transitions in argon in the domain mentioned. The data of Table 2 indicated that the agreement between theory and experiment is even better for crystalline argon than for a fluid and is 5% although the role of multiparticle interactions for the crystals should seemingly be greater since they possess greater density. However, it is well known [7] that for a suitable selection of the pairwise molecule interaction potential parameters crystals are described better in the additivity approximation than are fluids. This is explained by the intrinsic behavior of the multiparticle forces at different distances, which can result in their mutual compensation. Very much weaker dependences u(T) and v(T) for crystals are a result, which indeed assures better agreement between the theoretical relationship (4) and experiment for them.

In conclusion, let us note that the obtained relationship (4) is its own kind of indicator of the role of multiparticle molecule interactions in condensed media and, consequently, an investigation of the dependence of the heat of substance evaporation on its volume yields information about the non-additive component of the substance potential energy.

LITERATURE CITED

1. A. V. Voronel', Zh. Tekh. Fiz., 29, No. 3, 304-306 (1959).
2. I. Z. Fisher, Statistical Theory of Fluids [in Russian], Moscow (1961).
3. G. Temperly, J. Rashbrook, and J. Rawlinson (eds.) Physics of Simple Fluids [Russian translation], Moscow (1971).
4. N. B. Vargaftik, Handbook on Thermophysical Properties of Gases and Liquids [in Russian], Moscow (1963).
5. M. P. Malkov (ed.), Handbook on Physicotechnical Principles of Cryogenics [in Russian], Moscow (1973).
6. R. Reed, J. Prausnitz, and T. Sherwood, Properties of Gases and Fluids [Russian translation], Leningrad (1982).
7. I. G. Kaplan, Introduction to the Theory of Intermolecular Interactions [in Russian], Moscow (1983).

THERMAL CONDUCTIVITY OF N-ALKANES AND 1-ALKENES. UNDISTORTED BY RADIANT ENERGY TRANSPORT.

I. RESULTS OF EXPERIMENTAL STUDY

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Results are presented from an experimental study of molecular thermal conductivity of liquid n-alkanes and 1-alkenes using the hot wire method. Measurements were performed at pressures up to 50 MPa and at temperatures from 300 to 640 K. The new experimental data appear to be low by 10% or more when compared to accepted values.

1. The majority of organic compounds, including n-alkanes and 1-alkenes are among the materials which are semitransparent in the IR range of the spectrum. The thermal conductivity process in such substances is always accompanied by radiant energy transport, as a result of which the thermal flux is determined not by the temperature gradient at a given point, but by the temperature field over the entire system, and Fourier's law is not satisfied. As a consequence the effective thermal conductivity proves to depend not only on the properties of the medium, but also the system geometry.

Current reference data [1, 2] on thermal conductivity of organic liquids is based on experimental material obtained by traditional methods (coaxial cylinders, plane layer, hot

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wire, etc.). These methods directly measure the effective thermal conductivity value λ_{ef} which includes molecular (conductive) λ_m and radiant λ_v components, with λ_v depending on layer thickness and optical properties of the medium and boundary surfaces. Theoretical calculations and recent experimental data show that with increase in temperature the quantity λ_v increases intensely and may comprise 10-20% of the measured thermal conductivity value. The significant divergence (up to 10-14%) between results of various authors on effective thermal conductivity, for example, of liquid n-alkanes in the high temperature range [1] can apparently be explained to a significant degree by the varying value of the radiant component.

2. In recent years there have been significant achievements in development and utilization of rapid nonsteady state methods for thermal conductivity measurement, in which the thermal disturbance encompasses only thin layers (of the order of hundredths of an mm). Such thin layers of organic liquids are practically transparent to thermal radiation [3], and it becomes possible to measure molecular (conductive) thermal conductivity. There are two basic methods which can be used for such studies: the rapid (pulsed) hot wire method and the periodic heating method [1]. These methods have recently begun to be employed in the USSR and abroad for measurement of the molecular thermal conductivity of liquid organic compounds, including n-alkanes. Analysis of the available experimental material reveals that liquid n-alkanes have been studied over a relatively narrow temperature interval (from 273 to 370-400 K at pressures to 500-1000 MPa). The authors of [4, 5] performed a systematic study of thermal conductivity of liquid n-alkanes (from n-pentane to n-decane, as well as n-hexadecane) and extended the temperature range from 420-630 K at pressures to 30 MPa. Nevertheless the thermal conductivity of the higher (above C_{10}) members of the series (with the exception of n-hexadecane) remains unstudied at T > 373 K. It is known that the effect of the semitransparency of organic liquids on their thermal conductivity is most significant at high temperature. Hence follows the necessity of studying high molecular weight n-alkanes over a wide temperature interval at various pressures. No measurements of the molecular thermal conductivity of 1-alkenes have been performed previously.

