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Thermal Conductivity of Liquids: Prediction Based on a Group-Contribution Scheme

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A new semiempirical predictive scheme for the thermal conductivity of liquids, based on an extension of concepts derived from the rigid-sphere model of dense-fluid transport properties, is presented. The scheme makes use of the idea of group contributions to the molecular volume and is developed with the aid of accurate thermal conductivity data for the alkanes, the aromatic hydrocarbons, the alcohols, and the diols, along the saturation line and at elevated pressures. The procedure has been tested against other thermal conductivity data, not included in its formulation, and has been found to predict values within ±4% of the experimental data in the temperature range 110–370 K for pressures up to 600 MPa.

KEY WORDS: high pressure; liquids; prediction; thermal conductivity.

1. INTRODUCTION

The study of the thermal conductivity of liquids is important for the solution of design problems involving heat transfer. At present only for the case of monatomic gases at low density is an exact and routine calculation of their transport properties from the intermolecular potential available [1, 2]. As the systems become more complicated by virtue of increasing density or increasing molecular complexity, there is no formal kinetic theory which allows an exact evaluation of the thermal conductivity in terms of a realistic description of the molecular interactions. It must also be recognized that the industrial need for reliable thermophysical property data can never be met by measurement alone so that a soundly based scheme for interpolation and extrapolation of data is essential. Most

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existing schemes for the prediction of the thermal conductivity of liquids are based on entirely empirical procedures [3] and frequently they are to be applied at specified pressures. However, the simplest theories of transport in liquids that have proved most successful all indicate that it is the density of the fluid which is the most important variable, and not the pressure. For this reason, the present paper seeks to establish a predictive scheme for the thermal conductivity of liquids which makes use of this fact and therefore is more securely founded on theory. Beginning with an analysis of accurate thermal conductivity data for alkanes at elevated density, it is shown how the ideas of the rigid-sphere model of fluid transport naturally lead to a group-contribution scheme for the molecular volume. The extension of this scheme to other types of molecule is then examined with respect to equally accurate data under other conditions. Such extensions are seen to involve increasing empiricism but prove almost equally successful in correlating experimental data. These examinations of existing data have permitted a predictive scheme to be developed which can be tested against other information not included in its formulation.

2. THE RIGID-SPHERE MODEL

A heuristic application of the Enskog theory [4] to the van der Waals model of a dense fluid [5] suggests that the experimental quantity [6, 7]

$$\lambda^* = 1.9362 \times 10^7 \, (M/RT)^{1/2} \, \lambda \, \mathrm{V}^{2/3} \tag{1}$$

(in which all quantities are expressed in SI units), for a particular liquid is a function only of the ratio of the molar volume, V, to an effective core volume, V_0, so that

$$\lambda^* = F(V/V_0) \tag{2}$$

Here, M is the molecular weight, R the gas constant, and T the absolute temperature. In the initial model [6, 7], V_0 represented an effective core volume characteristic of the fluid, displaying a weak dependence on temperature only, which was related to the softness of the real repulsive wall of the intermolecular potential compared with that of a rigid sphere. As a consequence of this, the effective core volume, V_0, was expected to decrease with increasing temperature. Subsequent studies of this quantity for the experimental thermal conductivities of alcohols and water [9] showed that in the presence of an OH^- group, V_0 increased with temperature for the low-carbon number alcohols, while it decreased with temperature for the high-carbon number alcohols. This observation may be related, in a qualitative manner, to the importance of the attractive forces in systems containing the OH$^-$ group. The rigid-sphere model envisages just a weak uniform attractive potential throughout the fluid, whereas for hydrogen-bonded or associating fluids this is far from the case. For this reason the parameter V_0 should be interpreted more loosely than as a core volume for the fluid and is henceforth termed a "characteristic" molar volume.

