International Journal of Thermophysics, Vol. 7, No. 3, 1986

Comparison of the Thermal Conductivities of Water and Heavy Water[1]

R. Tufeu,[2] P. Bury,[2] Y. Garrabos,[2] and B. Le Neindre[2]

New measurements of the thermal conductivity of H_2O and D_2O have been performed from critical temperature up to 510°C and from atmospheric pressure up to 100 MPA. As these measurements have been made with the same cell, a precise analysis of the isotopic effect as a function of temperature and density is possible. Our analysis is presented in terms of corresponding states. It is shown that the critical thermal conductivity excesses for H_2O and D_2O reduced by their respective background thermal conductivity terms are represented by single reduced isotherms.

KEY WORDS: corresponding states; heavy water; thermal conductivity; water.

1. INTRODUCTION

In this paper, we present a comparison of the thermal conductivity of H_2O and D_2O based on new data obtained in the temperature range 377–510°C and from atmospheric pressure up to 100 MPa. The measurements were performed using the same coaxial cylinder cell in order to provide reliable and precise data for an analysis of isotopic effects on thermal conductivity of polyatomic molecules, for which the energy transfer depends on translational and internal contributions. Moreover, the two data sets obtained with the same apparatus are useful to build consistent representative equations for the transport properties of water and heavy water.

---

[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Laboratoire des Interactions Moléculaires et des Hautes Pressions, CNRS, Centre Universitaire Paris-Nord, 93430 Villetaneuse, France.

0195-928X/86/0500-0663$05.00/0

Table I. Critical Parameters and Reduction Constants

	H_2O	D_2O
T_c (K)	647.14	643.89
P_c (MPa)	22.06	21.6
ρ_c (kg m^{-3})	322	358
K_λ (SI units)	3.218E−7	3.40346E−7
K'_λ (SI units)	8.5913E−7	9.16275E−7

The densities and the other thermodynamic quantities have been calculated using the equation of state of Hill [1, 2] for D_2O and H_2O. These equations must have the same accuracy in the same pressure and temperature range. The critical parameters are given in Table I. The interpretation of the thermal conductivities measured relatively far from the critical point does not need the use of a critical EOS.

Our experimental results are shown in Figs. 1 and 2; they have been submitted for publication in the literature [3]. It must be noted that in the entire range of the experiment, the critical effect is present.

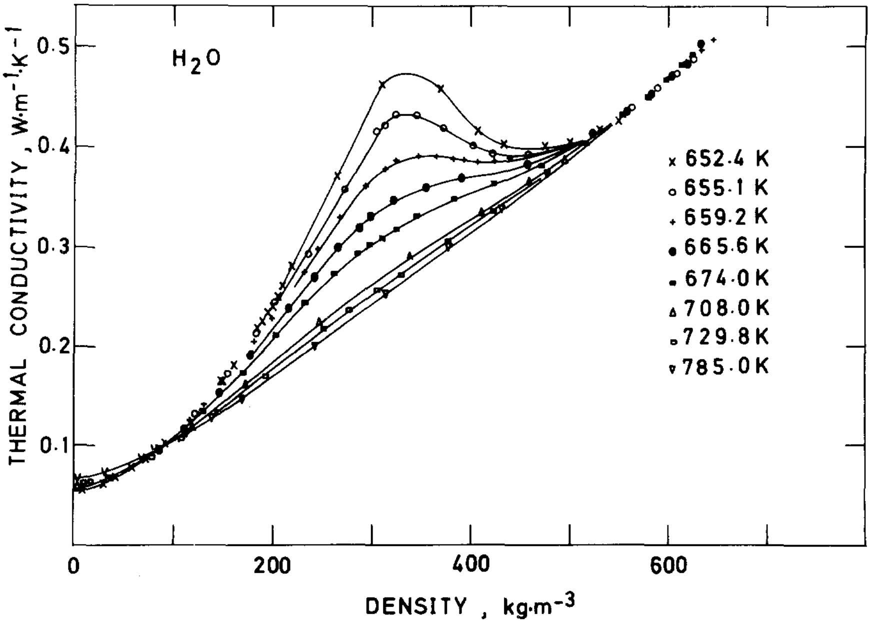

Fig. 1. Thermal conductivity of H_2O.

