GENERALIZATION OF EXPERIMENTAL DATA REGARDING THE THERMAL CONDUCTIVITY OF GAS MIXTURES FROM THE STRUCTURAL POINT OF VIEW

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On the basis of theoretical relationships and a generalization of experimental data, an equation is derived for calculating the thermal conductivity of binary mixtures of nonpolar gases.

Research workers have made repeated attempts at deriving convenient practical relationships for calculating the thermal conductivity of gas mixtures in a form simpler than that based on the derivations of the kinetic theory. Authors have based their considerations on a number of assumptions, for example, additive heat transfer by molecules of different kinds [6], the adequacy of the structure of the mixture and a certain ordered geometrical arrangement, etc. [1-3]. An inevitable result of these attempts has been either simplicity of the computing formula but a considerable discrepancy between the computed and experimental results or else complication of the computing method (for example, by introducing corrected thermal conductivities of the components) and an acceptable accuracy of the computed data. In this paper we shall attempt to derive valid computing relationships by generalizing experimental data; we consider that this kind of approach will enable all the special aspects of the transfer process in gas mixtures to be taken into account.

First we shall derive relationships for the thermal conductivity of a two-component structured material in which each component comprises inclusions of one shape or another (with sharp interfaces) and retains its individual transport properties. Let us consider the transfer of heat through a flat interlayer of such a material of thickness δ with constant temperatures T_0 and T_δ at the boundaries. Let us define the mean thermal conductivity of the layer material along a straight line parallel to the z axis (the z axis is directed perpendicular to the layer) passing through the point (x_0, y_0) in the following way:

$$\bar{\lambda}_{z(x_0,y_0)} = \frac{\int\limits_{\delta} \lambda(x_0, y_0, z) \frac{\partial T}{\partial z} dz}{\int\limits_{\delta} \frac{\partial T}{\partial z} dz}. \tag{1}$$

If we divide the integral in (1) into two sums of integrals, according to the number of inclusions N_1, N_2 of each component, assume that the properties of the components are independent of the temperature and coordinates, i.e., $\lambda_{1n} = \lambda_1$, $\lambda_{2n} = \lambda_2$, and remember that

$$\begin{gathered} \sum_{n=1}^{N_1} \int\limits_{\delta_{1n}} \frac{\partial T_{1n}}{\partial z} dz = \sum_{n=1}^{N_1} \Delta T_{1n} = \Delta T_1; \\ \sum_{n=1}^{N_2} \int\limits_{\delta_{2n}} \frac{\partial T_{2n}}{\partial z} dz = \sum_{n=1}^{N_2} \Delta T_{2n} = \Delta T_2, \end{gathered} \tag{2}$$

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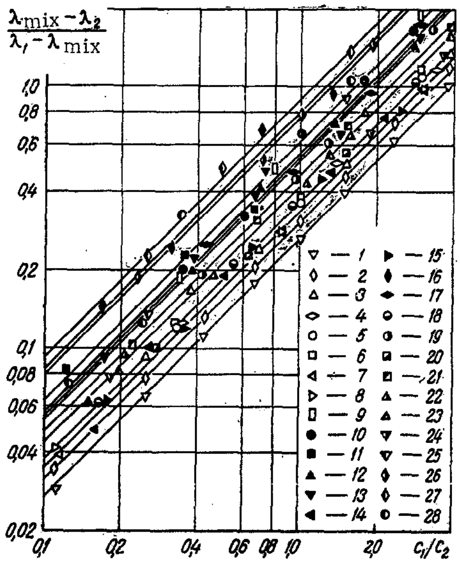

Fig. 1. Experimental dependence of the criterion $(\lambda_{mix} - \lambda_2)/(\lambda_1 - \lambda_{mix})$ on the relative volumetric concentrations of the components c_1/c_2 for gas mixtures. For notation see Table 1.

we shall obtain

$$\bar{\lambda}_{z(x_0,y_0)} = \frac{\lambda_1 \Delta T_1 + \lambda_2 \Delta T_2}{\Delta T_1 + \Delta T_2} = \frac{\lambda_1}{1 + \frac{\Delta T_2}{\Delta T_1}} + \frac{\lambda_2}{1 + \frac{\Delta T_1}{\Delta T_2}}, \tag{3}$$

where $\Delta T_1 + \Delta T_2 = T_0 - T_\delta$.

