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Thermal Conductivity of a Wide Range of Alternative Refrigerants Measured with an Improved Guarded Hot-Plate Apparatus[1]

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The thermal conductivity of the refrigerants R22, R123, R134a, R142b, R143a, and R152a has been determined as a function of temperature in the range from 300 to 460 K. Measurements were carried out at atmospheric pressure with an improved guarded hot-plate apparatus. The width of the instrument's gas layer and the temperature difference across the metering section were varied to detect any stray heat transfer. Radiation correction factors were derived from IR absorption spectra. The uncertainty of the measurements is estimated to be 2% at a standard deviation of less than 0.1%. All values are correlated with respect to temperature in the range covered. The equations are found to represent the results with average deviations of 1%. Our data sets are compared with corresponding hot wire results. In contrast to the generally preferred hot wire technique, with its possible electrical and chemical interactions between the wire and the polar refrigerant, there are no such difficulties using a guarded hot-plate apparatus. Our data sets may thus contribute to the discussions on discrepancies in thermal conductivity values from various authors using hot wire as one particular method.

KEY WORDS: guarded hot-plate apparatus; polar refrigerant; R22; R123; R134a; R142b; R143a; R152a; thermal conductivity.

1. INTRODUCTION

Thermal conductivity λ is the most important thermophysical transport property of the hydrochlorofluorocarbons (HCFC) substitutes, especially when they are used as blowing agents. The growing industrial demand for reliable λ values of these new fluids has prompted a worldwide measurement program leading to a number of reports. Almost all working groups

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use the currently predominating instrument, the transient hot wire cell, indicating an uncertainty of at most 1%. It is therefore somewhat alarming that there are discrepancies between various data sets which exceed 10%. Discussions on this unexpected observation have led to three possible systematic errors: the high dipole moment of the fluids under test, radiative heat transfer, and deviations from prescribed boundary conditions. (For further discussion of these discrepancies, see the papers by Assael et al. in the present Proceedings.)

The present paper deals with the thermal conductivity of the six refrigerants R22, R123, R134a, R142b, R143a, and R152a that are the most promising alternatives from an ozone depletion potential (ODP) and global warming potential (GWP) point of view. Data were taken at 0.1 MPa and temperatures from 298 to 463 K with a guarded hot-plate apparatus. Since this instrument has a sample volume of vanishing electrical potential and works at thermal equilibrium only, there may be no such errors as mentioned above. IR absorption spectra of the refrigerants helped to detect and correct for any radiative heat transfer.

2. EXPERIMENTS

Our guarded hot-plate apparatus (Fig. 1) has been described in detail elsewhere [1, 2]. It is designed exclusively for the use with fluids, and over many years of operation several improvements to it have been introduced, regarding particularly heat losses. The cylindrically shaped gap is bounded by the upper hot plate ($\phi = 100$ mm) and the lower cold plate ($\phi = 215$ mm). The gas not only fills this metering section but is extended to the whole guard section. This feature helps to prevent convective energy losses. The cold plate is fluid-cooled, while the hot plate and the guard are electrically heated. The temperature differences between the hot plate and the guard heaters are generally less than 0.01 K; the difference between the center and the edge of each respective surface does not exceed 0.002 K. The thermal conductivity λ at the sample's mean temperature T_m is determined from Fourier's linear law:

$$\lambda(T_m) = \frac{P}{A}\left(\frac{\Delta T}{d}\right)^{-1} \tag{1}$$

in which A gives the gas layer area and d(0.5,..., 2.0 mm) the height, which is adjusted with glass spacers ($\lambda_S = 0.596\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$). ΔT is the temperature drop. P, the electrical power $U*I$, fed to the hot-plate heater, equals the rate of heat flow through the gas layer. Since only measurements of power and the base units length and temperature are required, this instrument is an absolute one.

