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Measurements of the Thermal Conductivity of Refrigerants in the Vapor Phase[1]

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Measurements of the thermal conductivity of refrigerants R124, R125, and R134a in the vapor phase are presented. The measurements, performed in a newly developed transient hot-wire instrument, cover a temperature range from 273 to 333 K and a pressure range from about atmospheric up to below the saturation pressure. A finite-elements program developed allowed the reexamination of the major corrections employed in the analysis of the results. The uncertainty of the reported values is estimated to be better than ±1%. Comparisons with measurements of other investigators along the saturation line show a lack of reliable thermal conductivity data in the vapor phase for these compounds.

KEY WORDS: refrigerants; R124; R125; R134a; transient hot wire; vapor phase.

1. INTRODUCTION

During the last 4 years, a program of research aimed at measuring the thermal conductivity and viscosity, in the liquid and vapor phases of some of the new environmentally friendly refrigerants, has been undertaken. This paper, together with the companion paper on vapor-phase viscosity measurements [1], presents our latest measurement of the thermal conductivity of refrigerants R124, R125, and R134a, in the vapor phase and hence, in essence, concludes this program of work. The refrigerant

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1-chloro-1,2,2,2-tetrafluoroethane (R124) and pentafluoroethane (R125) are considered as possible replacements for R114 and R502, respectively, while tetrafluoroethane (R134a) has already been employed as a replacement of R12. It is, however, interesting that although many investigators have lately been involved in the measurement of the transport properties of these fluids, still the situation is nowhere as clear as, for example, in the case of the transport properties of the lower *n*-alkanes. It is shown in this paper that the discrepancies between various authors still exceed, by up to an order of magnitude, the claimed uncertainties.

The measurements were carried out in the vapor phase in the temperature range 273 to 333 K and a pressure range from about atmospheric up to below the saturation pressure.

2. EXPERIMENTS

As has clearly been stated elsewhere [2], the main problem in general in dealing with refrigerants is that most of them are polar fluids and act as very good solvents. Partial decomposition has also been observed in the presence of platinum, a material often employed for the wires in transient hot-wire instruments. Furthermore, in the specific case of low-pressure measurements performed with transient hot-wire instruments in the vapor or, more generally, in the gas phase, there are extra difficulties associated with the larger values of the thermal diffusivity encountered. Such large values of thermal diffusivity mean that the heat wave moves much faster in the gas toward the physical outer boundary surrounding the wire source. To overcome the latter problem, this physical boundary must be moved farther away, or equivalently the diameter of the wire sensor employed must be smaller.

Taking into consideration all the aforementioned propositions, in the present arrangement, tantalum wires were employed as the sensors. Upon anodization of tantalum, tantalum pentoxide, an electrical insulator, is formed on its surface. Hence the fluid is not in electrical contact with the heated wire. The tantalum wire employed was part of a specially made sample, kindly supplied by the National Engineering Laboratory, U.K., and had a diameter of 15.11 μm. To move farther away from the outer boundary, the diameter of the wire enclosure was increased from 10 to 12 mm. These precautions were found to be adequate.

Therefore, in the present cell, two tantalum wires were employed as both the heating source and the temperature sensor. The wires were mounted in a stainless-steel cell, composed of two cylindrical compartments formed by machining two cylindrical holes centered on the split diameter of a cylinder and parallel to its axis. One half carries the four wire supports and is, in essence, supported by the top plate of the pressure vessel. Similarly to the liquid-phase instrument [3], constant tensioning and verticality of the wires were achieved by a tantalum weight spot welded at the bottom of each wire. All electrical connections to the wires and leads through the pressure vessel were made out of tantalum and were all anodized together with the wires *in situ*. Thin PTFE tubing ensured that, in the places of support, the tantalum wire was not in electrical contact with the cell.

For these series of measurements, the same pressure-vessel arrangement for the liquid-phase measurements [3] was employed and placed in a closed, insulated 60-dm^3 water + ethylene glycol bath (60%, by weight, ethylene glycol).