The rapid (pulsed) hot wire method was used to study the thermal conductivity of n-alkenes and 1-alkenes without distortion by radiant energy transport. The electrical circuits and experimental technique were described in [6]. A thin platinum wire sensor (radius r = 2.5 μ, length ℓ = 35-73 mm, and resistance R_0 = 219-434 Ω) was installed vertically in a cell containing the liquid to be studied. Use of a wire of limitingly small diameter permits performing measurements at very brief heating times (30-100 msec). A chromel-alumel thermocouple (experimental device No. 1) or platinum (wire diameter 0.1 mm) resistance thermometer (device No. 2) was installed within the autoclave next to the sensor for calibration and stability monitoring.

Liquid thermal conductivity was determined from the equation [6]

$$\lambda = \frac{q}{4\pi} \frac{\ln(\tau/\tau_0)}{(\Delta T - \Delta T_0)}.$$

A significant advantage of the hot wire method as compared to others is that the measurement cell corresponds almost completely to the theoretical model of a linear source, so that the corrections to be introduced are small. The sum of all corrections comprises 1.5-2%. Moreover, as is evident from the equation, there is no need to measure cell dimensions, and the high resistance of the sensor enables more precise determination of ΔT. The uncertainty in the thermal conductivity measurements, as defined by government standard GOST 8.207-76 (at an 0.95 confidence level) is no more than 1%.

Two experimental devices were constructed, differing in the measurement cell configuration and the temperature stabilization system. In device No. 1, designed for measurements in the range T = 300-520 K and P = 0.1-50 MPa, the autoclave was placed in a liquid (PMS-200) thermostat. The sensor was mounted on a technically pure titanium body, having approx-

TABLE 1. Thermal Conductivity of n-Hexadecane ($C_{16}H_{34}$) at P = 0.1 MPa.

T, K	325,7	375,4	375,5	426,3	476,9	476,9	524,2
$\lambda \cdot 10^3$ W/(m·K)	135,1	124,3	124,4	112,9	102,3	103,3	93,0

TABLE 2. Thermal Conductivity of n-Alkanes $\lambda \cdot 10^3$ W/(m·K) at Various Temperatures and Pressures

T, K	P, мПа					
	P_s	5,0	10,0	20,0	30,0	50,0
			n-dodecane $C_{12}H_{26}$			
323,0	126,4	128,0	130,0	132,2	137,0	144,0
374,0	113,5	114,8	118,0	120,7	125,0	132,4
423,8	101,5	103,3	106,1	110,2	114,5	123,4
466,0	91,6	93,5	96,8	102,6	108,0	118,0
522,4	81,0	83,5	87,6	94,2	100,5	111,2
593,5*)	72,3	77,3	81,5	89,8	95,8	—
627,0*)	70,7	74,5	80,3	88,2	95,0	—
643,0*)	—	74,6	79,8	87,6	94,4	—
			n-tridecane $C_{13}H_{28}$			
323,0	129,4	130,1	132,1	135,2	139,0	145,0
371,3	117,5	118,6	121,5	124,6	129,0	136,5
423,7	105,2	107,7	110,5	114,2	118,7	126,8
471,0	94,7	97,4	100,9	105,0	110,0	118,2
520,3	—	87,9	92,6	97,5	102,8	111,4
			n-tetradecane $C_{14}H_{30}$			
300,0	136,6	138,1	139,8		146,4	153,2
371,5	119,8	121,5	124,0		129,6	138,3
423,5	108,7	110,0	113,0		121,5	129,0
465,4	99,5	101,0	104,0		113,3	123,5
520,5	—	91,2	95,0		107,0	116,0

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*Experimental data received for device No. 2.