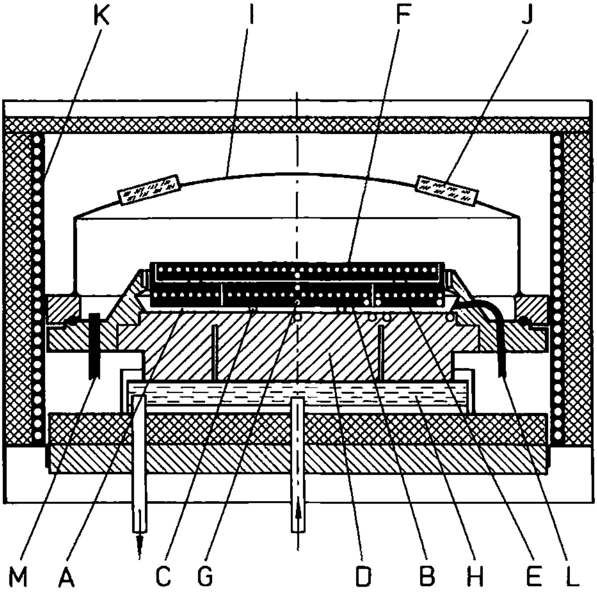

Fig. 1. Parallel-plate thermal conductivity apparatus for fluids. A, specimen (gap); B, heating unit; C, glass spacer; D, cooling unit; E, guard ring; F, guard plate; G, thermocouple (copper–constantan); H, thermostat volume; I, cap; J, glass window; K, protecting cap; L, liquid inlet; M, evacuation pipe.

It takes about 6 h to reach the steady state of the instrument and the originally pure gas may be contaminated by air. Just before a measurement the instrument is therefore flushed with preheated pure gas and refilled. Every experimental value is determined from six runs on the gas, three at a gap of $d = 0.5$ and another three at $d = 1.0$ mm to detect any natural convection. The corresponding mean values of the measurand λ for both these layers is corrected for any significant systematic error following [2]

$$P = U \cdot I - \sum P_V + P_X \tag{2a}$$

$$\Delta T = \Delta T_{ex} - \Delta T_m \tag{2b}$$

Estimates of the temperature correction ΔT_m to the measured temperature ΔT_{ex} and the correction factors for significant stray heat flows, P_V and P_X, at $\Delta T = 5$ K and $d = 0.5$ mm are listed in Table I. The radiative heat transfer, P_{VR}, was evaluated with the aid of infrared spectra to find potential bands of transmission. The temperature jump effect between the plate surfaces and the gas layer (at most 0.3%) was estimated according to [3].

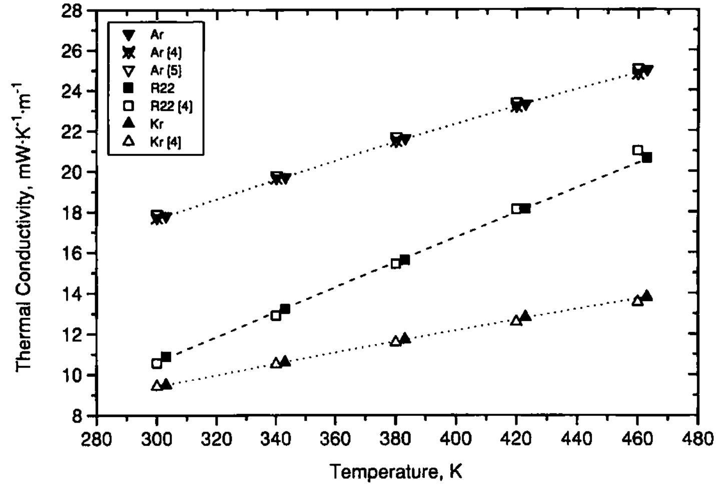

Fig. 2. Thermal conductivity for argon, krypton, and R22.

The values for the nickel–ethane system were used. That is why, first, the hot and cold plates are nickel coated and, second, there are no specific data of the fluids under test available from literature.

