

EXPERIMENTAL STUDY CONCERNING THE
COEFFICIENT OF THERMAL DIFFUSION AS A
FUNCTION OF THE CONCENTRATION AND THE
TEMPERATURE IN N_2 -Ar, N_2 -CO₂, AND
Ar-CO₂ SYSTEMS

A. G. Shashkov, A. F. Zolotukhina,
and T. N. Abramenko

UDC 533.735

The coefficients of thermal diffusion in N_2 -Ar, N_2 -CO₂, and Ar-CO₂ systems was measured with a bicameral apparatus. The test results are shown and compared with theoretical ones which take into account elastic and inelastic collisions.

Many theoretical and experimental studies have been made recently concerning the phenomenon of thermal diffusion.

The theoretical methods of analysis (elementary kinetic theory of gases and rigorous molecular theory of gases) are based, in the first case, on the representation of a molecule as an elastic sphere and on the concept of a mean-free path.

Thermal diffusion depends largely on the kind of collisions between molecules and, therefore, a description of such a collision on the basis of the elementary kinetic theory cannot be regarded adequate. Calculations of the coefficient of thermal diffusion α_T according to this theory [1-4] have yielded only a qualitative agreement with test data.

The methods based on the rigorous molecular-kinetic theory involve a systematically simplified description of natural processes and phenomena. An exact calculation of the coefficient of thermal diffusion is rather easy only in the case of isotopic mixtures, inasmuch as the collision integrals for identical and nonidentical molecules respectively differ by a factor which depends only on the molecular mass [5]. For nonisotopic mixtures these relations become much more intricate. In order to calculate the coefficient of thermal diffusion for such mixtures, therefore, one uses various approximations (1st, 2nd, 3rd, 4th, etc.) to the exact solution.

The coefficient of thermal diffusion α_T has been calculated in [6] for 27 different gas mixtures, as a function of the concentration and the temperature. These calculations have shown that the values based on the first and on the second approximation do not differ by more than 6%.

Those authors' calculations are also compared in [6] with test data and with values of α_T calculated for the exponential (exp-6). It is shown there that neither using the potential (exp-6) nor higher-order approximations for α_T will improve the numerical agreement between experimental and theoretical data. For all the mixtures considered there, the theoretical results describe only qualitatively the concentration characteristic and the temperature characteristic of α_T .

Of particular interest would be a study concerning the coefficient of thermal diffusion in the case of mixtures for which the molecular-kinetic theory does not yield even a qualitative agreement with test data. This applies to the concentration characteristic of α_T , for instance, which for several mixtures of polyatomic gases has a maximum or a minimum. Various views have been expressed on this subject in the technical literature. The authors of [7, 8] consider the data which yield a concentration characteristic

Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 24, No. 6, pp. 1045-1050, June, 1973. Original article submitted January 16, 1973.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

with an extremum (anomalous behavior) to be incorrect or to contain undetectable errors. The generally prevailing opinion of all authors is, however, that inelastic collisions have a decisive effect on the coefficient of the thermal diffusion.

The theory by Monchik et al. [9, 10], which accounts for the effect of inelastic collisions on the thermal diffusion of polyatomic gases, also does not render a complete answer to the problem. Calculations based on the occurrence of inelastic collisions do, at best, yield a remote agreement with test data.

It is to be noted that most systems with a maximum or a minimum coefficient of thermal diffusion, along its concentration characteristic, were studied by one author only. This has aroused all kinds of doubts as to the correctness of the results. The purpose of our study here, therefore, was to determine experimentally the concentration characteristic of α_T for N_2 -Ar, N_2 -CO₂, and Ar-CO₂ mixtures, which seemed to us to deserve special attention on this account.

Data pertaining to the temperature characteristics of α_T will also be shown here, for a narrow temperature range only. The measurements were performed in a bicameral apparatus which had been described in [11]. The method of analyzing a mixture was based on thermal conductivity measurements with high-sensitivity type STZ-18 thermistor elements.

The test results were then evaluated according to the method of least squares, on the basis of the polynomial approximation

$$\varphi(x) = A_0 + A_1x + A_2x^2 + A_3x^3 + A_4x^4.$$

The accuracy of the test data was estimated as 4% for the N_2 -Ar system, 5.5% for the N_2 -CO₂ system, and 6.4% for the Ar-CO₂ system.

