THERMAL CONDUCTIVITY OF METASTABLE FLUIDS

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The thermal conductivity of n-pentane and n-hexane was measured by a relative method in a coaxial cylindrical cell along the isobars at 0.4 and 1.0 bars including the transition into metastable states. The amount of fluid superheating above the saturation temperature reached 55°C. The applicability of linear extrapolation of λ along isotherms or isobars beyond the line of saturation is shown.

The intensification of processes which accompany phase transitions leads to the need to study the thermophysical properties of matter in the metastable state since the actual phase transition always occurs in a system displaced from equilibrium. Such studies are made complicated by the low stability of a system in a metastable state. For example, a liquid is easily superheated in small volumes [1], but in a measuring cell of large dimensions it is difficult to create and maintain a highly superheated fluid during the time of measurement.

There is no published data on the thermal conductivity of a superheated fluid. Although one would expect a smooth continuation of all thermophysical properties across the line of saturation from general considerations (with maintenance of the homogeneity of the material), it is necessary to obtain experimental verification of this. In addition, it is impossible to establish a priori the reliability of data extrapolation from the stable region into the metastable region. Thermal conductivity of fluids depends only slightly on pressure and the isotherms $\lambda = \lambda(p)$ are nearly straight lines; consequently, extrapolation of values of λ across the line of saturation along the isotherms represents a good method for which experimental verification is desirable.

In the proposed work, measurements of λ for superheated fluids (n-pentane, n-hexane) were first made by the relative method of coaxial cylinders [2]. The measuring cell was made of glass. The liquid studied filled a 0.6 mm gap between thin-walled vertical tubes; the outer tube was surrounded by a thermostatically controlled water bath. Mercury was poured into the internal cylinder (5 mm in diameter) and a

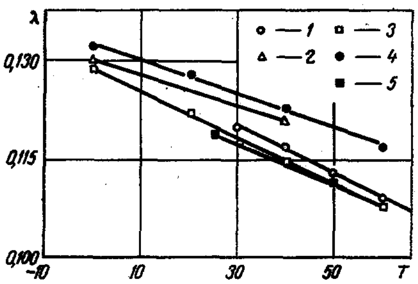

Fig. 1

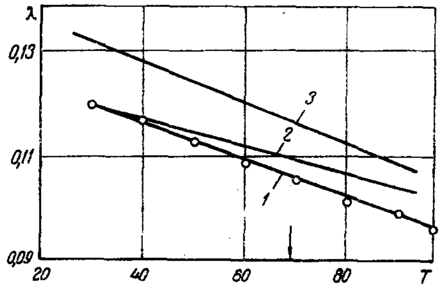

Fig. 2

Fig. 1. Thermal conductivity λ, W/m·deg, of liquid n-hexane as a function of the temperature T, °C: 1) present data; 2) [6]; 3) [7]; 4) [8]; 5) [5].

Fig. 2. Comparison of experimental values of the thermal conductivity λ, W/m·deg, for liquid n-hexane at various temperatures T, °C (1), with calculated results from the Weber–Predvoditelev formula (2), and the Filippov formula (3). Atmospheric pressure. The arrow indicates the boiling point.

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TABLE 1. Thermal Conductivity λ, W/m·deg, of N-Pentane and N-Hexane for Penetration into the Metastable Region

T, °C	n-pentane		n-hexane	
	$p = 1$ bar $T_s = 36{,}2$ °C	$p = 0{,}4$ bar $T_s = 11{,}2$ °C	$p = 1$ bar $T_s = 68{,}7$ °C	$p = 0{,}4$ bar $T_s = 41{,}7$ °C
30	0,114	0,114	0,120	0,120
40	0,111	0,111	0,117	0,117
50	0,108	0,108	0,113	0,113
60	0,105	0,105	0,109	0,109
70	—	—	0,106	0,106
80	—	—	0,102	0,102
90	—	—	0,099	0,099
97,4	—	—	0,096	0,096

heating element placed in it to create a controlled steady-state thermal flux in the cell. The temperature difference between the mercury and the water bath was measured by a differential copper—constantan thermocouple connected to a P-306 potentiometer. An automatic water-temperature control (±0.01 °C) hooked up in a photocompensation circuit was installed in an external thermostatic bath (Höppler type) from which water was supplied to the measuring cell and to which the water was returned.

