207.84	1245	205.41	1032	245.66	841
217.09	1202	217.93	999	249.19	833
225.88	1153	226.0	985	257.30	804
231.53	1134	234.26	958	263.01	779
244.92	1070	240.70	937	269.71	747
248.10	1056	246.42	925	277.8	720
258.54	1005	252.18	907	285.12	694
261.74	991	260.12	882	288.89	679
271.75	924	269.13	859	290.02	680
281.61	894	279.58	827		
284.38	883	284.78	813		
290.06	862	291.32	799		

Table II. Comparison of Densities Calculated by the Hankinson-Thomson Method with Recommended Values in the Liquid State

T (K)	P (MPa)	ρ_{cal} (kg·m^{-3})	ρ_{ref} (kg·m^{-3})	Dev. (%)
		Refrigerant R22 ($CHClF_2$)		
250	1.0	1359.0	1364.0	−0.37
300	1.0	1182.9	1183.2	−0.03
320	1.0	1089.6	1089.1	−0.05
		Refrigerant R152a ($C_2H_4F_2$)		
250	5.0	1017.4	1019.1	−0.17
300	5.0	909.5	910.0	−0.05
320	5.0	859.2	859.5	−0.03
		Refrigerant R134a ($C_2H_2F_4$)		
250	1.0	1369.5	1376.8	−0.53
300	1.0	1200.2	1204.2	−0.33
320	1.0	1115.0	1116.6	−0.14

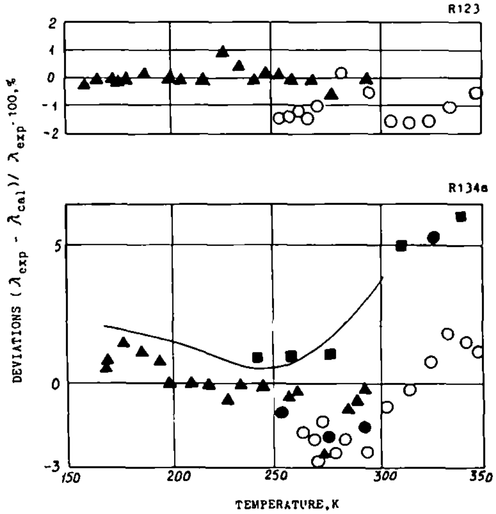

Fig. 2. Deviations of measured thermal conductivities of R123 and R134a from Eq. (4). (▲) Present work; (○) Ref. 4; (●) Ref. 5; (■) Ref. 7; (——) Ref. 6.

The thermal conductivity λ (as $10^4\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$) for the saturated liquid is represented by a linear function of the absolute temperature T in K

$$\lambda = C_0 + C_1 T \tag{4}$$

For refrigerant R123 it was found that $C_0 = 1587.81$ and $C_1 = -2.708$, for refrigerant R125 $C_0 = 1758.78$ and $C_1 = -3.720$, and for refrigerant R134a $C_0 = 2209.92$ and $C_1 = -4.647$.

In Fig. 2 we plot our results near the liquid saturation line and the results of other workers [4–7]. The present results agree well with those of Gross et al. [4] and of Ross et al. [5]. To our knowledge there are no data available for the thermal conductivity of refrigerants covering the range of low temperatures below 250 K or for the thermal conductivity of R125.

4. CALCULATED RESULTS AND DISCUSSION

Using the present measurements of liquid refrigerants we performed theoretical predictive calculations on the basis of the Predvoditelev–Vargaftik correlation:

$$\lambda = B\rho^n \tag{5}$$

$$B = AC_p M^{1/3} \tag{6}$$

Here M is the molar mass, ρ is the density, C_p is the specific heat at constant pressure, and A and B are adjustable parameters derived from a fit. We have made a comparison of the model, given by Eq. (5), with the

Table III. Coefficients in Eq. (5)

