International Journal of Thermophysics, Vol. 14, No. 2, 1993

Thermal Conductivity of R134a and R141b Within the Temperature Range 240–307 K at the Saturation Vapor Pressure

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Received December 29, 1992

New, absolute values of the thermal conductivity of two refrigerants, R134a and R141b, in the liquid phase at saturation are reported. The measurements have been performed in transient hot-wire instruments making use of electrically insulated tantalum wires within the temperature range 240–307 K. The results are estimated to have an accuracy of ±1%.

KEY WORDS: R134a; R141b; refrigerants; thermal conductivity.

1. INTRODUCTION

Early measurements of the thermal conductivity of some environmentally acceptable refrigerants in the liquid phase revealed significant discrepancies from each other [1]. The majority of these measurements was made with the transient hot-wire technique, but even so, the discrepancies reported have often been rather greater than the uncertainty claimed by the authors. Since the first measurements on R134a were reported [2, 3], it has been recognized that the polarity of the liquid refrigerants requires either that additional measures are taken in an experiment with bare platinum wires [2, 4] or that insulated wires are employed. In addition, it is possible that significant radiative heat transfer may play a role at elevated temperatures [5, 6]. In this work, we report on measurements of the thermal

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0195-928X/93/0300-0173$07.00/0

conductivity of liquid R134a and R141b within the temperature range 240 to 307 K at saturation carried out to enhance the preliminary results reported earlier [2].

2. EXPERIMENTS

The thermal conductivity measurements have been performed in the transient hot-wire instrument described elsewhere [7]. However, owing to the polar nature of the materials studied here and the difficulties encountered earlier [2], the hot-wire cells were, on this occasion, equipped with tantalum wires with a nominal diameter of 25 μm. A detailed description of these cells and their method of assembly is given in an earlier paper [8]. It suffices here to record that the wires were electrially insulated from the test fluid by means of an anodic coating of tantalum pentoxide deposited *in situ.*

During the course of the measurements reported here, two completely different sets of hot wires were employed. The cells containing the wires were those used for measurements on methanol and water [9, 10]. It will be shown later that the two sets of data obtained for R134a in the two independently assembled cells are entirely consistent. In addition, a check measurement of the thermal conductivity of normal pentane was performed for each wire assembly in order to provide independent confirmation of the absolute values of the thermal conductivity determined in the present work. This material was chosen, in place of the more conventional reference materials [11], owing to the ease with which it can be removed from the pressure vessel by evacuation. Following completion of all the measurements, a further check measurement of the thermal conductivity of water was carried out with the final set of hot-wire cells using a different pressure vessel. This procedure allows a direct comparison of the result for water with standard reference data [11]. For all of these measurements, the representation of the resistance-temperature characteristics for tantalum wires given by Assael *et al.* [12] was employed.

The working equations for the transient hot-wire method and, in particular, the specific corrections necessary to account for the effects of the insulating layer have been given in detail elsewhere [13]. All of the corrections contributing more than $\pm 0.01\%$ to the temperature rise of the wire have been applied consistently. The overriding demand of the theory of the method is that the corrected temperature rise of the wire should be a linear function of the logarithm of time. Only if such linearity can be demonstrated is it possible to assert that the practical instrument operates in accordance with the theory of it. Accordingly, Fig. 1 plots the deviations of the measured and corrected temperature rise, determined in a run with

R134a in the saturated liquid phase at a temperature of 273 K, from the best linear fit to the data. It can be seen that the maximum deviation amounts to one of 0.06%, which is commensurate with the combined uncertainty in the temperature rise and time measurements. Furthermore, there is no evidence of any systematic curvature, indicating the absence of any effects from radiative transmission of heat [14]. For all the runs reported here, the performance of the instrument is comparable with that contained in Fig. 1.

The samples of R134a and R141b were supplied by ICI, whereas the sample of normal pentane was supplied by the Aldrich Chemical Company. The purity of the R134a as supplied was confirmed to be in excess of 99.9%, as was that of the normal pentane. However, the purity of R141b was not as high, being better than 99.6%. For this reason, the uncertainty ascribed to the data for R141b is greater as a result of an estimate of the likely effect of the impurities upon the property. For both fluids, samples taken from the cells after measurement were again analyzed. There was no evidence of any change in the level of impurities.

