# MEASUREMENT OF THE THERMAL CONDUCTIVITY OF SUPERHEATED LIQUIDS

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The pulse method is used to study thermal conductivity of a number of organic liquids at atmospheric pressure. Measurements covered the region of superheated metastable states.

While the thermophysical properties of stable liquid states, in particular, the thermal conductivity, have been the object of a quite large number of studies, measurements in metastable liquid states are very few in number, and this state range is practically a "blank page" for experimental physicists. This situation is evidently connected with the experimental difficulties created by liquid instability on the saturation line.

The first experimental studies of the thermal conductivity of superheated liquids were reported in [1]. The authors studied the thermal conductivity of n-hexane and n-heptane at superheats from the equilibrium boiling point to 55°C and experimentally demonstrated the possibility of extrapolating thermal-conductivity data from the stable region beyond the saturation line.

The present study is a further investigation of the thermal conductivity of superheated liquids. Methodologically, it is a development of [2], which was an experimental study of the thermal activity of liquids in the metastable region. The method of [2] is based on the use of two voltage pulses acting on a resistive element located within the liquid under study. The first pulse, which we term the heating pulse, heats the resistive element and a thin layer of liquid adjacent to the element to a controlled temperature greater than the equilibrium boiling point of the liquid. Before the completion of this pulse, a second pulse is applied to the resistive element – the measurement pulse – by means of which the thermophysical parameter value is determined, using nonstationary measurement in an irregular thermal regime. The duration of the measurement pulse is significantly less than that of the heating pulse. Their ratio is chosen such that the temperature field generated by the heating pulse is "frozen" in comparison to the measurement-pulse temperature field. Another condition also affecting accuracy of the measurements is that the diffusion length of the heating-pulse temperature field must significantly exceed the corresponding characteristic of the measurement pulse. In that case it is justifiable to identify the resistive element temperature with the temperature of the liquid layer in which measurements are performed.

The transformation from measurement of thermal activity by the method described to determination of thermal conductivity is accomplished by replacing the planar resistive element with a linear one (fine wire). The experimental apparatus and technique remain unchanged; however, in the formulas of [2] we replace thermal activity by thermal conductivity (the thermal activity of the substrate by the thermal conductivity of the liquid under study). It should be noted that the method of nonstationary measurement in an irregular thermal regime by pulsed heating of a wire by an electrical current is quite well developed and studied (for example, in [3, 4]).

A necessary condition for study of superheated liquids with this method is the brevity of the measurement pulse. In this case the duration of the heating pulse can be set sufficiently low, with sufficiently rapid liquid heating, such that the liquid is superheated without boiling above the equilibrium boiling point. Since the duration of the measurement pulse is limited by the intrinsic heat capacity of the heat source, it is desirable to use a wire of limitingly small radius.

Platinum wires with a radius of $10^{-6}$ m were used. The probes constructed with these wires were described in [4]. Measurement and heating-pulse durations comprised $0.15 \cdot 10^{-3}$ and $15 \cdot 10^{-3}$ sec, respectively, i.e., their ratio was 1:100. The resistive elements had a length of 4-6 mm, and their maximum superheating during action of the measurement pulse did not exceed 5°C. Analytical grade toluene was used as a reference; its heat-capacity values in the stable region were used as a comparison [5].

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TABLE 1. Thermophysical Properties of Liquids

