COMPUTATION OF THE HEAT CONDUCTIVITY
OF BINARY GAS MIXTURES

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The results of computing the effective heat conductivity of gas mixtures with monatomic and polyatomic components are compared with experimental data.

A combination method of computing the heat conductivity of gas mixtures, based on the use of conceptions of the molecular-kinetic theory of the gas state in combination with a new phenomenological model of the structure of a gas mixture, was proposed in [1]. The functional dependence to compute the heat conductivity of a gas mixture λ is

$$\lambda = \lambda_1' \left[c^2 + v(1-c)^2 + \frac{2vc(1-c)}{vc + (1-c)} \right], \quad v = \frac{\lambda_2'}{\lambda_1'}. \tag{1}$$

Here c is a geometric parameter of the model associated with the volume concentration of the second component by means of the equation

$$m_2 = 2c^3 - 3c^2 + 1, \tag{2}$$

whose solution (the first root) can be represented as

$$c = 0.5 + a \cos \frac{\varphi}{3} \tag{3}$$

for

$$0 \leqslant m_2 \leqslant 0.5 \quad a = -1, \quad \varphi = \arccos(1 - 2m_2),$$
$$0.5 \leqslant m_2 \leqslant 1.0 \quad a = 1, \quad \varphi = \arccos(2m_2 - 1),$$

and the value of the angle φ is taken in the last quadrant, i.e., $270° \leq \varphi \leq 360°$.

The heat conductivity of a component in the mixture λ_i' is determined from the relationships of molecular-kinetic theory by analogy with [2, 3]:

$$\lambda_1' = \frac{\lambda_1}{m_1 + m_2 A_{12}} \; ; \; \lambda_2' = \frac{\lambda_2}{m_2 + m_1 A_{21}} . \tag{4}$$

Here the coefficients A_{ij} characterizing the intramolecular interaction depend on the relationships of the masses of the molecules of the components, and their geometric and force parameters. A large number of methods to compute the coefficients A_{ij} is presented in the literature [2-6]. Here we use the simplest relationships proposed in [3], namely:

$$A_{12} = \frac{\gamma_{12}}{\gamma_1} \left(\frac{\sigma}{\sigma_1} \right)^2 \sqrt{\frac{M_1 + M_2}{2M_2}} , \quad A_{21} = \frac{\gamma_{12}}{\gamma_2} \left(\frac{\sigma}{\sigma_2} \right) \sqrt{\frac{M_1 + M_2}{2M_1}} \tag{5}$$

with

$$\gamma_1 = 1 + \frac{S_1}{T}, \; \gamma_2 = 1 + \frac{S_2}{T}, \; \gamma_{12} = 1 + \frac{S_{12}}{T},$$