N_2 -Ar System. The temperature characteristic of α_T for this system has been studied in [6, 12-18] with $x_1 \approx x_2$ and, as shown in Fig. 1a, our data as well as those by various authors agreed closely within test accuracy.

The theoretical curve based on the Lennard-Jones potential (12-6) is in qualitative agreement with the test curves.

Ibbs, Grew, et al. [5] have analyzed the temperature characteristics of α_T for the N_2 -Ar system with three compositions: $x_1 = 0.46, 0.625, \text{ and } 0.70$ over the 150-270°K temperature range. The dispersion of test points was so large, however, that the actual trends of the $\alpha_T(x_1)$ relation could not be established at any temperature.

We measured the concentration characteristic of α_T at $T = 326^\circ\text{K}$ (Fig. 1b). The test data here reveal a minimum at an $x_1 \approx 0.4$ concentration.

It is to be noted that the N_2 -Ar system belongs to the class of mixtures where the effective collision diameter of the lighter component is larger than that of the heavier component (see Table 1), like H_2 -He or CH_4 -Ar also with a minimum on the concentration characteristic of α_T .

In order to give this minimum on the concentration characteristic of α_T for N_2 -Ar a physical interpretation, let us consider an elementary scheme for the thermal diffusion mechanism.

During the process of thermodiffusive separation, each component of the mixture moves from one temperature zone to another at a definite velocity which depends on both the mass and the size of its molecules. In principle, if the molecular masses of both components were equal but their molecular diameters were not, then the velocity of the component with the smaller molecules would be higher. With the heavier molecules having a smaller collision diameter, however, at certain concentrations the diffusion rate of the component with lighter molecules may be compensated by the larger quantity of heavier molecules with a smaller diameter, inasmuch as the "mass effect" and the "size effect" oppose each other so that the separation becomes slower and a minimum α_T along the concentration characteristic thus results. No such minimum is indicated according to the Chapman-Enskog theory. The theoretical curve calculated on the basis of the Kihar formula [19] with the Lennard-Jones potential (12-6) is a straight line slightly rising toward higher concentrations of the lighter component.

N_2 -CO₂ System. The concentration characteristic of α_T for this system has been studied most thoroughly in [20, 21], where the test curve was found to have a maximum.

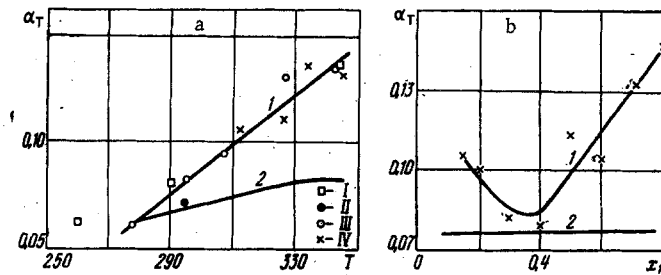


Fig. 1. Coefficient of thermal diffusion α_T for an N_2 -Ar mixture, as a function of a) the temperature (at $x_1 = 0.5$) and b) the concentration (at $T = 326^\circ K$). Test data: I) according to [12]; II) according to [17]; III) according to [15]; IV) according to these authors; 1) calculated by the method of least squares; 2) theoretical curves based on the Lennard-Jones potential (12-6).

TABLE 1. Effective Collision Diameters of Gas Molecules, according to the Lennard-Jones (12-6) [2] and the Morse [19] Potential Models

Gas	$\sigma, \text{\AA}$	
	Lennard-Jones potential (12-6)	Morse potential
He	2,576	2,687
H ₂	2,968	2,622
	2,915	2,898
Ar	3,418	3,461
	3,465	
N ₂	3,681	3,697
	3,749	
CH ₄	3,822	3,796
	3,796	

The theoretical values of α_T calculated according to the Kihar formula with the Lennard-Jones potential (12-6) do not agree, however, even qualitatively with the test data. Taking quadrupole moments into account does not narrow down the discrepancy. Curve B (Fig. 2a) lies only slightly below curve A and parallel to it, the latter having been calculated without quadrupole moments.

Furthermore, there is no maximum also within the ranges of extreme concentration levels, according to the data in [22].

