THERMAL CONDUCTIVITY OF BINARY GAS MIXTURES

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The main methods of analysis of heat transfer in mixtures of nonreacting gases are discussed. A new model and method of calculating the thermal conductivity is proposed.

There have been considerable number of theoretical studies of heat transfer in mixtures of nonreacting gases. Most of them represent a continuation and development of Boltzmann's fundamental work [1]. A gas or a gas mixture is a discrete medium with local aggregates of mass in the form of atoms, molecules, or associations of them, moving randomly in space. Using the ideas of molecular kinetic theory, Boltzmann derived the basic integrodifferential equation of the gas state, whose solution makes it possible to express analytically the transport coefficients, including the thermal conductivity, as a function of the controlling parameters (atomic or molecular weights and geometric dimensions of the components, radial distribution function, distribution of molecular velocities, form and parameters of intermolecular interaction potential). The difficulty of solving the equation is increased by the fact that the geometric parameters of gas molecules and the nature of their interaction have not yet been adequately investigated. Strictly speaking, the integrodifferential equation of the gas state applies to a uniform gas in conditions close to the equilibrium state, i.e., when the fluxes are linear in relation to the potential gradients.

Since the end of last century there have been two different approaches to the analytical determination of the thermal conductivity of a gas mixture.

1. Enskog [2] and Chapman [3] independently obtained an approximate analytical solution of the Boltzmann equation.

If the gas mixture is represented as a hypothetical uniform gas with reduced molecular parameters the solution of the equation of the gas state from [2, 3] can be used to obtain an expression for the thermal conductivity of a gas mixture as a function of the following controlling parameters

$$\lambda = f_1(M_i, \sigma_i, \varepsilon_i, T, m_i). \tag{1}$$

We note that the reduced molecular parameters (mass and diameter of molecules, parameters of intermolecular interaction) of a uniform gas are calculated on the basis of the combination rules, which contain some elements of arbitrariness [4].

In the solution of the Boltzmann equation the molecules are assumed to be spherically symmetrical, ideally elastic, and smooth, with a Maxwellian velocity distribution [2, 3].

The Enskog-Chapman method was developed in many subsequent studies involving more precise consideration of the effect of the asymmetry of shape and roughness of the molecules, the introduction of new kinds of interaction potentials, and a new distribution function. A thorough critical review of these investigations is given in [4]. The development of transport theory for multicomponent mixtures is also described in [4].

2. The second method of investigating the effective thermal conductivity of gas mixtures owes its origin to work of Wassiljewa [5]. Let us recall the main idea of this method. It is assumed that the effective thermal conductivity of a gas mixture is an additive function of the thermal conductivity of its components. The thermal conductivity of a component in a mixture can differ from the thermal conductivity of the pure gas, since the mean free path of the molecules in the mixture may be significantly altered. In this method of investigation the effective thermal conductivity of a gas mixture is expressed as a function of the following parameters:

$$\lambda = f_2(M_l, \sigma_i, T, \lambda_i, m_i). \tag{2}$$

In all the subsequent papers [6–11] in which Wassiljewa's method was developed, it was still assumed that there was an additive relationship between the effective thermal conductivity of a gas mixture and the thermal conductivity of its components. Since there is no obvious basis for this assumption, let us examine the justification given by Wassiljewa [5].

The thermal conductivity of a pure gas is determined from the formula obtained by Boltzmann [1]:

$$\lambda_i = \varkappa R \rho_i \bar{c}_{vi} l_i M_i^{-1} (\gamma_i - 1)^{-1}, \gamma_i = \frac{\bar{c}_{pi}}{\bar{c}_{vi}}. \tag{3}$$

For extension to a gas mixture Wassiljewa puts forward the following arguments: "We can imagine the total number n of molecules of a pure gas divided into two parts n_1 and n_2; $n_1 + n_2 = n$. Then the thermal conductivity (?)* can be represented as consisting of two parts in the form

$$\lambda_i = \frac{n_1}{n_1 + n_2} \frac{\varkappa R \rho_i \bar{c}_{vi} l_i}{(\gamma_i - 1) M_i} + \frac{n_2}{n_1 + n_2} \frac{\varkappa R \rho_i \bar{c}_{vi} l_i}{(\gamma_i - 1) M_i}. \tag{4}$$

All the quantities here have the same values as in formula (3) and relate to one gas. We leave the tempera-

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*The question mark here and later is ours.

ture and the pressure unaltered and imagine n_2 molecules of the one gas are replaced by the same number of molecules of the other gas. Then expression (4) retains (?) the same form, but in the second term of the right-hand side the subscripts of the components are changed. If the change in the mean free path of the molecules in the mixture is taken into account the expression for the thermal conductivity of a binary gas mixture takes the form

$$\lambda = \frac{n_1}{n_1+n_2}\,\frac{\varkappa R \rho_i \bar{c}_{vi} l_i'}{(\gamma_i - 1) M_i} + \frac{n_2}{n_1+n_2}\,\frac{\varkappa R \rho_j \bar{c}_{vj} l_j'}{(\gamma_j - 1) M_j}, \quad (5)$$

where l_i' and l_j' are the new mean free paths of the molecules of the mixture components."