| Liquid | $T_s$, °C | Parameter measured | Temperature | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20 | 40 | 60 | 80 | 100 | 110 | 120 | 130 | 140 | 150 | 160 | 170 | 180 | 190 | 200 | 210 | 220 |
| Benzene | 78 | $\lambda\times10^3$ | 146 | 139 | 133 | 126 | 118 | 115 | 112 | 110 | 107 | 105 | 103 | 101 | | | | | |
| | | $\varepsilon$ | 469 | 460 | 451 | 441 | 432 | 427 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 151 | 152 | 153 | 154 | 158 | 158 | | | | | | | | | | | |
| Benzyl chloride | 179 | $\lambda\times10^3$ | 139 | 134 | 130 | 126 | 123 | 121 | 119 | 117 | 115 | 113 | 111 | 109 | 107 | 105 | 103 | 101 | 99 |
| | | $\varepsilon$ | 460 | 461 | 452 | 443 | 435 | 430 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 158 | 158 | 157 | 156 | 154 | 153 | | | | | | | | | | | |
| Bromobenzene | 156 | $\lambda\times10^3$ | 112 | 108 | 104 | 99 | 95 | 93 | 92 | 90 | 89 | 87 | 86 | 85 | 84 | 82 | 81 | 80 | 79 |
| | | $\varepsilon$ | 401 | 398 | 394 | 391 | 387 | 385 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 144 | 147 | 149 | 154 | 157 | 159 | | | | | | | | | | | |
| Butyl acetate | 126 | $\lambda\times10^3$ | 139 | 134 | 128 | 123 | 118 | 115 | 112 | 110 | 107 | 104 | 102 | 99 | 96 | 93 | | | |
| | | $\varepsilon$ | 483 | 473 | 464 | 454 | 445 | 440 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 167 | 167 | 168 | 168 | 168 | 168 | | | | | | | | | | | |
| Dioxane | 100 | $\lambda\times10^3$ | 170 | 163 | 156 | 149 | 142 | 138 | 134 | 131 | 127 | 123 | 119 | 117 | 115 | 113 | 111 | 108 | 105 |
| | | $\varepsilon$ | 527 | 518 | 508 | 499 | 489 | 484 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 163 | 164 | 165 | 167 | 168 | 169 | | | | | | | | | | | |
| Styrene | 145 | $\lambda\times10^3$ | 140 | 136 | 132 | 128 | 125 | 123 | 121 | 119 | 117 | 115 | 113 | 111 | 109 | 107 | | | |
| | | $\varepsilon$ | 464 | 456 | 448 | 440 | 432 | 428 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 154 | 153 | 152 | 151 | 149 | 149 | | | | | | | | | | | |
| Carbon tetrachloride | 77 | $\lambda\times10^3$ | 104 | 100 | 95 | 90 | 86 | 85 | 83 | 81 | 79 | | | | | | | | |
| | | $\varepsilon$ | 367 | 358 | 349 | 342 | 331 | 327 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 129 | 128 | 128 | 129 | 127 | 126 | | | | | | | | | | | |
| Trichlorethylene | 90 | $\lambda\times10^3$ | 112 | 106 | 100 | 94 | 88 | 85 | 82 | 79 | 76 | 74 | 71 | 68 | 65 | 63 | | | |
| | | $\varepsilon$ | 395 | 385 | 375 | 366 | 357 | 352 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 139 | 140 | 141 | 142 | 144 | 145 | | | | | | | | | | | |
| 1,1,2,2-Tetrachlorethane | 146 | $\lambda\times10^3$ | 120 | 113 | 106 | 98 | 93 | 89 | 86 | 82 | 79 | 76 | 74 | 71 | 68 | 65 | 63 | | |
| | | $\varepsilon$ | 418 | 408 | 397 | 387 | 376 | 372 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 146 | 147 | 149 | 152 | 153 | 155 | | | | | | | | | | | |
| Cyclohexane | 81 | $\lambda\times10^3$ | 120 | 115 | 111 | 106 | 102 | 100 | 98 | 95 | 93 | 91 | | | | | | | |
| | | $\varepsilon$ | 414 | 410 | 404 | 399 | 395 | 392 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 143 | 146 | 147 | 150 | 152 | 153 | | | | | | | | | | | |
| Ethylbenzene | 136 | $\lambda\times10^3$ | 134 | 128 | 124 | 118 | 113 | 111 | 109 | 107 | 105 | 104 | 103 | 102 | 101 | 100 | 99 | | |
| | | $\varepsilon$ | 458 | 452 | 446 | 441 | 435 | 427 | | | | | | | | | | | |
| | | $\rho c\times10^{-4}$ | 157 | 160 | 161 | 164 | 167 | 167 | | | | | | | | | | | |

The "instantaneous" temperature (resistance) of the resistive element in the measurement probe was determined through calculations from the condition of "instantaneous" balance of the bridge, but in contrast to [2], balance was achieved by varying the resistance of a potentiometer located outside the compensation probe. In this case, as the bridge is being balanced, the current in the measurement arm does not vary, and the heating of the resistive element in that arm remains the same as in the action of a pair of pulses, i.e., in the thermal-conductivity measurements.

The thermal conductivity of a number of organic liquids of analytical and chemically pure grades was studied. Measurement results are presented in Table 1. The measurement range began in the stable region; temperature changes were effected both by changing the temperature of the thermostatic vessel containing the liquid and by changing the power of the heating pulse. Table 1 also shows the equilibrium boiling temperature of the liquids studied ($T_s$) under the experimental conditions — atmospheric pressure.

In analyzing the measurement uncertainty, the following factors were considered: intrinsic heat capacity of the wire, finite length of the wire, uncertainty in compensation indication, and temperature field of heating pulse. In estimating the error generated by the first two factors, the results of [3] were used; the presence of a compensation difference circuit reducing measurement error was considered. The resulting maximum

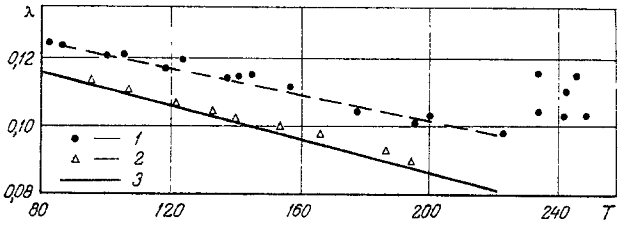

Fig. 1. Thermal conductivity of benzyl chloride and toluene: 1) benzyl chloride; 2) toluene; 3) reference data on toluene [5]; T, °C; λ, W/m • °K.

measurement error, without consideration of systematic error produced by uncertainty in the properties of the reference liquid, did not exceed 3%. Data scattering in the experiments did not exceed 2%.

