AN EXPERIMENTAL INVESTIGATION INTO THE COMPLEX OF THERMOPHYSICAL PROPERTIES OF LIQUIDS

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A setup is described, intended for the measurement of a complex of thermophysical characteristics of liquids and gases. It is based on the method of registering the fluctuations of temperature of wire transducers heated by alternating current. The merits of the method are analyzed. The results of an investigation into the thermophysical properties of toluol and n-hexane are presented.

Investigation of the thermophysical properties of liquids, in the first instance the thermal conductivity and heat capacity, is an integral element of the study of most important aspects of the nature of the liquid state of matter — the character of thermal motion and associated questions concerning the mechanism of transfer processes in these media. It is clear that the solution of these major problems of molecular-kinetic theory must resolve also the practical problem — development of methods of calculation and prediction of the corresponding properties. Up to now this work is conducted in a purely empirical plane and the study of the thermophysical properties has brought a distinctly insufficient contribution into physics of liquids. We can name two important causes which slow down the advance: 1) the complexity of the process of heat transfer in liquids, especially at high temperatures, as a result of which the temperature being measured in the majority of cases is distorted by the influence of radiative transfer, the magnitude of which is difficult to estimate; 2) incompleteness of the existing experimental material. For a real analysis of data on heat conduction, it is necessary to enlist information about the heat capacity of liquids and their thermal properties. At the present time heat capacity of liquids has been studied only for about 10% of materials for which data about thermal conductivity exist. Measurement of heat capacity, as a rule, embraces a very limited region of states, and the results of different authors far from always well agree with one another [1].

Taking into account what has been said, it is important to devise an experiment which would enable us to get rid of the two above-mentioned shortcomings at the same time, i.e., an experiment in which we would measure the purely molecular thermal conductivity (freed from the contribution of photon transfer) and simultaneously, under the same conditions, the thermal capacity. Such a complex experiment is proposed in [2]. It is based on the use of periodic heating of wire probes located in the liquid being investigated [3]. In an installation thus created, a thin platinum wire is heated by current of audio frequency, and the amplitude and phase of temperature oscillations of the wire are determined by the method of radio technology. Both quantities substantially depend on two thermophysical parameters — the thermal conductivity and the heat capacity of the liquid in which the probe is located. To determine each of these parameters, we require information about two quantities. There exist three variants of complex measurement methods. In the first of them we use information about the amplitudes of temperature oscillations at two sufficiently dispersed frequencies, in the second we need information about the phase at two frequencies, and in the third we require information about the amplitude and phase at a single frequency. All three variants of measurement methods can be examined on the installation depicted in Fig. 1.

A probe 1 of platinum wire with a diameter of a few microns is included in the arm of the branch C of an ac bridge formed by branches A, B, and C and has, respectively, three pairs of diagonal points AB, BC and AC. Branch A includes an analogous probe 2 placed in vacuum; it serves as a source of the base phase signal. During heating of the probes by current of audio frequency from generator 3, the temperature and, consequently, the resistance of the wires pulsates with the doubled frequency. Oscillations of the resistance make the scheme nonlinear and lead to the combinative, trebled frequency appearing. The bridges

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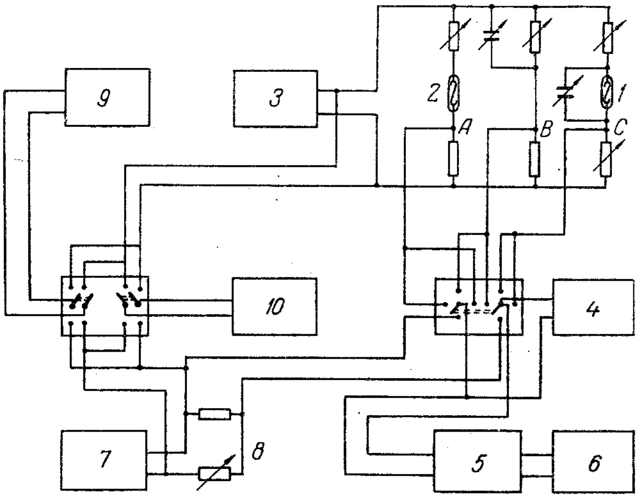

Fig. 1. Diagram of an installation for investigating the complex of thermophysical properties of liquids.