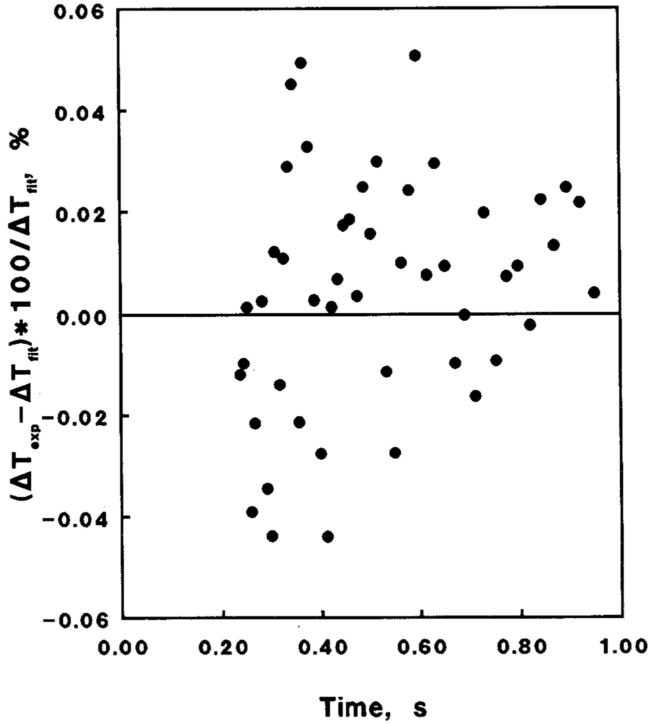

Fig. 1. Deviations of the experimental temperature rise from a linear fit vs ln*t* for a measurement in saturated liquid R134a at a temperature of 273 K.

The measurements have all been carried out a little above the saturation vapor pressure. Thus, in order to carry out the data reduction it is necessary to employ values for the density and isobaric heat capacity of the fluid under these conditions. For the density of R134a we have employed the equation given by McLinden [15] for this purpose, whereas the value of C_p has been obtained from the work of Saltoh *et al.* [16]. For R141b we have employed the density values reported by Maezawa *et al.* [17] and the heat capacity values deduced by application of the group contribution method of Missenard [18]. For normal pentane we employed the density data and heat capacity values tabulated by Vargaftik [19]. For water we employed the equation of state recommended by IAPS for both properties [20].

3. RESULTS

3.1. Normal Pentane

The thermal conductivity for *n*-pentane at saturation conditions and a temperature of 306 K was determined for each cell assembly. The present values listed in Table I are estimated to have an uncertainty of ±1%. The same table lists the value of the thermal conductivity for *n*-pentane determined in this laboratory in a completely independent study using a different set of hot-wire cells with platinum wires and an earlier version of the measurement bridge [21]. These earlier measurements were of a higher accuracy (±0.3%) than those reported here because the platinum wires were only 7 μm in diameter, reducing the magnitude of most corrections, and because the resistance temperature characteristics are better established for platinum. However, the earlier measurements did not extend to the saturation line so that a modest extrapolation to the saturated vapor pressure has been necessary. As a consequence, the estimated uncertainty for the reference thermal conductivity of *n*-pentane at saturation is one of

Table I. The Results of Check Measurements on the Thermal Conductivity of *n*-Pentane at Saturation Conditions and Water at a Pressure of 0.1 MPa

Fluid	Temp. (K)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)		
		First assembly	Second assembly	Ref. value
n-Pentane	306	110.7	110.7	110.6 [21]
Water	302		613.8	613.1 [11]

$\pm 0.5\%$. It can be seen from Table I that the values determined in both sets of tantalum cells are consistent with each other and with the reference value to within their mutual uncertainty.

For water the comparison in Table I is made with the standard reference values compiled by Nieto de Castro *et al.* [11], which have an estimated uncertainty of $\pm 1.0\%$. Once again, it can be seen that the agreement with the present values is compatible with the mutual uncertainty.

3.2. R134a

Table II contains the thermal conductivity data for liquid R134a along the saturation line as a function of temperature for the first and second cell assemblies, respectively. The uncertainty in each set of data is estimated to be one of $\pm 1\%$.

The present data acquired in the second cell assembly have been represented by the correlating equation

$$\lambda = 211.07 - 0.42784T \tag{1}$$

where λ is in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ and T is in K. Using this correlation as a basis, Fig. 2 shows plots of the deviations of the results of all measurements available to us from it.

It is first clear from Fig. 2 that the results obtained from the two sets of cells employed here are entirely consistent. Furthermore, while the present results lie below those of our earlier work [2] by up to 3%, this is acceptable in view of the preliminary nature of the previous work.