The most important result, for the present purposes, to be derived from Eq. (2), is the implication that it should be possible to superimpose plots of experimental curves of λ^* against ln V for a single fluid at a series of temperatures merely by imposing relative shifts along the ln V axis. Assigning a reference value to V_0 for one fluid at the lowest temperature for which accurate measurements of the thermal conductivity exist, the amount of shift required will produce the values of V_0 at every temperature. Li et al. [6] used the accurate measurements of 11 hydrocarbon liquids over the temperature range 110–370 K and for pressures up to 600 MPa to determine the function $F(V/V_0)$ of Eq. (2). The single curve of λ^* as a function of reduced molar volume can be represented by the equation,

$$\ln \lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{3}$$

Equations (1) and (3) represent the basis of our predicive scheme for the thermal conductivity of liquids.

3. THE PREDICTIVE SCHEME

The predictive scheme is based, in the first stage, on the correlation of the thermal conductivity of the alkanes. In Table I, the experimental data sets used for the thermal conductivity of the liquid phases of methane to tetradecane and the corresponding temperature and pressure ranges covered are presented. These particular data sets were used because they are the most accurate measurements available. The accuracy of these results is better than ±1%. Equations (1) and (3) were used to calculate the characteristic molar volume, V_0, at various temperatures for every hydrocarbon according to the above procedure. The resulting values for every hydrocarbon are shown as a function of the absolute temperature in Fig. 1. The temperature dependence of V_0 is seen to be almost linear. On the other hand, it can be seen from Fig. 1 that for one particular temperature, the dependence of V_0 on n_c, the number of carbon atoms in the alkane, is not linear although smooth.

It has been found by means of linear regression [8] that the best set of values of V_0 for the alkanes, denoted V_0^N, can be represented by the equation,

$$10^6 \, V_0^N(\theta, n_c) = \sum_{i=0}^{2} \sum_{j=0}^{3} a_{ij} n_c^j \theta^i \tag{4}$$

where,

$$\theta = T/273.15$$

is a nondimensional temperature chosen for computational convenience. The values of the coefficients a_{ij} securing the best representation of the data are shown in Table II. Obviously not all molecules with the same number of carbon atoms have the same characteristic molar volume. That is, one would expect that the addition of functional groups such as OH^- or the formation of a benzene ring would alter the characteristic molar volume. We postulate that the total characteristic molar volume for a molecule can be written in the form,

$$V_0 = V_0^{N} + V_0^{1B} + V_0^{1OH} + V_0^{2OH} \tag{5}$$

where because of limited experimental data, we must confine our analysis to alkanes (N), aromatic hydrocarbons with one benzene ring (1B), alcohols (1OH), and diols (1OH + 2OH). In order to examine whether a

Table I. The Experimental Thermal Conductivity Sets of Alkanes Used for the Scheme

Paraffin hydrocarbon	Ref.	No. of data	T (K)	P (MPa)
Methane	Mardolcar et al. [10]	30	110–160	0.2–9
Ethane	Roder et al. [11]	58	100–200	0.3–32
Propane	Roder et al. [12]	50	140–260	1–70
Butane	Castro et al. [13]	10	290–360	1–50
Pentane	Palavra et al. [14]	68	300–350	1.8–285
Hexane	Li [15]	66	300–360	1.8–645
	Assael et al. [16]	12	290–330	0.1
Heptane	Menashe et al. [17]	48	300–350	50–500
	Nagasaka et al. [18]	12	270–360	0.1
	Assael et al. [16]	13	300–360	0.1
Octane	Calado et al. [19]	75	300–360	0.1
	Li [15]	23	280–340	7–595
Nonane	Menashe et al. [20]	64	300–360	35–500
	Calado et al. [19]	20	280–360	0.1
Decane	Assael et al. [16]	13	300–360	0.1
Undecane	Menashe et al. [20]	49	300–350	45–400
	Calado et al. [19]	18	280–370	0.1
Dodecane	Kashiwagi et al. [21]	7	290–370	0.1
Tridecane	Mustafa et al. [22]	57	300–350	24–440
Tetradecane	Calado et al. [19]	22	300–370	0.1
Total		715		