Assuming that the layer is sufficiently thick relative to the size of the inhomogeneities in the structure, we may regard $\bar{\lambda}_z(x_0, y_0)$ as independent of the choice of coordinates (x_0, y_0) and in view of the isotropic nature of the material consider that $\bar{\lambda}_z$ is independent of direction, i.e., $\bar{\lambda}_z = \lambda_{mix}$.

Equation (3) establishes the initial dependence of the thermal conductivities of the components and contains the only undetermined parameter $\Delta T_1/\Delta T_2$. Solving Eq. (3) for $\Delta T_1/\Delta T_2$ we obtain

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\lambda_{mix} - \lambda_2}{\lambda_1 - \lambda_{mix}}. \tag{4}$$

From physical considerations we may expect this ratio to depend on the structure of the material and the concentrations and thermal conductivities of the components. The aim of our subsequent analysis is accordingly to establish qualitative and quantitative relationships between these parameters.

Figure 1 shows the results of an analysis of the experimental data in the form of a relationship between the complex $(\lambda_{mix} - \lambda_2)/(\lambda_1 - \lambda_{mix})$ and the ratio of the volumetric concentrations of the components c_1/c_2 for 28 mixtures of gases at 90-900°K.

It follows from Fig. 1 that for every mixture and for a variety of temperatures this relationship may be approximated to a high degree of accuracy by the equation

$$\frac{\lambda_{mix} - \lambda_2}{\lambda_1 - \lambda_{mix}} = K \frac{c_1}{c_2}. \tag{5}$$

The values of the proportionality factor K for the mixtures under consideration are shown in Table 1. Mixtures in which an extremum occurs in the $\lambda_{mix} = f(c_1)$ relationships cannot be analyzed in the manner indicated. These include mixtures containing a polar component (for example, water vapor or ammonia). Data relating to H_2–N_2 and H_2–CH_4 mixtures at high temperatures, and also mixtures containing Ne, are not described very satisfactorily in the manner indicated. As regards H_2–N_2 this fact was also noted by other research workers [2].

TABLE 1. Analysis of Experimental Data Regarding the Thermal Conductivities of Gas Mixtures

Composition of the mixture	T, °K	Experimental values of thermal conductivity, W/(m·deg)		K	Notation in the figures	Reference
		$\lambda_1 \cdot 10^3$	$\lambda_2 \cdot 10^3$			
He—Xe	273	143	5,1	0,265	1	[4]
	773	304,4	13,5	0,310	2	[4]
He—Ar	273,2	140,5	16,3	0,357	3	[4]
	308,2	151	18,4	0,358	4	[10]
	310,9	150,4	18,04	0,361	5	[9]
	374,2	179	21,4	0,370	6	[9]
He—Kr	308,2	151	9,65	0,329	7	[10]
	363,2	167,5	11,20	0,342	8	[10]
Ar—Kr	308,2	18,4	9,61	0,619	9	[10]
O_2—Kr	308,2	27	9,44	0,610	10	[11]
	318,2	28,1	9,78	0,620	11	[11]
O_2—Xe	308,2	27	5,43	0,525	12	[11]
	318,2	28,1	5,69	0,540	13	[11]
He—O_2	308,2	152,5	27	0,360	14	[11]
	318,2	158	28,1	0,365	15	[11]
Ne—O_2	308,2	48,7	27	0,77	16	[11]
	318,2	50,5	28,1	0,560	17	[11]
H_2—CO_2	273	169,2	15,07	0,360	18	[4]
	893	433,8	63,5	0,460	19	[4]
H_2—N_2O	273	169,2	15,9	0,370	20	[4]
H_2—Ar	273	169,2	16,34	0,470	21	[4]
H_2—C_2H_4	298	183,1	22,1	0,43	22	[4]
H_2—CO	273	169,2	22,2	0,43	23	[4]
H_2—N_2	300	179,9	25,9	0,413	24	[7]
H_2—O_2	273	167,5	24,9	0,57	25	[4]
H_2—D_2	273	169,2	129	0,81	26	[4]
N_2—Ar	273	23,7	16,1	0,92	27	[4]
	90	9,61	5,82	0,83	28	[5]

Equation (5) is valid both for limiting structures with maximum ($K = 1$) and minimum ($K = \lambda_2/\lambda_1$) conductivities (alternating plane layers oriented in a particular manner), and also for complicated compositions [$K = 2/3 + (1/3)(\lambda_2/\lambda_1)$] [8]; it may accordingly be regarded as a phenomenological relationship. This assertion is at the moment based on experimental data; however, if it is true, it should be possible to achieve a purely phenomenological derivation.

