TRANSPORT PROPERTIES OF BINARY MIXTURES OF MONATOMIC GASES

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A method is proposed for calculating the viscosity coefficient and thermal con-
ductivity. It is shown that the expressions for the thermal conductivity of a
binary mixture of monatomic gases can be formally generalized to polyatomic
gases. The results are compared with experimental data.

As is known, the transport properties of polyatomic gases and their mixtures have re-
ceived less experimental and theoretical attention from investigators than have monatomic
gases. In particular, there has been little study of the effect of internal degrees of
freedom of the molecules on the transport coefficients [1-4].

It was shown in [5] that the differences between experimental and theoretical data
for thermal conductivity are due not to deficiencies in the theory of Masson and Monchik
but to shortcomings of the model potentials that are used. The thermal properties (second
virial coefficient, Joule–Thomson coefficient) [6-8] and transport properties (viscosity,
thermal conductivity) [5] of nonpolar polyatomic gases are satisfactorily described by means
of a pairwise mode potential (12-7, δ) which considers the nonspherical shape of polyatomic
molecules. Here, the average number of collisions necessary to establish equilibrium be-
tween the translational and rotational degrees of freedom of molecules is calculated in
accordance with the theory of O'Neal and Brokaw [9] and does not require any empirical con-
stants other than those associated with the (12-7, δ) potential.

Here, the method of calculating the viscosity coefficient and thermal conductivity
is generalized to the case of binary mixtures. The expressions for the viscosity coefficient
of a binary gas mixture are well-known [1]. It should be noted that when calculations are
performed for mixtures, it is customary to introduce the coefficient of viscosity

$$\mu_{ij} = \frac{5}{16} \frac{\sqrt{\pi m_{ij} kT}}{\pi \sigma_{ij}^2 \Omega^{(22)}(T_{ij}^*, \delta_{ij})} \tag{1}$$

of a hypothetical gas having the molecular weight

$$m_{ij} = \frac{2m_i m_j}{m_i + m_j} \tag{2}$$

and interacting in accordance with the same potential as the components i and j. Table
1 shows the constants of the (12-7, δ) potential for the interaction between identical and
dissimilar molecules. The constants for the former case were calculated with the use of
modifications of the Kong combinatorial relations [10, 11] obtained on the basis of a theor-
etical approach.

We calculated the viscosity coefficients of binary gas mixtures and compared them with
available experimental data [12-16]. As a rule the deviations were within the range of
values corresponding to the results of the different studies. This range was thus taken
as an objective measure of the measurement error. As an example, Table 2 compares calcu-
lated and theoretical values for several binary mixtures whose components differ sharply
in their constants. The mean error for 21 experimental points is 1.0%, while the maximum
error is 2.2%.

The study [5] presented theoretical expressions of the nonlinearized theory of Masson
and Monchik for polyatomic gases [17] and compared calculations for the (12-7, δ) potential
with experimental data on thermal conductivity.

TABLE 1. Constants of the (12-7, δ) Potential

System	$\frac{\varepsilon}{k}$, K	$\sigma \cdot 10^8$, cm	$r_e \cdot 10^8$, cm	δ
He—He	10,2	2,550	0	0
N_2—N_2	140	3,471	1,098	0,1000
CO_2—CO_2	443	3,532	1,982	0,3149
CH_4—CH_4	208	3,566	0,896	0,0631
CF_4—CF_4	277	4,215	2,006	0,2265
He—N_2	24,5	3,178	0,776	0,0596
He—CO_2	45,4	3,210	1,401	0,1905
He—CH_4	25,6	3,289	0,634	0,0372
He—CF_4	23,8	3,730	1,418	0,1445

TABLE 2. Comparison of Theoretical Values of the Viscosity Coefficient of Binary Gas Mixtures and Experimental Data [12-14]; $\mu \cdot 10^8$, Pa·sec; T = 298.15 K

x_1	He—N_2		He—CO_2		He—CH_4		He—CF_4		
	[12]	theor.	[13]	theor.	[13]	theor.	x_1	[14]	theor.
0	1783	1768	1498	1477	1113	1100	0	1736	1700
0,2	1832	1820	1589	1567	1208	1198	0,3748	1879	1840
0,4	1886	1877	1701	1678	1330	1322	0,5209	1958	1916
0,6	1944	1938	1837	1812	1488	1481	0,9134	2123	2100
0,8	1992	1988	1980	1956	1701	1693	1,0	1986	1981
1,0	1986	1981	2000	1981	2000	1981			

Note. x_1 is the volume concentration of the first component (helium).

