APPROXIMATE METHOD OF CALCULATING THERMAL CONDUCTIVITY COEFFICIENTS OF DENSE GAS MIXTURES

V. Z. Svoiskii

UDC 536.23:533.27

A simple, theoretically-based, method is presented for calculating coefficients of thermal conductivity of multicomponent mixtures of gases of elevated density.

It was shown earlier in a series of papers [1-4] that the Enskog–Tarn theory [5] of binary mixtures of solid spheres and its generalization to multicomponent mixtures [6] furnish a basis for working out an approximate description of the compositional dependence of transfer coefficients of nonpolar gases. Important in this respect is a definition of an effective diameter of a solid sphere and the so-called pseudoradial distribution functions.

In the framework of the modified Enskog theory effective diameters may be calculated from values of the second virial coefficients and their thermal derivatives. The pseudoradial functions of the distribution of components are obtained from experimental data for transfer coefficients with the aid of the Enskog equations. Following this, the mixed pseudoradial distribution functions are calculated from the combined relations [1-4]. In this regard, difficulties may arise associated with the nonphysical behavior of the pseudoradial distribution functions for large densities. This may be explained by the fact that the Enskog theory does not account for the effects of correlated molecular motion [7]. The authors of [8] have proposed a method for determining the pseudoradial distribution functions by splicing together two branches of the solution at the minimum point of the ratios $\eta/(\eta^0\rho)$ or $\lambda/(\lambda^0\rho)$.

In the present paper we examine a version in which the pseudoradial distribution functions are replaced by known radial distribution functions [6] corresponding to the Mansoori, Carnahan, Starling, Leland (MCSL) equation of state for mixtures of solid spheres [9, 10]. Thus, there remains only the problem of determining the effective diameter of a solid sphere.

As usual, the thermal conductivity coefficient may be divided into two terms, taking into account translational energy transfer and internal degrees of freedom. The contribution of the translational degrees of freedom may be determined by a method proposed by the authors in [4]. The contribution of the internal degrees of freedom may be calculated with the aid of the Aiken–Hirschfelder formula.

We illustrate by calculating the thermal conductivity coefficient for mixtures of helium–neon, neon–argon–krypton, and nitrogen–oxygen (air) for a temperature of 300 K. Deviation of the results of our calculations from experimental data are within 2% for the helium–neon mixture [2], 4% for the neon–argon–krypton mixture [11]. For air the maximum deviation from the data [12] amounts to 10% up to pressures around 700 bar.

1. Method of Calculation. The approximate formula obtained by the author [4] for the thermal conductivity coefficient of dense multicomponent mixtures of monatomic gases has the form

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

where

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 2, pp. 296-301, February, 1990. Original article submitted August 22, 1988.

 0022-0841/90/5802-0232$12.50

$$y_i/x_i = 1 + \rho \sum_{j=1}^{v} \frac{2m_i m_j}{(m_i + m_j)^2} x_j \gamma_{ij} \bar{\chi}_{ij}, \tag{2}$$

$$k_{mix} = \frac{10}{9} \rho^2 \sum_{i,j=1}^{v} \frac{x_i x_j m_i m_j}{(m_i + m_j)^2} \lambda_{ij}^0 \gamma_{ij}^2 \bar{\chi}_{ij}. \tag{3}$$

The quantities γ_{ij}, appearing in formulas (2) and (3), are determined in terms of the diameter σ of the solid spheres σ [13]:

$$\gamma_{ii} = \gamma_i = \frac{6}{5} b_i = \frac{6}{5} b_{ii} = \frac{6}{5} \left(\frac{2}{3} \pi \sigma_i^3 \right),$$
$$\gamma_{ij} = \frac{6}{5} b_{ij} = \frac{6}{5} \left(\frac{2}{3} \pi \sigma_{ij}^3 \right), \tag{4}$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j), \tag{5}$$

$\bar{\chi}_{ij} = \bar{\chi}_{ji}$ are the pseudoradial distribution functions for molecules of kinds i and j in the presence of molecules of all the other components in the mixture.

Formula (1) was obtained assuming the nondiagonal elements of the matrix to be small in comparison with the diagonal elements (see [4]). It contains the whole class of approximate formulas depending on the parameters G_{ij}^{λ}. Selecting these in various ways, we can obtain different approximate formulas. Thus, if we specify G_{ij}^{λ} in the Maison–Saxson form

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

where

$$\frac{\lambda_i^0}{\lambda_{ij}^0} = \frac{1}{4} \left(\frac{2m_j}{m_i + m_j} \right)^{1/2} \left[1 + \left(\frac{m_i}{m_j} \right)^{1/4} \left(\frac{\lambda_i^0}{\lambda_j^0} \right)^{1/2} \right]^2, \tag{7}$$

we then have a generalization of the well-known Maison–Saxson formula to the case of dense gas mixtures. The quantities A_{ij}^* and B_{ij}^* represent dimensionless ratios of collision integrals, equal to one for solid spheres and close to one for other types of interaction.