Figure 2 shows the next stage in the analysis of the same data in the form of a relationship between the complex $K = [(\lambda_{mix} - \lambda_2)/(\lambda_1 - \lambda_{mix})] \cdot (c_2/c_1)$ and the ratio of the thermal conductivities of the components λ_2/λ_1. An analysis of Fig. 2 shows that the experimental points are best described (with a scatter of ±8%, apart from four mixtures) by the equation

$$\frac{\lambda_{mix} - \lambda_2}{\lambda_1 - \lambda_{mix}} \cdot \frac{c_2}{c_1} = 0.19 + 0{,}81 \left(\frac{\lambda_2}{\lambda_1}\right)^{\frac{2}{3}}. \qquad (6)$$

In Table 2 we compare the calculated and experimental values of the thermal conductivity for 47 mixtures of nonpolar gases. The mean-square deviation for these data is 4.3% (maximum deviation 13.7%).

Thus Eq. (6), which was obtained as a result of the generalization of experimental data, may be recommended for engineers' calculations of the thermal conductivity of mixtures of nonpolar gases over a wide range of temperatures and compositions. A comparison with the method of calculating the thermal conductivities proposed by Vasil'eva and Dul'nev [2, 6] shows that the method proposed here is simpler but gives the same accuracy.

The very fact of the correlation existing between experimental data regarding the thermal conductivity of binary gas mixtures when considered on the structural basis supports the existence of an analogy between heat transfer in the mixture and a certain geometrical arrangement, which we may fairly call the equivalent structure of the mixture.

TABLE 2. Comparison between the Calculated and Experimental Values of the Thermal Conductivities of Gas Mixtures with the Same Concentrations of the Components ($c_1 = c_2 = 0.5$; λ, W/(m · deg)

Composition of the mixture	T, °K	$\lambda_1 \cdot 10^3$	$\lambda_2 \cdot 10^3$	$\lambda_{mix.\ exp} \cdot 10^3$	$\lambda_{mix.\ cal} \cdot 10^3$	$(\lambda_{mix.\ cal} \cdot 10^3 - \lambda_{mix.cal}) / \lambda_{mix.\ cal}$, %	Reference
He—Xe	273	143	5,1	33,8	35	−3,43	[4]
	773	304,7	13,5	81,6	78,8	+3,3	[4]
He—Ar	273,2	140,5	16,3	49,2	50,6	−2,78	[4]
	308,2	151	18,4	53,5	55,4	−1,62	[10]
	310,9	150,4	18,04	52,08	55	−5,41	[9]
	374,2	179	21,4	64,0	65,4	−2,14	[9]
He—Kr	308,2	151	9,65	44,7	44,0	−1,59	[10]
	363,2	167,5	11,2	51	49,4	+3,24	[10]
Ar—Kr	308,2	18,4	9,61	13	13,2	−1,54	[10]
O_2—Kr	308,2	27	9,44	16,1	15,7	−2,55	[11]
	318,2	28,1	9,78	16,75	16,2	−3,4	[11]
O_2—Xe	308,2	27	5,43	12,80	12,3	+4,07	[11]
	318,2	28,1	5,69	13,45	12,85	+4,66	[11]
He—O_2	308,2	152,5	27	61,5	65,4	−6,1	[11]
	318,2	158	28,1	62,9	68	−7,35	[11]
Ne—O_2	308,2	48,7	27	36,4	36,4	0	[11]
	318,2	50,5	28,1	36,2	37,6	−3,73	[11]
Ne—Xe	291,2	48,5	5,52	16,7	17,3	−3,5	[5]
Ar—Xe	291,2	17,4	5,52	9,45	9,83	−4	[5]
Ne—Ar	291,2	52,5	17,5	2,92	3,0	−2,5	[5]
Kr—Xe	302,2	9,7	6	7,8	7,62	−2,2	[5]
He—CO_2	273,2	123	14,2	45,7	44,3	+2,94	[5]
D_2—Ar	308,2	135	18,3	54,4	51,8	+4,25	[5]
	363,2	154	21	63	59,3	−6,25	
H_2—Ne	303,2	192	46	85,7	94,5	−9,32	[5]
He—N_2	303,2	152	25,2	58,7	63,8	−8	[5]
N_2—Xe	303,2	21,7	7	11,75	12,3	−4,43	[5]
Ne—CO_2	273,2	44	14,3	25,1	25,1	0	[5]
Ar—C_6H_6	398,2	22,6	19,1	19,65	20,7	−5	[5]
N_2—CO_2	300	25,1	16,7	18,8	20,4	−7,85	[5]
N_2—N_2O	305,2	26,5	19	20,9	22,3	−6,26	[5]
NO—N_2O	323,7	27,5	19,8	22,6	23,3	−3	[5]
O_2—Ar	311,2	27,1	18,2	21,1	22,1	−4,53	[5]
O_2—N_2	692,2	48,6	44,6	46	46,5	−1,08	[5]
C_6H_{14}—C_6H_6	361	18,8	15,4	17,1	17	−0,59	[5]
NO—N_2	305,2	26,7	26,5	26,0	26,6	−2,25	[5]
N_2—CO	274,2	23,5	23,3	23,4	23,48	−0,426	[5]
H_2—CO_2	273,2	169,2	15,07	55,7	55	−1,27	[4]
	893	433,8	63,5	175	173	+1,15	[4]
H_2—N_2O	273	169,2	15,9	57,1	56,3	+1,42	[4]
H_2—Ar	273	169,2	16,3	56,8	65	−12,6	[4]
H_2—N_2	300	179,9	26,9	71,3	71	+0,5	[7]
H_2—C_2H_4	298	183,1	22,1	70,7	69	+2,3	[4]
H_2—CO	273	169,2	22,1	66,2	64,1	+3,28	[4]
H_2—O_2	273	167,5	24,9	76,2	67,0	+13,7	[4]
H_2—D_2	273	169,2	129	146,8	147,5	−0,5	[4]
N_2—Ar	273	23,7	16,1	19,75	19,6	+0,765	[4]
	90	9,61	5,82	7,8	7,9	−1,27	[5]