Prior to the measurements on the selected fluids, the reliability and precision of the apparatus were validated. Test measurements were carried out on krypton, argon, and R22 over the instrument's entire temperature

Table I. Maximum Temperature Correction (K) and Maximum Absolute Correction Factors (%) for Significant Stray Heat Flows Between Heater and Guard Ring, P_{V1}; Between Heater and Guard Plate, P_{V2}; Through Glass Spacers, P_{VS}; Between Heater and Cold Plate by Radiation, P_{VR}; and Due to the Thermocouples, P_X ($d = 0.5$ mm, $\Delta T = 5$ K)

Correction gas	P_{V1}	P_{V2}	P_{VS}	P_{VR}	P_X	ΔT_m
Ar	0.05	0.2	6.4	2.7	0.21	0.07
Kr	0.05	0.2	12	5	0.10	0.04
R22	0.04	0.3	6.5	1.2	0.15	0.05
R123	0.02	0.3	6.6	1.7	0.25	0.05
R134a	0.06	0.2	7.5	1.7	0.76	0.04
R142b	0.03	0.1	7.5	3.9	0.19	0.05
R143a	0.03	0.1	7.4	2.9	0.23	0.05
R152a	0.02	0.1	5.1	0.7	0.1	0.05

range. The noble gases (purity, 99.99%) were chosen because of their individual thermal conductivities, which, taken together, cover the expected conductivity range of the fluids under test and are precisely known. The third reference fluid, R22 (purity, 99.997%), is a widely analyzed working fluid and, thus, can easily serve as a laboratory reference for measurements on other refrigerants. Representative results for the three gases are given in Fig. 2. The overall uncertainty is estimated to be 2.1% for Kr, 1.2% for Ar, and 2% for R22. Deviations from the recommended values of Touloukian et al. [4] are within 0.5% for Ar, 1% for Kr, and 3% for R22. For Ar there is a very good agreement (0.5%) with the data of the IUPAC correlation [5] and two hot wire results [6, 7] on this gas near 300 K (0.6%). The latter result may be meaningful concerning the discussions about the hot wire results on the new refrigerants.

The stated purity of the test gases was 99.997% for R22, 99.69% for R123, 99.99% for R134a and R152a, and 99.95% in the cases of R142b and R143a.

3. RESULTS

The gaseous thermal conductivity measurements were performed at several mean temperatures within the range from 298 to 463 K at 0.1 MPa. All results listed in Table II are correlated by a polynomial of temperature:

$$\lambda(T, p=0.1\ \mathrm{MPa}) = a_2 T^2 + a_1 T + a_0 \tag{3}$$

Table II. Experimental Thermal Conductivities ($\mathrm{mW \cdot K^{-1} \cdot m^{-1}}$) at Different Mean Temperatures T_m (K)

	Gas							
T_m (K)	Ar	Kr	R22	R123	R134a	R142b	R143a	R152a
298						12.49	12.3	
303	17.77	9.51	10.89		13.76			14.91
308				9.77			13.00	
318				10.41		13.94		
343	19.74	10.63	13.21	11.73	16.92	15.79	15.70	19.45
368				13.14				
383	21.58	11.70	15.61		20.39	18.79	18.73	22.81
393				14.56				
418				15.99		21.40	21.40	
423	23.32	12.85	18.12		23.96			25.92
443				17.53				
463	25.12	13.72	20.64	18.61	27.58			30.40

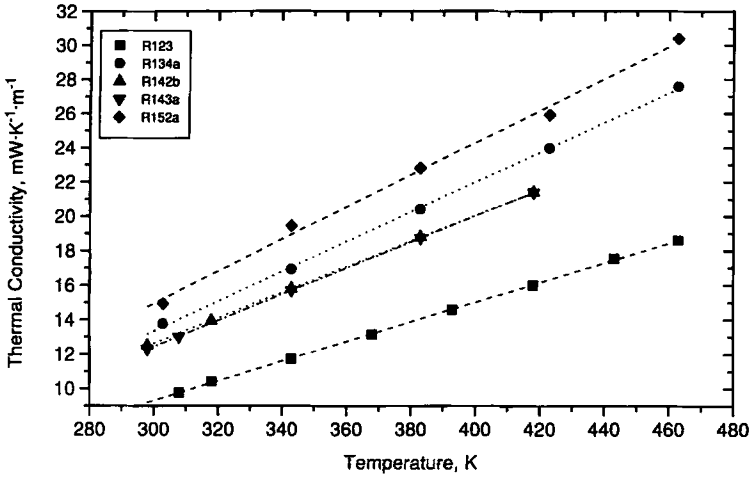

Fig. 3. Thermal conductivity for R123, R134a, R142b, R143a, and R152a.