The calibration of the wires to determine their temperature coefficient of resistance was carried out *in situ* over the temperature range 240 to 350 K and was found to be in full agreement with our previous reported one [3], that is,

$$R(T) = R(273.15)[1 + 3.4345 \times 10^{-3}(T - 273.15) - 4.8844 \times 10^{-7}(T - 273.15)^2] \tag{1}$$

The wire-resistance change, and consequently the temperature rise of the wires, is recorded by incorporating the two wires in the two arms of a Wheatstone-type computer-driven automatic bridge [3, 4]. Finally, to ensure stability of the oxide layer on both wires, a bias was applied to them, by means of a DC supply, so that the wires were always positive with respect to the vessel, which in itself was maintained at ground potential. This arrangement, although necessary for measurements in the liquid phase, in the case of the vapor-phase measurements was only precautionarily employed.

To check the continuing good operation of the instrument, the thermal conductivity of argon was measured over the whole temperature and pressure range. The measurements were found to agree with established literature values [5], well within ±0.5%. The thermal conductivity of argon was also measured before and after every fluid as a further check of continuing good operation. Considering all possible errors, the uncertainty of the present measurements is estimated to be much better than ±1%, while the reproducibility of the present instrument was found to be better than ±0.3%.

The refrigerant samples of R124 and R125 were supplied by Du Pont de Nemours International S.A. at purities better than 99.95% for both fluids. The R134a sample was provided by ICI Chemicals Polymers Ltd. with a purity of better than 99.9%. All purity values were confirmed by chromatographic analysis. It should also be pointed out that the R134a sample was part of an international round-robin project [6] currently taking place under the auspices of the Subcommittee on Transport Properties of Commission I.2 on Thermodynamics of IUPAC.

3. ANALYSIS OF DATA

In the transient hot-wire technique, a thin and straight wire immersed in an isotropic gas and initially at equilibrium with it is subjected, at time $t = 0$, to a step change in the voltage applied to it. Following this change, the wire appears as a line source of heat, while the time evolution of the temperature of the wire is determined by the thermal conductivity of the gas. The ideal line source solution of the Fourier heat conduction equation predicts [7] that the thermal conductivity is obtained from the slope of the straight line of the temperature rise versus the logarithm of the time.

Two corrections were proposed to the real experimental situation to follow accurately the aforementioned ideal model. The first one, being more important at short times, is related to the finite heat capacity of the wires. The second one, referring to longer times, deals with the necessary physical presence of an outer boundary. For both these corrections approximate analytic expressions have been put forward [7].

The transient hot-wire technique has been employed successfully for the measurement of the thermal conductivity of liquids and gases, the only exception being the low-pressure gas region, where values higher than expected were always obtained.

In the case of the present low-pressure vapor thermal-conductivity measurements, the aforementioned corrections were carefully reexamined. Therefore, in both cases, instead of the existing approximate solutions [7], more accurate ones were adopted. In the case of the heat-capacity correction, the full solution to the problem given by Carslaw and Jaeger [8, p. 347] was preferred. Hence, the described semiinfinite integral, whose integrand contained Bessel functions, was transformed into a definite one and computed numerically using the 3/4 Simpson's method. In the case of the outer boundary correction, instead of the asymptotic solution usually adopted [7], the more complex one given by Carslaw and Jaeger [8, p. 332] was also employed. Consequently, the correction was based on the roots of the Bessel-functions equation, calculated for the exact geometry employed here. For this present chosen geometry, employing the full solution of the outer boundary correction had almost no effect.

However, employing the full solution for the heat-capacity correction had an effect on the calculated value of the thermal conductivity, which was in the region of 1–2%

To test that the resulting solution represented the experimental setup well, a finite-elements program was constructed, solving the Fourier equation not only in the fluid region, but also in the wire region. This meant that the program took into consideration (a) the finite radius of the wire and (b) the finite properties of the wire, and, as a consequence, the heat flux used in the wire to increase its temperature. In addition, the imposition of boundary conditions at the outer cell circumference was accomplished by imposing the existence of a real isothermal wall at a finite distance, and not at infinity. The experimentally obtained temperature rise at distinct time intervals was input to the program. After an iterative process, the calculated thermal conductivity of the vapor was found to agree fully with the previously described analysis.

