THERMAL CONDUCTIVITIES OF LIQUID n-ALKANES AND 1-ALKENES CORRECTED FOR RADIATIVE ENERGY TRANSPORT. Part 2. DATA FITTING FOR A WIDE STATE-PARAMETER RANGE

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An equation is proposed to describe the molecular thermal conductivities of liquid n-alkanes and 1-alkenes over wide ranges in the state parameters, which is based on the law of corresponding states. Measurements on the whole deviate from the equation by not more than 2-3%. The measurements on n-alkanes and 1-alkenes have been used in the fitting.

1. The reference literature [1, 2] for liquid organic compounds gives effective thermal conductivities, which include radiation transport components. Molecular-kinetic theory can be advanced and similarity theory applied if one has data on the molecular (conductive) thermal conductivities unaffected by the optical parameters of the media and bounding surfaces. One also needs to know the conductive thermal conductivity in order to determine the total heat transport under particular conditions.

Nonstationary methods have recently been used [3] to measure molecular thermal conductivities for various organic liquids, including n-alkanes and 1-alkenes. We have fitted the measurements for those two classes of hydrocarbons over wide ranges in temperature and pressure by means of the law of corresponding states [4], which is based on general similarity theory. That theory employs a restricted volume of measurements in order to determine the properties of similar substances that have not been measured thoroughly or at all.

Heated-wire and periodic-heating methods have been used to measure the molecular conductivities of the liquid n-alkanes from n-pentane C_5H_{12} to n-hexadecane $C_{16}H_{34}$. The temperature range covered was 250-650 K and the pressure range from 0.1 to 500-100 MPa. The following detailed measurements have been made: n-pentane [5, 6], n-hexane [5, 7, 8], n-heptane [7, 9-12], n-octane [5-7, 13-16], n-nonane [12, 14, 15, 17], n-decane [5, 7, 12, 13], n-undecane [15, 17, 18], n-dodecane [3, 7], n-tridecane [3, 19, 20], n-tetradecane [3, 15, 18], n-pentadecane [3, 18], and n-hexadecane [3, 5, 18]. The molecular thermal conductivities of 1-alkenes (1-hexene, 1-octene, and 1-nonene) have been measured in only one study [3] at 300-600 K and 0.1-50 MPa.

2. The above measurements on the saturation lines may be represented in reduced coordinates

$$\lambda_\tau/\lambda_{\tau=0,5}=f(\tau), \tag{1}$$

in which $\tau=T/T_c$, T_c is the critical temperature in K, and $\lambda_{\tau=0,5}$ is the thermal conductivity for $\tau = 0.5$.

The reduced temperature $\tau = 0.5$ was selected to cover all the measurements. Also, the absolute temperatures corresponding to $\tau = 0.5$ should not exceed 300-350 K because we have information only on the effective thermal conductivities [1, 2] for the high-molecular 1-alkenes (with the number of carbon atoms in the molecule $n_C \geqslant 10$). To determine $\lambda_{\tau=0,5}$ for those substances, one has to make a correction for the radiative component, which was taken the same as for the n-alkanes at the same T and did not exceed 1-3%.

Figure 1 shows the processing results in reduced coordinates. The points for the n-alkanes (from n-pentane to n-hexadecane) and the 1-alkenes (from 1-hexene to 1-nonene) fit closely to a single curve described by

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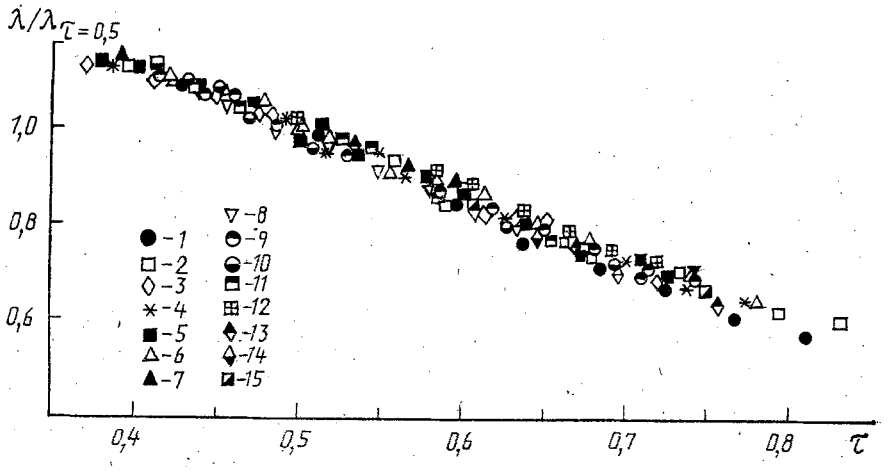

Fig. 1. Behavior of $\lambda/\lambda_{\tau=0.5}=f(\tau)$ for the n-alkanes (*1* — C_5H_{12}; *2* — C_6H_{14}; *3* — C_7H_{16}; *4* — C_8H_{18}; *5* — C_9H_{20}; *6* — $C_{10}H_{22}$; *7* — $C_{11}H_{24}$; *8* — $C_{12}H_{26}$; *9* — $C_{13}H_{28}$; *10* — $C_{14}H_{30}$; *11* — $C_{15}H_{32}$; *12* — $C_{16}H_{34}$) and 1-alkenes (*13* — C_6H_{12}; *14* — C_8H_{16}; *15* — C_9H_{18}).

