MOLECULAR THERMAL CONDUCTIVITY OF HEAVY-WATER VAPOR AT PRESSURES UP TO 30 MPa AND TEMPERATURES UP TO 700°C

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The results of an experimental investigation of the molecular thermal conductivity of heavy-water vapor by the method of pulsed heating of a thin wire are presented.

Heavy water D_2O is one of the chief coolants used in nuclear power plants. As a result its properties, including the thermal conductivity λ, have been intensively studied, both in this country and abroad. In 1984 the International Association on the Properties of Water Vapor (IAPWV) adopted standards for the thermal conductivity of heavy water and vapor at temperatures of up to 550°C and pressures up to 100 MPa [1]. In developing these standards the existing experimental data, a significant part of which were obtained by Soviet scientists, were taken into account. The thermal conductivity λ of heavy water vapor at high pressures is usually studied using experimental cells in the form of coaxial cylinders and a flat layer, prepared from stainless steels and alloys. At high temperatures the correction for radiation reaches 15-25%.

As is well known heavy-water vapor, especially at high pressures, is a semitransparent medium with a complicated radiation spectrum. Because there is no information on the optical properties of heavy-water vapor for the corresponding values of P and t the data on the thermal conductivity are obtained under the assumption that heavy-water vapor is transparent to thermal radiation. As a result the values of the thermal conductivity of D_2O vapor, used as the basis for the international standard, strictly speaking, do not correspond to the true molecular thermal conductivity. Therefore, the values of λ contain an error, which has not been accounted for, associated with the semitransparency of D_2O at high pressures.

In the last few years significant progress has been made in the development and employment of methods for measuring the thermal conductivity that permit obtaining data with virtually no radiation component. The method of pulsed (short-time) heating of a thin wire is such a method. In implementing this method the measurements were performed during short (not exceeding 20-60 msec) time intervals after the start of heating, and the thermal perturbation encompasses only thin layers (less than 0.1 mm). Such thin layers of heavy-water vapor are virtually transparent to thermal radiation.

A thin platinum wire probe 1 (see Fig. 1), placed in the liquid (gas) under study, was heated with a constant electric current (4-20 mA) with a definite duration. The temperature of the filament and of the surrounding medium increased monotonically. The probe corresponds almost completely to an ideal model of a linear source of heat with constant power, for which an expression for the increment to the temperature of the wire between the times τ and T_0 can be written down [2]:

$$\Delta T(\tau) - \Delta T(\tau_0) = \frac{q}{4\pi\lambda} \ln \frac{\tau}{\tau_0}. \quad (1)$$

From here we derive an equation for determining the thermal conductivity of the liquid (gas)

$$\lambda = \frac{q}{4\pi} \frac{\ln(\tau/\tau_0)}{\Delta T(\tau) - \Delta T(\tau_0)}, \quad (2)$$

which, strictly speaking, is valid only for an ideal model of an infinitely long, linear heat source. Although only thin platinum wires (the length to diameter ratio exceeds 5000) are employed in the measuring cell, some corrections taking into account the deviation from an ideal model must be introduced [2]: for the thermal inertia of the filament, radiation

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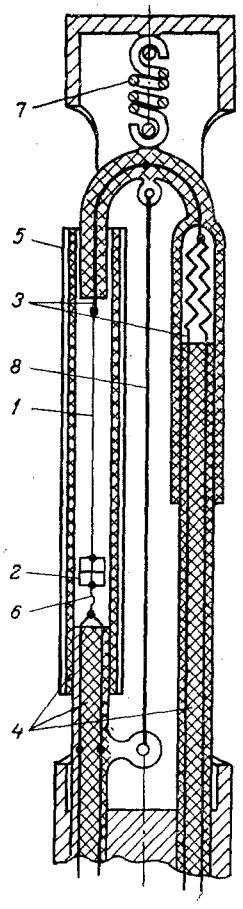

Fig. 1

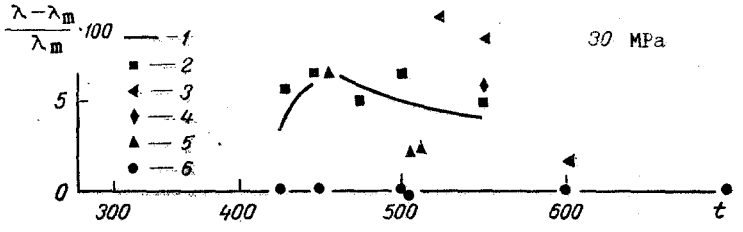

Fig. 2

Fig. 1. Construction of the measurement cell.