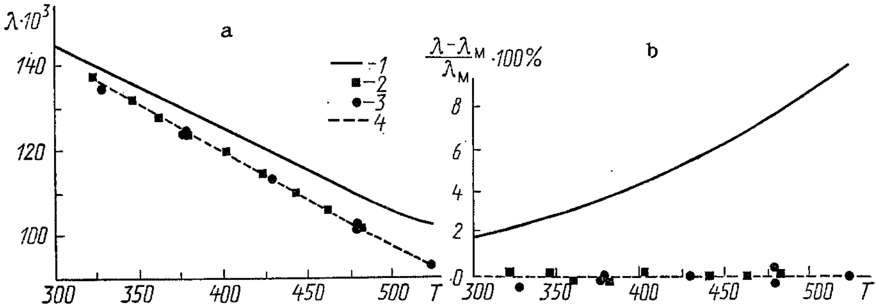

Fig. 1. Comparison of experimental λ_m values obtained for n-hexadecane at P = 0.1 MPa with data from literature: 1-hexene 1, [2]; 2, [5]; 3, present study; 4, averaged λ_m value. λ_1, W/(m·K); T, K.

imately the same coefficient of linear expansion as the platinum. To increase the temperature range of the study device No. 2 was constructed, to measure thermal conductivity of n-dodecane and 1-nonene at temperatures to 650 and 600 K respectively (at higher temperatures thermal decomposition of the materials set in). The autoclave was temperature stabilized by four electric heaters. In the measurement cell thermal expansion and deviation from straightness of the platinum wire were compensated by a platinum weight (3.8 mg). Pressure application and measurement in both devices were carried out by an MP2500 class 0.02 piston manometer.

Chemically pure grade materials were used for the study, corresponding to specifications: n-hexadecane TU-6-09-3659-74, n-dodecane TU-6-09-3730-74, n-tridecane TU-6-09-3732-74, n-tetradecane TU-6-09-3705-74, 1-hexene TU-6-09-3812-74, 1-octene TU-6-09-14-1994-78, 1-nonene TU-6-09-832-78. Measurements were performed along isotherms. From five to eight isotherms were taken for each liquid. The heating current was in the range 5-10 mA, with the sensor heating by 1-2 K. The compounds n-octane, n-pentane, and n-hexadecane were studied at atmospheric pressure. Data for n-octane were presented in [6]. For n-pentadecane one point was obtained at T = 520 K and P = 0.1 MPa, $\lambda = 92 \cdot 10^{-3}$ W/(m·K). Results for n-hexadecane are presented in Table 1. The experimental data for molecular thermal conductiv-

TABLE 3. Thermal Conductivity of 1-Alkenes $\lambda \cdot 10^3$, W/(m·K) at Various Temperatures and Pressures

T, K	P, MPa					
	P_s	5,0	10,0	20,0	30,0	50,0
			n-decane C_6H_{12}			
300,3	113,0	141,1	116,1	120,0	122,5	
323,4	104,7	106,8	109,6	114,0	116,4	
373,0	—	93,8	96,4	102,6	106,2	
422,0	—	82,4	85,9	93,0	97,8	
			1-octene C_8H_{16}			
324,5	111,1	113,7	115,1	120,0	123,1	
371,5	97,0	99,5	103,0	109,5	113,6	
422,0	83,4	87,6	92,0	97,2	102,7	
472,0	71,0	76,0	81,8	88,4	95,2	
520,0	—	68,0	75,3	82,5	89,6	
			1-nonene C_9H_{18}			
323,4	112,1	114,8	118.2	123,0	127,0	133,5
372,9	100,1	102,4	105,8	110,7	116,2	123,8
423,0	87,1	90,2	93,8	100,0	104,4	—
472,4	74,9	78,8	83,4	90,0	94,4	—
522,0	65,4	70,0	76,5	82,6	89,8	—
497,0*)	—	73,6	80,2	85,3	—	—
597,0*)	—	62,3	70,4	78,3	—	98,4

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*Experimental data received for device No. 2.

TABLE 4. Pressure Dependence of Effective and Molecular Thermal Conductivity of Certain Organic Liquids

Material	T, K			
	470		520	
	[8]	present data	[8]	present data
n-dodecane	1,23	1,26	1,26	1,29
n-tridecane	1,20	1,21	1,26	1,27
n-tetradecane	1,20	1,22	1,24	1,27
n-nonene	1,30	1,32	1,37	1,38

ity of n-dodecane, n-tridecane, and n-tetradecane are presented in Table 2, while those for 1-hexene, 1-octene, and 1-nonene are given in Table 3, where P_s is pressure on the saturation line.

