

NOTATION

a , thermal diffusivity of gas, $b = \sqrt{\lambda c_p \gamma}$ and b_0 , thermal activity coefficients of gas at pressures P and P_0 ; c and c_p , specific heats of sensor material and gas; $d = \sqrt{\omega/2c\rho\delta}$, a quantity characterizing the speed of response of the sensor; e , measured signal; g , temperature discontinuity coefficient; h , radiative heat transfer coefficient; m , mass of sensor; R_0 and R_1 , resistance of sensor and bridge arm in series; \bar{T} , mean gas temperature; θ_0 , amplitude of sensor temperature oscillations; V_+ and V_- , constant and variable voltage components at bridge input; $\alpha = 1/R_0 \cdot dR_0/dT$, ρ , and δ , temperature coefficient of resistance, density, and thickness of sensor; γ and λ , density and thermal conductivity of gas; φ , difference in phase between temperature and power oscillations; ω , cyclic frequency of supply alternating current.

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KNUDSEN EFFECT IN DETERMINING THE THERMAL CONDUCTIVITY OF GASES BY THE COAXIAL- CYLINDER METHOD

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UDC 536.23

The properties of the thermal conductivity of gases are investigated by the coaxial-cylinder method at low pressures. It is established that there is a temperature-jump effect, which must be taken into account, especially for light gases at $P \approx 1$ atm and room temperature.

Macroscopic transfer theory has been formulated for molecular free path lengths less than all the macroscopic parameters of the experiment. In this case the gas behaves as a continuous medium, and the concepts of local density, velocity, and temperature gradient have a perfectly definite physical meaning. In particular, in a pure gas, the thermal conductivity λ is defined as the coefficient of proportionality relating the energy flux q_c to the thermodynamic force ∇T

$$q_c = -\lambda \nabla T. \quad (1)$$

Experimental values of q_c and ∇T allow the value of λ to be determined.

In the commonly used steady-state methods (parallel-plate, coaxial-cylinder, or heated-fiber methods), ∇T , which is assumed to be unidirectional in the first of these methods and axisymmetry in the other two, is practically determined from the temperature difference between two solid surfaces bounding the investigated gas.

At low pressures this definition of the thermal conductivity is problematic, since the temperature gradient becomes discontinuous in the vicinity of the wall. For example, if two plane-parallel solid walls at tem-

Paris, France. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 36, No. 3, pp. 472-479, March, 1979. Original article submitted December 6, 1977.

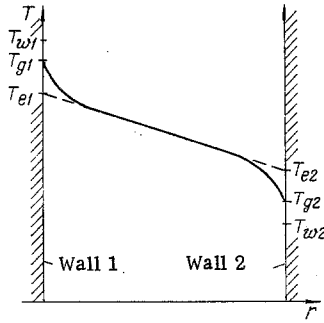


Fig. 1

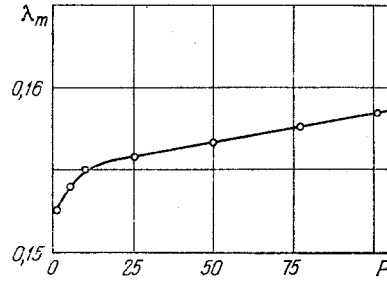


Fig. 2

Fig. 1. Explanation of the temperature jump encountered in determining the thermal conductivity of a gas confined between two parallel plates, a distance e apart, at temperatures of T_{w1} and T_{w2} ; T_{e1} and T_{e2} are the temperatures which the gas would have at the walls if the temperature gradient were constant; T_{g1} and T_{g2} are the actual gas temperatures at the walls.

Fig. 2. Pressure dependence of the apparent thermal conductivity of helium. λ_m , $W \cdot m^{-1} \cdot C^{-1}$; P , $10^5 N \cdot m^{-2}$.

peratures T_{w1} and T_{w2} are considered, it is evident that the temperature gradient does not remain constant in the vicinity of the walls (the temperature distribution is shown in Fig. 1).

These conditions are known as "temperature-jump" conditions. The temperature jump at the wall is defined as the difference between the wall temperature T_{w1} and the temperature T_{e1} obtained by extrapolation of the straight line representing the temperature distribution in the gas.

The value of the thermal conductivity obtained from experimental measurements without taking account of the temperature jump is lower than the value obtained when the temperature jump is taken into account.