Fig. 2. Discrepancy between the data obtained in this work and data obtained by different authors on the thermal conductivity of heavy-water vapor: 1) international standard [1]; 2) [4]; 3) [5]; 4) [6]; 5) [7]: 6) this work (r_1 = 2.5 μm). $(\lambda-\lambda_m)/\lambda_m$, %; t, °C.

from its surface, change in the length of the filament with temperature, and leakage of heat from the tips of the filament. The sum of all corrections made in the case of measurement of λ_m of heavy-water vapor in the studied range of state parameters did not exceed 2-4% (for r_1 = 2.5 μm), while the correction to radiation from the surface of the wire did not exceed 1%.

The procedure employed in the electrical measurements and in the experiments and the results for a number of organic liquids and gaseous nitrogen have been published previously [3].

Because of the electrical conductivity heavy-water vapor and its corrosive action against the constructional materials, the method of pulsed heating has thus far not been employed for measuring the thermal conductivity of heavy water vapor. In designing the experimental apparatus the special difficulties of studying the thermal conductivity of heavy water vapor were taken into account. Thus, for example, the use of a 30D101A optronic switch in the electric measurement circuit [3] enabled complete decoupling of the circuit powering the bridge circuit from "ground," which reduced the external noise from 200 to 5 μV. To ensure good electric insulation the platinum current-carrying wires 3 were insulated with quartz capillaries 4 (Fig. 1). To prevent displacement of the thin wire in the medium under study under the action of Ampère's force at the moment the current pulse passed, the probe was covered with a screen 5 made of nickel foil. A weight 2 with a mass of 10-38 mg was suspended to the bottom end of the wire to ensure that the probe is straight. The required deflection of the compensating loop 6 was achieved with the help of a tension apparatus, consisting of a tungsten spring 7 and a weight 8, made from, like the current-carrying wires 3, platinum with a diameter of 0.2 mm. A spring ensures that the connecting rod 8 is always in a tensed state,

TABLE 1. Results of Measurements of the Thermal Conductivity of D_2O Vapor

t, °C	P, MPa	$\lambda \cdot 10^{-3}$, W/(m·K)
First series of expts. Probe № 1 $r_1 = 5$ μm, $L = 37{,}52$ mm		
502,6	2,5	70,8
502,6	5,0	71,9
502,8	10,0	75,9
502,8	15,0	80,5
502,8	20,0	87,5
600,9	5,0	85,4
600,9	10,0	87,6
600,9	15,0	92,2
600,9	20,0	96,7
Second series of expts. Probe № 2 $r_1 = 2{,}5$ μm $L = 47{,}47$ mm		
305,2	1,0	45,0
305,1	2,5	46,5
303,8	5,0	50,9
302,8	7,5	63,2
357,6	1,0	51,3
356,9	2,5	51,8
352,7	5,0	53,4
354,5	7,5	57,9
351,3	10,0	64,7
350,6	12,5	74,8
350,8	12,5	74,7
377,5	1,0	53,7
378,7	2,5	54,0
377,5	5,0	55,3
377,6	5,0	55,3
377,6	7,5	58,2
376,9	10,0	63,5
377,1	10,0	63,5
375,8	12,5	70,1
375,1	15,0	82,9
373,6	17,5	100,1
373,8	20,0	131,5
409,2	1,0	57,9
408,2	2,5	58,8
402,5	5,0	58,8
410,0	5,0	59,7
410,1	7,5	62,5
404,0	10,0	64,5
401,0	12,5	69,7
401,3	15,0	75,0
399,5	17,5	85,9
400,8	20,0	95,3
399,4	22,5	119,5
430,9	1,0	61,2
427,8	2,5	61,1
427,9	5,0	62,0
427,8	5,0	62,0
427,9	5,0	61,5
424,2	7,5	63,2
429,1	10,0	66,5
427,1	12,5	70,8
500,1	7,5	73,5
499,0	10,0	75,5
498,0	12,5	77,5
497,5	15,0	80,49
496,5	17,5	82,13
495,3	20,0	85,50
496,8	22,5	88,22
497,0	25,0	93,30
496,5	27,5	98,29
494,4	30,0	105,2
Probe № 4 $r_1 = 2{,}5$ μm, $L = 46{,}20$ mm		
496,6	2,5	70,8
492,2	5,0	70,7
496,8	5,0	71,8
495,2	15,0	79,8
492,6	20,0	85,0
495,1	25,0	94,6
495,1	27,5	100,1
493,2	30,0	106,3
600,3	1,0	84,9
603,2	1,0	85,4
600,8	2,5	85,7
599,9	5,0	86,4
600,3	7,5	87,4
600,4	10,0	88,8
602,7	12,5	91,0
599,8	15,0	92,0
600,0	30,0	108,1
Probe № 6 $r_1 = 2{,}5$ μm, $L = 45{,}89$ mm		
705,6	1,0	100,0
704,9	5,0	101,6
705,6	5,0	101,2
703,1	10,0	102,9
702,1	15,0	105,2
703,9	20,0	108,4
701,1	22,5	110,2
701,6	25,0	112,5
701,3	27,5	115,0
701,1	30,0	118,0

and this provides the necessary deflection of the compensating loop irrespective of the temperature. The length of the compensating loop 6, made of the same wire as the main part of the sensor, was incorporated in the computed length.