Wassiljewa determined the values l_i' and l_j' from the formulas [1]

$$l_i' = \pi^{-1}\left[\sigma_i^2 n_i \sqrt{2} + \sigma^2 n_j \sqrt{(M_i + M_j) M_j^{-1}}\,\right]^{-1},$$
$$l_j' = \pi^{-1}\left[\sigma_j^2 n_j \sqrt{2} + \sigma^2 n_i \sqrt{(M_i + M_j) M_i^{-1}}\,\right]^{-1},$$
$$\sigma = 0{,}5(\sigma_i + \sigma_j). \quad (6)$$

Wassiljewa subsequently converted relationship (5) to the form

$$\lambda = \lambda_1 \left(1 + A_{12} \frac{m_2}{m_1}\right)^{-1} + \lambda_2 \left(1 + A_{21} \frac{m_1}{m_2}\right)^{-1}. \quad (7)$$

Here m_1 and m_2 are the volume concentrations of the components in the mixture,

$$m_1 = n_1 (n_1 + n_2)^{-1}, \quad m_2 = n_2 (n_1 + n_2)^{-1},$$

and the parameter A has the following form:

$$A_{ij} = K \left(\frac{\sigma}{\sigma_i}\right)^2 \sqrt{\frac{M_i + M_j}{2M_j}}, \quad (8)$$

where k = 1.38 is an empirical coefficient.

Relationship (7) is known in the literature as Wassiljewa's formula.

For convenience of further analysis we put expression (7) in the form

$$\lambda = \lambda_1' m_1 + \lambda_2' m_2, \quad (9)$$

where λ_1' and λ_2'—the new values of the thermal conductivity of the pure components in the mixture—are given by the expressions

$$\lambda_1' = \frac{\lambda_1}{m_1 + m_2 A_{12}}, \quad \lambda_2' = \frac{\lambda_2}{m_2 + m_1 A_{21}}. \quad (10)$$

We will show that the above justification of the additive nature of relationship (9) is not sound. In fact, it is easy to show that by using the same arguments we could justify the following form, for instance, of the relationship between the effective thermal conductivity and thermal conductivity of the components:

$$\frac{1}{\lambda} = \frac{m_1}{\lambda_1'} + \frac{m_2}{\lambda_2'}. \quad (11)$$

We note that relationships (4), (5), and (9) assume a definite structure in the arrangement of the components in the gas mixture, viz., components 1 and 2 form flat layers (Fig. 1a) oriented parallel to the heat flux. The nature of formulas (4) and (5) will be the same for two layers consisting of components 1 and 2 and for an infinite number of infinitely thin layers.

If components 1 and 2 form alternating flat layers oriented perpendicular to the heat flux, then we arrive at formula (11).

We emphasize that neither of these cases truly represents the actual arrangement of the components in the gas mixture. In fact, the molecules are arranged randomly in the gas mixture. The ascription of a definite structure to the arrangement of the components must be regarded as a formal approach, which, as the investigations of Wassiljewa and his successors have shown, can be of great value for calculation of the thermal conductivity of a gas mixture. Relationships (9) and (11) relate to two extreme models of the structure of a mixture and represent cases of minimum (9) and maximum (11) thermal resistance. Such models of a gas mixture are anisotropic and the components of the mixture in the model are geometrically nonequivalent. Any intermediate isotropic model will presumably be closer to the structure of a real gas mixture. On this basis we can predict straight away that relationships (9) and (11) can lead to differences between calculated data and experimental results. Relationship (9) will lead to overestimated results and (11) to underestimates.

This probably explains why Wassiljewa had to introduce the empirical correction factor K = 1.38 into formula (9).

Wassiljewa's basic assumption of an additive relationship between the effective thermal conductivity of a gas mixture and the thermal conductivity of its components has been treated very critically by some investigators.

Enskog thinks that in general the thermal conductivity of a mixture cannot be expressed by an additive function of its components [2].