As is known [17], the thermal conductivity of a binary mixture of polyatomic gases decomposes into three terms describing translational and internal degrees of freedom, as well as into cross terms. Here, the contribution of the translational degrees of freedom is calculated from the formulas for a binary mixture of monatomic gases. The contribution of the internal degrees of freedom is calculated from the empirical Hirschfelder expression [1]:

$$\lambda_{mx}^{inter} = \frac{\lambda_{11} - \lambda_{11}^0}{1 + \frac{x_2}{x_1} \frac{D_{11}}{D_{12}}} + \frac{\lambda_{22} - \lambda_{22}^0}{1 + \frac{x_1}{x_2} \frac{D_{22}}{D_{12}}} . \tag{3}$$

Here, D_{ij} are the diffusion coefficients, while

$$\lambda_{ij}^0 = \frac{75}{64} \frac{k \sqrt{\frac{\pi k T}{m_{ij}}}}{\pi \sigma_{ij}^2 \Omega^{(22)} (T_{ij}^*, \delta_{ij})} \tag{4}$$

is the thermal conductivity of a monatomic gas.

The third terms are extremely cumbersome and of low magnitude. They are usually ignored (Hirschfelder—Eiken approximation). Using this method and allowing for the cross terms, we performed calculations for several binary systems. For mixtures having components that differed greatly in their constants, the deviations from the experimental data in [18-23] were significantly greater than the measurement errors. The situation was almost the same when the contribution of the translational degrees of freedom was calculated from the formulas for a binary mixture of monatomic gases but the effect of inelastic collisions was considered in the computation of λ_{ij}. The completed studies showed that the method of calculation can be simplified and the agreement with the experimental data improved if the expression for the thermal conductivities of a binary mixture of monatomic gases are formally generalized to polyatomic gases.

To do this it is necessary to introduce the thermal conductivity λ_{ij} in a form analogous to the viscosity coefficient μ_{ij}:

$$\lambda_{ij} = \lambda_{ij}^{tran} + \lambda_{ij}^{inter}, \tag{5}$$

$$\lambda_{ij}^{tran} = \lambda_{ij}^0 \left(1 - \frac{2}{3} \Delta_{ij} \frac{c_{ij}^{inter}}{R} \right), \tag{6}$$

TABLE 3. Comparison of Theoretical Values of the Thermal Conductivity of Binary Gas Mixtures and Experimental Data [18-21]; $\lambda \cdot 10^2$, W/(m·K); T = 300.65 K

He–N₂			He–CO₂			He–CH₄			He–CF₄		
x_1	[18]	theor.	x_1	[19]	theor.	x_1	[20]	theor.	x_1	[21]	theor.
0	2,603	2,613	0	1,685	1,708	0	3,493	3,440	0	1,603	1,593
0,2202	3,832	3,825	0,2936	3,243	3,352	0,2013	4,538	4,605	0,2785	2,823	2,714
0,5432	6,456	6,607	0,4615	4,624	4,737	0,4459	6,291	6,539	0,4812	4,200	4,104
0,8370	11,17	11,18	0,6956	7,519	7,661	0,7538	10,04	10,34	0,8047	8,662	8,699
1,0	15,59	15,51	1,0	15,59	15,51	1,0	15,59	15,51	1,0	15,59	15,51

$$\lambda_{ij}^{\text{inter}} = \frac{\frac{12}{5} R A_{ij}^*}{m_i + m_j} \, \mu_{ij} (1 + \Delta_{ij}) \, \frac{c_{ij}^{\text{inter}}}{R}, \qquad (7)$$

where

$$\Delta_{ij} = \frac{5}{\pi} (1 - 0{,}48 A_{ij}^*) \frac{R u_{ij}}{Z_{ij}^{\text{rot}} A_{ij}^{\text{mm}} c_{ij}^{\text{inter}}}; \qquad (8)$$

$$A_{ij}^{\text{mm}} = 1 + \frac{2 R y_{ij}}{\pi Z_{ij}^{\text{rot}} c_{ij}^{\text{inter}}} \left(\frac{5}{3} \frac{c_{ij}^{\text{inter}}}{R} + \frac{6}{5} A_{ij}^* \right); \qquad (9)$$

$$(Z_{ij}^{\text{rot}})^{-1} = \frac{5\pi}{12} \frac{\delta_{ij}}{(1 + \delta_{ij})^2 \, \Omega^{(2.2)} (T_{ij}^*, \delta_{ij})} \exp\left(\frac{\varepsilon_{ij}}{kT} \right); \qquad (10)$$

$$y_{ij} = \frac{c_{ij}^{\text{rot}}}{R} = \frac{1}{2} (y_i + y_i), \quad c_{ij}^{\text{inter}} = \frac{1}{2} (c_i^{\text{inter}} + c_j^{\text{inter}}). \qquad (11)$$