AB, BC, and AC are balanced at the fundamental frequency, the balance is checked by the zero index 4. Signals of the trebled frequency, carrying information about the properties of the liquid, from the diagonals of bridges AB, BC, and AC enter into the selective amplifier 5 and are registered by digital voltmeter 6. For the calibration of the registering channel we use a circuit of reference signal 8 supplied from generator 7 tuned to the trebled frequency. The voltage and frequency of the generators are measured by digital voltmeter 9 and frequency meter 10.

The process of measurements basically reduces to registering two signals of the doubled frequency from the diagonals AC and BC.

An analysis of the conditions under which the experiment is conducted, and the estimate of the measurements compels us to give preference to the amplitude—phase variant. Under the typical conditions of the experiment, the systematic error of measurement of thermal conductivity amounts to 1-1.5% and the error for thermal capacity 1.5-2%.

One of the most important peculiarities of the method is the fact that the wave of the temperature wave in the liquid at frequencies of periodic heating ∿100 Hz turns out to be very small. As a result, the convective flows which can arise in the volume of the medium, practically have no effect on the results of thermal conductivity measurement. Another important consequence of the same peculiarity is the relative smallness of the radiative flux in the overall heat flux, the possibility of obtaining results on thermal conductivity which are not distorted by the effect of radiation.

The solution of the problem of radiative—convective heat exchange of a plane transducer being heated by alternating current in a semitransparent medium [4], and the estimation of the radiative flux from a cylindrical transducer with a blackbody placed in a transparent medium, indicate that under the conditions of the experiment being carried out by us the radiative flux in transparent and semitransparent media is approximately two orders less than in experiments utilizing stationary methods for determining the thermal conductivity in the case of a gap width of ∿1 mm. The absence of the role of radiative transfer in experiments by the method under consideration is confirmed by the absence of any notable dependence of the measurement results on the heating frequency when the latter varies from 23 to 600 Hz.

An undoubted merit of the method is simplicity and the minuteness of the probe and the small dimensions of the measuring cell, enabling us to carry out investigations into the thermophysical properties under extremal conditions, including conditions close to the critical point. Combination of the different variants of the method of periodic heating of low-inertia probes of wire and foil, and also the possibility of wide variation of the conditions of carrying out the experiment allow us to study the region of states of the material from a dense liquid to vapors of low pressure. There exists a variant of the method which is specifically foreseen for investigating the properties of gases and vapors at temperatures up to 1500°K.

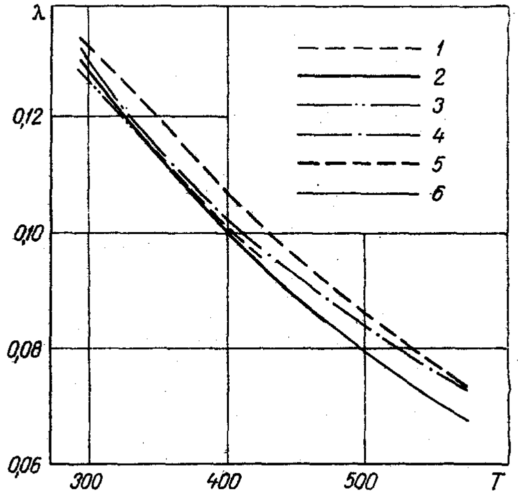

Fig. 2. Results of investigating the thermal conductivity (W/m·deg K) of toluene on the saturation line: 1) method of heated wire (extrapolation to $\delta = 0$); 2) method of a plane layer and coaxial cylinders ($\delta = 0$); for the construction of 1 and 2 the results of [7-19] have been used; 3) method of rapid heating of wire [6]; 4) method of heated wire for a gap width of ~3 mm [7]; 5) data recommended in [5], obtained by averaging of the results of 43 experimental investigations, and relating to a gap of about 1 mm; 6) our results.

The rapid action of the installation, its high resolving capability, sensitivity, and productivity are connected both with the peculiarity of the method and with the use of the modern radio-technical apparatus which is convenient for the creation of partially or fully automated systems for investigation of the complex of thermophysical properties of liquids and gases.

The method of measurement just described is used for the investigation of the complex of thermophysical properties of a wide circle of materials. Below we shall present some of the results obtained.