Chemical formula of refrigerant	$10^5 B$		Temp. range (K)
	Min.	Max.	
R113 ($C_2F_3Cl_3$)	29.8	31.1	243–353
R114 ($C_2F_4Cl_2$)	29.4	32.6	213–373
R115 (C_2F_5Cl)	29.6	31.6	193–313
R123 ($C_2HF_3Cl_2$)	36.2	37.0	159–291
R125 (C_2HF_5)	38.9	44.4	172–290
R134a ($C_2H_2F_4$)	55.8	57.6	170–290
R142b ($C_2H_3ClF_2$)	69.0	72.9	243–363
R143 ($C_2H_3F_3$)	76.4	79.3	213–293
R152a ($C_2H_4F_2$)	122.0	129.4	170–300

experimental thermal conductivity for the refrigerants in question and for R152a, R113, R114, R115, R142b, and R143 obtained from generally accepted references [1, 3]. The required density values were obtained from Refs. 7–10 or calculated from the compilation study of Hankinson–Thomson [11]. In Table II we compare the values of the density calculated from the equation of state and from the Hankinson–Thomson compilation. A good degree of consistency can be seen between values shown in Table II.

The resulting λ values were used to obtain the exponent n in Eq. (5). A mean value of the exponent $n = 2$ was accepted for all refrigerants mentioned. For all refrigerants the values of parameters B defined in Eq. (5) are shown in Table III. The actual critical values of the refrigerants are presented in Table IV.

Some qualitative features may be observed. Table III shows that the B values rise continuously with an increasing number of H atoms in the molecule of the refrigerant. However, Table III also shows a relation between parameter B and the number of F atoms in the molecule. Parameter B shifts to a higher value monotonously with increasing fluorine number.

The scheme described can be used to present parameter B of a refrigerant with a given hydrogen number as a function of the fluor number only. Furthermore, using this scheme it is possible to predict the B parameter of refrigerants R133a, R124, and R116, expressing it as a function of fluorine number contributions.

Table IV. Critical Constants

Refrigerant	M $(\mathrm{kg \cdot kmol^{-1}})$	T_{cr} (K)	P_{cr} (MPa)	ρ_{cr} $(\mathrm{kg \cdot m^{-3}})$
R113	187.38	487.30	3.414	576.4
R114	170.92	418.90	3.263	581.7
R115	154.47	353.15	3.158	613.1
R116	138.01	292.85	2.883	638.1
R123	152.93	456.94	3.674	550.0
R123a	152.93	457.15	3.732	554.3
R124	136.48	395.65	3.634	560.0
R125	120.02	339.40	3.631	572.0
R132b	134.94	491.15	4.150	509.0
R133a	118.49	427.15	4.050	524.0
R134a	102.00	374.15	4.067	512.3
R142b	100.50	410.25	4.246	459.0
R143a	84.04	346.25	3.811	434.0
R152a	66.05	386.44	4.520	365.0

Therefore parameter B_{124} for R124 (C_2HF_4Cl) was expressed as

$$B_{124} = B_{123} + \Delta B_2 \tag{7}$$

with

$$\Delta B_2 = (B_{125} - B_{123})/2$$

Parameter B_{116} for R116 (C_2F_6) is

$$B_{116} = B_{115} + \Delta B_1 \tag{8}$$

with

$$\Delta B_1 = B_{115} - B_{114}$$

Since the B values for R133a are unknown, we have assumed that $\Delta B_2 = \Delta B_3$ so that the result for R133a ($C_2H_2F_3Cl$) is

$$B_{133} = B_{134} - \Delta B_3 \tag{9}$$

with

$$\Delta B_3 = (B_{125} - B_{123})/2$$

The thermal conductivity is then calculated from Eq. (5) with the densities given in Refs. 7–11.

Tables V–VII show a comparison between the calculated values and the experimental data obtained from Refs. 1 and 3. It is seen that the scheme is capable of reproducing the thermal conductivity of liquid refrigerants with a maximum deviation not exceeding +5%. Not only does this fact confirm the applicability of this scheme, but also it indicates, in relation to our previous work for halocarbons [1], that it is likely to be able to express parameter B as a function of atom contributions.