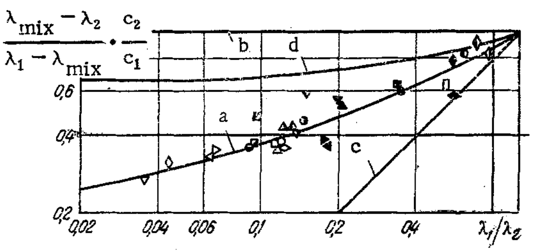

Fig. 2. Experimental dependence of the complex $K = [(\lambda_{mix} - \lambda_2)/(\lambda_1 - \lambda_{mix})] \cdot (c_2/c_1)$ on the ratio of the thermal conductivities of the components for various mixtures of gases (notation as in Fig. 1): a) average curve; b) curve of maximum conductivity; d) curve based on the Odelevskii formula [8].

NOTATION

$\bar{\lambda}_z(x_0, y_0)$, mean thermal conductivity of the interlayer along a straight line parallel to the z axis and passing through the point (x_0, y_0); $\lambda(x_0, y_0, z)$, current thermal conductivity; λ_1, λ_2, thermal conductivities of the components; λ_{1n}, λ_{2n}, thermal conductivities of components 1 and 2 in the n-th inclusion; δ, thickness of the interlayer; T_0, T_δ, temperatures at the boundaries of the interlayer; z, direction along which the thermal conductivity of the interlayer is defined; n, serial number of inclusions of components 1, 2 along the straight line under consideration; N_1, N_2, number of inclusions of the components; δ_{1n}, δ_{2n}, extent of the inclusions of components 1, 2 along the straight line; ΔT_{1n}, ΔT_{2n}, temperature drop in the n-th inclusion of components 1, 2; ΔT_1, ΔT_2, total temperature drops in the components along the straight line; λ_{mix}, thermal conductivity of the mixture; c_1, c_2, volumetric concentrations of components 1, 2.

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MEASUREMENT OF THE THERMAL ACTIVITY OF LIQUIDS IN THE METASTABLE REGION

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A method of measuring the thermal activity of superheated liquids is described. Transition through the saturation line is effected under isobaric conditions by the pulsed heating of a thin layer of liquid bordering the resistive element used as the heater.

Owing to the instability of liquids in the region beyond the saturation line, any experimental analysis of their properties is very difficult. The specific volumes [1-3] and viscosity [4] of a number of liquids have been measured, but the literature contains no data at all regarding the thermophysical characteristics of superheated liquids. Yet the properties of liquids in this region need to be known for a whole series of theoretical and practical reasons. At present, such data are usually obtained by extrapolating the results obtained in the stable region. The validity of this extrapolation lacks experimental verification.

We have accordingly developed a pulse measuring method in which shock heating of the liquid briefly realizes the superheated state and at the same time enables

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