To test the two approaches, thermal-conductivity measurements on argon were performed from 3 down to 0.1 MPa. In all measurements, both the presently described approach and the finite-elements program were found to produce the same thermal conductivity values, with the temperature-rise versus the logarithm of the time lines always being linear. It was hence concluded that performing the two corrections in the described manner certainly solved some of the low-pressure discrepancies. Nevertheless, below 0.2 MPa, where the thermal diffusivity of argon is about $2 \times 10^{-5}\ \mathrm{m \cdot s^{-1}}$, the measured thermal conductivity of argon was found to differ by 1.5% from the known value. This difference was eliminated at about 1 MPa, where the thermal diffusivity of argon is about $2 \times 10^{-6}\ \mathrm{m \cdot s^{-1}}$, that is, 10 times smaller, and hence all corrections become less important. Therefore although some progress has been made, further investigation is still to be carried out here, especially when the thermal diffusivity is larger then $10^{-5}\ \mathrm{m \cdot s^{-1}}$.

In the special case of the thermal conductivity measurements of the vapor refrigerants considered in this work, the thermal diffusivity even at the lowest pressures reported is never larger than $3.5 \times 10^{-6}\ \mathrm{m \cdot s^{-1}}$. Hence, according to the aforementioned discussion, it is believed that this "low-pressure" effect does not influence the present measurement.

4. RESULTS

The thermal-conductivity measurements were performed from just above the atmospheric pressure up to 2–3 atm below the saturation pressure, along the 273.15, 283.15, 293.15, 303.15, 313.15, 323.15, and 333.15 K isotherms (except in the case of R125, where they were restricted to 313.15 K). As already mentioned, the thermal conductivity of argon was measured before and after each fluid, to ensure the continuing good operation of the instrument.

To calculate the thermal conductivity of R124, the density measurements of Kubota et al. [9] were employed. These values cover a temperature range of 298–423 K. Since no other experimental density measurements of vapor R124 that cover a wider temperature range could be found in the literature, the equation proposed by Kubota was extrapolated to 273 K. No density measurements could be found in the literature for R125 corresponding to the temperature and pressure ranges

Table I. Thermal Conductivity of Vapor R124

P (MPa)	T (K)	$\lambda(T, P)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\rho(T_n, P)$ $(\mathrm{kg \cdot m^{-3}})$	$\lambda(T_n, P)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
		$T_n = 283.15$ K		
0.14	282.88	10.48	8.446	10.52
		$T_n = 293.15$ K		
0.28	293.40	11.58	17.00	11.56
0.13	293.43	11.41	7.516	11.37
		$T_n = 303.15$ K		
0.30	303.26	12.36	17.52	12.35
0.16	303.05	12.21	8.980	12.22
		$T_n = 313.15$ K		
0.31	312.68	13.04	17.40	13.08
0.18	313.07	12.97	9.786	12.99
		$T_n = 323.15$ K		
0.34	323.32	13.80	18.47	13.78
0.19	323.16	13.67	9.993	13.68
		$T_n = 333.15$ K		
0.59	333.24	14.59	32.61	14.59
0.33	333.13	14.40	17.23	14.41
0.18	333.11	14.32	9.137	14.31

of the present work and thus the densities were calculated from the equation of state proposed by Outcalt and McLinden [10]. Tillner-Roth and Baehr [11] measured the density of R134a with an uncertainty of about ±0.03% and within a temperature range of 293–453 K. This equation was also extrapolated to cover the temperature range of the present thermal conductivity measurements.

The results of the thermal-conductivity measurements of the three refrigerants are presented in Tables I, II, and III. Values corrected to nominal temperatures (employing a surface regression analysis) are also given.

Table II. Thermal Conductivity of Vapor R125

P (MPa)	T (K)	$\lambda(T, P)$ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	$\rho(T_n, P)$ ($\mathrm{kg \cdot m^{-3}}$)	$\lambda(T_n, P)$ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
		$T_n = 273.15$ K		
0.57	272.98	12.46	34.64	12.48
0.35	272.90	12.28	20.02	12.28
0.16	273.02	12.23	8.748	12.24
		$T_n = 283.15$ K		
0.77	283.19	13.60	46.69	13.58
0.44	283.23	13.13	24.51	13.11
0.16	283.20	12.99	8.404	12.97
		$T_n = 293.15$ K		
1.09	293.16	14.92	67.84	14.92
0.69	293.21	14.12	38.68	14.10
0.44	293.17	13.86	23.41	13.84
0.17	293.16	13.69	8.610	13.70
		$T_n = 303.15$ K		
1.13	303.28	15.52	66.22	15.50
0.84	303.23	14.96	46.11	14.95
0.61	303.00	14.63	32.03	14.65
0.20	303.15	14.45	9.809	14.45
		$T_n = 313.15$ K		
1.05	313.08	15.73	56.93	15.74
0.79	313.11	15.40	40.88	15.37
0.18	313.07	15.22	8.496	15.22