On the basis of [1, 2], Kennard [3] developed a kinetic theory of the temperature jump. The assumptions of the Kennard theory were refined in [4, 5]. In this theory a temperature-jump length g is introduced; it is defined as a function of a , the so-called accommodation coefficient*

$$T_w - T_e = -g \frac{\partial T}{\partial r}, \quad (2)$$

$$g = A \left(2\pi \frac{R}{M} T \right)^{1/2} \frac{\lambda}{(\gamma + 1) C_v P}, \quad (3)$$

where $A = (2 - a)/a$; R is the gas constant; $\gamma = C_p/C_v$.

In the case of coaxial cylinders of the same material, with diameters r_1 and r_2 , the relation between the measured (λ_m) and actual (λ) thermal conductivity may be written, assuming that $T_{w1} \neq T_{w2}$ and λ is a function of the temperature, in the form

$$\frac{1}{\lambda_m} = \frac{1}{\lambda} + \frac{C}{P}, \quad (4)$$

where

$$C = \sqrt{\frac{2\pi M}{R}} \cdot \frac{A}{2 \left(\frac{C_v}{R} + \frac{1}{2} \right)} \cdot \frac{1}{\log \frac{r_2}{r_1}} \left(\frac{\sqrt{T_{w1}}}{r_1} + \frac{\sqrt{T_{w2}}}{r_2} \right). \quad (5)$$

*The accommodation coefficient $a = \lim_{E_w \rightarrow E_0} \frac{E_d - E_0}{E_w - E_0}$, where E_0 is the energy of the incident particles; E_w is the energy of the molecules at the wall; E_d is the energy of the reflected particles; $E_w \leq E_d - E_0$. For a monoatomic gas, $a = \lim_{T_w \rightarrow T_0} \frac{T_d - T_0}{T_w - T_0}$.

Introducing the parameter $e = r_2 - r_1$ and setting $r_1 \neq r_2 \gg e$, Eq. (4) is transformed to give

$$\frac{1}{\lambda_m} = \frac{1}{\lambda} + \sqrt{\frac{2\pi M}{R}} \cdot \frac{A}{\left(\frac{C_v}{R} + \frac{1}{2}\right)} \cdot \frac{\sqrt{T}}{e} \cdot \frac{1}{P}. \quad (6)$$

The temperature-jump effect has been taken into account in several measurements of the thermal conductivity of gases at low densities [6-8]. This has confirmed the theoretical linear dependence of $1/\lambda_m$ on $1/P$ and, by extrapolation to $1/P = 0$, has led to corrected values for the thermal conductivity of attenuated gases.

The thermal conductivity of He measured at $P > 1$ atm in [9, 10] is much reduced at low pressures (Fig. 2). No theoretical explanation was offered for this unexpected behavior of the thermal conductivity in [9, 10]. In [11], data obtained at $P > 1$ atm for helium were analyzed, and values of the accommodation coefficient at high pressure were obtained.

Below, data obtained by the coaxial-cylinder method are given for the thermal conductivity of various gases as a function of the pressure (including pressures less than 1 atm).

It is shown that:

- 1) the temperature-jump effect may be important even at pressures for which the free path length is small in comparison with the distance between the cylinders;
- 2) if the real value of the thermal conductivity is to be determined in the limiting case of low density, it must be measured as a function of the pressure.

Several series of thermal-conductivity measurements were made using three cells which differed only in the distance e between the cylinders. The surfaces were carefully polished. A complete description of the measurement cell is given in [12].

In the cell with a gap of $e = 0.260$ mm (No. 1), neon and helium were investigated at room temperature and pressures from $P \approx 0.013 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$ (100 mm Hg) to $100 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$. Above room temperature the thermal conductivity of the same gases was measured at $P > 100 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$.

In the cell with a gap of $e = 0.225$ mm (No. 2), the thermal conductivity of water vapor and nitrogen was measured at room temperature and above (up to 520°C) for $P > 1$ atm.

In the cell with $e = 0.325$ mm (No. 3), nitrogen and water vapor were investigated at $T > 420^\circ\text{C}$ and pressures below atmospheric. The values of λ_m obtained are given in Table 1.

In addition, an analysis was made of the experimental data for He obtained in [9], where a cell similar to these used in the present investigation was used for temperatures $30\text{--}365^\circ\text{C}$ and pressures $0.1\text{--}20$ atm. The gap in this cell was $e = 0.200$ mm (cell No. 4). Finally, the results of [13] for He at 686°C were used. The cell used in [13] was of coaxial-cylinder type and made of silver; the gap size was 0.600 mm.