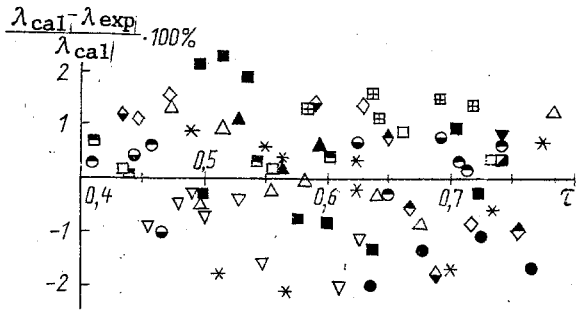

Fig. 2. Deviation of the measured values λ_m from those calculated from (2) for P = Ps; symbols are in Fig. 1.

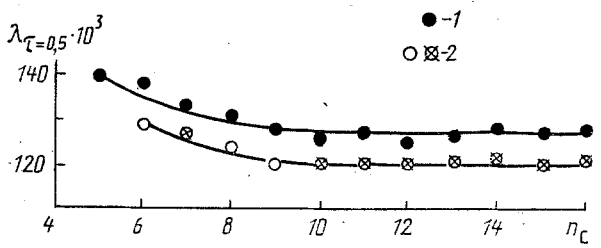

Fig. 3. Dependence of $\lambda_{\tau=0.5}$ on number of carbon atoms: 1) n-alkanes: 2) 1-alkenes. $\lambda_{\tau=0.5}$, W/(m·K).

$$\lambda_\tau/\lambda_{\tau=0,5} = (1{,}7911 + 1{,}8273\tau + 0{,}4714\tau^2). \qquad (2)$$

This applies for τ = 0.4-0.8. Figure 2 compares the measurements with (2) and shows that in nearly all cases the deviations do not exceed 2% (maximum deviation 2.3%). The deviations are also not systematic, i.e., the thermal conductivities for the two classes agree satisfactorily with the law of corresponding states.

Figure 3 shows the n_C dependence of $\lambda_{\tau=0.5}$ (crosses are given for those 1-alkenes for which there are no measurements on the molecular thermal conductivity). As n_C increases, $\lambda_{\tau=0.5}$ decrease, and for $n_C>9$ tend to become constant. The dependence of $\lambda_{\tau=0.5}$ on the number of carbon atoms for the n-alkanes is

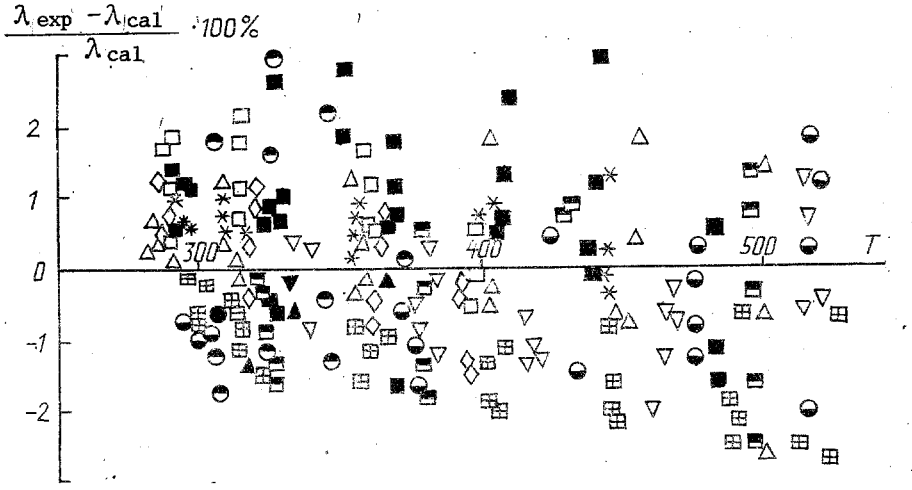

Fig. 4. Deviations in the measured λ_m from various sources with various state parameters from those calculated from (5); symbols as in Fig. 1. T in K.

$$\lambda_{\tau=0.5} = 0{,}168 - 70{,}0\cdot10^{-4}n_C + 28{,}6\cdot10^{-5}n_C^2 \text{ for } n_C = 5-9, \qquad (3)$$
$$\lambda_{\tau=0,5} = 0{,}1265 \text{ W/(m·K) for } n_C = 10-16$$

and for the 1-alkenes

$$\lambda_{\tau=0,5} = 0{,}174 - 96{,}6\cdot10^{-4}n_C + 42{,}9\cdot10^{-5}n_C^2 \text{ for } n_C = 6-9, \qquad (4)$$
$$\lambda_{\tau=0,5} = 0{,}1205 \text{ W/(m·K) for } n_C = 10-16.$$

Equations (2)-(4) enable to calculate the molecular thermal conductivities for these compounds on the saturation lines over wide ranges in temperature, and they include substances for which there are no measurements. It is merely necessary to know T_c, which has been given for many substances in [21].