TABLE 1. Heat Conductivity of Gas Mixtures

Gas mixture	Temper-ature, °K	Number of points	Deviations		Reference
			arith. mean	rms	
Monatomic gas mixtures					
Ar—He	273	4	2,2	3,3	[16]
Ar—He	311	4	0,5	2,0	[19]
Ar—Ne	311	4	0,1	0,55	[19]
Ar—Ne	793	3	—0,2	1,37	[19]
Ar—Kr	291	5	—2,0	2,6	
Ar—Kr	311	4	1,4	1,54	[19]
Ar—Kr	793	3	—0,2	0,87	
Ar—Xe	291	5	—0,3	0,7	[19]
Ar—Xe	311	4	0,3	1,53	[19]
Ar—Xe	793	3	0,4	1,16	[19]
He—Kr	291	5	6,2	7,1	[19]
He—Xe	291	10	0,7	2,0	[19]
He—Xe	311	4	2,1	5,0	[19]
He—Xe	793	4	1,6	4,0	[19]
Monatomic and polyatomic gas mixtures					
He—O_2	303	6	0,6	2,2	[14]
He—O_2	318	6	0,6	2,5	[14]
Ne—O_2	303	5	0,4	0,8	[14]
Ne—O_2	318	6	—1,1	2,6	[14]
Ar—H_2	273	4	12,6	12,6	[15]
Ar—N_2	273	4	2,6	2,6	[15]
Ar—C_6H_6	351	3	0,1	0,01	[16]
Ar—CH_3OH	351	3	1,2	1,2	[16]
Kr—O_2	303	6	1,5	3,6	[14]
Kr—O_2	318	5	3,1	4,9	[14]
Xe—O_2	303	6	5,2	6,1	[14]
Xe—O_2	318	6	—6,4	6,9	[14]
N_2—CO	274	3	—1,6	1,7	[18]
N_2—CO	673	3	—1,4	1,4	[18]
N_2—CO	1085	3	—0,6	1,1	[18]
CO—CO_2	433	4	—1,0	1,6	[18]
CO—CO_2	774	3	1,0	1,2	[18]
CO — air	291	4	—1,8	2,0	[15]
CH_4 — air	295	4	1,7	1,8	[15]
C_2H_4— air	293	5	1,9	2,0	[15]
C_2H_4— air	338	4	2,9	3,0	[15]
C_2H_4— H_2	273	4	4,2	4,7	[17]
H_2—N_2	299	9	11,9	12,2	[17]
H_2—N_2	348	5	13,3	13,6	[17]
H_2—N_2	423	4	12,3	12,3	[17]
H_2—O_2	295	5	7,8	9,2	[17]
H_2—CO	273	5	6,5	7,1	[15]
H_2—N_2	372	5	12,5	12,9	[17]
H_2—CO_2	273	3	12,7	12,8	[15]
H_2—C_2H_4	298	5	12,4	12,5	[15]
Polyatomic gas mixtures with polar components					
N_2—NH_3	274	3	—3,3	3,4	[17]
N_2—NH_3	299	9	—0,1	0,6	[17]
N_2—NH_3	348	5	5,3	5,4	[17]
N_2—NH_3	372	4	0,4	2,8	[17]
N_2—NH_3	423	3	1,5	2,9	[17]
NH_3—CO	295	4	0,8	0,8	[17]
NH_3—air	293	4	0,0	0,6	[15]
NH_3—air	353	4	1,5	1,6	[15]
NH_3—C_2H_4	298	3	2,3	2,3	[15]
N_2—H_2O	338	4	2,4	2,7	[16]
H_2O—air	353	4	1,3	1,3	[15]
H_2—NH_3	299	10	8,2	8,5	[17]
H_2—NH_3	348	5	11,9	12,0	[17]
H_2—NH_3	372	5	9,1	9,8	[17]
H_2—NH_3	423	5	8,6	8,7	[17]
H_2—N_2O	273	4	5,5	6,7	[15]

where S_1, S_2 are Sutherland constants characterizing the intramolecular interaction. For a mixture of non-polar gases the quantity S_{12} is determined from the expression $S_{12} = \sqrt{S_1 S_2}$, and for mixtures with polar components $S_{12} = 0.733 \sqrt{S_1 S_2}$ [3]. Hence $\sigma = 0.5(\sigma_1 + \sigma_2)$.

Let us examine methods and errors in determining the separate parameters used in computing the heat conductivity of a gas mixture by means of (1)-(5), and let us estimate the probable error in the computation. The molecular weights of the components are determined with less than 0.1% error. The error in determining the volume concentration of the components can be less than 1% [5]. The heat conductivity of the pure components is measured with an accuracy of 3-6% [12]. The parameters listed above are determined by direct measurements. However, the kinetic-gas diameter of the molecules and the interaction force parameters S_i or ε_i cannot be measured directly at the present time. The indirect methods of determining the geometric and force parameters by converting them from experimental data by means of the
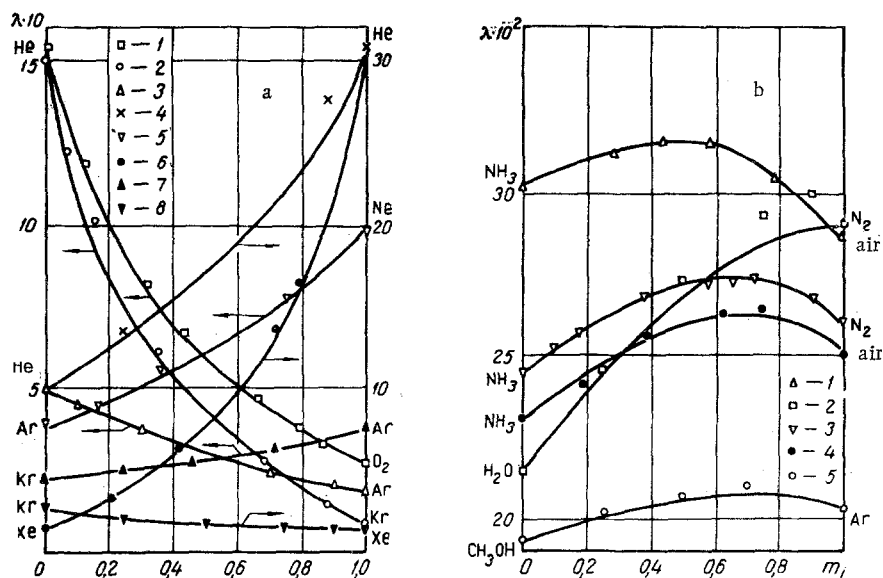
Fig. 1. Heat conductivity (W/m · deg) of gas mixtures: a) mixtures
with nonpolar components [1) He—O_2, T = 303°K; 2) He—Kr, T = 291°K;
3) Ne—Ar, T = 311°K; 4) Ne—He, T = 793°K; 5) Ar—Ne, T = 793°K; 6)
Xe—He, T = 793°K; 7) Kr—Ar, T = 793°K; 8) Kr—Xe, T = 793°K]; b)
mixtures with polar components [1) NH_3—air, T = 388°K; 2) H_2O—N_2,
T = 338°K; 3) NH_3—N_2, T = 299°K; 4) NH_3—air, T = 293°K; 5) CH_3OH
—Ar, T = 351°K].