Heavy water, deaerated beforehand with argon, with an isotope content of 99.7% in the isotope-substituted position and a specific electric conductivity $3 \cdot 10^{-6}$ $\Omega^{-1} \cdot cm^{-1}$ was employed for the studies.

Two series of experiments were performed in measuring the thermal conductivity of heavy-water vapor: in the first series sensors with r_1 = 5 μm were employed, and in the second series r_1 = 2.5 μm. The results of these experiments are in complete agreement with one another (the discrepancies do not exceed 1.5-2%). The measurements of the thermal conductivity of D_2O vapor were performed at t = 300-700°C and P = 1.0-30.0 MPa. the experiments were performed along isotherms. Table 1 gives the measurements of λ_m and the basic dimensions of the sensors employed.

The error in measuring the thermal conductivity with a sensor made from a wire with r_1 = 2.5 μm, determined based on GOST 8.207-76 (with a confidence probability of 0.95), did not exceed 1%; for the sensor with r_1 = 5 μm the error did not exceed 1.3%.

Comparison of the experimental data obtained for λ_m (Fig. 2) with the values of the thermal conductivity of heavy-water vapor presented in the international standard [1] shows that the new experimental data are lower (by up to 4-7%). As the temperature is increased (for t > 450°C) the discrepancies decrease. Figure 2 also shows a comparison of the new data with the results of [4-6], employed in preparing the international standard on the thermal conductivity of D_2O, and with the recently published data obtained by French scientists [7]. To somewhat high values of the thermal conductivity of the international standard [1] and the data of [4-7] are explained by the fact that the experimental results obtained previously by traditional methods, do not take into account the semitransparency of heavy-water vapor at high pressures. It should be noted that the new experimental results permit extending the international standard on the thermal conductivity of D_2O from 550 to 700°C, where in the past there were no experimental data at high pressures.

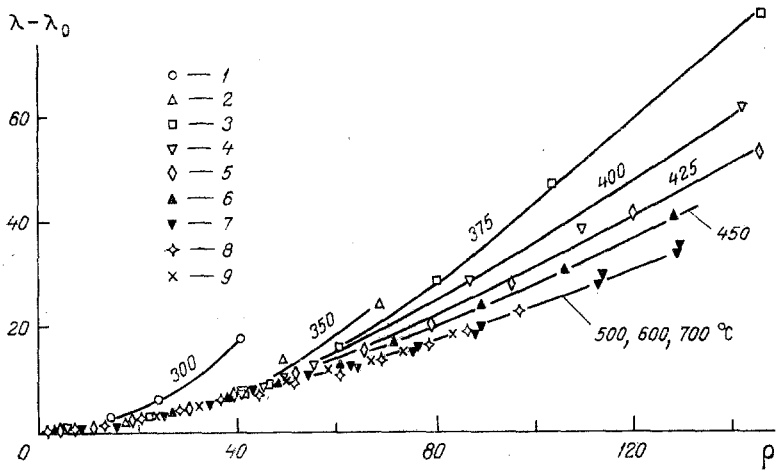

Fig. 3. $\lambda - \lambda_0$ versus the density of heavy-water vapor: 1) 300°C; 2) 350; 3) 375; 4) 400; 5) 425; 6) 450; 7) 500; 8) 600; 9) 700°C. $(\lambda - \lambda_0)$, W/(m·K); ρ, kg/m³.

To generalize the experimental data and to construct tables of the thermal conductivity of gases in a large range of values of P and t a single-valued dependence of the excess thermal conductivity $\Delta\lambda$ on the density ρ is often employed:

$$\Delta\lambda = f(\rho), \tag{3}$$

where $\Delta\lambda = \lambda - \lambda_0$, and λ and λ_0 are the thermal conductivity at pressures P and $P_0 = 0.1$ MPa and at the same temperature.

As one can see from Fig. 3, in the $\Delta\lambda - \rho$ plane the experimental points on D_2O on the isotherms 500, 600, and 700°C fall on virtually the same bottom curve, while the remaining isotherms diverge from one another. Based on an analysis of the figure, we shall approximate the experimental data obtained on the thermal conductivity of D_2O vapor with the equation

$$\lambda = \lambda_0 + \Delta\lambda + \Delta\bar{\lambda}, \tag{4}$$

where $\Delta\lambda$ is determined based on Eq. (3), while $\Delta\bar{\lambda} = f(\rho, T)$ takes into account the deviation from Eq. (3).

