HEAT-CONDUCTION COEFFICIENT OF GAS MIXTURES AT HIGH DENSITIES

V. Z. Svoiskii

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An approximate formula is obtained to compute the heat-conduction coefficient of multicomponent dense gas mixtures.

The modified Enskog theory [1] turns out to be useful for calculating the transport coefficients of pure gases. The Enskog–Thorn theory of binary mixtures of solid spheres [2] and its extension to a multicomponent mixture [3] has been used successfully to compute the transport coefficients of gas mixtures. A computation of the viscosity and heat-conduction coefficients of a number of mixtures [4, 5] showed the reliability and high accuracy of the method. Although it is quite tedius, its theoretical foundation should especially be emphasized.

In this paper the original method [4, 5] is simplified without a noticeable reduction in the accuracy of the results. Simplification is achieved by using the assumption, borrowed from kinetic rarefied gas theory, about the smallness of the nondiagonal elements of the matrix as compared with the diagonal elements. An approximate formula is obtained to compute the heat-conduction coefficient of multicomponent dense gas mixtures that is analogous to the formula for the viscosity coefficient [6]. In the limit both formulas go over into the known Sutherland–Vasil'eva expressions for zero density. A computation of the heat-conduction coefficient for air and a helium–neon mixture is performed. Comparison of the computation results with generalized data [7] and with a computation by the original method [5] shows agreement with 1-2% limits.

1. Computation Method

The original formula for the heat-conduction coefficient of a multicomponent dense mixture of solid spheres is written in the form [5]

$$\lambda_{\text{mix}} = -\frac{\begin{vmatrix} L_{11} & \dots & L_{1\nu}y_1 \\ \vdots & & \vdots \\ L_{\nu 1} & \dots & L_{\nu\nu}y_\nu \\ y_1 & \dots & y_\nu \;\; 0 \end{vmatrix}}{\begin{vmatrix} L_{11} & \dots & L_{1\nu} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ L_{\nu 1} & \dots & L_{\nu\nu} \end{vmatrix}} + k_{\text{mix}}, \tag{1}$$

where

$$y_i = x_i\left[1 + n\sum_{j=1}^{\nu}\frac{2m_im_j}{(m_i+m_j)^2}\,x_j\gamma_{ij}\bar{\chi}_{ij}\right]; \tag{2}$$

$$L_{ii} = \frac{x_i^2\bar{\chi}_{ii}}{\lambda_i^0} + \sum_{\substack{j=1\\ j\neq i}}^{\nu}\frac{x_ix_j\bar{\chi}_{ij}}{2\lambda_{ij}^0A_{ij}^*(m_i+m_j)^2}\left(\frac{15}{2}m_i^2 + \frac{25}{4}m_j^2 - 3m_j^2B_{ij}^* + 4m_im_jA_{ij}^*\right); \tag{3}$$

$$L_{ij}\,(i\neq j) = -\frac{m_im_jx_ix_j\bar{\chi}_{ij}}{2\lambda_{ij}^0A_{ij}^*(m_i+m_j)^2}\left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right); \tag{4}$$

$$k_{\text{mix}} = \frac{10}{9}n^2\sum_{i,j=1}^{\nu}\frac{x_ix_jm_im_j}{(m_i+m_j)^2}\,\lambda_{ij}^0\gamma_{ij}^2\bar{\chi}_{ij}. \tag{5}$$

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The quantities γ_{ij} in (1)-(5) are defined in terms of the diameter of the solid spheres σ:

$$\gamma_{ii} = \gamma_i = \frac{6}{5} b_i = \frac{6}{5} b_{ii} = \frac{6}{5}\left(\frac{2}{3}\pi\sigma_i^3\right), \tag{6}$$

$$\gamma_{ij} = \frac{6}{5} b_{ij} = \frac{6}{5}\left(\frac{2}{3}\pi\sigma_{ij}^3\right), \tag{7}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j),$$

$\bar{\chi}_{ij} = \bar{\chi}_{ji}$ are pseudoradial distribution functions for the molecules of species i and j in the presence of molecules of all the other components in the mixture. They are denoted by bars up above to distinguish them from the true radial distribution functions χ_{ij} related to the equation of state. The quantities A_{ij}^* and B_{ij}^* are dimensionless ratios of collision integrals, equal to one for solid spheres, and close to one for other kinds of interaction.