Papers [6–11] give various empirical relationships for calculation of the numerical coefficients in Wassiljewa's formula. These relationships use experimental data for the diffusion or viscosity coefficients of the components forming the mixture. Attempts to provide a rigorous theoretical basis for the use of these coefficients have been unsuccessful. The view that the thermal conductivity of the mixture will have an intermediate value between the results obtained from formulas (9) and (11) has been expressed by several investigators. For instance, Brokaw [8] proposed

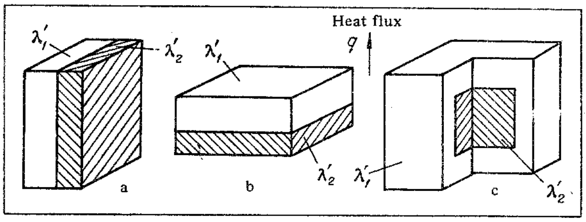

Fig. 1. Models of structure of gas mixture: a) Wassiljewa's model [5]; b) Brokaw's model [8]; c) Missenard's model [12].

that the thermal conductivity of a mixture should be calculated as the arithmetic mean of the results obtained from formulas (9) and (11). Missenard [12] proposed the following model of a gas mixture. Isolated inclusions of component 2 are scattered throughout the connecting component 1 (Fig. 1c). The relationship between the effective thermal conductivity of such a model and the thermal conductivity of the components and their volume concentration has the form

$$\lambda = \lambda_1' \left\{ 1 + m_2 \left(1 - \frac{\lambda_1'}{\lambda_2'}\right) \left[1 - m_2^{1/3}\left(1 - \frac{\lambda_1'}{\lambda_2'}\right)\right]^{-1} \right\}. \qquad (12)$$

In this model components 1 and 2 are also geometrically nonequivalent, i.e., the subscripts cannot be interchanged in formula (12). To remove this contradiction Missenard suggested calculating two values of the thermal conductivity of the mixture by interchanging the subscripts of the components in (12) and taking their arithmetic means.

The calculation methods proposed by Brokaw and Missenard seem very artificial to us. We think that the structural model chosen for the gas mixture should correspond with the main aspect of the distribution of the components in the gas mixture, viz., the components in the mixture do not form alternating layers (Wassiljewa's and Brokaw's model) do not consist of closed macroinclusions of one component in the other (Missenard's model), but form a random system composed of interpenetrating components. The two components in this case will be geometrically equivalent. Let us attempt to construct a structural model of the gas mixture corresponding to the formulated requirements. Imagine the position of the molecules of the binary gas mixture as fixed at an arbitrary instant (see Fig. 2a). We now divide the whole volume occupied by the gas mixture between the individual components (see Fig. 2b) in proportion to their volume concentration. We obtain a random three-dimensional spatial lattice rather like a sponge with communicating pores. Each random spatial lattice, as Fig. 2b shows, contains molecules of only one component, and the