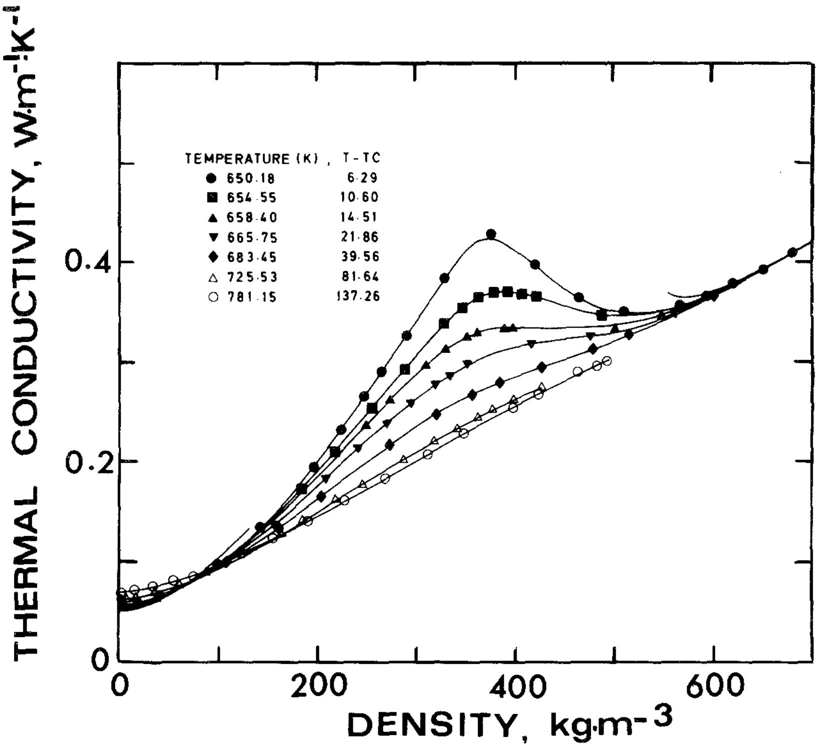

Fig. 2. Thermal conductivity of D_2O.

2. DILUTE-GAS THERMAL CONDUCTIVITY OF H_2O AND D_2O

The dilute-gas thermal conductivity of H_2O and D_2O was obtained by extrapolating the values at higher densities to avoid accommodation effects.

Table II. Coefficients a_i for $\lambda_0(T)$

H_2O	D_2O
$a_0 = 8.9372\ E-4$	$a_0 = -0.0126116$
$a_1 = 4.90018E-5$	$a_1 = 1.22144E-4$
$a_2 = 2.56541E-8$	$a_2 = -8.00026E-8$
$a_3 = 4.127\ E-11$	$a_3 = -1.17434E-11$
$a_4 = -8.73764E-15$	$a_4 = 2.02829E-13$
$a_5 = -1.55286E-17$	$a_5 = -1.13526E-16$
$a_6 = 4.81493E-21$	$a_6 = -5.09018E-21$

The values can be correlated by the following equation:

$$\lambda_0(T) = \sum_{i=0}^{6} a_i T^i \tag{1}$$

The a_i are given in Table II; T is in K.

To calculate these coefficients, we have included other sets of data outside the temperature range of our study. For H_2O we have taken into account the tabulated data by IAPS above 500°C [4]. For D_2O, we included the data of Vargaftik [5] above 500°C.