To calculate the coefficient of thermal conductivity from formula (1), it is necessary to specify the molecular masses m_i, the effective diameters σ_i of the solid spheres, the thermal conductivity coefficients λ_i^0 of components with small density, as well as the mixed pseudoradial distribution functions $\bar{\chi}_{ij}$.

In [1-4] the functions $\bar{\chi}_{ij}$ are determined from the functions χ_i for the noble components. The latter in turn may be calculated from experimental data for coefficients of thermal conductivity (viscosity).

In the present paper, instead of the pseudoradial distribution functions $\bar{\chi}_{ij}$, we use the known radial distribution functions g_{ij} corresponding to the equation of state for mixtures of solid spheres [9, 10]:

$$Z_{MCSL} = \frac{1 + \zeta + \zeta^2 - \zeta^3}{(1 - \zeta)^3} - \frac{\zeta [3(t_1 + t_2\zeta) - (t_1 + t_2)\zeta^2]}{(1 - \zeta)^3}, \tag{8}$$

where

$$\zeta = \frac{1}{6} \pi \rho \Sigma_3, \quad \Sigma_s = \sum_{k=1}^{v} x_k \sigma_k^s; \tag{9}$$

$$t_1 = 1 - \frac{\Sigma_1 \cdot \Sigma_2}{\Sigma_3}; \quad t_2 = \frac{\Sigma_1 \cdot \Sigma_2}{\Sigma_3} - \frac{\Sigma_2^3}{\Sigma_3^2}; \quad t_3 = \frac{\Sigma_2^3}{\Sigma_3^2}. \tag{10}$$

The radial distribution functions g_{ij} in contact, corresponding to equation (8), may be written in the form [6]:

$$g_{ij}(\sigma_{ij}) = (1-\zeta)^{-1} + \frac{3}{(1-\zeta)^2}\left(\frac{\sigma_i\sigma_j}{\sigma_i+\sigma_j}\zeta\frac{\Sigma_2}{\Sigma_3}\right) + \\ + \frac{2}{(1-\zeta)^3}\left(\frac{\sigma_i\sigma_j}{\sigma_i+\sigma_j}\zeta\frac{\Sigma_2}{\Sigma_3}\right)^2. \quad (11)$$

In calculating the thermal conductivity coefficient of a mixture of monatomic gases, the contribution λ(mon) of the translational degrees of freedom may be determined from equation (1). The contribution λ(int) of the internal degrees of freedom may be calculated with the aid of the Aiken–Hirschfelder formula [2]:

$$\lambda(\text{int}) = \sum_{i=1}^{\nu}\left[\frac{\lambda_i^0 - \lambda_i^0(\text{mon})}{g_{ii}}\right]\left[1 + \sum_{\substack{j=1\\ j\neq i}}^{\nu}\frac{x_j}{x_i}\frac{\lambda_i^0(\text{mon})}{\lambda_{ij}^0(\text{mon})}\frac{g_{ij}}{g_{ii}}\right]^{-1}. \quad (12)$$

2. Computational Results and Discussion. According to the method presented in this paper, the solid sphere effective diameters may be calculated from experimental values of the thermal conductivity coefficients of the components at high density. From the condition for coincidence of minima of the quantity $\lambda/(\lambda^0\rho)$, also given experimentally by the Enskog formula

$$\frac{\lambda_i}{\lambda_i^0} = \frac{1}{\delta_i}\rho b_i\left(\delta_i\frac{1}{\rho b_i\chi_i} + 1.2 + 0.757\rho b_i\chi_i\right), \quad (13)$$

where

$$\delta_i = \lambda_i^0/\lambda_i^0(\text{mon}), \quad \lambda_i^0(\text{mon}) = \frac{15}{4}\frac{R}{M_i}\eta_i^0,$$

it follows that

$$b_i = \left(\frac{\lambda_i}{\lambda_i^0\rho}\right)_{\min}\frac{\delta_i}{1.2 + 2\sqrt{0.757\delta_i}}. \quad (14)$$

Here the quantity $\lambda_i/(\lambda_i^0\rho)$ may be considered as a function of the density at some temperature.

