THERMAL CONDUCTIVITY OF A MIXTURE OF HELIUM AND AIR

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The thermal conductivity of a helium–air mixture was measured for molar concentrations from 0 to 100%.

At room temperature the thermal conductivities of helium and air are quite different [1]. For many practical applications it is of interest to measure the thermal conductivity of a mixture of the gases as a function of its composition.

The measurements were made by the heated-filament method [2], which in essence consists in the following. A thin filament stretched along the axis of a cylindrical container filled with the gas under study is heated by a current. The heat evolved is transmitted to the container wall by conduction through the gas, radiation, and flow through the supports. The heat-balance equation has the form [2]

$$[2\pi l/\ln(r_2/r_1)]\int_{T_2}^{T_1}\lambda(T)\,dT + \sigma(T_1^4 - T_2^4) + j\Delta T = I^2R, \tag{1}$$

where l and r_1 are the length and radius of the filament; r_2, radius of the cylindrical container; λ, thermal conductivity of the gas at the temperature T; $\Delta T = T_1 - T_2$, temperature difference between the filament and the container wall; j, heat-transfer coefficient through the filament supports; I, current through the filament, R, resistance of the filament. The temperature jumps at the surfaces of the filament and container, and thermal effects due to convection, are not taken into account.

To determine the first term in Eq. (1) it is necessary to know the temperature dependence of λ. Data in [1,2] for a mixture of helium and nitrogen in the 200-400°K temperature range show that this dependence is practically linear. Consequently, if the measurements are made in such a way that the temperatures of the filament and container are kept constant while the composition of the gas is varied, Eq. (1) can be written in the form

$$I^2 = A\lambda(T_{av}) + B, \tag{2}$$

where $T_{av} = {}^1/_2(T_1 + T_2)$, and A and B are constants which can be determined from measurements with pure air and helium.

A type LT-4M transducer containing a thin filament heated by a current, and a Chromel–Copel thermocouple for measuring the filament temperature was used to measure the thermal conductivity. The diameter of the filament was $\sim 10^{-4}$ m, which is much smaller than the size of the container ($\sim 2 \cdot 10^{-2}$ m), and under these conditions the logarithmic dependence of heat transfer from the filament on the ratio r_2/r_1 (the first term in Eq. (1)) is such that at distances of the order of the size of the container the temperature of the gas is practically the same everywhere. Thus, the fact that filament is not stretched along the axis of the transducer is unimportant from the point of view of the applicability of Eqs. (1) or (2).

At a gas pressure of more than 10^4 N/m² the mean free path of gas molecules becomes less than the filament diameter, and the thermal conductivity of the gas ceases to depend on the pressure. In this range of pressures the transducer cannot be used to measure vacuum, but it can be employed to measure thermal conductivity.

First a test was made to determine whether the transducer operates according to Eq. (2). Measurements were performed on three samples of type LT-4M transducers which were simultaneously filled with pure gas to a pressure of $1.5 \cdot 10^4$ N/m². This choice of pressure will be justified. Gases with various thermal conductivities were used: argon, air, neon, and helium. The current through the filament of each transducer was kept constant to within 5

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TABLE 1. Results of Determination of Parameters of Trans-ɹcers ducers (TD)

Gas		Argon	Air	Neon	Helium	$A \pm \Delta A$	$B \pm \Delta B$
I_{ex} in A for TD No.							
	1	0,260	0,305	0,405	0,690	3,007+0,005	0,0117+0,0004
	2	0,260	0,310	0,410	0,700	3,102±0,008	0,0110±0,0007
	3	0,260	0,310	0,400	0,700	3,111±0,051	0,0085±0,0040
Thermal conduct. at T_{av} = 315°K W/m·deg K		0,0184	0,0271	0,0508	0,1544		

mA for a thermoelectromotive force of the thermocouple equal to 3 mV, which corresponds to an average gas temperature of 315°K. The results, averaged over several measurements of the current, are listed in Table 1. The table also lists the values of the thermal conductivities of the gases at 315°K [2], the parameters A^2 ($A^2 \cdot$m·deg K/W) and B (A^2) of the straight line (2) calculated by the least-squares method, and their errors determined by the deviation of the experimental points from the straight line. The accuracy of the measurement of λ is