Our experimental values and values given by the representative equations [4, 6] are within the error bands for H_2O and D_2O considered separately, but the ratio $\lambda_0(D_2O)/\lambda_0(H_20)$ as a function of temperature is found to be slightly different. At 500°C, $(D_2O)/(H_2O) = 1.03$, while the proposed equations [4, 6] yield $\lambda_0(D_20)/\lambda_0(H_2O) = 1.05$. This last value is close to the experimental ratio obtained by Vargaftik [7]. In Fig. 3, we have represented the experimental ratio obtained by different authors. The agreement is excellent with the previous measurements made by

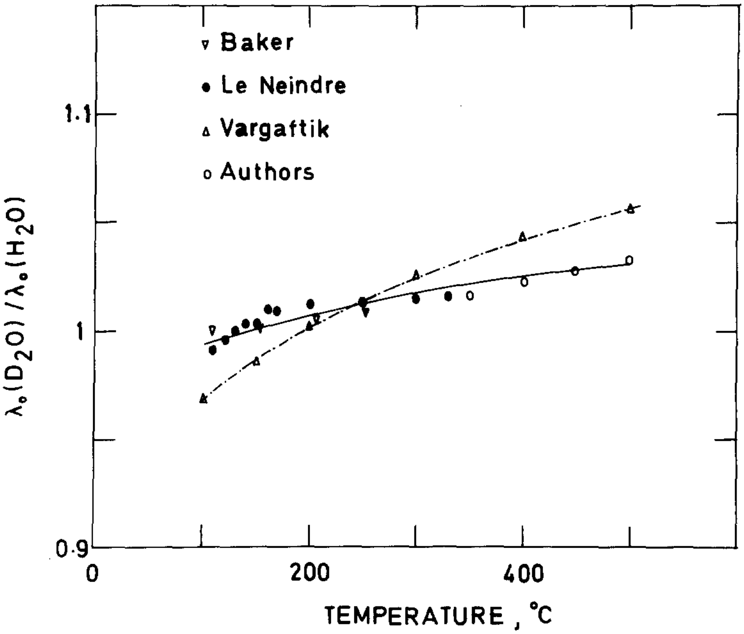

Fig. 3. Ratio of $\lambda_0(D_2O)$ to $\lambda_0(H_2O)$ at atmospheric pressure as a function of temperature.

Le Neindre *et al.* [8] with the same type of cell and with the values obtained by Baker and Brokaw [9].

If H_2O and D_20 were composed of simple spherical molecules differing only by their mass m, $\lambda_0(D_2O)$ would be smaller than $\lambda_0(H_20)$ by a factor

$$\sqrt{m(D_2O)/m(H_2O)} = 1.05 \qquad (2)$$

Some theoretical work was developed to explain the observed isotopic effects (see, for example, Ref. 9). It was demonstrated that for these polyatomic molecules, the internal modes play an important role in the energy transfer process. This is clearly shown by considering the Eucken factor $\lambda/\eta C_v$ (η is the shear viscosity and C_v is the specific heat at constant volume), which is 1.4, a value very different from the value of 2.5 obtained for simple spherical molecules (noble gases). It is interesting and surprising that the Eucken factors calculated from our experimental thermal conductivity values, using the viscosity coefficient calculated from the representative equation [6, 10] and C_v calculated from the equations of state [1, 2], have exactly the same value, 1.40, for the two substances in the temperature range 377–510°C, although the molecules have different moments of inertia and consequently different collision numbers.

3. CORRESPONDING STATES

The thermal conductivities of H_2O and D_2O can be compared after being reduced by using the coordinates of their critical points T_c, P_c, and ρ_c and represented as a function of the reduced temperature $T_r = T/T_c$, the reduced pressure $P_r = P/P_c$, or the reduced density $\rho_r = \rho/\rho_c$. Two expressions are obtained:

$$\lambda_r(T_r, \rho_r) = \lambda K_\lambda \qquad (3)$$

with

$$K_\lambda = M^{1/2} T_c^{-1/2} \tilde{\rho}_c^{-2/3} R^{-3/2} \qquad (4)$$

or

$$\lambda'_r(T_r, P_r) = \lambda K'_\lambda \qquad (5)$$

with

$$K'_\lambda = M^{1/2} P_c^{-2/3} (RT_c)^{1/6} R^{-1} \qquad (6)$$

In Eqs. (4) and (6), M is the molar weight, $\tilde{\rho}_c$ is the critical molar density, and R is the molar gas constant.