equations of state or transport yield distorted values of the absolute quantities because of experimental er-
ror, the imperfections of the model on whose basis the computational relations are founded (the selection of
the kind and parameters of interaction potential), the conditionality of the combination rules and the approxi-
mate solution of the gas state equation.

In this connection, there is a certain wonder about the values of the molecule diameter and the poten-
tial interaction parameters presented in the literature [9-11] to four significant figures, while the error in
the experimental data from which the mentioned parameters have been calculated, is 2-3% in the best case,
and grows with temperature. Moreover, the geometric and force parameters obtained by an inverse con-
version from experimental results for mixtures, will not agree with the parameters calculated by the com-
bination rules from the properties of the pure components. The discrepancy may be 15% in the magnitude
of the kinetic-gas diameter and 25% in the interaction potential parameters [7, 8]. At the same time, com-
putations show that the heat conductivity of the individual components and the mixture depends substantially
on the initial value of the kinetic-gas diameter. Thus, for example, a 10% change in the magnitude of the
kinetic-gas diameter for a He—Xe mixture will result in a 20% change in the computed value of the mixture
heat conductivity.

A computation method so noticeably responsive to a change in the initial data of the parameters in-
evitably obliges seeking some foundation for the choice of the parameters σ_i, S_i, ε_i obtained by different
methods.

At present it is impossible to give rigorously founded recommendations for the selection of the molec-
ular parameters for the computation. Only certain qualitative considerations can be presented, according
to which it is expedient to use values of σ_i, S_i, or ε_i evaluated from experimental transport parameters
rather than from the equation of state, to compute the heat conductivity. Since only separate data on the
magnitude of σ_i, S_i, ε_i found from experimental values of the coefficient of heat conductivity are presented
in the literature, values of these parameters determined from test results on viscosity [9] are ordinarily
used in the computation. In our opinion, the minimal discrepancy between the computation and test results
on the heat conductivity of a gas mixture should not be less than the error in an experimental determination
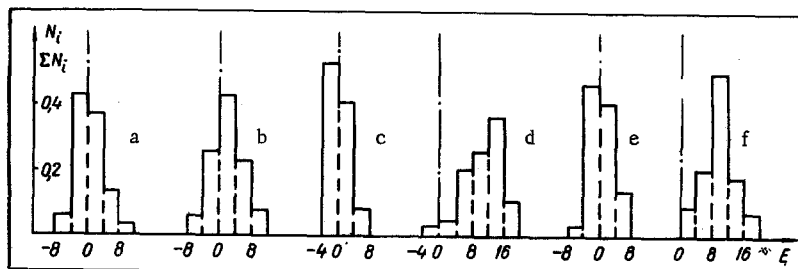of the heat conductivity of the pure components, i.e., ±3-5%.

Fig. 2. Deviation histogram (E in %): a) monatomic gas mixture; b, c) mixtures of monatomic and polyatomic, hydrogen-free non-polar gases; d) nonpolar monatomic gas mixtures with hydrogen; e) hydrogen-free mixtures with polar components; f) mixtures of polar components with hydrogen.