Here, Δ_{ij} is the Masson–Monchik correction for inelastic collisions; A_{ij}^{mm} is the multiplier in the nonlinearized Masson–Monchik theory; Z_{ij}^{rot} is the mean number of collisions necessary to establish equilibrium between the rotational and translational degrees of freedom. Also, we can approximately take $A_{ij}^* = 1.100$ and $B_{ij}^* = 1.250$. These two quantities depend slightly on the corrected temperature T_{ij}^* and the nonsphericity parameter δ_{ij}.

The calculation is simplified in this case, while the deviations from the experimental data [18-23] do not exceed ±4.0%. As an example, Table 3 compares theoretical and experimental values of the thermal conductivity of several mixtures containing helium. The mean deviation for 21 experimental points is 1.4%, while the maximum deviation is 4.0%. It should be considered that the thermal conductivities of these mixtures are much more heavily dependent on the concentrations of the components than is viscosity. Thus, the additional errors associated with the establishment of thermodynamic equilibrium in the mixture and the determination of its composition are greater when thermal conductivity is being measured.

LITERATURE CITED

1. J. Hirschfelder, J. Curtiss, and R. Baird, Molecular Theory of Gases and Liquids [Russian translation], Moscow (1961).
2. G. C. Maitland, M. Mustafa, and W. Wakeham, J. Chem. Soc. Faraday Trans, 1, 163-172 (1983).
3. N. Imashi, J. Kestin, and W. Wakeham, Physica, 123A, No. 1, 50-71 (1983).
4. M. Assael, M. Mustafa, and W. Wakeham, High Temp. High Pressures, 17, No. 3, 291-302 (1985).
5. R. M. Sevast'yanov and K. I. Voroshilova, Inzh. Fiz. Zh., 53, No. 6, 983-986 (1987).
6. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh. Fiz. Zh., 51, No. 1, 122-124 (1986).
7. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh. Fiz. Zh., 52, No. 6, 974-977 (1987).
8. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh. Fiz. Zh., 53, No. 4, 589-593 (1987).
9. C. O'Neal and R. S. Brokaw, Phys. Fluids, 6, No. 12, 1675-1682 (1963).
10. C. L. Kong, J. Chem. Phys., 59, No. 5, 2464-2467 (1973).
11. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh. Fiz. Zh., 48, No. 2, 263-266 (1985).
12. J. Kestin, S. T. Ro, and W. Wakeham, J. Chem. Phys., 56, No. 8 (1972).

13. J. Kestin and S. T. Ro, Ber. Bunsenges Phys. Chem., 80, No. 7, 619-625 (1976).

14. J. Kestin, H. E. Khalifa, S. T. Ro, and W. Wakeham, Physica, 88A, No. 2, 242-260 (1977).

15. Y. Abe, J. Kestin, H. E. Khalifa, and W. Wakeham, Physica, 93A, No. 2, 155-170 (1978).

16. I. F. Golubev and N. E. Gnezdilov, Viscosity of Gas Mixtures [in Russian], Moscow (1971).

17. L. Monchik, A. N. Pereira, and E. A. Masson, J. Chem. Phys., 42, 3241-3247 (1965).

18. R. D. Fleeter, J. Kestin, R. Paul, and W. Wakeham, Physica, 108A, No. 2-3, 371-401 (1981).

19. J. Kestin, Y. Nagasaka, and W. Wakeham, Physica, 113A, No. 1, 1-26 (1982).

20. R. Fleeter, J. Kestin, R. Paul, and W. Wakeham, Ber. Bunsenges Phys. Chem., 85, No. 3, 215-220 (1981).

21. N. Imaishi, J. Kestin, and R. Paul, Int. J. Thermophys., 6, No. 1, 3-20 (1985).

22. J. Kestin, Y. Nagasaka, and W. Wakeham, Ber. Bunsenges Phys. Chem., 86, No. 7, 632-636 (1982).

23. J. Kestin, S. T. Ro, and Y. Nagasaka, Ber. Bunsenges Phys. Chem., 86, No. 10, 945-948 (1982).