We have represented in Figs. 4 and 5 $\lambda_r(T_r, \rho_r)$ for four quasi-isotherms ($T_r = 1.012$, $T_r = 1.040$, $T_r = 1.125$, and $T_r = 1.215$). It is clear

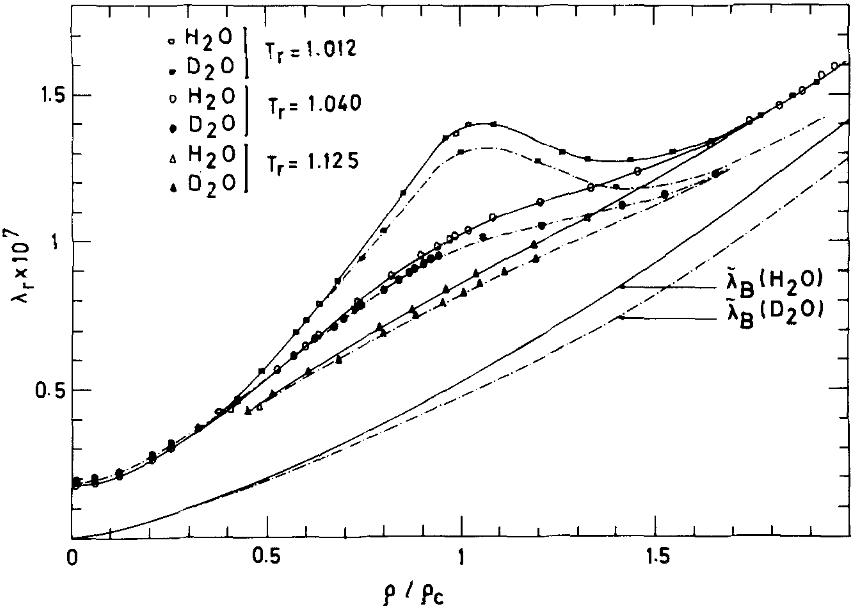

Fig. 4. Reduced thermal conductivity of H_2O and D_2O (T_c and ρ_c parameters).

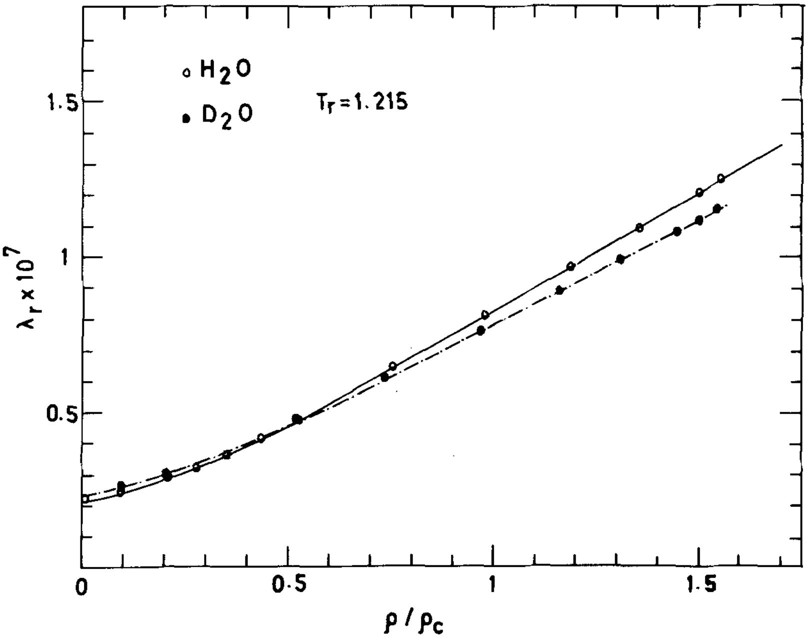

Fig. 5. Reduced thermal conductivity of H_2O and D_2O (T_c and ρ_c parameters).