It is apparently expedient to compute the domain of possible values of the coefficient of heat conductivity of gas mixtures. The dimensions of this domain should depend on the error with which the parameters in the computational formula are known.

Let us compare the results of computing the heat conductivity of gas mixtures with experimental data. The geometric (σ_i) and force (S_i) parameters used in the computation, which are borrowed from [9, 13], are evaluated from viscosity measurements.

Mixtures of Monatomic Gases. Presented in Table 1 are the results of computing the heat conductivity of mixtures of monatomic gases by means of (1)-(5). A comparison of the results of computation in a broad range of variation of the volume concentrations of the components, the temperature, and the relationship of the molecule masses, shows satisfactory agreement with experiment (see Fig. 1a). It can be noted that a tendency to increase the discrepancy between test and computation is observed in the domain of low concentrations of the heavy component (He−Kr, He−Xe mixtures) for a sharp difference in the molecular masses of the components. The magnitude of the deviations, their sign and frequency of manifestation are easily clarified by analyzing the histogram (see Fig. 2a). The distribution of the deviations is practically symmetrical, and the shape of the histogram is similar to a normal distribution curve. Bias is not observed in the histogram.

Monatomic and Polyatomic Gas Mixtures. The results of computing the heat conductivity of monatomic gas mixtures with nonpolar and polar components and of monatomic gases are shown in Table 1 and in Fig. 1a. Presented in Fig. 2b is a histogram of the deviations, which is similar in shape to a normal distribution curve whose maximum has been shifted approximately 2% on the positive side. The shift indicates the appearance of some systematic error,i.e.,a reduction in the results of the computation relative to the experiment. Agreement can be considered satisfactory on the whole, in the whole range of variation of the volume concentration of components.

Polyatomic Gas Mixtures. The results of computing the heat conductivity of polyatomic gas mixtures with nonpolar components are presented in Table 1 and in Fig. 1b. Shown in Figs. 2c, e separately are histograms of the deviations for mixtures with and without hydrogen. A systematic divergence of the computation from test of on the average 12% towards a reduction in the computational results is observed in the whole range of concentration changes for mixtures with hydrogen. The hydrogen-free mixtures have no systematic deviations and show good agreement with experiment.

The significant difference in the masses of the components in mixtures with hydrogen (up to 20-fold) is apparently not the sole cause for such noticeable deviations of systematic nature. Indeed, the mean error in a He−Kr mixture with the same difference between the masses of the molecules is about 6% and the maximum does not exceed 11%, while in the He−Xe mixture with a 30-fold difference in the masses the maximum divergence is 5%.

An analogous picture is observed for gas mixtures with polar components (see Table 1 and Fig. 1b). As in the previous case, hydrogen-free mixtures disclose no systematic deviations and result in satisfactory agreement between computation and experiment. Polar gas mixtures with hydrogen also disclose a systematic deviation towards a 10% reduction in the computational results on the average.

The comparison made between the results of a computation and the experimental data of various researchers (see Fig. 1) permits the conclusion that the proposed model of the structure of a gas mixture and the method of computing the heat conductivity describe the qualitative nature of the changes in the heat conductivity (see Fig. 1) as a function of the concentration (concavity, linearity, and convexity of the concentration dependences) in a broad range of variation of the governing parameters, namely: the species of gas, the relationships between the masses, the concentrations and heat conductivities of the components in the range of temperature variation from 273 to 1100°K. For the majority of cases, with the exception of mixtures with hydrogen, the method yields satisfactory quantitative agreement with experiment, the deviations are random, and as a rule, do not exceed $\pm 4\%$.

To clarify the causes for the systematic deviation for mixtures with hydrogen it is expedient to conduct a special investigation and to verify other methods of computing the coefficients A_{ij}, which have been presented in [4-6], for example. Verification of the suitability of the proposed method of computation in the low-temperature range is of interest. The possibility of a systematic error in the experimental determination of the heat conductivity of gas mixtures containing hydrogen is also not excluded.

NOTATION

λ	is the effective heat conductivity of a gas mixture, W/m·deg;
λ_i	is the heat conductivity of the i-th component in the mixture, W/m·deg;
c	is the geometric model parameter;
m_i	is the volume concentration of the i-th component;
M_i	is the molecular weight;
σ_i	is the kinetic-gas diameter of the molecule;
S_i	is the Sutherland constant, deg;
ε_i	is the depth of the potential wall, erg.

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