While the conductivity of each refrigerant under test can be fitted to a linear function ($a_2 = 0$), this property of the noble gases is represented best by a second-order polynomial. The corresponding regression coefficients of Eq. (3) are listed in Table III together with the correlation coefficient r^2, the standard deviation σ (95%), and additional information on the range of application. The deviation between any data point and its correlation does not exceed 1%. Figure 3 shows the thermal conductivity as a function of temperature for the five fluids.

Comparing our correlated hot-plate data, λ_{calc}, with those obtained from hot wire measurements, λ_{exp}, we found results that correspond in temperature and pressure only for R123, R134a, and R152a. The percentage deviations were calculated through the relation $(\lambda_{\text{exp}} - \lambda_{\text{calc}})/\lambda_{\text{calc}} \cdot 100$

Table III. Coefficients in Eq. (3) with λ ($\text{mW} \cdot \text{K}^{-1} \cdot \text{m}^{-1}$) and T (K); Range of Applicability, 300–460 K

	Gas							
Coeff.	Ar	Kr	R22	R123	R134a	R142b	R143a	R152a
a_2	$-1.96 * 10^{-5}$	$-1.88 * 10^{-5}$	0	0	0	0	0	0
a_1	0.061	0.041	0.061	0.057	0.087	0.075	0.076	0.094
a_0	1.184	−1.196	−7.68	−7.78	−12.68	−9.78	−10.52	−13.16
σ	0.04%	0.07%	0.06%	0.05%	0.13%	0.04%	0.07%	0.37%
r^2	0.9999	0.9992	0.9997	0.9997	0.9993	0.9999	0.9997	0.9953

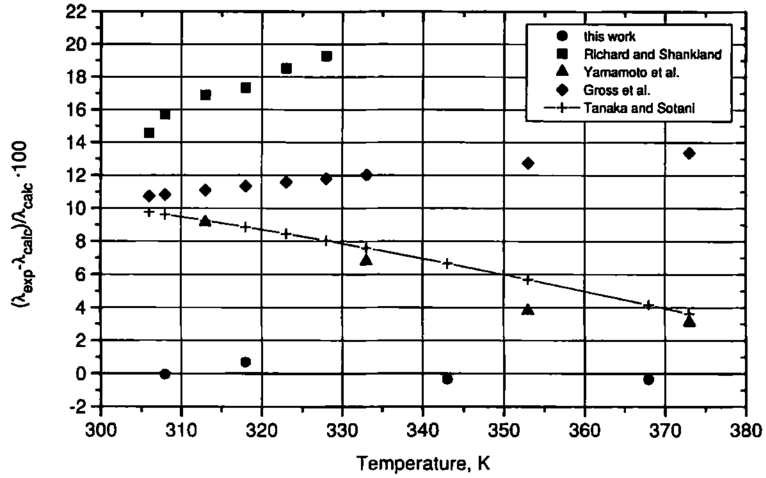

Fig. 4. Comparison of presents steady-state thermal conductivity data for R123 with corresponding transient hot wire data.

and plotted against temperature between 300 and 380 K (Figs. 4–6). The results are indeed somewhat alarming: Most of the cited data sets are outside a range of +5% and spread with increasing temperature. For R123 and R134a most of the data are systematically higher than ours, in one single case [10] even up to 40% at 373 K. The cited results are lower for R152a.