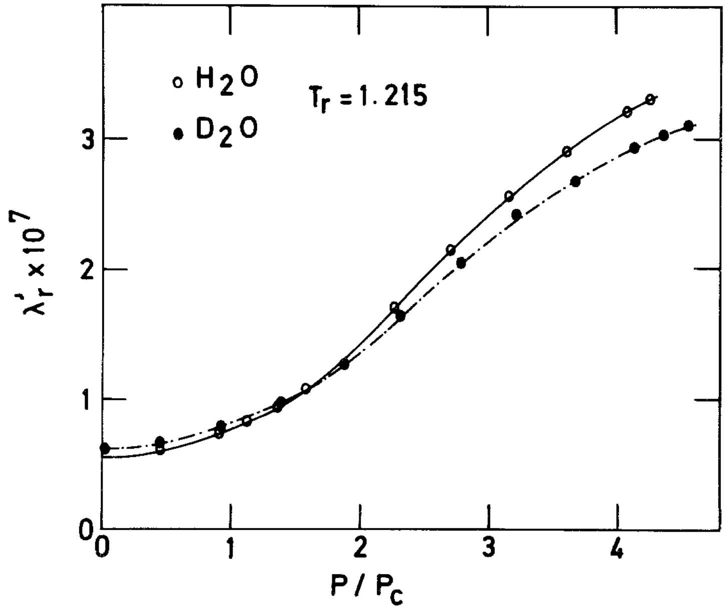

Fig. 6. Reduced thermal conductivity of H_2O and D_2O (T_c and P_c parameters).

that the experimental reduced thermal conductivity does not lie on a single curve at a given reduced temperature, even when the critical effect becomes small at high and low densities and high temperatures [at $\rho = 2\rho_c$, $\lambda_r(H_2O)/\lambda_r(D_2O) = 1.06$].

The experimental values $\lambda_r'(T_r, P_r)$ obtained for the $T_r = 1.215$ reduced isotherm are represented in Fig. 6. As for the reduction by T_c and ρ_c, we do not obtain a single curve for the two substances.

A simple corresponding-state approach does not provide a way to deduce the thermal conductivity of one isotope relative to the other within the 1.5% accepted uncertainty. The comparison of the viscosity of H_2O and D_2O yields the same conclusion as for the thermal conductivity.

4. THE CRITICAL THERMAL CONDUCTIVITY EXCESS OF H_2O AND D_2O

Classically the thermal conductivity is separated into two parts, a background term λ_B and a critical term $\Delta\lambda$.

$$\lambda(\rho, T) = \lambda_B(\rho, T) + \Delta\lambda(\rho, T) \quad (7)$$

with

$$\lambda_B(\rho, T) = \lambda_0(T) + \bar{\lambda}_B(\rho, T) \tag{8}$$

$\lambda_0(T)$ is the dilute-gas thermal conductivity, which has been discussed, and $\bar{\lambda}_B(\rho, T)$ is the "normal" density effect.

For H_2O and D_2O, $\lambda_B(\rho, T)$ is not easy to estimate, mainly because $\lambda(\rho)$ are not available at temperatures sufficiently high to neglect $\Delta\lambda$. So we have proceeded as follows. The critical thermal conductivity excess $\Delta\lambda$ has been theoretically calculated at $\rho = \rho_c$. It is given by the relation obtained from the mode–mode coupling theory:

$$\Delta\lambda_c(\rho_c, T) = \Lambda \frac{k_B T}{6\pi\eta\xi} \rho C_P^c \tag{9}$$

where ξ is the long-range correlation length, η is the shear viscosity, C_P^c is the critical specific heat at constant pressure, and Λ is a numerical constant.

For H_2O, we have used the values proposed by Sengers *et al.* [4] and calculated $\Delta\lambda_c(\rho_c, T)$ at $t = (T - T_c)/T_c = 1.2 \times 10^{-2}$:

$$\Delta\lambda_c = 0.213 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

For this temperature, our experimental thermal conductivity is

$$\lambda(H_2O) = 0.428 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

and we deduce

$$\lambda_B(\rho_c, T_c) = 0.214 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

For D_2O, the interpolation of our data at $T_r = 1.012$ gives

$$\lambda(D_2O) = 0.385 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

assuming that $\Delta\lambda_c(\rho_c, t = 1.2 \times 10^{-2})/\lambda_B(\rho_c, T_c) = 1.00$ is verified for H_2O and D_2O (point A in Figs. 7 and 8), we obtain for D_2O

$$\lambda_B(\rho_c, T_c) = 0.192 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

As a second hypothesis, the density effect $\bar{\lambda}_B$ is supposed to be temperature independent. Moreover, we assume that $\Delta\lambda = 0$ for $\rho = 0$ and $\rho = 2\rho_c$ and is symmetrical for $0.7 < \rho/\rho_c < 1.3$.