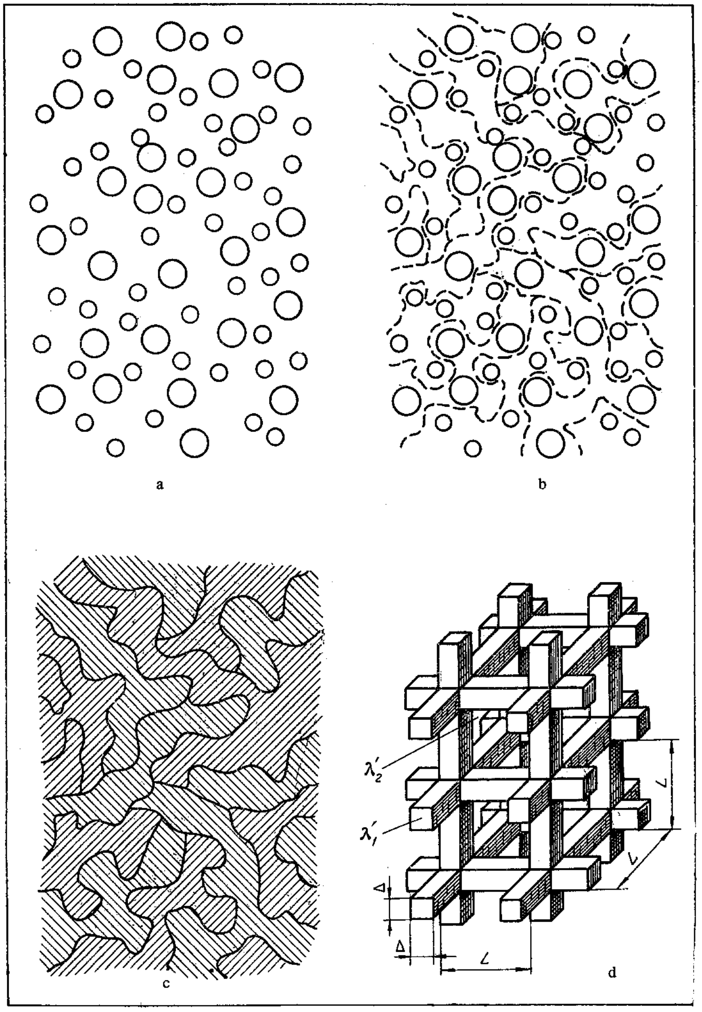

Fig. 2. For derivation of a model of a gas mixture in the form of interpenetrating components: a) schematic representation of binary gas mixture; b) distribution of free volume between components; c) schematic representation of irregular three-dimensional structure; d) ordered model of three-dimensional structure of mixture [13].

volumes occupied by the different components are contiguous with one another. Figure 2b also shows that the cross sections of the microlattice are commensurable with the distance between the molecules.

Assume that part of the volume assigned to each component is filled with a continuous isotropic medium with a thermal conductivity corresponding to the altered thermal conductivity of the components in the mixture (see Fig. 2c). The thermal conductivity of such a random three-dimensional structure can be investigated on an ordered model.

In [13] we considered a model structure of a two-component mixture (see Fig. 2d) corresponding to the requirements formulated earlier for the model of a gas mixture. In fact, the model of [13] is an ordered system of interpenetrating lattices. It is isotropic and the components in it are geometrically equivalent and uniformly distributed throughout the volume of the mixture. The functional relationship for calculation of the thermal conductivity has the form

$$\lambda = \lambda_1' \left[C^2 + \nu (1 - C)^2 + \frac{2\nu C (1 - C)}{\nu C + (1 - C)} \right],$$
$$\nu = \frac{\lambda_2'}{\lambda_1'} . \tag{13}$$

Here C = Δ/L is a dimensionless quantity characterizing the relationship between the parameters of the spatial lattice of the model (see Fig. 2d). The quantity C depends only on the volume concentration of the components and is given by the equation

$$m_2 = 2C^3 - 3C^2 + 1, \tag{14}$$

whose real and positive solution (first root) has the form

$$C = 0{,}5 + a \cos \frac{\varphi}{3}, \tag{15}$$

and for

$$0 \leqslant m_2 \leqslant 0{,}5, \ a = -1 \quad \varphi = \arccos (1 - 2m_2);$$
$$0{,}5 \leqslant m_2 \leqslant 1{,}0, \ a = 1 \quad \varphi = \arccos (2m_2 - 1),$$

and the values of the angle φ are real only in the last quadrant, i.e., $270^\circ \le \varphi \le 360^\circ$.

The third root of the cubic equation (14) is also a real positive solution, but is less suitable for calculations.

For rough calculations we can use the graphic solution of Eq. (14) given in Fig. 3.

We obtain the thermal conductivities λ_1' and λ_2' of the components of the mixture from relationship (11)

$$\lambda_1' = \lambda_1 (m_1 + m_2 A_{12}')^{-1}, \quad \lambda_2' = \lambda_2 (m_2 + m_1 A_{21}')^{-1} . \tag{16}$$

To calculate coefficients A_{12}' and A_{21}' we use the very simple relationships proposed in [6]:

$$A_{12}' = \frac{\gamma_{12}}{\gamma_1} \left(\frac{\sigma}{\sigma_1} \right)^2 \sqrt{\frac{M_1 + M_2}{2M_2}},$$
$$A_{21}' = \frac{\gamma_{12}}{\gamma_2} \left(\frac{\sigma}{\sigma_2} \right)^2 \sqrt{\frac{M_1 + M_2}{2M_1}},$$
$$\gamma_1 = 1 + \frac{S_1}{T}, \quad \gamma_2 = 1 + \frac{S_2}{T}, \quad \gamma_{12} = 1 + \frac{S_{12}}{T} . \tag{17}$$

Here S_1 and S_2—the Sutherland constants—characterize the forces of intermolecular interaction. The value of S_{12} for a mixture of nonpolar gases is determined from the expression [14] $S_{12} = \sqrt{S_1 S_2}$, and for mixtures with polar components [6] $S_{12} = 0.73 \sqrt{S_1 S_2}$. The coefficients A_{ij}' can also be calculated from other recently obtained, more accurate relationships [7–11, 15, 16].