A choice for an effective diameter of a solid sphere, in accordance with formula (14), is, generally speaking, not uniquely possible. If the coefficients of viscosity of components of the mixture for small density are known, the effective solid sphere diameter can be selected so as to obtain an experimental value for the viscosity coefficient η_i^0 of a rarefied gas in accordance with the expression:

$$\eta_i^0 = \frac{5.08}{16\sigma_i^2}\left(\frac{m_i kT}{\pi}\right)^{1/2}. \quad (15)$$

In this case, as shown in [14], the Enskog theory yields satisfactory values (±1%) for the transfer coefficients of monatomic noble gases for the densities $b\rho < 0.4$ cited.

In [15] the Van der Waals approach was used to study transfer properties in dense gases. The temperature dependence of the effective solid sphere diameter obtained by the authors makes it possible to calculate transfer coefficients of inert gases from the Enskog theory with an error of less than 10% (for temperatures and densities larger than critical).

TABLE 1. Thermal Conductivity Coefficient of Helium–Neon Mixture, mW/(m·K)

ρ, kmole/m³	x_1=0,182			x_1=0,416			x_1=0,586			x_1=0,788		
	[4]	[2]	this paper	[4]	[2]	this paper	[4]	[2]	this paper	[4]	[2]	this paper
0	60,60	60,0	60,61	79,40	79,0	79,42	96,76	94,5	96,77	122,2	121,5	122,3
1	60,98	61,0	60,97	79,74	79,3	79,76	97,18	95,0	97,23	122,8	122,0	123,0
2	61,41	61,5	61,37	80,10	80,0	80,14	97,65	95,5	97,71	123,4	122,8	123,8
3	61,90	62,0	61,79	80,53	80,5	80,54	98,13	96,0	98,23	124,4	123,5	124,6
4	61,42	62,7	62,23	80,99	80,99	80,97	98,69	96,6	98,78	125,1	124,3	125,4
5	62,97	63,0	62,71	81,52	81,3	81,42	99,34	97,0	99,36	126,0	125,3	126,3
6	63,52	64,0	63,21	82,08	82,0	81,91	100,0	98,0	99,98	126,9	126,2	127,3
7	64,13	64,5	63,74	82,64	82,5	82,43	100,6	98,0	100,6	127,9	127,0	128,3
8	64,78	65,0	64,29	83,24	83,0	82,97	101,3	98,5	101,3	128,9	127,9	129,3
9	65,45	65,5	64,88	83,89	83,7	83,55	102,2	99,5	102,0	130,1	128,8	130,4

TABLE 2. Thermal Conductivity Coefficient of Neon–Argon–Krypton Mixture, mW/(m·K) (x_{Ne} = 0.4887; x_{Ar} = 0.2565; x_{Kr} = 0.2548)

P, MPa	ρ, kmole/m³	λ		P, MPa	ρ, kmole/m³	λ	
		expt. [11]	calc.			expt. [11]	calc.
—	0,0000	—	25,65	3,61	1,446	25,63	26,04
0,595	0,2399	24,84	25,70	4,15	1,665	25,78	26,11
1,08	0,4335	24,97	25,76	4,61	1,847	25,90	26,16
1,58	0,6341	25,10	25,81	5,15	2,059	25,98	26,23
2,10	0,8395	25,24	25,86	5,64	2,261	26,13	26,30
2,63	1,053	25,39	25,92	6,17	2,474	26,23	26,38
3,10	1,241	25,47	25,98	6,90	2,759	26,47	26,48

TABLE 3. Thermal Conductivity Coefficient of Air, mW/(m·K)

P, MPa	ρ, kmole/m³	λ		
		[4]	[12]	this paper
	0	26,02	26,31	25,99
2,473	1	27,18	27,58	26,51
4,929	2	28,54	28,93	27,18
7,390	3	30,00	30,11	28,01
9,884	4	31,64	31,96	29,01
12,42	5	33,41	33,69	30,21
15,04	6	35,31	35,44	31,61
17,76	7	37,35	37,35	33,25
20,63	8	39,50	39,41	35,16
23,67	9	41,76	41,62	37,36
P, MPa	ρ, kmole/m³	λ		
		[4]	[12]	this paper
26,92	10	44,19	43,93	39,88
30,48	11	46,73	46,55	42,76
34,31	12	49,41	49,30	46,04
38,55	13	52,25	52,28	49,76
43,23	14	55,23	55,48	53,99
48,47	15	58,39	58,94	58,78
54,37	16	61,80	62,72	64,20
60,98	17		66,78	70,33
68,46	18		71,15	77,25
77,05	19		75,99	85,08

If the second virial coefficient and its thermal derivative are known for all components of the mixture, the effective diameters can then be chosen according to the modified Enskog theory [14, 16]:

$$b_i = B_i + T\frac{dB_i}{dT}. \tag{16}$$

Choice of an effective diameter in accordance with expression (16) is the choice most preferred since it does not require knowledge of the transfer coefficients of components at high densities. In this connection, however, no upper limit with respect to density is known; meanwhile, in using relation (14), we can take as such an upper limit the density at the minimum point of the quantity $\lambda/(\lambda^0\rho)$ (or $\eta/(\eta^0\rho)$).