The change in $1/\lambda_m$ as a function of $1/P$ is shown in Fig. 3 for He, Ne, N_2 , and H_2O . The results shown were obtained at $P < 0.2 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$, where λ should be independent of pressure. The lighter the gas, the larger the slope of the straight lines in Fig. 3.

Consider the results obtained for He (cell No. 1). At atmospheric pressure and 28°C , the difference between the measured value and the value extrapolated to $1/P = 0$ is 1.6% . Although the free path length $L \approx 3 \cdot 10^{-4}$ mm is small in comparison with $e = 2.6 \cdot 10^{-1}$ mm, there is a marked difference in the value of the thermal conductivity.

It is evident from Eq. (2) that the temperature-jump length g is on the order of $6L$. Note that multiatomic and monoatomic gases behave in the same way, although energy transfer between the gas molecules is a more complex process in the case of multiatomic molecules, since all the degrees of freedom of the molecule must be taken into account.

If a linear variation of $1/\lambda_m$ as a function of $1/P$ is necessary for the evaluation of the temperature-jump effect, it is necessary to verify the value of the accommodation coefficient a obtained from Eq. (4).

For He at 28°C , $a \approx 0.3$; for Ne at 22°C , $a \approx 0.6$. These values are comparable in order of magnitude with the values of a in the case of tungsten or nickel surfaces ($0.18 < a < 0.47$ for He and $0.3 < a < 0.8$ for Ne).

The ratio $a_{\text{Ne}}/a_{\text{He}}$ is very close to the ratio $\sqrt{M_{\text{Ne}}}/\sqrt{M_{\text{He}}}$, which is as predicted theoretically for the

TABLE 1. Experimental Values of the Thermal Conductivity of Helium, Neon, Nitrogen, and Water Vapor

| | | Cell № 1 | | $e_1 = 0,260$ mm | | | | |
|-------------|--|---------------------------|-------|------------------|-------|-------|-------|-------|
| Helium | | $T = 28^\circ\text{C}$ | | | | | | |
| P | | 0,070 | 0,115 | 0,20 | 0,47 | 0,77 | 4,56 | |
| λ_m | | 129,0 | 136,3 | 142,6 | 148,4 | 149,9 | 152,4 | |
| | | $T = 31^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 5,1 | 10,0 | 25,2 | 50,7 | 101,7 | |
| λ_m | | 152,3 | 153,8 | 154,9 | 155,8 | 156,7 | 158,5 | |
| | | $T = 121^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 10,1 | 25,3 | 50,7 | 101,5 | 159 | |
| λ_m | | 181,8 | 184,8 | 186,0 | 187,0 | 188,8 | 190,6 | |
| | | $T = 186^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 9,8 | 25,2 | 50,7 | 76,4 | 101,7 | 149 |
| λ_m | | 201,6 | 205,5 | 206,6 | 207,4 | 208,3 | 208,8 | 210,1 |
| | | $T = 270,5^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 10,1 | 25,3 | 50,9 | 101,7 | 200 | |
| λ_m | | 225,3 | 231,4 | 232,4 | 233,4 | 234,5 | 237,3 | |
| Neon | | $T = 22^\circ\text{C}$ | | | | | | |
| P | | 0,093 | 0,114 | 0,178 | 0,256 | 0,568 | 0,981 | 1,05 |
| λ_m | | 46,09 | 46,59 | 47,47 | 47,86 | 48,18 | 48,47 | 48,40 |
| | | $T = 33^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 10,1 | 25,3 | 50,7 | 73,8 | 110,4 | |
| λ_m | | 49,63 | 50,27 | 50,66 | 51,34 | 51,77 | 52,80 | |
| | | $T = 333,2^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 10,1 | 25,3 | 50,7 | 101,8 | 200 | |
| λ_m | | 77,11 | 78,0 | 78,27 | 78,73 | 79,54 | 81,18 | |
| | | Cell № 2 | | $e_2 = 0,225$ mm | | | | |
| Nitrogen | | $T = 296^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 25 | 50 | 100 | 187 | | |
| λ_m | | 42,2 | 43,6 | 44,2 | 45,5 | 47,7 | | |
| Steam | | $T = 406,4^\circ\text{C}$ | | | | | | |
| P | | 1 | 25 | 50 | 100 | | | |
| λ_m | | 54,6 | 56,4 | 57,9 | 64,7 | | | |
| | | $T = 475^\circ\text{C}$ | | | | | | |
| P | | 1,01 | 25 | 50 | 75 | 100 | 125 | |
| λ_m | | 63,1 | 64,6 | 65,9 | 67,4 | 69,6 | 72,7 | |
| | | Cell № 3 | | $e_3 = 0,325$ mm | | | | |
| Nitrogen | | $T = 208^\circ\text{C}$ | | | | | | |
| P | | 0,093 | 0,123 | 0,164 | 0,266 | 0,291 | 0,629 | 1,01 |
| λ_m | | 35,73 | 36,12 | 36,70 | 37,04 | 37,31 | 37,68 | 38,00 |
| | | $T = 410^\circ\text{C}$ | | | | | | |
| P | | 0,120 | 0,150 | 0,169 | 0,407 | 0,789 | 1,01 | |
| λ_m | | 44,31 | 44,94 | 45,3 | 47,73 | 48,31 | 48,6 | |
| Seam | | $T = 420^\circ\text{C}$ | | | | | | |
| P | | 0,173 | 0,267 | 0,541 | 0,817 | 0,99 | 0,99 | |
| λ_m | | 53,4 | 54,4 | 55,04 | 55,8 | 56,0 | 56,3 | |