The maximum liquid superheat in relation to normal boiling point reached 100°C (for benzene, dioxane, and trichloroethane). Factors permitting the achievement of such high superheating were the brevity of the heating, the small volume of the superheated liquid, and, finally, the small surface area of the wire bordering on the liquid. This surface serves as a source of artificial vapor-formation centers.

The thermal-conductivity measurement range was limited above by liquid boiling. The boiling process was clearly expressed. At the moment of boiling the wire temperature decreased sharply, after which irregular temperature oscillations were observed. As a rule, even when operating with one sensor, the boiling temperature was not reproducible for a sequence of identical pulses applied to the bridge, although for a train of 3-5 pulses reproducibility did occur often. This nonreproducibility complicated the thermal-conductivity study in the vicinity of the boiling temperature. Also noted was a rise in thermal conductivity before boiling. Figure 1 shows the results of thermal-conductivity measurements for benzyl chloride and toluene, including the preboiling region. The growth in thermal conductivity in this region is irregular in nature. This is evidently because even before explosive boiling, the liquid contains traces of nucleation accompanied by heat absorption. The presence of heat sinks in the liquid volume diminishes the temperature increase of the wire as it is heated somewhat, leading to measured heat-capacity values which are too high.

Results of thermal-conductivity studies in the metastable region show that the dependence of thermal conductivity on temperature is close to the analogous dependence on the saturation line, within the limits of experimental error. In particular, Fig. 1 compares experimental data for toluene with data from [5] characterizing the saturation line.

Together with thermal conductivity, Table 1 shows thermal activity (ε) values measured in accordance with [2] for the various liquids. The temperature range of these measurements is 20-110°C. For a number of liquids – benzene, cyclohexane, carbon tetrachloride, trichloroethane, and dioxane – the measurements encompassed the superheated state with a maximum heating above normal boiling point of about 30°C. The error in ε measurement, without consideration of systematic error in the properties of the reference liquid (toluene), does not exceed 2%.

It is evident from Table 1 that upon transition through the equilibrium boiling point the temperature dependences of the thermophysical characteristics studied maintains a smooth character; this fact confirms the validity of extrapolating experimental data from the stable region where it was obtained to the metastable region. This assumption is valid for sufficiently large penetration depths into the metastable region. However, there do remain unaccessible to the present study further removed and theoretically more interesting regions of the metastable state, including the spinodal region. This limitation exists because of liquid boiling on artificial vapor-formation centers.

The analysis of [6] reveals that suppression of boiling at such centers is possible upon realization of a shock heating of the metal wire more rapid than that used in the present study. This, in turn, presupposes the use of heat sources with lower intrinsic heat capacity, i.e., use of a wire of smaller radius (estimates indicate reduction by a factor of about three).

The possibilities of the method described are not limited to superheated liquids; it may be used to establish the temperature dependence of thermal conductivity and to study the thermal conductivity of liquid systems which do not tolerate lengthy stationary heating.

## NOTATION

$T_s$ is the equilibrium boiling temperature;
$\lambda$ is the conductivity;
$\varepsilon$ is the thermal activity coefficient;
$\rho c$ is the volumetric heat capacity.

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# MEASUREMENT OF THERMAL DIFFUSIVITY OF MASSIVE METALLIC SPECIMENS BY THE PULSE METHOD

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A pulse method for measuring the thermal diffusivity of semi-infinite specimens is described. Results of thermal-diffusivity measurements on iron and tin are presented.

The present authors have previously described a pulse method of measuring the thermal diffusivity of metals [1, 2] useful for specimens of hemispherical form. For thin plane-parallel plates the well-known method presented by Parker et al. [3-5] is usually used. However, in many cases creation of specimens with such geometry is difficult, and it is of great interest to consider the possibility of using the pulse method for measurement of the thermal diffusivity of specimens of the simplest form – a semi-infinite mass. Use of powerful point-laser sources permits a quite simple solution of this problem in principle.

The general solution of the thermal-conductivity differential equation

$$\frac{\partial T(x,\ y,\ z,\ \tau)}{\partial \tau} = a\nabla^2 T(x,\ y,\ z,\ \tau) \tag{1}$$

for $-\infty < x,\ y, < \infty,\ 0 < z < \infty$, and $\tau > 0$ with initial

$$\tau_0 = 0,\quad T(x,\ y,\ z,\ \tau) = 0$$

and boundary

$$T(\infty,\ y,\ z,\ \tau) = T(x,\ \infty,\ z,\ \tau) = T(x,\ y,\ \infty,\ \tau) = 0,$$

$$\frac{\partial T(\pm\infty,\ y,\ z,\ \tau)}{\partial x} = \frac{\partial T(x,\ \pm\infty,\ z,\ \tau)}{\partial y} = \frac{\partial T(x,\ y,\ \infty,\ \tau)}{\partial z} = 0$$

conditions for an instantaneous heat source at a point ($x_1$, $y_1$, $z_1$) on the surface of a semi-infinite-mass specimen is given by the function [6, 7]

$$T(x,\ y,\ z,\ \tau;\ x_1,\ y_1,\ z_1) = \frac{q_0}{8(\pi a\tau)^{3/2} c_p\rho} \exp\left[-\frac{(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2}{4a\tau}\right]. \tag{2}$$

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