The pressure dependence of the conductivities was incorporated via the following expression based on a one-parameter generalization of the law of corresponding states:

$$\lambda_{\tau,\pi} = \lambda_\tau + \Delta\lambda(\tau, \pi), \qquad (5)$$

in which $\Delta\lambda(\tau, \pi) = (\pi/10^3)\ (0{,}4556 - 0{,}6838\tau + 1{,}925\tau^2)F$; $\pi = (P - P_s)/P_c$; P_s is the pressure on the saturation line in MPa, P_c the critical pressure in MPa, F = 1 for n_C = 10-16, and F = 2-S for n_C = 5-9, with S the acentricity factor [21]:

$$S = \frac{3}{7}\frac{T_b/T_c}{1 - T_b/T_c} - \lg(10P_c) - 1;$$

and T_b the boiling point at atmospheric pressure in K.

Equation (5) describes the measurement data for τ = 0.4-0.8 (temperatures from 250 to 560 K) and π = 0.02-20 (pressures from 0.1 to 50 MPa). Figure 4 shows that the deviations in the various results from (5) at high pressures do not exceed 3%.

3. (2)-(5) can be used reliably to calculate molecular thermal conductivities for liquid n-alkanes and 1-alkenes over wide ranges in the state parameters.

NOTATION

λ thermal conductivity, W/m·K; T temperature in K; $\tau = T/T_c$ reduced temperature; n number of atoms; P pressure in MPa; $\pi = (P-P_s)/P_c$ reduced pressure; S acentricity factor. Subscripts: τ at reduced temperature; τ = 0.5 at reduced temperature of 0.5; C carbon; c critical; s on saturation line; b boiling.

LITERATURE CITED

1. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, Thermal Conductivities of Liquids and Gases [in Russian], Moscow (1978).
2. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, Thermal Conductivities of Polyatomic Liquids and Gases [in Russian], Moscow (1981).
3. A. A. Tarzimanov, R. A. Sharafutdinov, and F. R. Gabitov, Inzh.-Fiz. Zh., 59, No. 4, 662-667 (1990).
4. L. P. Filippov, The Law of Corresponding States [in Russian], Moscow (1983).
5. S. N. Kravchun, Measurements on the Thermophysical Parameters of Liquids by the Periodic-Heating Method: Ph. D. Thesis [in Russian], Moscow (1983).
6. V. M. Shul'ga, A Balance Method of Periodic Heating for Measuring the Thermal Parameters of Liquids over a Wide Temperature Range at Pressures Up to 1000 MPa: Ph. D. Thesis [in Russian], Moscow (1985).
7. H. Kashiwagi, M. Oishi, J. Tanaka, H. Kubata, and T. Makita, Int. J. Thermophys., 3, No. 2, 32-36 (1982).
8. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, Ber. Bunsenges. Phys. Chem., 88, No. 1, 32-36 (1984).
9. C. A. Nieto de Castro, J. C. G. Calado, and W. A. Wakeham, Proc. 7th Int. Symp. Thermophys. Properties (1977), pp. 730-738.
10. S. N. Nefedov and L. P. Filippov, Zh. Fiz. Khim., 53, No. 8, 2112-2113 (1979).
11. J. Menashe and W. A. Wakeham, Ber. Bunsenges. Phys. Chem., 85, No. 4, 340-347 (1981).
12. A. A. Kuyumchev, V. M. Shul'ga, and Yu. A. Atanov, Teplofiz. Vys. Temp., 26, No. 4, 727-732 (1988).
13. C. A. Nieto de Castro, J. C. G. Calado, and W. A. Wakeham, High Temp. High Press., 11, No. 5, 551-559 (1979).
14. C. A. Nieto de Castro, J. M. N. Fareteire, and J. C. G. Calado, Proc. 8th Symp. Thermophys. Properties, Vol. 1 (1981), pp. 247-253.
15. J. C. G. Calado, J. M. N. A. Fareleira, C. A. Nieto de Castro, and W. A. Wakeham, Int. J. Thermophys., 4, No. 3, 193-208 (1983).
16. A. A. Tarzimanov, F. R. Gabitov, and R. A. Sharafutdinov, Heat and Mass Transfer in Chemical Engineering: Intercollegiate Coll. [in Russian], Kazan' (1985), pp. 14-17.
17. J. Menashe and W. A. Wakeham, Ber. Bunsenges. Phys. Chem., 86, No. 6, 541-545 (1982).
18. J. Wada, J. Nagasaka, and A. Nagashima, Int. J. Thermophys., 6, No. 3, 251-265 (1985).
19. M. Mustafa, M. Sage, and W. A. Wakeham, Int. J. Thermophys., 3, No. 3, 101-116 (1982).
20. A. S. Tleubaev, Automated Systems for Measuring Thermophysical Parameters: Thermal Conductivity and Specific Heat for Some Organofluorine Liquids: Ph. D. Thesis [in Russian], Moscow (1986).
21. R. Read, J. Prausniz, and T. Sherwood, The Properties of Gases and Liquids [Russian translation], Leningrad (1982).