The theory of the method has been explained [2]. The computational formula for the determination of λ takes the form

$$(\varkappa - \beta)\lambda = C. \tag{1}$$

Here, $\varkappa = e/E^2$, e is the emf of the differential thermocouple in the steady-state mode, and E is the heater voltage. The parameters C and β, which depend on temperature, are determined by calibration of the instrument with two materials having a known thermal conductivity (toluol [3] and water [4]). The parameter β takes into account the temperature drops in the glass walls of the internal and external tubes. Measurements were made for two values of ΔT in the range 1-2°. The value of $\varkappa$ for each material was independent of heater voltage, which indicates the absence of marked convection in the cell. This was confirmed by evaluation of the Rayleigh number for the experimental conditions ($\mathrm{Ra} = 60\text{-}250 < \mathrm{Ra}_{\mathrm{cr}}$).

Materials used were of cp grade. To remove gases, the liquids were distilled before an experiment or were boiled in a flask connected to a reflux condenser.

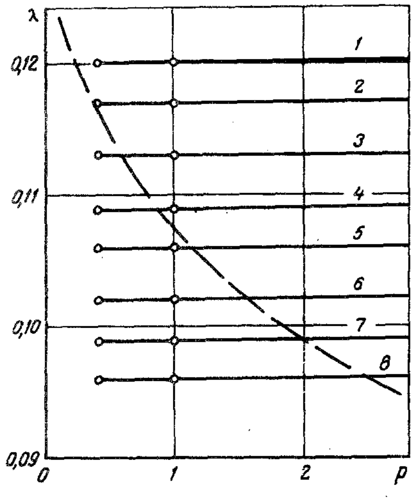

Fig. 3. Dependence of thermal conductivity λ, W/m·deg, of liquid n-hexane on pressure p, bar, in the stable and metastable regions (points denote present data, dashed line is line of saturation, and the solid lines are isotherms, for T, °C): 1) 30.0; 2) 40.0; 3) 50.0; 4) 60.0; 5) 70.0; 6) 80.0; 7) 90.0; 8) 97.4.

Measurements of the thermal conductivity of n-pentane and n-hexane for deep penetration into the metastable region were made at two pressures, 1.0 and 0.4 bar. The error in the determination of λ was 3%. Pressure below atmospheric was produced by connecting the measuring cell to a previously pumped-down reservoir and was monitored with a standard vacuum gauge.

The experimental results are shown in Table 1. A comparison with the measurements of other authors for stable states of n-hexane is shown in Fig. 1. Figure 2 shows that transition along an isobar through the boiling point is accompanied by no change whatever in the temperature dependence of λ. The thermal conductivity of n-hexane along isotherms is shown in Fig. 3. The slope of the isotherms is taken from [5]. The measured values of the thermal conductivity for n-hexane are compared in Fig. 2 with calculated values based on the Weber—Predvoditelev formula

$$\lambda = B\rho^{4/3} \tag{2}$$

and on the Filippov formula [6]

$$\lambda = 0.307\,u\,(C_p\rho)^{2/3}\,(\beta T)^{1/3}\,. \tag{3}$$

The constant B was determined from the experimental value of λ at T = 30°C. Equation (2) gives a temperature coefficient of variation for λ which does not agree with experiment. The thermal conductivity calculated from Eq. (3) is systematically approximately 10% higher than measured values.

The experiments performed allow one to conclude that the change in thermal conductivity of a fluid during the transition from the stable region to the metastable region occurs smoothly without discontinuities. Such a behavior of λ during superheating is evidence of the lack of specific changes in the nature of thermal motion and in the structure of the fluid. The results indicate the permissibility of linear extrapolation of λ along isotherms and isobars into the metastable region. Extrapolation along isotherms is more convenient because of the weak dependence of λ on pressure.

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