Determination of the parameters γ_{ij} and $\bar{\chi}_{ij}$ is central to the utilization of (1). As in the modified Enskog theory [1], γ_{ij} is expressed in terms of the second virial coefficient and its temperature derivative:

$$\gamma_{ij} = \frac{6}{5} b_{ij} = \frac{6}{5}\left[B_{ij} + T\frac{dB_{ij}}{dT}\right]. \tag{8}$$

Since experimental values of B_{ij} are often missing for $i \neq j$, the combination rule (7) can be used and we can obtain

$$\gamma_{ij}^{1/3} = \frac{1}{2}(\gamma_{ii}^{1/3} + \gamma_{jj}^{1/3}). \tag{9}$$

The pseudoradial distribution functions $\bar{\chi}_i$ of the pure gases comprising the mixture are evaluated from the Enskog equation

$$\frac{\lambda_i}{\lambda_i^0} = \frac{1}{\delta_i} nb_i \left(\delta_i \frac{1}{nb_i\chi_i} + 1.2 + 0.757 nb_i\chi_i\right), \tag{10}$$

where

$$\delta_i = \lambda_i^0/\lambda_i^0(\text{mon});\ \lambda_i^0(\text{mon}) = \frac{15}{4}\frac{R}{M_i}\eta_i^0. \tag{11}$$

The values of $\lambda_i(n, T)$, λ_i°, and η_i° are considered known from experiment, and b_i is found in conformity with (8).

Equation (10) is written down for a polyatomic gas [1]. If the gas is monatomic, then $\delta_i = 1$ and the equation has the usual form. To simplify the writing it is convenient to introduce the notation

$$z = bn\bar{\chi};\ \lambda/(\lambda^0 bn) = c. \tag{12}$$

Taking (12) into account, (10) is reduced to a quadratic equation in z

$$\frac{0.757}{\delta} z^2 + \left(\frac{1.2}{\delta} - c\right) z + 1 = 0. \tag{13}$$

Then one of the two branches of the solution of (13) is selected that corresponds to the minus sign before the square root:

$$z = \left[\left(c - \frac{1,2}{\delta}\right) - \sqrt{\left(c - \frac{1.2}{\delta}\right)^2 - 4\frac{0.757}{\delta}}\right] \Big/ \left(2\frac{0.757}{\delta}\right) \tag{14}$$

$$= \frac{2}{\left(c - \frac{1,2}{\delta}\right) + \sqrt{\left(c - \frac{1.2}{\delta}\right)^2 - 4\frac{0.757}{\delta}}}.$$

On this branch $z \to 0$ as $n \to 0$.

The constraint $b < b_{lim}$ results from (14) where

$$b_{\lim} = \frac{\lambda}{\lambda^0 n} \frac{\delta}{1,2 + 2\sqrt{0.757\delta}}. \tag{15}$$

With respect to the functions $\bar{\chi}_i$ determined by means of (14) from measurements of the heat-conduction coefficient, all assertions in [6] about the functions $\bar{\chi}_i$ obtained from measurements of the viscosity coefficient are valid. We add that they often are not in agreement with each other [5].