The properties of toluene have been investigated by us within the temperature interval 293-643°K under pressures from 2 to 30 MPa. The data on thermal conductivity of toluene (W/m·deg K) on the saturation line within the interval 293-573°K is approximated by the polynomial

$$\lambda(p_s, T) = 0.1375 - 3.26\cdot10^{-4}(T - 273.2) + 3.28\cdot10^{-7}(T - 273.2)^2 \qquad (1)$$

and is shown in Fig. 2. The mean-square error of approximation amounts to 0.5%.

From Fig. 2 it is seen that there exists a systematic difference of the data thus obtained from the data recommended in [5] towards lower values. The difference, amounting to 1.3% at the temperature 293°K, increases with increase in the temperature and at 473°K reaches 8%. This discrepancy can be explained by the role of radiative heat transfer, which is not singled out in the data [5]. The validity of this conclusion is confirmed also by the closeness of the results obtained to the data of [6], carried out by the method of rapid heating, in which the role of radiative transfer is also small. This is confirmed by the agreement of the two curves in Fig. 2 obtained by extrapolation of the results of experiments of two types to zero gap thickness, i.e., to the value of molecular thermal conductivity (the results of [7-19] have been used).

The effect of pressure on the thermal conductivity of liquid toluene, representable by the ratio $\lambda(p, T)/\lambda(p_s, T)$, according to the results of our measurements turned out to be close to that obtained by other methods. This ratio within the interval 293-573°K under pressures up to 30 MPa agrees with the recommendations [5] within the limits of 2-3%, a fact which bears witness to the relatively small influence of pressure on radiative transfer. The

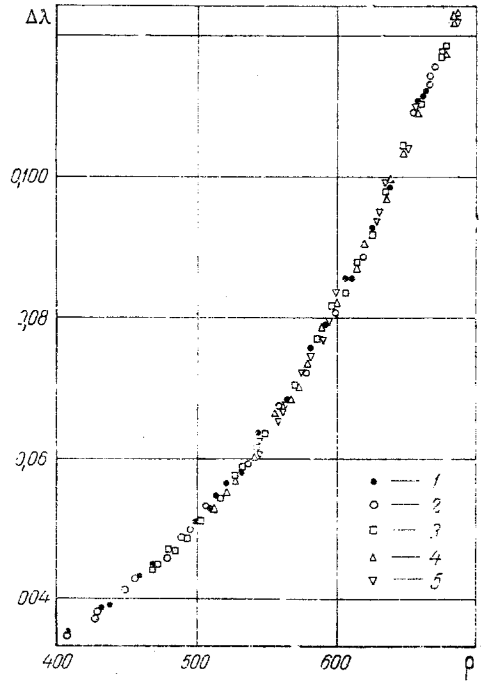

Fig. 3. Dependence of the surplus thermal conductivity Δλ, W/m·deg K, on density ρ, kg/m³: 1) on the saturation line; 2) 5 MPa; 3) 10 MPa; 4) 20 MPa; 5) 30 MPa.

thermophysical properties of n-hexane (283-573°K; 0.1-30 MPa) were investigated by means of wire transducers of various diameters: ∿1, ∿2.5, ∿5 μm. Altogether on four isobars (5, 10, 20 and 30 MPa) and saturation lines more than 200 experimental points were obtained. Any notable systematic discrepancy between the data obtained with transducers of different diameters within the entire region of states of n-hexane were not discovered. The results of investigation of thermal conductivity of n-hexane on the saturation line in the temperature range 282-475°K are approximated by the polynomial

$$\lambda(p_s,\ T) = 0{,}128 - 3{,}95\cdot 10^{-4}(T - 273{,}2) + 5{,}75\cdot 10^{-7}(T - 273{,}2)^2.$$

The mean-square deviation of the experimental data from the approximating curve amounts to 0.6%. These results, just as those in the case of toluene, systematically differ from the results recommended in [5], and they allow us to draw the conclusion that the fraction of radiative transfer in n-hexane in layers of thickness ∿0.7 mm [5] at 300°K amounts to ∿3%, and at 500°K it is 12%.