To describe the terms in Eq. (4) the following expressions are proposed:

$$\lambda_0 = (T/T_{cr})^{1/2} \sum_{i=0}^{3} a_i (T/T_{cr})^i, \tag{5}$$

$$\Delta\lambda = b_0 + b_1(\rho/\rho_{cr}) + b_2 \exp\{B_1[(\rho/\rho_{cr}) + B_2]^2\}, \tag{6}$$

$$\Delta\bar{\lambda} = [d_1(T_{cr}/T)^{C_1} + d_2](\rho/\rho_{cr})^{C_2} \exp\{C_3[1 - (\rho/\rho_{cr})^{C_2}]\}. \tag{7}$$

The coefficients in the equations (5)-(7) were determined by the method of least squares on a computer and are given below: $a_0 = 0.00568296$; $a_1 = 0.0355836$; $a_2 = 0.0156146$; $a_3 = -0.00422464$ W/(m·K); $B_1 = -1.3$; $B_2 = 2.39219$; $b_0 = -0.01687682$; $b_1 = 0.1389958$; $b_2 = 29.162086$ W/(m·K); $C_1 = 17$; $C_2 = 2.8$; $C_3 = 3.0$; $d_1 = 0.0345709$; $d_2 = 0.00109454$ W/(m·K).

The following values of the critical parameters were adopted: $T_{cr} = 643.89$ K and $\rho_{cr} = 358$ kg/m³ [1].

The discrepancies between our data and Eq. (4), with rare exceptions, do not exceed 2%.

Thus, analysis of new experimental data, not distorted by radiation transport of heat, combined with the results of previous studies leads to the conclusion that changes must be made in the internation al standard on the thermal conductivity of D_2O.

NOTATION

λ, thermal conductivity of the liquid (gas); P, pressure; t and T, temperature in C and K, respectively; L, length of the probe; τ, time; $\Delta T(\tau)$ and $\Delta T(\tau_0)$, increments to the temper-

ature of the sensor at the times τ and τ_0; q, heat flux per unit length; r_1, radius of the probe wire; and ρ, density. The indices are as follows: m, molecular, refers to values of the international standard, and cr, critical parameter.

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STUDY OF THE STRAIN-RESISTANCE PROPERTIES OF MASSIVE SAMPLES OF $Bi_2Te_3-Sb_2Te_3$ AND $Bi_2Te_3-Bi_2Se_3$

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The coefficients of strain sensitivity of polycrystalline samples of ternary alloys based on bismuth and antimony chalcogenides were measured and the strain sensitivity of Peltier thermocouples of low height under real working conditions were evaluated.

The semiconductor materials Bi_2Te_3 [1, 2], Sb_2Te_3 [3], and their solid solutions [4] with a complicated multiellipsoidal band structure exhibit a significant sensitivity to strain. Under anisotropic strain in these semiconductors, like in Ge, Si, and PbTe, the energy extrema become nonequivalent, the current carriers are redistributed between states near different extrema, and, as a consequence, a large reversible change in the electric resistance occurs.

The strain sensitivity of polycrystalline films prepared using a special method from the compounds $Bi_2Te_3-Sb_2Te_3$ is significantly higher (by two to three orders of magnitude) than that of the bulk samples of these solid solutions, so that most measurements of the strain sensitivity have been performed on films [5, 6]. Nonetheless it is useful to compare the coefficients of strain sensitivity of films and bulk samples in order to determine the mechanism of the strain-sensitivity in films. Bulk samples of the solid solutions $(Bi_{0.25}Sb_{0.75})_2Te_3$ and $Bi_2(Te_{0.9}Se_{0.1})_3$ are employed to fabricate the positive and negative branches of thermocouples, respectively. The coefficient of strain sensitivity of a thermocouple must be known in order to use the method of strain measurement to predict the behavior of thermocouples under conditions of high temperature gradients [7].

In this work we measured the coefficients of strain sensitivity in bulk, large-crystalline samples of p-type $(Bi_{0.25}Sb_{0.75})_2Te_3$ and n-type $(Te_{0.9}Se_{0.1})_3$, prepared by growing by the method of zone melting. Samples 12 mm long, 2 mm wide, and from 0.3 to 0.8 mm thick were cut out on an electric-spark stand, after which they were subjected to chemical etching. The samples so obtained were glued to an elastic steel plate, and after drying at 100°C for 6 h copper wires for feeding current were soldered to them. The strain-sensitive elements were strained by the method illustrated in Fig. 1.

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