# HEAT CONDUCTIVITY OF WATER NEAR 4°C

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The results of short-term nonsteady-state measurements do not confirm the view that the heat conductivity of water behaves abnormally in the vicinity of 4°C.

Water is one of the most thoroughly studied objects. It was shown in [1] that the error of measurement of its heat conductivity in the range 0-200°C amounts to 1%. In this range it is recommended to use water as a reference substance. This recommendation is widely used in thermophysical experiments. Therefore, any nonconformity or contradiction in experimental results had to be carefully examined. Such a contradiction arose in particular in connection with the publication of [2], which presents the results of measurements of the heat conductivity of water obtained by the steady-state method of the plane layer. Attention should be given to two aspects of [2]: 1) it follows from the article that the heat conductivity of water increases suddenly (by about 7%) upon transition through 4°C, and 2) the obtained values of heat conductivity are about 10% higher than the recommended values. This last is due to the fact that, according to the authors' statement, contact resistance at the interface between the liquid and the solid wall had not been taken into account, and consequently the experimental values of heat conductivity obtained were lower than the true values. In these authors' opinion, their own method eliminated the effect of contact resistances, and therefore the results of their measurements of heat conductivity (with measurement errors of 1.5-2%) corresponded to the true values.

To verify the results of [2], we investigated the heat conductivity of water in the range 0-10°C by an unsteady method at the stage of irregular thermal regime. In the experiments we used elements with low inertia, viz., platinum threads with a radius of about 1 $\mu$m; this made it possible to reduce the length of impulse measurement to $10^{-3}$ sec. This in turn made it possible to measure heat conductivity in an extremely thin layer (10 $\mu$m) directly adjacent to the thread. The method of measurement was previously dealt with in [3]. The standard was toluene. The values of heat conductivity of toluene took into account the correction for radiation, i.e., they directly expressed molecular heat conductivity [1]. In the experiments, the impulse measurements lasted 3 msec, maximum heating of the thread under the effect of the impulse did not exceed 2°C.

The measurements were carried out in distilled water. In order to reduce electrical shunting to a minimum, all sections of the conductors, and also the ends of the thread were covered with paraffin before the copper coating of the platinum wire was electrolytically stripped. After the paraffin had been applied, the probe was immersed in nitric acid where electrolytic stripping proceeded on the parts of the copper coating adjacent to the acid. The forming platinum wire (its length was about 3 cm) had a small area of contact with the water, in consequence of which the effect of shunting was small and did not have much influence on the results of measuring the thermal conductivity.

The obtained experimental results are presented in Fig. 1. The error of the relative measurements was estimated to be 2%. The error is somewhat larger than in [2] because the dissolution of paraffin by toluene makes its use as a standard difficult. In relative measurements the heat conductivity of water was therefore determined with the aid of oil (industrial) whose heat conductivity in accordance with [3] was determined from toluene.

It follows from the experimental results that there is no jump of heat conductivity in the investigated region (this conclusion is correct within the mentioned error of the relative measurements), and there is satisfactory agreement between the experimental results and the known literature data [4]. Thus, the experimental data of the present work do not confirm the conclusions of [2]. Let us deal with this in more detail.

First we will examine the problem of the so-called contact resistances (called by the author of [2] Wärmeübergangzahl). What is involved here is a matter of principle because if the results of [2] were confirmed, the data on the heat conductivity, not only of water, but of other liquids as well, would have to be reviewed. The authors assume that such a resistance exists at the interface between the liquid and the solid wall; in [2] the contact face is the ground surface of a copper cylinder in contact with the water. When the steady-state temperature distribution is written, the existence of the resistance is introduced in the following manner:

$$\frac{L}{\lambda}+\frac{2}{\alpha}=\frac{T_0-T_L}{q}, \qquad (1)$$

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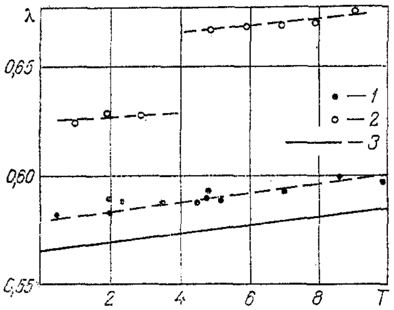

Fig. 1

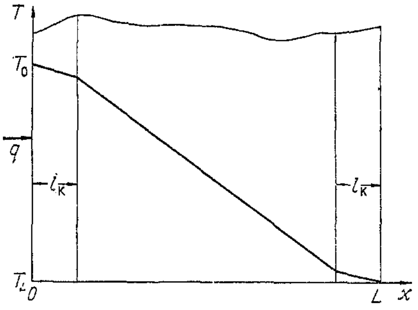

Fig. 2

Fig. 1. Heat conductivity of water: 1) experimental data of the present work; 2) [2]; 3) [4]; λ, W/m·deg K; T, °C.