Note. P , $10^5 \text{ N} \cdot \text{m}^{-2}$; λ_m , $10^{-3} \text{ W} \cdot \text{m}^{-1} \cdot ^\circ\text{C}^{-1}$.

accommodation coefficients on pure surfaces.

From this viewpoint, it may be concluded that the decrease observed in λ_m at pressures on the order of 1 atm for light gases in experiments with coaxial cylinders is a result of the temperature-jump effect.

The temperature-jump theory is approximate and, whereas it has now been developed for the determination of the accommodation coefficient, the theory of the accommodation effect of gases has, as far as is known, not yet been developed. Hence, to obtain a corrected value of λ at low pressures, it must be measured as a function of the pressure.

There is a choice of two possible methods:

a) extrapolation of the value of λ from the low-pressure region, considering the region where λ is independent of pressure (attenuated gas);

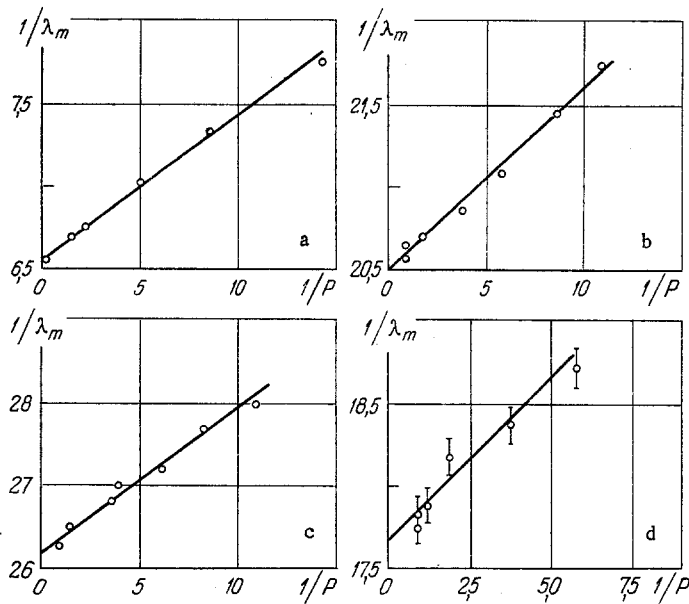


Fig. 3. Inverse of apparent thermal conductivity as a function of the inverse pressure: a) helium, $T = 28^\circ\text{C}$; b) neon, $T = 22^\circ\text{C}$; c) nitrogen, $T = 208^\circ\text{C}$; d) steam, $T = 420^\circ\text{C}$. λ_m , $\text{W}^{-1} \cdot \text{m} \cdot ^\circ\text{C}$; $1/P$ $(10^5 \text{ N} \cdot \text{m}^{-2})^{-1}$.