Table II. The Thermal Conductivity of Liquid R134a Along the Saturation Line

Temp. (K)	Thermal conductivity ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	
	First assembly	Second assembly
240.4		108.2
242.7	108.5	
252.3	104.4	
256.3		101.4
261.8	99.8	
272.5	94.8	
273.1		94.3
289.4		87.2
306.8		79.6

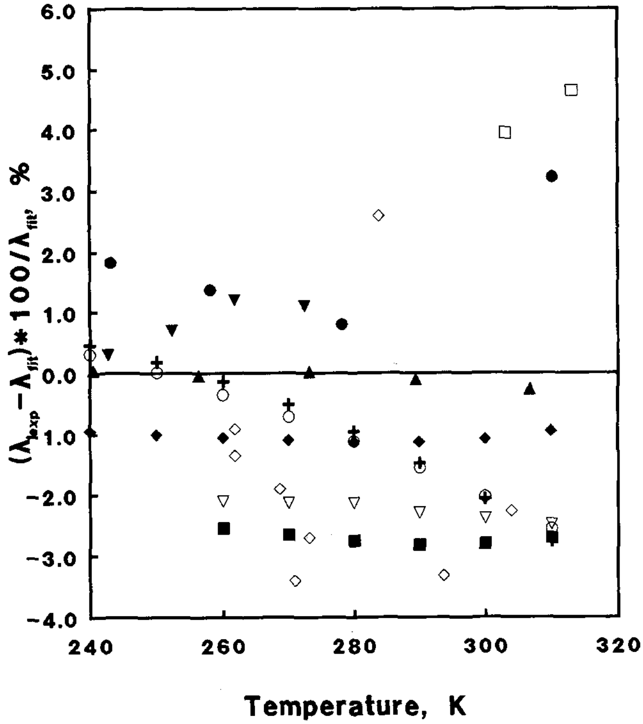

Fig. 2. Deviations of the results of measurements of the thermal conductivity of liquid R134a along the saturation line from the correlation of Eq. (1). (▼) Present work, first assembly; (▲) present work, second assembly; (●) Ross *et al.* [2]; (○) Perkins *et al.* [4]; (◆) Ueno *et al.* [22]; (▽) Yata [24]; (■) Assael and Karagiannidis [23]; (◇) Gross *et al.* [3]; (+) Laesecke *et al.* [25]; (□) Kruppa and Straub [26].

The comparison with other independent measurements shows a greater disparity. Thus, the measurements of Ueno *et al.* [22] lie uniformly 1% below the present data, and those of Assael and Karagiannidis [23] almost uniformly 2.5% below them, with the results of Yata [24] showing a similar behavior. The measurements of Gross *et al.* [3] show a scatter which is sufficiently large that we are unable to discern any systematic trend. On the other hand, the results of Perkins *et al.* [4] and Laesecke *et al.* [25], extrapolated from higher pressures, show a markedly different temperature dependence, although the deviation never exceeds 3%. All of these measurements were made using transient hot-wire instruments so that the discrepancies apparent are of some concern, especially since the accuracy claimed by each author is often superior to the differences observed. One set of measurements of the thermal diffusivity reported by

Table III. The Thermal Conductivity of Liquid R141b Along the Saturation Line

Temp. (K)	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)
248.6	109.1
257.8	106.5
267.6	103.0
277.2	99.5
286.0	96.8
303.9	91.6

Kruppa and Straub [26] has been performed by a light-scattering method. Their thermal diffusivity data have been converted to thermal conductivity using the density reported in the same paper [26] and heat capacity values referred to earlier and it can be seen that the values lie up to 4% above the present results.

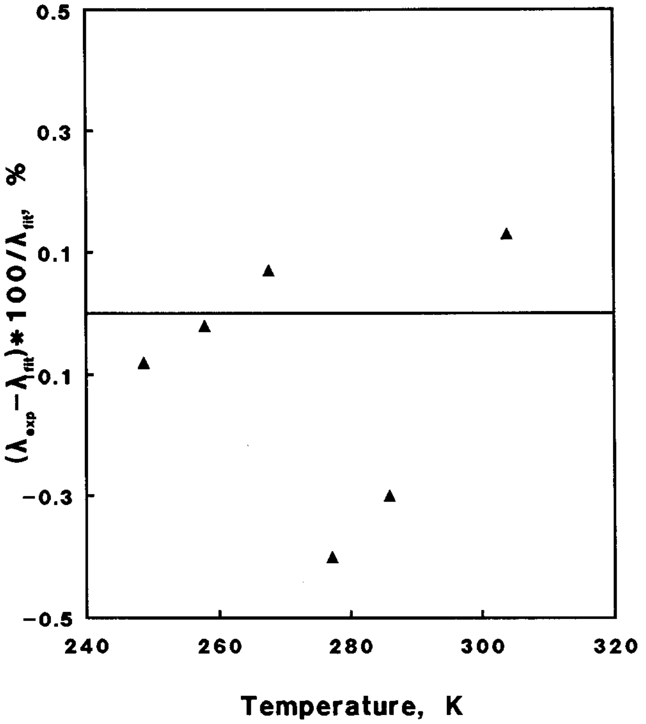

Fig. 3. Deviations of the results of measurements of the thermal conductivity of liquid R141b along the saturation line from the correlation of Eq. (2). (▲) Present work (first assembly).