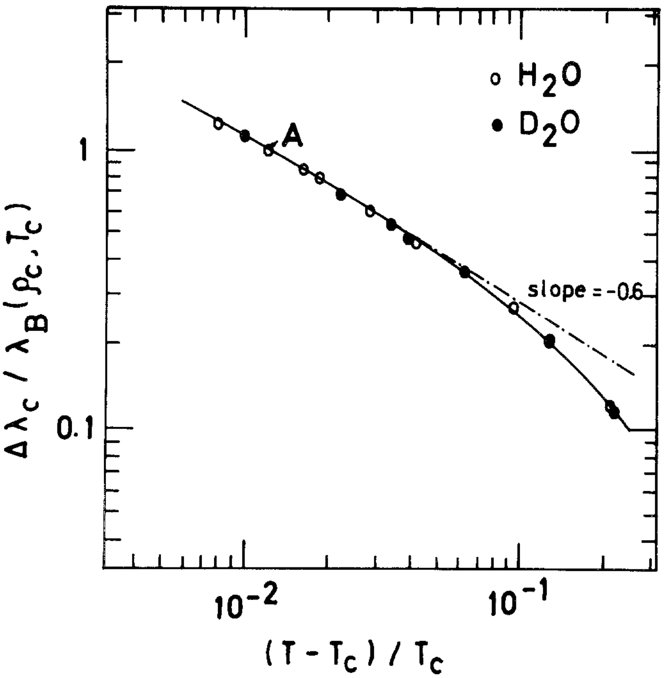

Fig. 7. Critical thermal conductivity excess of H_2O and D_2O at critical density.

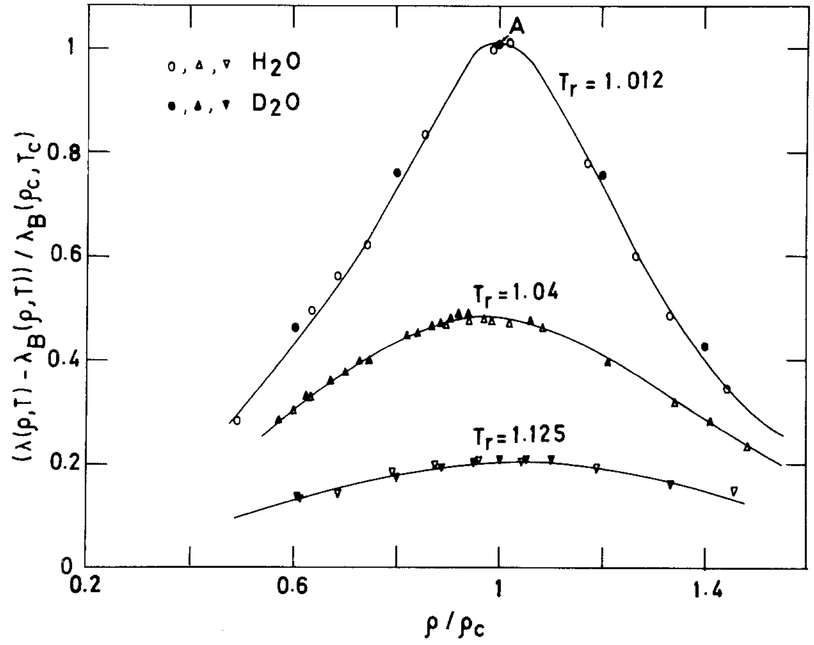

Fig. 8. Critical thermal conductivity excess of H_2O and D_2O as a function of reduced temperature and density.