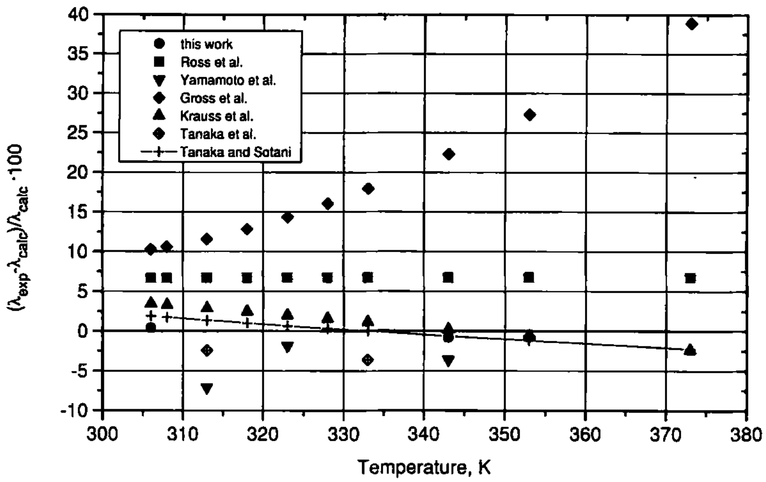

Fig. 5. Comparison of present steady-state thermal conductivity data for R134a with corresponding transient hot wire data.

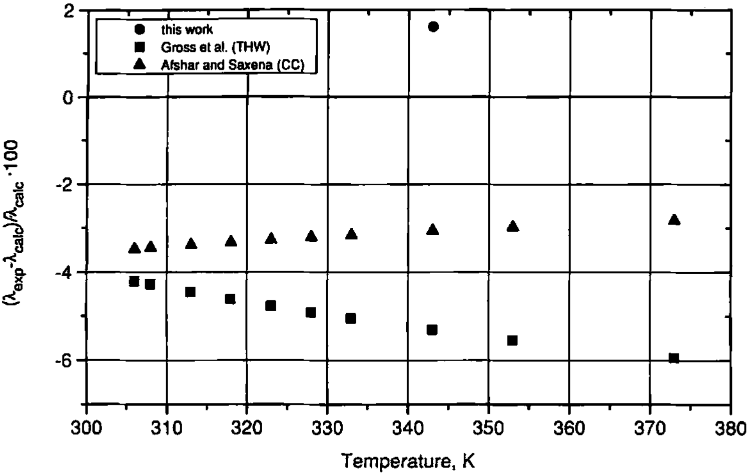

Fig. 6. Comparison of present steady-state thermal conductivity data for R152a with corresponding transient hot wire data and thermal conductivity column instrument data.

For R123 (Fig. 4) it seems that the data taken from Refs. 8–11 start at 300 K, with nearly the same deviation of about 10% from ours. Then the data sets of Richard and Shankland [8] and Gross et al. [10] increase with temperature to about 20% and 12%, respectively, at 328 K and Yamamoto and co-workers' [9] data and the correlated set of Tanaka and Sotani [11] decrease to 3% at 373 K.

In the case of R134a there is a spread from about +5% at 300 K to −2.5 or nearly 40% at the highest plotted temperature. Nevertheless, the correlation of Tanaka and Sotani [11] as well as the data of Krauss et al. [13] and Tanaka et al. [14] lie within a range of ±4% around our correlation. In the general scheme of spreading data the set of Ross et al. [12] is an exception: Its deviation is nearly constant at 6.7%.

For R152a we found hot wire results only from Gross et al. [10]; however, there is a set of data measured by Afshar and Saxena [15] with the (relative) thermal conductivity column instrument. These compare best with ours. They are found within a range of about 3% tending slightly to closer values with increasing temperature.

4. CONCLUSION

The thermal conductivity of six selected refrigerants has been determined with a guarded hot-plate apparatus. Compared with representative hot wire results, there are, in some cases, large deviations as well as a wide spread in the data with increasing temperature. This cannot be explained simply by electrical or chemical interactions between the hot wire and the fluid.

At the moment nearly all measurements of the thermal conductivity of alternative refrigerants have been carried out with the transient hot wire instrument and this has led to serious discrepancies among them. To broaden the basis of the current discussion it would be helpful to improve the reproducibility of data. This can be done by using steady-state methods in addition to the transient hot wire technique.

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