The mixed pseudoradial distribution functions $\bar{\chi}_{ij}$ can be obtained from $\bar{\chi}_i$ if the combination rule (7) and the virial expansion of the functions χ_i and χ_{ij} [5] are used. We write down an expression for the mixed pseudoradial distribution functions χ_{ij} of a binary mixture:

$$\bar{\chi}_{11} = 1 + x_1(\bar{\chi}_1 - 1) + \frac{1}{5}x_2(\bar{\chi}_1 - 1) + \frac{2}{5}x_2[(\bar{\chi}_1 - 1)^{1/3} + (\bar{\chi}_2 - 1)^{1/3}]^3 - \tag{16}$$

$$- \frac{3}{5}x_2(\bar{\chi}_1 - 1)^{1/3}[(\bar{\chi}_1 - 1)^{1/3} + (\bar{\chi}_2 - 1)^{1/3}]^2,$$

$$\bar{\chi}_{12} = x_1\bar{\chi}_1 + x_2\bar{\chi}_2 + \frac{3}{5}[x_1(\bar{\chi}_1 - 1) - x_2(\bar{\chi}_2 - 1)][(\bar{\chi}_2 - 1)^{1/3} - (\bar{\chi}_1 - 1)^{1/3}][(\bar{\chi}_2 - 1)^{1/3} + (\bar{\chi}_1 - 1)^{1/3}]^{-1}. \tag{17}$$

Here $\bar{\chi}_{22}$ is obtained from $\bar{\chi}_{11}$ by a change of subscript $1 \to 2$, $2 \to 1$.

Let us make a remark. The value of the functions $\bar{\chi}_i$ evaluated by means of (14) by using (8) for b_i can turn out to be a complex number for a certain density [5]. Then b_i is determined from the minimum on the curve of the dependence of the quantity $\lambda/(\lambda^0 n)$ on the density [8]:

$$b = b_{\min} = \left(\frac{\lambda}{\lambda^0 n}\right)_{\min} \frac{\delta}{1.2 + 2\sqrt{0.757\delta}}. \tag{18}$$

2. Approximate Formulas

Derivation of the approximate formula for the heat-conduction coefficient of a multicomponent dense mixture of monatomic gases is performed analogously to the derivation of the corresponding formula for the viscosity coefficient [6]. We write down just the final result

$$\lambda_{\text{mix}} = \sum_{i=1}^{\nu} \frac{(y_i/x_i)^2(\lambda_i^0/\bar{\chi}_{ii})}{1 + \sum_{\substack{j=1 \\ j \neq i}}^{\nu} (x_j/x_i) G_{ij}^{\lambda} (\bar{\chi}_{ii}/\bar{\chi}_{ii})} + k_{\text{mix}}, \tag{19}$$

where y_i and k_{mix} are given by (2) and (5)

$$G_{ij}^{\lambda} = \frac{1}{2A_{ij}^*} \frac{(m_i - m_j)\left[3m_jB_{ij}^* + \frac{5}{4}(6m_i - 5m_j)\right] + 8m_im_jA_{ij}^*}{(m_i + m_j)^2} \frac{\lambda_i^0}{\lambda_{ij}^0}. \tag{20}$$

TABLE 1. Heat-Conduction Coefficient of a Helium–Neon Mixture, MW/m·K

n, kmole/m³	x_1=0,182		x_1=0,416		x_1=0,586		x_1=0,788	
	comp.	[5]	comp.	[5]	comp.	[5]	comp.	[5]
0	60,60	60	79,40	79	96,76	94,5	122,2	121,5
1	60,98	61	79,74	79,3	97,18	95	122,8	122,0
2	61,41	61,5	80,10	80	97,65	95,5	123,4	122,8
3	61,90	62	80,53	80,5	98,13	96,0	124,4	123,5
4	62,42	62,7	80,99	80,99	98,69	96,6	125,1	124,3
5	62,97	63	81,52	81,3	99,34	97,0	126,0	125,3
6	63,52	64	82,08	82	100,0	98,0	126,9	126,2
7	64,13	64,5	82,64	82,5	100,6	98	127,9	127,0
8	64,78	65	83,24	83	101,3	98,5	128,9	127,9
9	65,45	65,5	80,89	83,7	102,2	99,5	130,1	128,8