TABLE 2

| Material | Gap size, mm | T , $^\circ\text{C}$ | δ , % | δ' , % | δe , arb. units | $\delta e'$, arb. units |
|------------------|---------------|------------------------|--------------|---------------|-------------------------|--------------------------|
| He | $e_1 = 0,260$ | 28 | 1,6 | | 4,2 | |
| | | 31 | | 1,7 | | 4,4 |
| | | 122 | | 1,9 | | 5,0 |
| | | 186 | | 2,1 | | 5,5 |
| | | 270 | | 3,0 | | 7,8 |
| He | $e_1 = 0,200$ | 30 | | 2,4 | | 4,8 |
| | | 99 | | 3,3 | | 6,6 |
| | | 198 | | 3,6 | | 7,2 |
| | | 299,5 | | 3,2 | | 6,4 |
| | | 356 | | 4,5 | | 9,0 |
| He | $e_3 = 0,600$ | 686 | | 5,4 | | 31,2 |
| Ne | $e_1 = 0,260$ | 22 | 0,6 | | 1,6 | |
| | | 33 | | 0,7 | | 1,8 |
| | | 333 | | 1,1 | | 2,9 |
| N ₂ | $e_2 = 0,225$ | 296 | | 1,8 | | 4,0 |
| N ₂ | $e_3 = 0,325$ | 209 | 0,6 | | 2,0 | |
| | | 410 | | 1,4 | | 4,6 |
| H ₂ O | $e_2 = 0,225$ | 406 | | 1,4 | | 3,2 |
| | | 475 | | 1,4 | | 3,2 |
| H ₂ O | $e_3 = 0,325$ | 420 | 1,1 | | 3,5 | |

b) extrapolation from the high-pressure region, giving attention to data which take no account of the temperature jump, and assuming that λ changes monotonically as a function of the density.

For each gas it is expedient to consider the relative deviation

$$\delta = \frac{(1/\lambda_m)_1 - (1/\lambda_m)_\infty}{(1/\lambda_m)_\infty} \cdot 100,$$

where the value of $(1/\lambda_m)_1$ is taken at 1 atm and $(1/\lambda_m)_\infty$ is extrapolated to the pressure $1/P = 0$ (λ_m is the thermal conductivity at $P < 1$ atm), or the deviation

$$\delta' = \frac{\lambda_{m,1} - \lambda_{ext,1}}{\lambda_{ext,1}} \cdot 100$$

between the thermal conductivity observed at 1 atm and the value extrapolated to 1 atm from higher pressure.

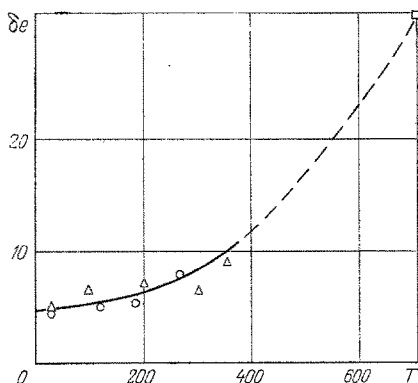


Fig. 4. Temperature dependence of the characteristic quantity δe for helium. T , $^{\circ}\text{C}$.

Within the limits of experimental error, extrapolation of the results for $P < 0.1 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$ and those for $P > 0.1 \text{ M} \cdot \text{N} \cdot \text{m}^{-2}$ leads to the same value of λ (for He at $T \approx 30^{\circ}\text{C}$, $\delta \neq \delta' = 1.6\%$; for Ne at room temperature, $\delta \neq \delta' \approx 0.6\%$). Then δe and $\delta'e$ may be considered for different cells. Temperature-jump theory predicts that δe should be constant for a given type of cell and a given gas at the same temperature. Table 2 shows that δe may be regarded as constant within the limits of accuracy of the data.

Curves of δe and $\delta'e$ against the temperature for He may be presented as the conclusion of this work (Fig. 4). These curves characterize the temperature-jump correction which may be applied in the case when the thermal conductivity is measured at $P = 1 \text{ atm}$. The correction becomes significantly larger at high temperatures, for which there are two possible explanations.

1) Since the free path length at high temperatures is large, the temperature-jump length g increases.

2) The surface conditions change with increase in temperature. The number of adsorbed molecules decreases, so that a decreases (0.32 at 28°C and 0.18 at 688°C), reaching eventually the value of a for a pure surface, which is an order of magnitude lower for He, for example. This behavior of a is similar to that observed in [20] in the case of the nitrogen-tungsten system.

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