Table III. Thermal Conductivity of Vapor R134a

P (MPa)	T (K)	$\lambda(T, P)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\rho(T_n, P)$ $(\mathrm{kg \cdot m^{-3}})$	$\lambda(T_n, P)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
		$T_n = 273.15$ K		
0.22	272.99	11.50	10.56	11.53
		$T_n = 283.15$ K		
0.30	283.14	12.48	14.09	12.48
0.17	283.19	12.31	7.692	12.28
		$T_n = 293.15$ K		
0.54	293.56	13.60	25.95	13.55
0.14	293.17	13.09	6.043	13.11
		$T_n = 303.15$ K		
0.60	303.04	14.29	27.78	14.31
0.36	302.97	14.04	15.69	14.06
0.17	303.11	13.99	7.112	13.97
		$T_n = 313.15$ K		
0.70	313.22	15.15	31.54	15.14
0.45	313.30	14.91	19.16	14.88
0.15	313.15	14.82	6.031	14.81
		$T_n = 323.15$ K		
1.00	323.25	16.40	45.87	16.38
0.67	323.29	15.86	28.54	15.84
0.39	323.14	15.62	15.76	15.62
0.13	323.09	15.59	5.035	15.61
		$T_n = 333.15$ K		
1.30	333.45	17.80	60.30	17.76
1.00	333.40	17.12	43.35	17.10
0.65	333.41	16.62	26.39	16.60
0.35	333.40	16.45	13.54	16.42

5. DISCUSSION

The thermal-conductivity values given in Tables I, II, and III were employed to extrapolate to saturation conditions. The values obtained are presented in Table IV. For comparison purposes, these values at saturation were fitted to an equation of the form

$$\frac{\lambda_S}{\lambda_S(298.15)} = \sum_{i=0}^{3} a_i \left(\frac{T}{298.15}\right)^i \tag{2}$$

Table IV. Thermal Conductivity of Vapor R124, R125, and R134a at Saturation

T_s (K)	P_s (MPa)	$\rho(T_s, P_s)$ ($kg \cdot m^{-3}$)	$\lambda(T_s, P_s)$ ($mW \cdot m^{-1} \cdot K^{-1}$)
	R124		
283.15	0.234	14.64	10.67
293.15	0.327	20.24	11.62
303.15	0.445	27.41	12.49
313.15	0.593	36.56	13.29
323.15	0.775	48.11	14.07
333.15	0.996	62.66	14.85
	R125		
273.15	0.671	41.74	12.63
283.15	0.909	57.24	13.87
293.15	1.206	77.58	15.22
303.15	1.571	104.5	16.73
313.15	2.014	141.3	18.64
	R134a		
273.15	0.293	14.43	11.70
283.15	0.415	20.23	12.68
293.15	0.572	27.77	13.60
303.15	0.770	37.49	14.59
313.15	1.016	50.02	15.75
323.15	1.317	66.19	17.19
333.15	1.680	87.23	18.92

In Table V, the required constants are given together with the standard deviation of the three fits. The maximum standard deviation is ±0.07%.

Equation (2) can be employed for the comparison of thermal-conductivity values produced by other investigators. This comparison is presented in Fig. 1. It should be noted that, due to the lack of experimental

Table V. Coefficients of Eq. (2)

Fluid	$\lambda_s(298.15)$ ($mW \cdot m^{-1} \cdot K^{-1}$)	a_0	a_1	a_2	a_3	σ (%)
R124	12.06	−15.043	41.146	−36.294	11.192	±0.07
R125	15.93	−34.067	107.48	−112.62	40.207	±0.06
R134a	14.09	−26.815	82.782	−84.228	29.260	±0.07