It would be unwise, at this stage, to try to argue which sets of results may be incorrect since there is insufficient evidence available. However, there is an extremely strong case for further measurements of the thermal conductivity of R134a, preferably by techniques not so far employed. It is possible that some of the discrepancy arises from variations in purity of the samples studied, although earlier reports do not provide sufficient information to be able to assert this with certainty.

3.3 R141b

The present results for this fluid are listed in Table III, and it is estimated that they have an uncertainty of ±1.5% for the reasons noted earlier.

The data have been represented by the equation

$$\lambda = 188.787 - 0.32050T \tag{2}$$

where λ is in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ and T is in K. Figure 3 plots the deviation of the experimental values from this optimum representation of them. The maximum deviation is one of 0.5%.

There are no other results of measurements of the thermal conductivity of R141b available to us at present.

4. CONCLUSIONS

New measurements of the thermal conductivity of refrigerants R134a and R141b in the liquid phase at saturation have been reported. Substantial care has been taken to demonstrate that the transient hot-wire instrument employed operates in accordance with the theoretical model of it and that the absolute value of the thermal conductivity obtained is consistent with reference data. There remain significant differences among the data of various fluids for R134a which are still to be resolved.

REFERENCES

1. R. Krauss and K. Stephan, *Int. J. Thermophys.* (in press).
2. M. Ross, J. P. M. Trusler, W. A. Wakeham, and M. Zalaf, in *Proc. IIF/IRR Comm. B1 Meet.*, Herzlia, Israel (1990), p. 89.
3. U. Gross, Y. W. Song, J. Kallweit, and E. Hahne, in *Proc. IIF/IIR Comm. B1 Meet.*, Herzlia, Israel (1990), p. 103.
4. R. A. Perkins, A. Laesecke, and C. A. Nieto de Castro, *Fluid Phase Equil.* **80**:275 (1992).
5. G. H. Wang, J. E. S. Venart, and R. C. Prasad, *Proc. 3rd Asian Thermophys. Prop. Conf.* (International Academic, Beijing, 1992), p. 399.
6. C. A. Nieto de Castro, R. A. Perkins, and H. M. Roder, *Int. J. Thermophys.* **12**:985 (1991).

7. G. C. Maitland, M. Mustafa, M. Ross, R. D. Trengove, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **7**:245 (1986).
8. W. A. Wakeham and M. Zalaf, *Physica* **139/140B**:105 (1986).
9. M. Dix, W. A. Wakeham, and M. Zalaf, *Thermal Conductivity 20* (Plenum Press, New York, 1989), p. 185.
10. W. A. Wakeham, M. Zalaf, and H. Yu, *Proc. 2nd Asian Thermophys. Prop. Conf.* (1989), p. 211.
11. C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, R. D. Trengove, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **15**:1073 (1986).
12. M. J. Assael, E. Karagiannidis, and W. A. Wakeham, *Int. J. Thermophys.* **13**:735 (1992).
13. M. J. Assael, C. A. Nieto de Castro, H. M. Roder, and W. A. Wakeham, in *Experimental Thermodynamics, Vol. III. Measurement of the Transport Properties of Fluids,* W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds., (Blackwell Scientific, Oxford, 1991), Chap. 7.
14. C. A. Nieto de Castro, S. F. Y. Li, G. C. Maitland, and W. A. Wakehal, *Int. J. Thermophys.* **4**:311 (1983).
15. M. O. McLinden, *Rev. Int. Froid* **13**:149 (1990).
16. A. Saltoh, S. Nakagawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **35**:107 (1990).
17. Y. Maezawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **36**:151 (1991).
18. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw Hill, New York, 1987), p. 136.
19. N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed. (Hemisphere, Washington, DC, 1975), p. 255.
20. L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables* (Hemisphere, Washington DC, 1984).
21. A. M. F. Palavra, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **8**:305 (1987).
22. Y. Ueno, M. Sekikawa, Y. Nagasaka, and A. Nagashima, *Proc. 11th Jap. Symp. Thermophys. Prop.* Tokyo (1990), p. 123.
23. M. J. Assael and E. Karagiannidis, *Int. J. Thermophys.* (in press).
24. J. Yata, *Proc. 11th Jap. Symp. Thermophys. Prop.*, Tokyo (1990), p. 143.
25. A. Laesecke, R. A. Perkins, and C. A. Nieto de Castro, *Fluid Phase Equil.* **80**:263 (1992).
26. B. Kruppa and J. Straub, *Proc. 11th Symp. Thermophys. Prop.*, Boulder, CO, June (1991), p. 21.