Table V. Comparison of the Thermal Conductivity Calculated by the Present Method with Recommended Data [1, 3] Near the Saturation Line for Refrigerant R124

T (K)	$T \cdot T_{cr}^{-1}$	ρ_{cal} ($kg \cdot m^{-3}$)	$10^4 \lambda_{cal}$ ($W \cdot m^{-1} \cdot K^{-1}$)	$10^4 \lambda_{ref}$ ($W \cdot m^{-1} \cdot K^{-1}$)	Dev. (%)
230	0.581	1561	892	916	−2.6
250	0.632	1505	829	849	−2.4
270	0.682	1445	764	784	−2.6
290	0.733	1382	699	720	−2.9
310	0.784	1313	631	659	−4.2

Table VI. Comparison of the Thermal Conductivity Calculated by the Present Method with Recommended Data [1, 3] Near the Saturation Line for Refrigerant R133a

T (K)	$T \cdot T_{cr}^{-1}$	ρ_{cal} ($kg \cdot m^{-3}$)	$10^4 \lambda_{cal}$ ($W \cdot m^{-1} \cdot K^{-1}$)	$10^4 \lambda_{ref}$ ($W \cdot m^{-1} \cdot K^{-1}$)	Dev. (%)
190	0.445	1556	1317	1275	2.5
210	0.492	1512	1244	1202	3.5
230	0.538	1467	1171	1130	3.6
250	0.585	1421	1099	1058	3.9
270	0.632	1373	1026	986	4.1
290	0.679	1322	951	914	4.1
310	0.726	1268	875	841	4.1
320	0.749	1239	835	805	3.7

Table VII. Comparison of the Thermal Conductivity Calculated by the Present Method with Recommended Data [12] Near the Saturation Line for Refrigerant R116

T (K)	$T \cdot T_{cr}^{-1}$	ρ_{ref} ($kg \cdot m^{-3}$)	$10^4 \lambda_{cal}$ ($W \cdot m^{-1} \cdot K^{-1}$)	$10^4 \lambda_{ref}$ ($W \cdot m^{-1} \cdot K^{-1}$)	Dev. (%)
180	0.615	1673	848	840	1.0
200	0.683	1588	764	760	0.5
220	0.751	1494	676	680	−0.6
240	0.820	1385	581	600	−3.2

Table VIII. Comparison of the Specific Heat at Constant Pressure Calculated with Experimental Values [12] for Refrigerant R116 Near the Liquid Saturation Line

T (K)	$T \cdot T_{cr}^{-1}$	ρ_{ref} ($kg \cdot m^{-3}$)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)	$C_{p,cal}$ ($J \cdot kg^{-1} \cdot K^{-1}$)	$C_{p,exp}$ ($J \cdot kg^{-1} \cdot K^{-1}$)	Dev. (%)
180	0.615	1673	840	923	920	0.3
200	0.683	1588	760	979	954	2.6
220	0.751	1494	680	1036	1007	2.9
240	0.820	1385	600	1121	1081	3.7
260	0.878	1254	510	1206	1213	−0.6

Table IX. Calculated Values of the Specific Heat at Constant Pressure for Refrigerants R132b and R133a Near the Liquid Saturation Line

T (K)	$T \cdot T_{cr}^{-1}$	ρ_{cal} (kg · m^{-3})	$C_{p,cal}$ (J · kg^{-1} · K^{-1})
		Refrigerant R133a	
270	0.632	1373	1143
290	0.679	1322	1215
310	0.726	1268	1296
320	0.749	1239	1327
		Refrigerant R132b	
300	0.611	1416	1074
310	0.631	1394	1101
320	0.652	1372	1128

It is necessary to mention here that the values of C_p can also be deduced from Eq. (5). The calculation of C_p then follows the procedure to express C_p by

$$C_p = \lambda/(AM^{1/3}\rho) \qquad (10)$$

A calculation of the specific heat at constant pressure requires a value for the product of $AM^{1/3}$.

A procedure similar to the analysis described above was employed to represent the $AM^{1/3}$ product for this family of liquids. Thus for refrigerant R116, $AM^{1/3}$ should be found from the values derived for refrigerants R114 and R115, and for refrigerants R133a and R132b the product $AM^{1/3}$ may be assumed to be equal to the value found for refrigerant R134a.

The results for C_p of R116 are summarized in Table VIII. The results of the calculations on the basis of Eq. (10) for R133a and R132b are presented in Table IX. Comparison with earlier measurements was possible only for R116.

Based on the results of this paper, it is apparent that much further work is required to obtain a correlation between B and $AM^{1/3}$ values found from thermal-conductivity measurements for different systems. Preliminary calculations developed for the thermal conductivity and the specific heat at constant pressure for refrigerants yield interesting results.

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