TABLE 2. Heat-Conduction Coefficient of Air, MW/m·K

P, bar	n, kmole/m³	λ		P, bar	n, kmole/m³	λ	
		comp.	[7]			comp.	[7]
	0	26,02	26,31	236,7	9	41,76	41,62
24,73	1	27,18	27,58	269,2	10	44,19	43,99
49,29	2	28,54	28,93	304,8	11	46,73	46,55
73,90	3	30,00	30,11	343,1	12	49,41	49,30
98,84	4	31,64	31,96	385,5	13	52,25	52,28
124,2	5	33,41	33,69	432,3	14	55,23	55,48
150,4	6	35,31	35,44	484,7	15	58,39	58,94
177,6	7	37,35	37,35	543,7	16	61,80	62,72
206,3	8	39,50	39,41				

The ratio $\lambda_i^0/\lambda_{ij}^0$ can be written in the Mason–Saxon form

$$\frac{\lambda_i^0}{\lambda_{ij}^0} = \frac{1}{4}\left(\frac{2m_j}{m_i+m_j}\right)^{1/2}\left[1+\left(\frac{m_i}{m_j}\right)^{1/4}\left(\frac{\lambda_i^0}{\lambda_j^0}\right)^{1/2}\right]^2. \tag{21}$$

For a binary gas mixture (19) has the form

$$\lambda_{\text{mix}} = \frac{(y_1/x_1)^2\lambda_1^0/\bar{\chi}_{11}}{1+G_{12}^{\lambda}(x_2/x_1)(\bar{\chi}_{12}/\bar{\chi}_{11})} + \frac{(y_2/x_2)^2\lambda_2^0/\bar{\chi}_{22}}{1+G_{21}^{\lambda}(x_1/x_2)(\bar{\chi}_{21}/\bar{\chi}_{22})} + k_{\text{mix}}. \tag{22}$$

Let us examine two particular cases of (22).

1. The pseudoradial functions $\bar{\chi}_i$ of the components comprising the mixture are equal to each other (for instance, for a He–Ne mixture this assumption is valid to 1% accuracy at 300°K). Then the mixed pseudoradial distribution functions $\bar{\chi}_{ij}$ are in agreement, i.e.,

$$\bar{\chi}_1 = \bar{\chi}_2 = \bar{\chi}_{11} = \bar{\chi}_{22} = \bar{\chi}_{12} = \bar{\chi}. \tag{23}$$

Formula (22) simplifies to

$$\lambda_{\text{mix}} = \frac{1}{\bar{\chi}}\left[\frac{(y_1/x_1)^2\lambda_1^0}{1+G_{12}^{\lambda}(x_2/x_1)} + \frac{(y_2/x_2)^2\lambda_2^0}{1+G_{21}^{\lambda}(x_1/x_2)}\right] + k_{\text{mix}}. \tag{24}$$

2. One of the functions $\bar{\chi}_i$ equals 1 identically (as is valid, for instance, for oxygen, in a mixture with nitrogen at 300°K to around 2% accuracy).

In this case (16) and (17) reduce to the following

$$\bar{\chi}_{11} = 1 + x_1(\bar{\chi}_1 - 1), \tag{25}$$

TABLE 3. Quantities Used in Computing the Heat-Conduction Coefficient

Parameter	He	Ne	He-Ne mixture	N_2	O_2	Air
$\gamma_{ij} \cdot 10^3$, $m^3/kmole$	16,58	21,07	18,58	73,99	66,62	70,24
λ_{ij}^0, $\frac{MW}{m \cdot K}$	155,9	49,45	101,1	25,85	26,59	—
λ_{ij}^0(mon), $\frac{MW}{m \cdot K}$	155,9	49,45	101,1	19,84	20,19	20,03

$$\bar{\chi}_{12} = \bar{\chi}_{22} = 1 + \frac{2}{5}(\bar{\chi}_1 - 1). \tag{26}$$