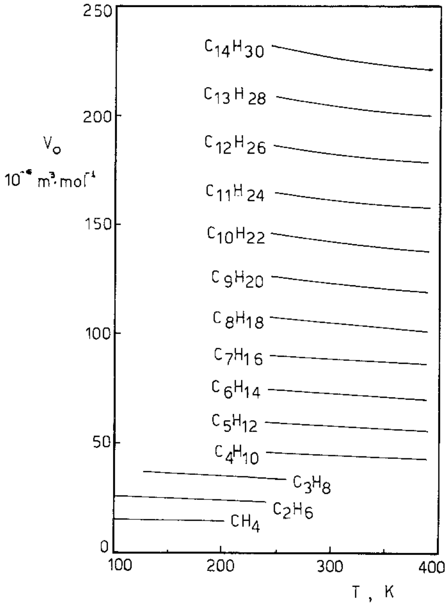

Fig. 1. The characteristic molar volume for the alkanes as a function of temperature.

Table II. The Coefficients a_{ij}, b_{ij}, c_{ij}, and d_j of Eq. (7)

		m³·mol⁻¹			
i	j	a_{ij}	b_{ij}	c_{ij}	d_j
0	0	+6.3918	−14.700	−0.1630	+4.40
0	1	+9.7389	−2.8280	−4.5280	+0.70
0	2	+0.84785	—	+0.7807	—
0	3	−0.013132	—	—	—
1	0	0	+8.1945	+1.7209	—
1	1	−4.57722	−0.52991	+4.4797	—
1	2	0	—	−0.69653	—
1	3	0	—	—	—
2	0	0	—	—	—
2	1	+1.40555	—	—	—
2	2	0	—	—	—
2	3	0	—	—	—

group-contribution scheme to V_0 of this type is useful, each contribution, V_0^{1B}, V_0^{1OH}, and V_0^{2OH}, has been deduced from experimental data at atmospheric pressure in the following way.

First, for the case of the aromatic hydrocarbons, the total characteristic molar volume V_0 is calculated from the experimental data for benzene [16], toluene [23], and the three xylene isomers [24], using Eqs. (1) and (3). The experimental thermal conductivity values used covered a temperature range 290–360 K and were obtained at atmospheric pressure. The contribution of the benzene ring was then obtained by subtracting the characteristic molar volume of the alkanes, V_0^{N}, from this total molar volume. The derived values of V_0^{1B} were found by means of linear regression to be represented by the equation,

$$10^6\, V_0^{1B}(\theta, n_c) = \sum_{i=0}^{1} \sum_{j=0}^{1} b_{ij} n_c^j \theta^i \tag{6}$$

The coefficients b_{ij} are shown in Table II.

The same procedure was adopted for the alcohols and the diols. The experimental thermal conductivity values used for the alcohols, methanol to hexanol [9, 25], were at atmospheric pressure and covered the temperature range 290–360 K. For the diols, atmospheric-pressure experimental thermal conductivities for ethanediol and propanediol [26] that covered the temperature range 290–360 K were used.

The final equation for the total characteristic molar volume, expressed as group contributions, is

$$V_0 = V_0^{N} + V_0^{1B} + V_0^{1OH} + V_0^{2OH} \tag{7}$$

where

$$10^6\, V_0^{N}(\theta, n_c) = \sum_{i=0}^{2} \sum_{j=0}^{3} a_{ij} n_c^j \theta^i$$

$$10^6\, V_0^{1B}(\theta, n_c) = \sum_{i=0}^{1} \sum_{j=0}^{1} b_{ij} n_c^j \theta^i$$

$$10^6\, V_0^{1OH}(\theta, n_c) = \sum_{i=0}^{1} \sum_{j=0}^{2} c_{ij} n_c^j \theta^i$$

$$10^6\, V_0^{2OH}(n_c) = \sum_{j=0}^{1} d_j n_c^j$$

where θ is the nondimensional temperature defined earlier and n_c is the total number of carbon atoms in the molecule. In this equation for the total characteristic molar volume, the first term represents the contribution to V_0 if the chain is a straight chain of n_c carbon atoms. The second term represents an additive contribution to the first term, if six of the carbon atoms were in a benzene-ring arrangement. The third term represents an additive contribution for the case where one hydrogen atom is substituted by an OH^- group, while the fourth term refers to the case where a second OH^- group substitutes a second hydrogen atom.