Table III. Coefficients b_i for $\tilde{\lambda}_B$

H_2O	D_2O
$b_1 = 1.79795E-4$	$b_1 = 1.26794E-4$
$b_2 = 1.72671E-6$	$b_2 = 1.75816E-6$
$b_3 = -2.81557E-9$	$b_3 = -4.32592E-9$
$b_4 = -2.50847E-13$	$b_4 = 3.31701E-12$
$b_5 = 1.07363E-14$	$b_5 = 4.53499E-15$
$b_6 = -1.46857E-17$	$b_6 = -7.18731E-18$
$b_7 = 5.70163E-21$	$b_7 = 2.24572E-21$

We propose for $\tilde{\lambda}_B$ the following virial expansions:

$$\tilde{\lambda}_B = \sum_{i=1}^{7} b_i \rho^i \tag{10}$$

The b_i are given in Table III; ρ is in $\text{kg} \cdot \text{m}^{-3}$. Note that $(\tilde{\lambda}_B)_r$ reduced by T_c and ρ_c does not verify the simple corresponding-state principle as shown in Fig. 4.

We now plot the thermal conductivity excess $\Delta\lambda_c$ at the critical density ρ_c for H_2O and D_2O reduced by their respective background thermal conductivity $\lambda_B(T_c, \rho_c)$ as a function of $t = (T - T_c)/T_c$. Figure 7 shows that a single curve is obtained. It can be fitted by the equation

$$\Delta\lambda_c(\rho_c, t)/\lambda_B(\rho_c, T_c) = 0.085 t^{-0.57}(1 - 0.3t^{0.5} - 1.2t) \tag{11}$$

The reduced $\Delta\lambda(\rho, T)$ by $\lambda_B(\rho_c, T_c)$ are plotted in Fig. 8. Single reduced isotherms are obtained for the two substances in the density range $0.6 < \rho_r < 1.4$. Our choice of λ_B leads to a unique reduced thermal conductivity excess for H_2O and D_2O.

5. CONCLUSION

The present analysis of our thermal conductivity data on water and heavy water measured with the same apparatus in the supercritical range has shown that this transport coefficient cannot be predicted within the experimental accuracy for one isotope relative to the other through simple corresponding-state arguments.

From our experimental results, we have shown some features that should be retained to build consistent representative equations for the thermal conductivity of the two substances. These features are, for example, related to the ratio of the thermal conductivity of H_2O and D_2O as a function of temperature in the dilute-gas state or to the critical enhancement of the thermal conductivity, which can be represented by single reduced isotherms in restricted temperature and density ranges when reduced by the background thermal conductivity estimated at the respective critical temperature and critical density.

REFERENCES

1. P. G. Hill, R. D. C. McMillan, and V. Lee, *J. Phys. Chem. Ref. Data.* **11**:1 (1982), **12**:1065 (1983).
2. P. G. Hill and E. LeFèvre, Formulation of unified equation of state for H_2O. IAPS release (1983).
3. R. Tufeu and B. Le Neindre, *J. Chem. Eng. Data* (in press).
4. J. V. Sengers, J. T. R. Watson, R. S. Basu, B. Kamgar-Parsi, and R. C. Hendricks, *J. Phys. Chem. Ref. Data* **13**:893 (1984).
5. N. B. Vargaftik, N. A. Navicheva, and L. V. Yakush, *Inzh. Fiz. Zh.* **25**:336 (1973).
6. N. Matsunaga and A. Nagashima, *J. Phys. Chem. Ref. Data* **12**:933 (1983).
7. N. B. Vargaftik, in *7th International Conference on the Properties of Steam* (American Society of Mechanical Engineers, New York, 1970).
8. B. Le Neindre, P. Bury, R. Tufeu, P. Johannin, and B. Vodar, in *7th International Conference on the Properties of Steam* (American Society of Mechanical Engineers, New York, 1970), p. 231.
9. C. E. Baker and R. J. Brokaw, *J. Chem. Phys.* **40**:1523 (1964).
10. J. V. Sengers and B. Kamgar-Parsi, *J. Phys. Chem. Ref. Data* **13**:185 (1984).