Thus, we can propose the following scheme for calculation of the thermal conductivity of a gas mixture. From (15), (16) we find the thermal conductivity of the components of the mixture, i.e.,

$$\lambda_i' = f_3 (\lambda_1, \lambda_2, m_1, m_2, \sigma_1, \sigma_2, S_1, S_2, M_1, M_2). \tag{18}$$

The found values of λ_1', λ_2' and the volume concentrations m_1 and m_2 are substituted in relationship (13) and the effective thermal conductivity of the gas mixture

$$\lambda = f_4 (\lambda_1', \lambda_2', m_1, m_2) \tag{19}$$

is calculated.

Let us investigate the effect of individual parameters on the effective thermal conductivity of the gas mixture calculated by the proposed method.

A general quantitative analysis of (13) is rather difficult, since the effective thermal conductivity of the mixture is a function of ten parameters and, hence, in this paper we confine ourselves to a few limiting cases and an investigation of the qualitative effect of the individual parameters.

1. We consider several limiting cases in formula (13), which lead to obvious results: a) $\lambda_1' = \lambda_2'$, then $\nu = 1$ and $\lambda = \lambda_1' = \lambda_2'$; b) when $m_2 = 0$, $\lambda = \lambda_1' = \lambda_1$; c) when $m_1 = 0$, $\lambda = \lambda_2' = \lambda_2$; d) when $A_{12}' = A_{21}' = 1$ we obtain $\lambda_1' = \lambda_1$, $\lambda_2' = \lambda_2$.

2. We note that in the region $0.7 \le \nu \le 1.6$ the relationship $\lambda = f_4(\lambda_1', \lambda_2', m_1, m_2)$ is almost linear.

3. Consideration of the effect of polarity of the components when $\nu \approx 1$ leads to a reduction of the coefficient A_{ij}' and the appearance of a positive deviation of the effective thermal conductivity from the additivity rule.

4. If there is a significant difference in the masses of the molecules and their diameters we can expect the appearance of negative deviations of the effective thermal conductivity of a gas mixture from the additivity rule.

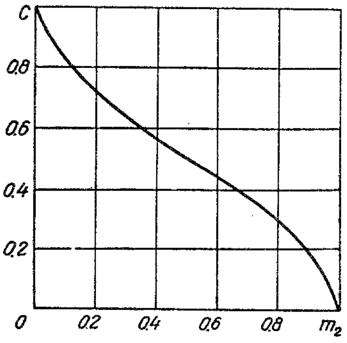

Fig. 3. Relationship between parameter C and volume concentration of components.

To test the suitability of the proposed method we calculated the thermal conductivity of 30 mixtures of inert, polyatomic, and polar gases in the whole range of variation of the concentration of the components at temperatures of 273 to 800° K. The mean difference between calculation and experiment was 2–5%. The maximum difference for mixtures of inert gases (about 10%) occurred in the case of a He–Kr mixture at T = 793° K in the region of low concentrations of the heavy component.

For mixtures of polyatomic gases the maximum deviation (up to 14%) was observed for a H_2-CO_2 mixture, also in the region of low volume concentration of CO_2. Considerable deviations between experiment and calculation (up to 10%) for H_2-CO_2, H_2-N_2, and H_2-C_2H_4 mixtures have been observed by other researchers [8, 20] and probably require special consideration.

It is believed that present analytical methods of calculation of the thermal conductivity of gas mixtures give results which deviate from the experimental data by only 2–3% on the average. In view of this an average discrepancy of 5–8% can be regarded as a fault of the calculation method.

We regard this viewpoint as strange, since the error in the experimental determination of the thermal conductivity of pure components and the differences between the data of different authors are ±(2–5%) [17] and increase with temperature increase. In addition, the initial calculation parameters σ_i, ε_i, and S_i differ significantly in different papers [4, 16, 18, 19]. At the same time, calculations show that for a He-Xe mixture a change of 10% in σ_i leads to a change of 25% in the thermal conductivity of the gas mixture. This indicates the need for a critical attitude to the prevalent view on the postulated error of various methods of calculation. The considered questions and a comparison of the results of calculations by the proposed method with experimental data will be dealt with in a special paper.

NOTATION

λ is the effective thermal conductivity of gas mixture; λ_i is the thermal conductivity of pure i-th component; σ_i and M_i are the diameter and the mass of molecular components; ε_i and S_i are the constants characterizing intermolecular interaction; m_i is the volume concentration of components; T is temperature; q is the heat flux, °K; l_i is the mean free path of molecules of pure gas; l_i' is the mean free path of molecules of i-th gas in mixture; $\varkappa$ is a numerical coefficient; R is the gas constant; ρ_i is the gas density; c_{pi} and c_{vi} are the mean specific heat of gas at constant pressure and volume.

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