8. R. A. Mustafaev, "Equipment for complex thermophysical studies of the thermal conductivity of liquids at high pressures in the monotonic heating regime," Izv. Vyssh. Uchebn. Zaved., Neft Gaz, No. 8, 69–74 (1975).
9. A. Meissner, Thermal Conductivity of Solids, Liquids, and Gases and Their Compositions [Russian translation], Mir, Moscow (1968).

THERMAL DIFFUSION IN BINARY GAS MIXTURES

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The temperature dependence and the pressure dependence of the thermal diffusion coefficient as well as its dependence on the concentrations of interdiffusing components is evaluated with the aid of the (12—7, δ) model potential. The results of calculations are found to agree with experimental data within the accuracy of measurements.

Study of thermal diffusion is known to be an important way to study intermolecular interactions [1, 2]. That possibility is seriously limited, however, because of a lack of reliable experimental data. Systematic measurements of thermal diffusion in binary gas mixtures were begun only during the past five years [3-11]. The mean difference between generalized data in one such study [4] and the results of another study [5] pertaining to equimolar mixtures of monoatomic gases at 300°K temperature is ±4%, the maximum difference being ±10%. These figures must evidently be accepted as objective estimates of the error of experimental data. It therefore is not worthwhile to use for calculations the extremely unwieldy expression [12] for higher-order approximations in the Chapman—Cowling method.

In this study the thermal diffusion coefficient for binary mixtures of nonpolar gases will be calculated in the first Chapman—Cowling approximation [1, 2]. Only the results for mixtures containing helium are reported here. Those mixtures were also studied experimentally in the most systematic and thorough manner. Calculations were made using the paired model potential (12—7, δ) [13] and the Kong combining rules [14]. It has been demonstrated in earlier studies [13, 15-17] that the (12—7, δ) potential consistently describes experimental data on the second virial coefficient, the viscosity, and the thermal conductivity of nonpolar gases as well as of their mixtures at low density levels.

Since the thermal diffusion coefficient is an intricate function of concentrations, temperatures, pressures, and molecular masses of the components, the dependence on each of these influencing factors was evaluated separately.

Theoretical values and experimental values [5-7] of the thermal diffusion coefficient for molar mixtures with helium concentrations of 0.2-0.8 are compared in Table 1. The agreement is close, the mean difference being 4.7% and the maximum difference being 10.6%.

TABLE 1. Concentration Dependence of Thermal Diffusion Coefficient. Comparison of Calculations with Experimental Data [5, 6, 7] (T = 300°K, P = 0.03 MPa, x_1 — molar concentration of helium)

x_1	He—Ne		He—Ar		He—Kr		He—Xe		He—N$_2$		He—CH$_4$	
	[5]	calc.	[5]	calc.	[5]	calc.	[5]	calc.	[6]	calc.	[7]	calc.
0,20	0,277	0,290	0,316	0,320	0,344	0,332	0,355	0,340	0,293	0,262	0,246	0,250
0,50	0,316	0,336	0,396	0,411	0,442	0,440	0,471	0,462	0,370	0,363	0,311	0,317
0,80	0,367	0,405	0,531	0,577	0,620	0,650	0,699	0,723	0,503	0,554	0,423	0,440

TABLE 2. Temperature Dependence of Thermal Diffusion Coefficient. Comparison of Calculations with Generalized Experimental Data [4] (P = 0.03 MPa, $x_1 = x_2 = 0.5$)

T, K	200	300	400	500	600	700	800	Mean difference, %	Maximum difference, %
He—Ne	0,341	0,343	0,332	0,318	0,305	0,294	0,283	8,0	19,1
	0,332	0,336	0,337	0,337	0,337	0,337	0,337		
He—Ar	0,379	0,398	0,400	0,398	0,395	0,390	0,386	5,1	7,5
	0,399	0,411	0,414	0,415	0,415	0,415	0,415		
He—Kr	0,417	0,428	0,430	0,430	0,428	0,427	0,425	3,4	4,5
	0,428	0,440	0,443	0,444	0,444	0,444	0,444		
He—Xe	0,427	0,425	0,430	0,436	0,441	0,447	0,451	5,9	8,7
	0,453	0,462	0,464	0,464	0,464	0,464	0,464		

Note: Experimental values [4] in upper case, theoretical values in lower case.

The temperature dependence of the thermal diffusion coefficient for mixtures with equimolar concentrations of components is indicated by the data in Table 2. The differences between theoretical and generalized experimental data [4] does not, as a rule, exceed ±10%. The noticeably lower experimental values of the thermal diffusion coefficient for the helium—neon mixture at temperatures above 400°K cannot be explained theoretically, they are evidently attributable to a hidden measurement error.

The concentration dependence and the pressure dependence of the thermal diffusion coefficient for He—Ar, He—CO$_2$, and He—SF$_6$ mixtures are indicated by the data in Table 3. These data include, besides the thermal diffusion coefficient α_T^0 at low pressures (densities), also the first correction $\tilde{B}_T$ for pressure.