$$\Delta\lambda/\lambda = \Delta(I^2 - B)/(I^2 - B) + \Delta A/A. \tag{3}$$

Taking account of the fact that $I^2 \gg B$ and $\Delta I^2 \gg \Delta B$, we see that for a variation of the thermal conductivity by almost an order of magnitude (with an accuracy $\Delta\lambda/\lambda \approx 2$-4%) the operation of the transducer is described by Eq. (2). This is illustrated in Fig. 1 for the first LT-4M transducer. It should be emphasized that the spread of values of the coefficient A is an order of magnitude smaller than the spread of values of B; for helium and air $A\lambda \gg B$.

A schematic diagram of the experimental arrangement is shown in Fig. 2. Chamber 1 is pumped down to a pressure of 10 N/m² and then filled with helium evaporated from the Dewar flask 7 and atmospheric air. The molar concentration X was determined by the ratio of the partial pressures. The transducer was first evacuated and then filled to the required pressure with the air–helium mixture. Using a VT-3 vacuum gauge a current of proper magnitude was passed through the filament so that the potential of the Chromel–Copel thermocouple used to measure the filament temperature was 3 mV. In this method of measurement the average temperature of the gas surrounding the filament was constant and equal to 315°K.

The results of the measurements of I(P, X) for T_{av} = 315°K given in Fig. 3 show that for air in the pressure range from 10^4 to 10^5 N/m² the variation of current with pressure does not exceed 20%. As the helium concentration in the mixture is increased, this dependence is weakened, and for helium concentrations of 80% and more the current is practically independent of pressure up to 10^5 N/m². This is apparently related to convection in the gas in the transducer which appears both at high pressures and for a high density of the mixture of gases, and leads to a change in the heat release from the filament. Similar results were obtained at T_{av} = 330°K.

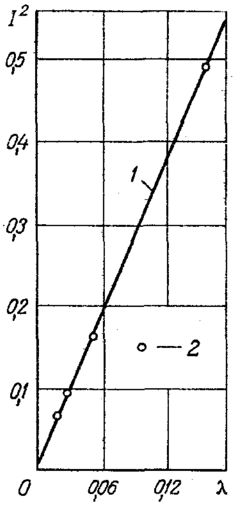

Fig. 1. Square of the TD filament current I^2 in A^2 as a function of the thermal conductivity λ in W/m·deg K of the gas filling the TD: 1) $I^2 = A\lambda + B$; 2) results of experiment with TD-1; the straight line is drawn by the least-squares method.

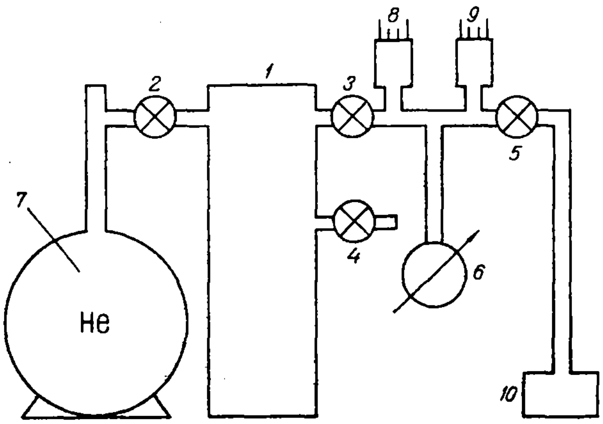

Fig. 2. Schematic diagram of experimental arrangement: 1) chamber; 2-5) valves; 6) standard vacuum gauge; 7) Dewar flask with liquid helium; 8-9) LT-4M transducers; 10) NVR-5D pump.