Equations (1), (3), and (7) represent a consistent way of calculating the thermal conductivity of the following group of liquids:

(1) straight-chain molecules (no double bonds) with carbon and hydrogen atoms and up to two OH^- groups present and

(2) liquids of case 1 where six of the carbon atoms are in a benzene-ring arrangement.

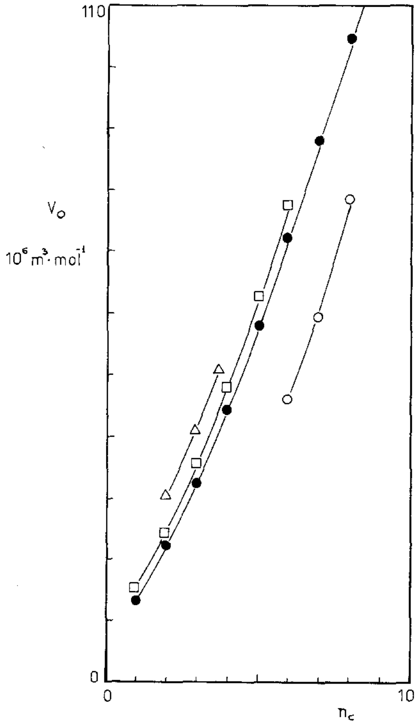

Fig. 2. The characteristic molar volume as a function of the carbon atoms at 290 K, Eq. (7). (—●—) Paraffins; (—○—) aromatic hydrocarbons; (—□—) alcohols; (—△—) glycols.

It should also be noticed that no real distinction between isomers is possible at present in this scheme. When isomers are present this scheme predicts an "average" thermal conductivity. As, however, each isomer has a slightly different molar volume, there is a corresponding variation in the predicted thermal conductivity values.

Equation (7) is plotted in Fig. 2, where the decrease in the characteristic molar volume, when the benzene-ring substitutes a straight chain of six carbon atoms, can be seen. The increase in V_0 in the presence of one OH^- or two OH^- groups is also shown.

4. THE PREDICTIVE POWER OF THE PROPOSED SCHEME

As this scheme is based on the correlation of the values obtained from the alkanes, Fig. 3 shows the deviation of the experimental values used from the proposed scheme. It can be seen that the maximum deviation is less than ±4%, although data extend up to 600 MPa. In Fig. 4, the deviations of the experimental data at atmospheric pressure, used for the contribution terms for the aromatic hydrocarbons, alcohols, and diols, are shown. It can also be seen that the maximum deviation is well under ±4%.

Recently, accurate thermal conductivity data at pressures up to 600 MPa have been reported for benzene [27], toluene [28], and the three

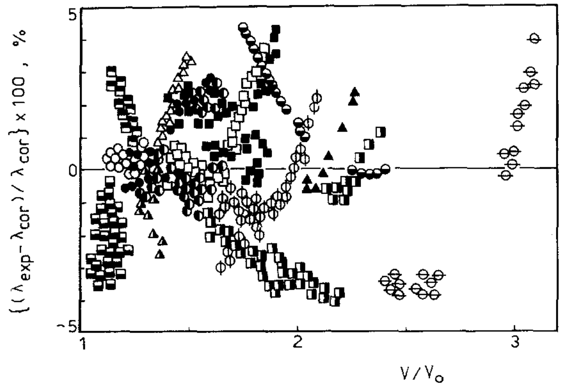

Fig. 3. Deviations of the experimental thermal conductivity values of alkanes from those predicted by the scheme of Eqs. (1), (3), and (7). (—⊖—) Methane; (⬙) ethane; (◨) propane; (▲) butane; (ɸ) pentane; (■) hexane; (□) heptane; (◐) octane; (●) nonane; (△) decane; (○) undecane; (▲) dodecane; (⬓) tridecane; (⬒) tetradecane.