The total thermal diffusion coefficient at moderate pressures is [8]

$$\alpha_T = \alpha_T^0 (1 + \tilde{B}_T p), \tag{1}$$

where

$$\tilde{B}_T = 4x_1 x_2 E + \frac{1}{\alpha_T^0} (x_2 \Delta \tilde{\Phi}_2 - x_1 \Delta \tilde{\Phi}_1), \tag{2}$$

with x_1 and x_2 denoting the molar concentrations of components, and

$$E = B_{12} - \frac{1}{2} (B_{11} + B_{22}); \tag{3}$$

$$\Delta \tilde{\Phi}_1 = \frac{\Phi_{11} - \Phi_{12}}{RT}; \quad \Delta \tilde{\Phi}_2 = \frac{\Phi_{22} - \Phi_{12}}{RT}; \tag{4}$$

$$\Phi_{ij} = \left(T \frac{dB_{ij}}{dT} - B_{ij} \right), \quad ij = 11, 12, 22, \tag{5}$$

TABLE 3. Concentration Dependence and Pressure Dependence of Thermal Diffusion Coefficient. Comparison of Calculations with Experimental Data [8] (T = 300°K, x_1 — molar concentration of helium)

x_1	He—Ar				He—CO$_2$				He—SF$_6$			
	α_T^0		$\tilde{B}_T$, MPa^{-1}		α_T^0		$\tilde{B}_T$, MPa^{-1}		α_T^0		$\tilde{B}_T$, MPa^{-1}	
	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
0,15	0,304	0,309	0,147	0,109	0,303	0,306	0,531	0,478	0,329	0,333	1,25	1,01
0,20	0,315	0,320	0,126	0,100	0,315	0,319	0,483	0,436	0,355	0,350	0,966	0,907
0,50	0,396	0,411	0,053	0,053	0,407	0,425	0,290	0,223	0,496	0,504	0,483	0,440
0,80	0,531	0,577	0,021	0,016	0,597	0,639	0,063	0,069	0,826	0,904	0,130	0,123

where B_{ij} is the second virial coefficient, E is the "excess" second virial coefficient, and Φ_{ij} is the Joule—Thompson coefficient.

The values of the first correction for pressure calculated on the basis of the (12—7, δ) potential agree with the experimental data [8] within the accuracy of measurements.

The results indicate that the thermal diffusion coefficient depends much more strongly on the pressure (density) than do other transfer properties. For mixtures containing heavy monoatomic gases at a 300°K temperature this dependence is already strong at the P = 0.1 atm level.

It is noteworthy that for none of the mixtures in this study did the calculated thermal diffusion coefficient pass through an extremum as the concentrations of components were varied at temperatures ranging from 200 to 800°K. At very low temperatures, however, the calculated thermal coefficient had a minimum whose magnitude and location for an argon—krypton mixture agreed closely with experimental data [3].

LITERATURE CITED

1. J. O. Hirschfelder et al., Molecular Theory of Gases and Liquids, Wiley (1964).
2. J. H. Ferziger and H. G. Kaper, Mathematical Theory of Transport Processes in Gases, Elsevier (1972).
3. V. L. Zhdanov and O. A. Kolenchits, "Evaluation of thermal diffusion constant for argon—krypton mixture at low temperatures," Inzh.-Fiz. Zh., 37, No. 1, 83-90 (1979).
4. W. L. Taylor, "Thermal diffusion factors for binary noble gas mixtures," J. Chem. Phys., 72, No. 9, 4973-4981 (1980).
5. R. D. Trengove, H. L. Robjohns, T. N. Bell, et al., "Thermal diffusion factors at 300°K for seven binary noble gas systems containing helium or neon," Physics, 108A, Nos. 2-3, 488-501 (1981).
6. R. D. Trengove and P. J. Dunlop, "Diffusion coefficients and thermal diffusion factors for five binary systems of nitrogen and noble gases," Physica, 115A, 339-359 (1982).
7. R. D. Trengove, H. L. Robjohns, and P. J. Dunlop, "Diffusion coefficients and thermal diffusion factors for five binary systems of methane with noble gases," Ber. Bunsenges., Phys. Chem., 86, No. 10, 951-955 (1982).
8. R. D. Trengove, H. L. Robjohns, M. L. Martin, and P. J. Dunlop, "Pressure dependence of thermal diffusion factors for He—Ar, He—CO$_2$, and He—SF$_6$ systems at 300°K," Physica, 108A, Nos. 2-3, 502-510 (1981).
9. R. D. Trengove and P. J. Dunlop, "Temperature dependence of thermal diffusion factors for binary systems of nitrogen with five noble gases and of helium with argon," Ber. Bunsenges., Phys. Chem., 87, No. 10, 874-877 (1983).
10. R. D. Trengove, H. L. Robjohns, and P. J. Dunlop, "Diffusion coefficients and thermal diffusion factors for H$_2$—N$_2$, D$_2$—N$_2$ and H$_2$—O$_2$, D$_2$—O$_2$ systems," Ber. Bunsenges., 87, No. 12, 1187-1190 (1983).
11. A. G. Shashkov, T. N. Abramenko, A. F. Zolotukhina, and V. L. Zhdanov, "Experimental study of thermodiffusional separation in gas mixtures," Teplofiz. Svoistva Veshch. Mater., No. 17, 139-142 (1982).
12. E. A. Mason, "Third Chapman—Cowling approximation for thermal diffusion factors," J. Chem. Phys., 27, No. 1, 75-82 (1957).
13. R. M. Sevast'yanov and I. K. Zykov, "Interaction potential of nonpolar polyatomic molecules," Inzh.-Fiz. Zh., 38, No. 4, 639-643 (1980).
14. C. L. Kong, "Combining rules for intermolecular-potential parameters," J. Chem. Phys., 59, No. 5, 2464-2467 (1973).
15. R. M. Sevast'yanov and N. A. Zykov, "Potential energy of interaction between unlike nonpolar molecules," Inzh.-Fiz. Zh., 40, No. 1, 120-125 (1981).
16. R. M. Sevast'yanov and N. A. Zykov, "Transfer coefficients for binary mixtures of monoatomic gases," Trudy Tsentr. Aerogidrodin. Inst., No. 1873 (1977).
17. N. A. Zykov, R. M. Sevast'yanov, and K. I. Voroshilova, "Transfer properties of nitrogen, oxygen, carbon dioxide, and air at low densities at temperatures from 50 to 3000°K," Inzh.-Fiz. Zh., 43, No. 1, 77-81 (1982).