To compute the heat-conduction coefficient of a mixture of polyatomic gases, it is split into parts specified by the translational (mon) and internal (int) degrees of freedom

$$\lambda = \lambda(\text{mon}) + \lambda(\text{int}). \tag{27}$$

Making the assumption that the energy of the internal degrees of freedom is transported just by diffusion, as well as the assumption about independence of the quantities A_{ij}^* and B_{ij}^* from the inelastic collisions, we represent λ(int) by using the Hirschfelder–Aiken formula [5]

$$\lambda(\text{int}) = \sum_{i=1}^{v} \left[\frac{\lambda_i^0 - \lambda_i^0(\text{mon})}{\bar{\chi}_{ii}} \right] \left[1 + \sum_{\substack{j=1 \\ j \neq i}}^{v} \frac{x_j}{x_i} \frac{D_{ii}}{D_{ij}} \right]^{-1}. \tag{28}$$

If known relationships of kinetic theory for the diffusion coefficients D_{ij} are used [5], we obtain the following relationship in place of (28)

$$\lambda(\text{int}) = \sum_{i=1}^{v} \left[\frac{\lambda_i^0 - \lambda_i^0(\text{mon})}{\bar{\chi}_{ii}} \right] \left[1 + \sum_{\substack{j=1 \\ j \neq i}}^{v} \frac{x_j}{x_i} \frac{\lambda_i^0(\text{mon})}{\lambda_{ij}^0(\text{mon})} \frac{\bar{\chi}_{ii}}{\bar{\chi}_{ii}} \right]^{-1}. \tag{29}$$

The part of the heat-conduction coefficient due to the translational degrees of freedom λ(mon) is calculated by using (19).

3. Results of a Computation

As examples of the utilization of the approximate formulas, we calculated the heat-conduction coefficients of the monatomic He–Ne gas mixtures, the mixture $0.78N_2 + 0.22O_2$, and the mixture $0.354He + 0.646N_2$ at a 300°K temperature.

Formula (24) was used in computing the heat-conduction coefficient of the He–Ne mixture. Values of λ_i^0 are borrowed from [9], and of γ_{ij} and $\bar{\chi}$ from [5].

A comparison of the results obtained by the approximate methodology (formula (24)), with a computation by the original method (formula (11)) performed in [5] is given in Table 1. The difference reaches 2% only for the 58.6% He composition.

Formulas (22) and (29) together with the relationships (25) and (26) were used in the computation of the heat conduction for the mixtures $0.78N_2 + 0.22O_2$ and $0.354He + 0.646N_2$. Values of λ_i and η_i^0 are borrowed from [7] and [9].

A comparison between the calculated results and the generalized data in [7] is given for air in Table 2. The deviation does not exceed 1.6%.

The computed values of the heat-conduction coefficient for the mixture $0.354He + 0.646N_2$ were compared with the experimental data in [10]. The deviation is within the limits of experimental data error (2%) at all pressures with the exception of 200 bar, where it is 6-8%.

However, it should be noted that the experimental values of the heat-conduction coefficient at this pressure and the temperature 299.46°K (see [10]) disturb the monotonic growth of the heat-conduction coefficient with temperature by forming a local minimum at the 200-bar isobar.

Values of γ_{ij} and λ°_{ij} used in the computations are presented in Table 3.

The results obtained show that the proposed methodology permits computation of the heat-conduction coefficient of gas mixtures of elevated density with high accuracy.

NOTATION

n, density; m, molecular mass; x_i, molar fraction of the i-th component; ν, number of mixture components; λ, heat-conduction coefficient; the superscript 0 denotes quantities for a rarefied gas, subscripts are used to number the mixture components; λ°_{ij}, heat-conduction coefficient of a rarefied gas with the molecular mass $2m_im_j(m_i + m_j)$.

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