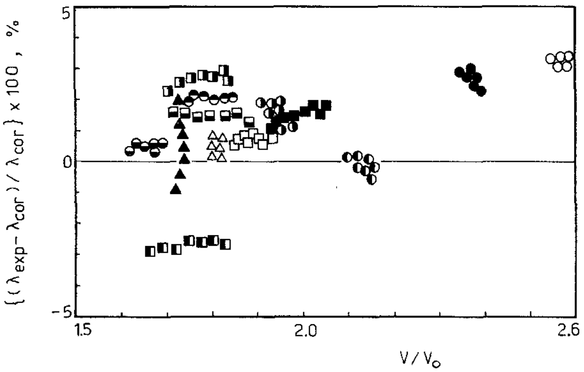

Fig. 4. Deviations of the experimental thermal conductivity values of aromatic hydrocarbons, alcohols, and diols from those predicted by the scheme of Eqs. (1), (3), and (7). (■) Benzene; (□) toluene; (◧) *o*-xylene; (◨) *m*-xylene; (⬓) *p*-xylene; (○) methanol; (●) ethanol; (◐) propanol; (◑) butanol; (◓) pentanol; (◒) hexanol; (△) ethanediol; (▲) propanediol.

xylene isomers [29]. These results enable us to examine the predictive power of this scheme, because the aromatic contribution term was calculated based on data at atmospheric pressure. Figure 5 shows the deviations of these high-pressure experimental data from the predicted with this scheme values. The maximum deviation here is ±2%. Thus the scheme enables prediction to high pressures with great accuracy.

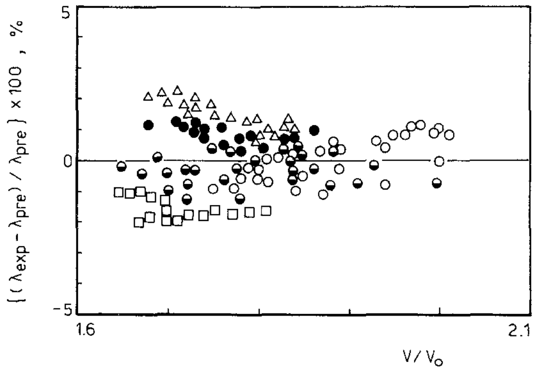

Fig. 5. Deviations of the high-pressure experimental thermal conductivity values of aromatic hydrocarbons from those predicted by the scheme of Eqs. (1), (3), and (7). (□) Benzene [27]; (△) toluene [28]; (●) *o*-xylene [29]; (○) *m*-xylene [29]; (◒) *p*-xylene [29].

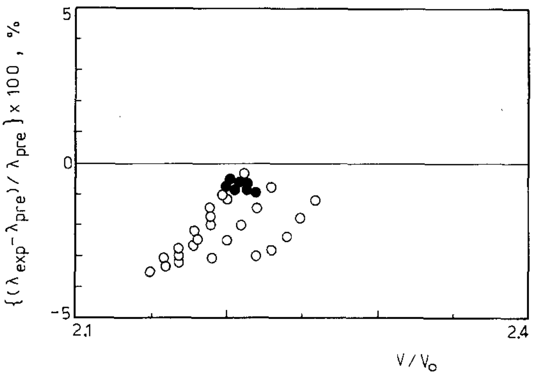

Fig. 6. Deviations of the high-pressure experimental thermal conductivity values of water from those predicted by the scheme of Eqs. (1), (3), and (7). (●) Ref. 25; (○) Ref. 30.