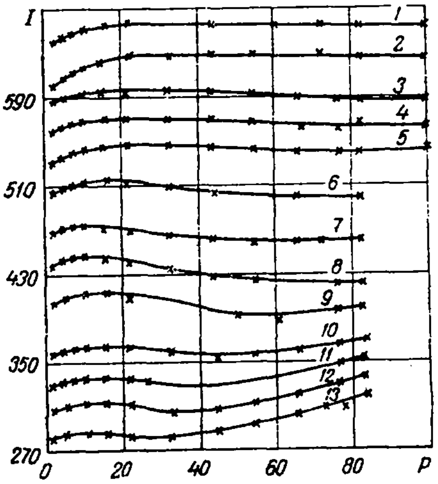

Fig. 3. Filament current as a function of pressure for various helium concentrations in mixture (emf of thermocouple 3 mV, T_{av} = 315°K): 1) helium; 2) X = 0.95; 3) 0.9; 4) 0.85; 5) 0.8; 6) 0.7; 7) 0.6; 8) 0.5; 9) 0.4; 10) 0.3; 11) 0.2; 12) X = 0.1; 13) air. I in mA, P in 10^3 N/m^2.

Thus, in order to employ Eq. (2) to determine the dependence of the thermal conductivity λ of the mixture on its molar concentration X, it is necessary to use the I(X) dependence in the range of pressures where convection is unimportant, and at the same time the thermal conductivity does not depend on the pressure. Figure 4 shows the results of measurements at $P = 1.5 \cdot 10^4$ N/m^2, and λ as a function of X given by Eq. (2) for T_{av} = 315 and 330°K. The figure also shows the experimental values for a helium–nitrogen mixture taken from [1, 2] and converted to the indicated temperatures.

The deviation from the linear equation $\lambda = \lambda_1 X + \lambda_2 (1 - X)$ determined in the present work is characteristic of most mixtures of monatomic and polyatomic gases [2]. This results from the fact that the contribution of the lighter component to the thermal conductivity is decreased because of collisions with the heavier components of the mixture. Many calculations (cf. [2]) have been made of the thermal conductivity of a multicomponent mixture on the basis of the kinetic theory of gases, but it is hardly expedient to compare these with the results of the present work, since the composition of the air was not strictly controlled in the measuring process. For practical purposes it makes sense to compare our results with the semiempirical formula [3]

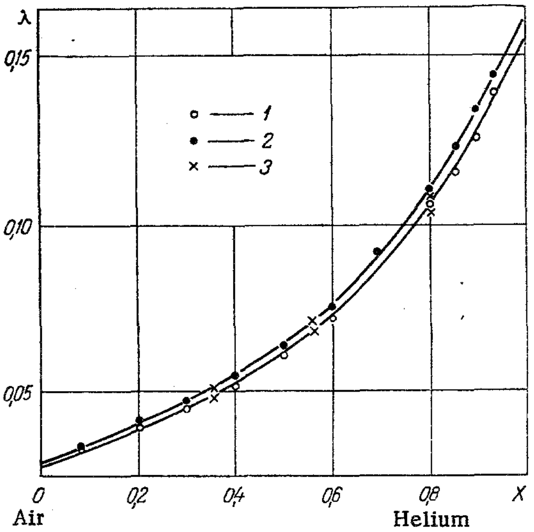

Fig. 4. Thermal conductivity of mixture as a function of helium concentration according to Eq. (2): 1) T_{av} = 315; 2) 330°K; 3) extrapolated values for a helium–nitrogen mixture, taken from [1,2].

TABLE 2. Comparison of Measured and Calculated Parameters of the Curve for the Thermal Conductivity λ as a Function of the Concentration X (4)

T_{av}, °K	A_{ik}^{ex}	W	A_{12}^{ex}/A_{21}^{ex}	A_{ik}	A_{12}/A_{21}
315	$A_{12}=2{,}74\pm0{,}05$ $A_{21}=0{,}183\pm0{,}003$	0,004613	15,0	$A_{12}=2{,}00$ $A_{21}=0{,}131$	15,3
330	$A_{12}=2{,}81\pm0{,}003$ $A_{21}=0{,}148\pm0{,}001$	0,0011774	19,0	$A_{12}=1{,}99$ $A_{21}=0{,}132$	15,1

$$\lambda = \lambda_1/[1 + A_{12}(1 - X)/X] + \lambda_2/[1 + A_{21}X/(1 - X)], \tag{4}$$

which was derived by taking account of the resistance of molecules of one component to the transport of heat by molecules of the other.