Analysis of the data obtained indicates that the presence of the double bond in the 1-alkenes leads to decrease in both the value of thermal conductivity and its temperature coefficient as compared to n-alkanes.

As was expected, the results of our measurements on all the materials studied lie systematically lower than the reference standards of [1, 2], which present effective thermal conductivity values corresponding to some mean layer thickness 0.5-0.7 mm. As is evident from Fig. 1, there is good agreement (divergence not greater than 1%) between our data and that of [5], which used the periodic heating method. At room temperature ($T \approx 300$ K) the data of [2] are elevated by 1.5-2%, and the divergence increases with increase in temperature, reaching 10% at T = 525 K. These values agree well with the fact that $\lambda_v \sim T^3$ [7]. A similar pattern can be seen for the 1-alkenes. Figure 2 compares our data for thermal conductivity of 1-nonene at P = 5.0 MPa with the results of [8], which were used in preparing reference [1].

Table 4 presents information on the dependence of the effective [8] and molecular (present data) thermal conductivity of certain organic liquids on pressure ($P_2 = 50$ MPa and $P_1 = 5$ MPa) at temperatures of 470 and 520 K. It is evident that the pressure dependence of thermal conductivity is identical within the overall limits of experimental uncertainty in both cases, i.e., the fraction of radiant transport in the case of organic liquids is practically independent of pressure (up to 50 MPa). A similar conclusion was made earlier in [7] for n-alkanes at pressures to 30 MPa.

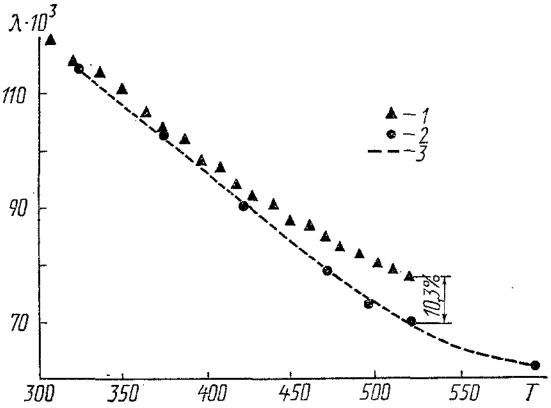

Fig. 2. Comparison of experimental λ_m values obtained for 1-nonene at P = 5.0 MPa with results of [8]: 1, [8]; 2, present study; 3, averaged λ_m value.

3. As the above demonstrates, reference data on effective thermal conductivity of organic liquids differs significantly, especially at high temperatures, from conductive thermal conductivity values, so that it will be necessary to collect the latter type of experimental data and develop methods for its generalization.

NOTATION

λ, liquid thermal conductivity coefficient, W/(m·K); T, temperature, K; P, pressure, MPa; r, radius; ℓ, length; R, resistance; q, thermal flux per unit length; ΔT and ΔT_0, sensor temperature increments at times τ and τ_0. Subscripts: m, molecular; ef, effective; r, radiant; 0, at 0°C or initial time; s, on saturation line.

LITERATURE CITED

1. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, Thermal Conductivity of Liquids and Gases [in Russian], Moscow (1978).
2. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, Thermal Conductivity of Multiatomic Liquids and Gases [in Russian], Moscow (1981).
3. B. I. Il'in, V. F. Salokhin, and G. G. Spirin, Inzh. Fiz. Zh., 30, No. 6, 972-978 (1976).
4. S. N. Nefedov and L. P. Filippov, Zh. Fiz. Khim., 53, No. 8, 2112-2113 (1979).
5. S. N. Kravchun, Study of Thermophysical Properties of Liquids by the Periodic Heating Method. Author's Abstract, Candidate's Dissertation [in Russian], Moscow (1983).
6. A. A. Tarzimanov, R. A. Sharafutdinov, and F. R. Gabitov, Metrolog., No. 1, 29-34 (1989).
7. S. N. Kravchun and L. P. Filippov, Heat and Mass Exchange in Chemical Technology: Inter-VUZ Handbook [in Russian], Kazan' (1985), pp. 3-6.
8. R. A. Mustafaev, Thermophysical Properties of Hydrocarbons at High State Parameters [in Russian], Moscow (1980).