The results on thermal conductivity of n-hexane and toluene allow us to find out that the surplus thermal conductivity $\Delta\lambda = \lambda(p, T) - \lambda(0, T)$, where $\lambda(0, T)$ is the thermal conductivity of the rarefied gas, is a single-valued and monotonic function of density (Fig. 3). This function for n-hexane is approximated by the polynomial (the values of $\lambda(0, T)$ are taken from [5])

$$\Delta\lambda(\rho) = 0.2036\cdot 10^{-3}\rho - 6.75\cdot 10^{-7}\rho^2 + 9.29\cdot 10^{-10}\rho^3.$$

For toluene the results can be represented in the form

$$\Delta\lambda(\rho) = 0.154\cdot 10^{-3}\rho - 4.2\cdot 10^{-7}\rho^2 + 4.68\cdot 10^{-10}\rho^3.$$

The results of measurements of the heat capacity of toluene and n-hexane agree with data from [20,21] within the limits of an error 1.5-2%.

When discussing data on capacity, it is advisable to draw attention to the weak temperature dependence of isobaric heat capacity of unit volume $c_p\rho$ on the temperature. This dependence, having the character of a very shallow maximum, is virtually the same for different isobars, with the exception of the region directly adjacent to the critical point, but much narrower than for c_p. The relationship under consideration can be conveniently used to interpolate and extrapolate data on heat capacity. We should also mention the relatively weak and purely linear dependence of thermal activity $\lambda/\sqrt{a}$ on the temperature.

Concluding, we present observations about the possibilities of developing this work.

The results presented above are the first step of a large program of investigations including: derivation of new results on molecular thermal conductivity of a large number of organic liquids; analysis of the role of radiative heat transfer; study of the laws of behavior of the heat capacity of liquids in a broad range of states, in connection with the problem about the character of thermal motion of molecules of liquids; and investigation of the interconnection of transfer, calorific, and thermal quantities from the viewpoint of heat transfer in liquids.

NOTATION

λ, thermal conductivity; a, thermal diffusibility; c_p, heat capacity at constant pressure; T, absolute temperature; p, pressure; p_s, pressure of saturated vapors; $\Delta\lambda$, excess thermal conductivity of liquid; ρ, density.

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MEASUREMENT OF THE VISCOSITY OF LIQUIDS AND THE DIMENSIONS OF SUSPENDED PARTICLES BY THE METHOD OF CORRELATION OPTICAL-MIXING SPECTROSCOPY

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The Brownian motion of spherical particles in water is investigated using optical-mixing spectroscopy. The diameters of the particles and the viscosity of the liquid are measured. Multiple scattering was found to affect the results.

One of the most promising applications of optical-mixing spectroscopy is the measurement of the shear viscosity of transparent liquids. In this method small spherical particles are introduced into the liquid being investigated and their diffusion coefficient is measured.

The diffusion coefficient is defined using the results of measurements of the width of the unbiased (central) component in the spectrum of the scattered light using an optical-mixing spectrometer [1]

$$\Gamma = DK^2. \tag{1}$$

Further, using the Einstein–Stokes formula, which describes the Brownian motion of spherical particles [2], one of two quantities is determined, viz., the viscosity of the liquid or the radius of the particles (if the second quantity is known)

$$D = \frac{k_B T}{6\pi\eta r_0}. \tag{2}$$

To determine the experimentally attainable measurement accuracy and possible limitations of the method, we investigated the diffusion of spherical particles of polystyrene latex in water. The experimental arrangement employed is shown in Fig. 1.

The radiation of an LG-36A He–Ne laser (λ = 0.633 μm) is focused by a lens L of long focal length onto the center of a cuvette containing the specimen. The cuvette is placed in a thermostat which keeps the temperature constant to within ±0.02°K. The temperature of the specimen is measured with a TSPN-2V platinum thermometer with an error of 1 mK. The light scattered at an angle ϑ is received by an FÉU-79 photomultiplier, operating as a photon counter. The output signal of the photomultiplier is applied to a 72-channel digital correlator [3] which measures the autocorrelation function of the scattered light $G(\tau)$. The value of Γ was found by processing the measured autocorrelation function on an ES-1022 computer using the least-squares method [4]. The experimental data were approximated by an exponential function, which corresponds to the scattering of light for the case of monodisperse spherical particles

$$G(\tau) = A \exp \Gamma\tau + B, \tag{3}$$

where Γ, A, and B are the varied parameters in the least-squares method.

A more detailed description of the equipment, the method of measurement, and the method of processing the results can be found in [5].

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