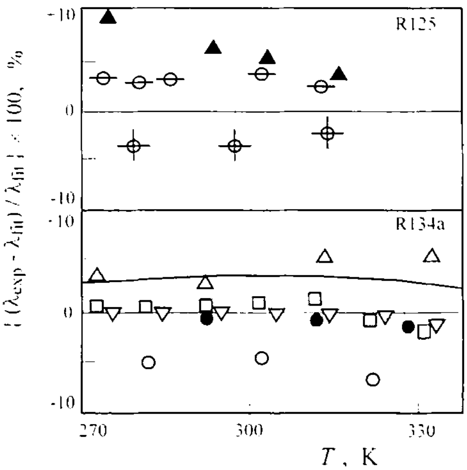

Fig. 1. Percentage deviations of the thermal conductivity measurements of R125 and R134a along the saturation line, from Eq. (2). (⊖) Tsvetkov et al. [12]; (⊕) Tanaka et al. [13]; (▲) Gross and Song [14]; (▽) Ueno et al. [15]; (●) Tanaka et al. [16]; ( ) Yamamoto et al. [17]; (□) Laesecke et al. [18]; (△) Gross et al. [19]; (- -) Krauss et al. [20].

thermal-conductivity data for R124, no comparison can be made and so R124 is not included in this figure. It should also be pointed out, that only measurements taking place in the last 5 years are included in Fig. 1.

In the case of the thermal conductivity of refrigerant R125 in the vapor phase, Tsvetkov et al. [12] employed a steady-state coaxial-cylinders instrument calibrated with R11 and R12. The values, obtained near saturation with a quoted uncertainty of ±2–3%, agree well with these presented here. In the same year, 1994, Tanaka et al. [13] employed a two-platinum wire transient hot-wire instrument, on a relative basis, calibrated with nitrogen and argon. Although a ±1% uncertainty is quoted, the extrapolated-to-saturation values deviate from the present ones by up to −4%. An even larger deviation, +10%, is observed between the present values and the extrapolated-to-saturation measurements of Gross and Song [14] also performed in 1994. Gross and Song employed, on a relative basis, a two-platinum wire transient hot-wire instrument, with a quoted uncertainty of ±2.0%. Hence, in the case of the thermal conductivity of

R125, although the three investigators presented here all performed their measurements during the last 2 years with a quoted uncertainty of about ±2%, the scan between their data extends up to 14%.

In the case of R134a, more measurements do exist in the literature. Ueno et al. [15], in 1991 employed a transient hot-wire instrument for the measurement, on a relative basis, of the thermal conductivity very near the saturation line, with a quoted uncertainty of about ±1%. These measurements are in excellent agreement with the present values. In the same year, Tanaka et al. [16] employed a steady-state coaxial cylinder method, on a relative basis, for the measurement of the thermal conductivity of R134a. The instrument was calibrated with monatomic gases and a ±2% uncertainty was quoted. These extrapolated-to-saturation values were also found to be in excellent agreement with the present ones described by Eq. (2). However, the same group, in 1993, published new measurements [17] performed in a two-tantalum wire transient hot-wire instrument, with an improved uncertainty of ±1%. These new values, being much lower than their previous ones, were found to differ by the present ones up to ±6%. Transient hot-wire instruments with platinum wires were also employed by Laesecke et al. [18] and Gross et al. [19]. Although the extrapolated-to-saturation values of Laesecke et al. [18] agree excellently with the present set, the values of Gross et al. [19] are higher than those of all other investigators, up to 7% from the present set. In the same figure, the recent correlation of Krauss et al. [20], based on critically evaluated data, covering the whole fluid range with an uncertainty of about ±4%, is also shown. The present measurements are in good agreement with the values produced by this correlation.

It should finally be pointed out that, although the comparison was made under saturation conditions, measurements performed in the vapor phase at pressures other than saturation conditions follow a very similar pattern.

6. CONCLUSION

New measurements of the thermal conductivity of R124, R125, and R134a were presented. The measurements were performed with a transient hot-wire instrument with two 15.11 μm-diameter tantalum wires, with an estimated uncertainty of ±1% and a reproducibility of better than ±0.3%. The results that refer to the saturation boundary, fitted to simple polynomials, showed the lack of reliable vapor-phase thermal-conductivity values.

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