To illustrate applicability of the proposed method of calculation to real gas mixtures, we calculated thermal conductivity coefficients for mixtures of monatomic gases: helium–neon, neon–argon–krypton, and the mixture $0.78\,N_2 + 0.22O_2$ (air) at temperature 300 K. Choice of this last mixture as a substitute for air is justified by the small fraction of argon and carbon dioxide gas present in its makeup, and also by the approximate nature of the whole theory.

Tables 1 and 2 furnish a comparison of the results of our calculations with data of other authors for mixtures of monatomic gases; Table 3 gives a comparison with generalized data [12] for air. A comparison is also given of calculated values of the thermal conductivity of an Ar–CF_4 mixture with experimental data from [17]. The maximum deviation amounts to 11%.

As might be expected, the proposed method, based on the Enskog–Tarn theory for mixtures of solid spheres, yields more precise results in the case of mixtures of monatomic gases.

NOTATION

ρ, density; m, molecular mass; x_i, mole fraction of i-th component; ν, number of components of mixture; λ, thermal conductivity coefficient; λ^0_{ij}, thermal conductivity coefficient of rarefied gas with molecular mass $2m_im_j/(m_i + m_j)$. Superscript 0 indicates rarefied gas quantity; subscripts indicate numbering of mixture components.

LITERATURE CITED

1. R. Di Poppo, J. R. Dorfman, and J. Kestin, et al., Physica, 86A, 205-223 (1977).
2. E. A. Mason, H. E. Khalifa, and J. Kestin, et al., Physica, 91A, 377-392 (1978).
3. V. Z. Svoiskii, Uchen. Zap. TsAGI, 13, No. 4, 141-147 (1982).
4. V. Z. Svoiskii, Inzh.-Fiz. Zh., 48, No. 3, 418-424 (1985).
5. S. Chapman and G. Cowling, Mathematical Theory of Nonhomogeneous Gases [Russian translation], Moscow (1960).
6. M. K. Tham and K. E. Gubbins, J. Chem. Phys., 55, No. 1, 268-279 (1971).
7. B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys., 53, No. 10, 3813-3826 (1970).
8. S. I. Sandler and J. K. Fiszdon, Physica, 95A, 602-608 (1979).
9. G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, J. Chem. Phys., 54. No. 4, 1523-1525 (1971).
10. L. Ponce-Ramirez, J. Chem. Phys., 72, No. 10, 5789-5790 (1980).
11. A. A. Clifford, R. Fleeter, J. Kestin, and W. A. Wakeham, Physica, 98A, 467-490 (1979).
12. A. A. Vasserman, Ya. Z. Kazavchinskii, and V. A. Rabinovich, Thermophysical Properties of Air and Its Components [in Russian], Moscow (1966).
13. J. Hirschfelder, C. Curtiss, and R. Baird, Molecular Theory of Gases and Liquids, Wiley, New York (1964).
14. J. V. Sengers, Int. J. Heat Mass Trans., 8, 1103-1115 (1965).
15. J. H. Dymond and B. J. Alder, J. Chem. Phys., 45, No. 6, 2061-2068 (1966).
16. H. J. Hanley, R. D. McCarty, and E. G. D. Cohen, Physica, 60, 322-356 (1972).
17. N. Imaishi, J. Kestin, and R. Paul, Int. J. Thermophys., 6, No. 1, 3-20 (1985).

COMMENTS ON DESIGNING A DIAPHRAGMLESS REACTOR FOR THE PRODUCTION OF ELECTROLYTIC HYDROGEN

A. G. Shashkov, P. G. Khramtsov, I. I. Bortnikov, and N. P. Matveiko

UDC 621.357

Criterial relations generalizing the functional interrelationship between a number of dimensionless complexes of hydrodynamics and voltage in a reactor cell are obtained from the differential equations that describe the electrochemical process.

Hydrogen is becoming increasingly important with each year as an energy carrier and a raw material for many branches of industry. A potential demand for it in the near future may come from the microbiological industry, where hydrogen is used as a raw material for the production of feed protein, and in the future will perhaps be used to produce protein for human consumption [1, 2]. Although they are profitable, however, existing methods of producing hydrogen, particularly chemical methods, cannot satisfy the demand of this branch of industry for high-quality hydrogen. In this respect much attention should be focused on the

Institute of Applied Physics, Academy of Sciences of the Belorussian SSR, Minsk.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 2, pp. 301-307, February, 1990. Original article submitted December 28, 1988.

0022-0841/90/5802-0236$12.50