Fig. 2. Diagram of the temperature field in the layer in the case of contact resistances.

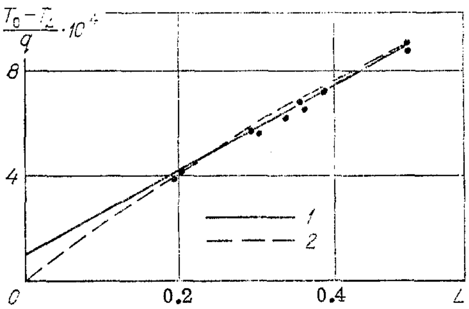

Fig. 3. Dependence of $(T_0 - T_L)/q$ (km²/W) on L (mm) according to the results of [2] (for T = 2°C): 1) authors' extrapolation; 2) possible variant of the extrapolation; dots: data of [2].

where $\alpha$ is a coefficient characterizing the contact resistance.

The experiment was carried out with several thicknesses of the layer, and the heat conductivity was determined by the slope of the linear function $T_0 - T_L/q$.

The coefficient $\alpha$ can be lucidly interpreted on the assumption that at the wall–liquid interface there is a uniform layer $l_K$ thick whose heat conductivity $\lambda_K$ differs from the heat conductivity within the bulk (Fig. 2). In this case

$$\frac{T_0 - T_L}{q} = \frac{2l_K}{\lambda_K} + \frac{(L - 2l_K)}{\lambda}$$

or, assuming that $l_K \ll L$,

$$\frac{L}{\lambda} + \frac{2l_K}{\lambda_K} = \frac{T_0 - T_L}{q}, \tag{2}$$

which coincide with (1) when $l_K/\lambda_K = 1/\alpha$.

If we calculate with the value $\alpha$ given in [2] (0.25 W/cm²·deg K) and assume that the hypothetical layer under examination is $10^{-5}$ m thick, we obtain for its heat conductivity a value of 0.025 W/m·deg K. The conditions of carrying out short-term measurements (depth of probing the liquid by a temperature field of about $10^{-5}$ m) corresponded to the measurements in the contact layer but the results did not yield lower values of heat conductivity.

Another assumption may be admitted: that the contact resistance is due to gas bubbles settling on the walls. But then it would have to be assumed that this factor is in the nature of a systematic error of all the measurements and previously not taken into account. However, against this assumption speaks the good agreement of the results obtained by different researchers and different methods. It is difficult to believe that such agreement would occur if an irreproducible factor such as the presence of gas bubbles on the wall would be involved.

It is therefore most probable that the discrepancy between the results and the known literature data is due to a methodical error of [2]. Its source may be noticeable heat losses in the water layer. According to the authors' own estimate, the changes in heat flux in dependence on the thickness of the layer fluctuated in the experiments between 2 and 12%. A correct calculation of the distribution of the temperature field in the liquid layer has to take the magnitude of these losses into account. If we assume that the heat flux passing through the section x has the form $q(x) = q_0 - \delta q(x)$, where $\delta q(x)$ corresponds to the losses, we can write the temperature field in the form

$$T_0 - T(x) = \frac{1}{\lambda} q_0 L - \frac{1}{\lambda} \int_0^x \delta q(x)\, dx$$

or for a layer with thickness L

$$\frac{T_0 - T_L}{q_0} = \frac{L}{\lambda} + f(L), \tag{3}$$

where $f(L) = \frac{1}{\lambda} \int_0^L \frac{\delta q(x)}{q_0}\, dx$.

The authors of [2] assumed that the heat flux is constant, and they took it as equal to $q = (q_0 + q_L)/2$. Such an assumption is justified only in the case of a linear change of the heat flux across the layer. In reality, however, this dependence may be of a more complex nature. In that case it follows from (3) that linear extrapolation of the values $(T_0 - T_L)/q$ (Fig. 3) to zero thickness of the layer is inadmissible. But it was precisely this extrapolation which was used for detecting contact resistances, and its results are higher values of the heat conductivity. Figure 3 shows, in particular, a possible form of the function $(T_0 - T_L)/q$ for $f(L) \neq \text{const}$.

As regards the jumplike increase in heat conductivity at 4°C, the reason here, too, is apparently a methodical error. Its source could be, specifically, that convection was not taken into account. The authors of [2] checked the absence of convection by the coincidence of the results of measurements in heating from below and from above. However, around 4°, where the water attains its maximum density, such a method of checking may be ineffectual.

## NOTATION

L, thickness of the liquid layer, m; T, temperature, °K; q, heat flux, W/m$^2$; λ, thermal conductivity, W/m·deg K. Indices 0 and L denote the beginning and end of the layer, respectively.

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