A Nairi computer was used to find the values of the parameters A_{12} and A_{21} which minimize the dispersion

$$W = \Big[\sum_n (\lambda_n^{ex} - \lambda_n)^2\Big]^{1/2} \tag{5}$$

of the experimental data. Table 2 gives the values found for A_{ik}^{ex} and the dispersion W for two temperatures. The accuracies of the parameters indicated in the table correspond to $\Delta \ln W = 0.001$. Within the limits of accuracy of the measurements the experimental results agree with the curves plotted in Fig. 4 by using Eq. (4).

It is interesting to compare the values found for the parameters A_{ik}^{ex} with those calculated from the expression [4]

$$A_{ik} = (1.065/2\sqrt{2})[1 + (\lambda_i/\lambda_k)^{1/2}(m_i/m_k)^{1/4}]^2/[1 + (m_i/m_k)]. \tag{6}$$

The values of A_{ik} calculated from this equation, with gram molecular weights of helium and air taken equal to 4 and 28.6 g, respectively, are also listed in Table 2. It is clear that the difference between A_{ik} and A_{ik}^{ex} does not exceed 30%. The table also lists the values of the ratios A_{12}/A_{21} and A_{12}^{ex}/A_{21}^{ex}, which agree considerably better.

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INTERACTION POTENTIAL OF NONPOLAR POLYATOMIC MOLECULES

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The extension of the (12—7)-pair potential model to nonpolar polyatomic molecules is proposed. It is demonstrated that this model consistently fits diverse experimental data.

It has been demonstrated in previous studies [1-3] that the (12—7)-pair potential model

$$\varphi(r) = 5.1042\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{7}\right] \tag{1}$$

consistently fits diverse experimental data pertaining to all monatomic gases over the entire range of measurements, except for discrepancies between the results obtained by various authors. With the (12—7) potential, in other words, the law of corresponding states is actually satisfied for equilibrium and transport properties of gases with spherical nonpolar molecules at low temperatures. It has been possible on this basis to calculate the properties of monatomic gases at temperatures at which direct measurements are not possible [3].

Many gases are not monatomic, however, and their molecular structures are most diverse. The potential energy of interaction involving two polyatomic molecules depends not only on the distance between their centers of inertia but also on their orientations. It is well known [4-6] that, by averaging the pair potential of interaction over all possible orientations, one can theoretically calculate the corrections for asphericity of molecules, these corrections depending only on the intermolecular distance. This greatly simplifies calculations of the macroscopic properties, inasmuch as the effective pair potential of polyatomic molecules can be expressed in terms of a spherically symmetric function.

The simplest model of interaction of polyatomic molecules is the Kihara—Midzuno—Kaneko model [5]. Here every molecule is represented as a distribution of potential sources corresponding to individual atoms and the interparticle potential between two molecules represents interaction of the distributed sources which represent these two molecules. According to this model, the effective pair potential can be expressed as a power series in r_e^2 [5]:

$$\varphi = \varphi_0 + \frac{r_e^2}{12}\left(\varphi_0'' + 2\frac{\varphi_0'}{r}\right) + \cdots, \tag{2}$$

where φ_0 is the interaction potential of two sources and r_e is a linear dimension which characterizes the asphericity of molecules (core). For homonuclear diatomic molecules (hydrogen, nitrogen, oxygen) and also for the linear symmetric CO_2 molecule, this core dimension is equal to the equilibrium distance between the two extreme nuclei in a molecule.

Strictly speaking, expression (2) is valid for large distances between the cores of molecules ($r \gg r_e$), where the far-range component of potential energy is dominant. Assuming that there

$$\varphi_0 = -cr^{-7}, \tag{3}$$

as is the case in the model potential (1), we have for polyatomic molecules

$$\varphi = -cr^{-7}\left(1 + \frac{7}{2}\frac{r_e^2}{r^2}\right) \tag{4}$$

in the first approximation.

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