A further test that one can make of the scheme is to examine the thermal conductivity of water. Water can be considered, according to the aforementioned discussion, as a straight-chain alcohol with no carbon atoms. Taking thus the first and third terms only in Eq. (7) and placing $n_c = 0$, one can calculate the thermal conductivity of water at various densities. In Fig. 6, we show the deviations of our experimental measurements of water [25] and the measurements of Nagasaka et al. [30] up to 40 MPa in the temperature range 274–363 K, from the predicted values. It can be seen that the maximum deviation is ±3.2%.

The predictive power of the proposed scheme can be further

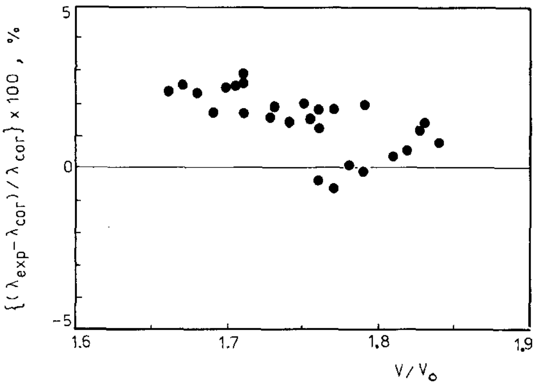

Fig. 7. Deviations of the high-pressure experimental thermal conductivity values of ethyl benzene from those predicted by the scheme of Eqs. (1), (3), and (7). (●) Ref. 31.

Table III. Comparison of Predicted Thermal Conductivity Values with Measured Values at 290 K and Atmospheric Pressure, for Various Liquids

Liquid	Thermal conductivity ($mW \cdot m^{-1} \cdot K^{-1}$)		Deviation $(\lambda_{exp} - \lambda_{pre})/\lambda_{pre}$ (%)	Ref. No.
	Predicted	Measured		
Benzyl alcohol ($C_6H_5CH_2OH$)	158.4	159.9	+1.0	32
Phenol (C_6H_5OH)	158.4	157.0	−0.8	33
o-Cresol ($CH_3C_6H_4OH$)	152.0	153.0	+0.6	33
Decanol ($C_{10}H_{21}OH$)	151.6	157.0	+3.5	34
Tetradecanol ($C_{14}H_{29}OH$)	152.0	158.0	+4.0	35
Isopropyl benzene ($C_6H_5C_3H_7$)	126.1	124.7	−1.1	36

demonstrated in the case of ethylbenzene. Recently, very accurate thermal conductivity data for ethylbenzene have been reported [31] in the temperature range 300–360 K and pressures up to 500 MPa. In Fig. 7 the deviations of the experimental thermal conductivity values from the predicted values are shown. The comparison is restricted to 50 MPa, as density values above this pressure were not available. It can be seen that the maximum deviation is 3%.

No other high-accuracy measurements at various temperatures and pressures for such liquids are available. We have, however, used the scheme to predict the thermal conductivity of various liquids for which less accurate measurements are available. In Table III, predicted values for the thermal conductivity of benzyl alcohol, phenol, *o*-cresol, decanol, tetradecanol, and isopropyl benzene are compared with measured values at 290 K and atmospheric pressure. Deviations are still within ±4%, even when we predict tetradecanol from a scheme based on methanol to hexanol. It is also worthwhile noting that the scheme can predict the thermal conductivity of liquids such as benzyl alcohol, phenol, or *o*-cresol, which are aromatic alcohols, although no data for aromatic alcohols were used.

5. CONCLUSIONS

A new semiempirical scheme has been presented for the prediction of the thermal conductivity of liquids at temperatures of 110–370 K and pressures up to 600 MPa. Liquids covered by this scheme are straight-chain alkanes, alcohols, diols, and water, as well as liquids with a benzene ring such as aromatic hydrocarbons and cyclic alcohols. The accuracy of the predictive scheme seems to be better than ±4% by comparison with existing accurate measurements of the thermal conductivity.

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