For this reason, we considered a supplementary study of this system worthwhile. We measured the concentration characteristic of α_T at $T = 326^\circ K$, a temperature $2^\circ K$ higher than in the study made by the authors of [21]. According to Fig. 2a, the widest discrepancy between our values and those in [21] occurs at concentrations $x_1 = 0.2$ and 0.8 . Our data indicate a slight maximum at the concentration $x_1 = 0.5$.

The temperature characteristic of α_T for the N_2 -CO₂ system is shown in Fig. 2b. The difference between our test data and those in [21, 22] does not exceed 10%. The theoretical curve calculated on the basis of the Lennard-Jones potential (12-6) does qualitatively describe the trend of α_T as a function of the temperature.

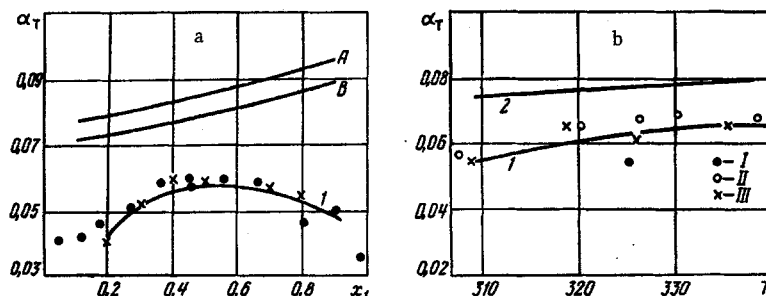


Fig. 2. Coefficient of thermal diffusion α_T for an N_2 -CO₂ mixture, as a function of a) the concentration (at $T = 326^\circ K$) and b) the temperature (at $x_1 = 0.5$). Test data: I) according to [21] at $T = 324^\circ K$; II) interpolated from [22]; III) according to these authors; 1) calculated by the method of least squares; 2, A) theoretical curves based on the Lennard-Jones potential (12-6); B) theoretical curve based on the Lennard-Jones potential (12-6) with quadrupole moments taken into account.

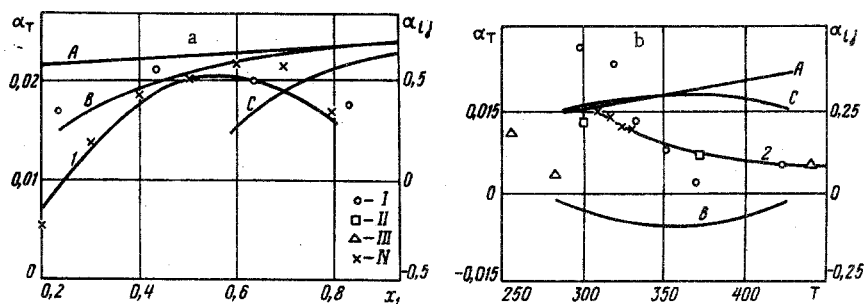


Fig. 3. Coefficient of thermal diffusion α_T for an Ar-CO₂ mixture, as a function of a) the concentration (at $T = 324^\circ\text{K}$) and b) the temperature (at $x_1 = 0.5$). Test data: I) according to [23]; II) according to [17]; III) according to [24]; IV) according to these authors; 1) curve calculated by the method of least squares; 2) averaging curve to fit the test points; A) theoretical curve based on the Lennard-Jones potential (12-6) with elastic collisions taken into account; B) theoretical curve with inelastic collisions taken into account and with $\tilde{Q}_{ij}^{00,10} \neq 0$; C) theoretical curve with inelastic collisions taken into account and with $\tilde{Q}_{ij}^{00,01} = 0$.

Ar-CO₂ System. The "anomaly" of the other systems was noted, essentially, in the concentration characteristics of α_T . The dependence of α_T on the temperature can be explained theoretically. We note that this trend is typical of most systems. From this standpoint, the Ar-CO₂ system seems unique. Namely, its coefficient of thermal diffusion decreases with increasing temperature [16, 23, 24].

We measured the temperature characteristic of α_T for an equimolar mixture at four temperatures: 308.5, 316.4, 324.2, and 328.5°K. Our data also confirm the general trend of α_T becoming smaller at higher temperatures (Fig. 3b). However, our values differ appreciably from those obtained by other authors.

The concentration characteristic of α_T is shown in Fig. 3a. We also have interpolated the data in [23], for comparison, and have found a close agreement within test accuracy. The theoretical curves with the effect of both elastic and inelastic collisions taken into account have been interpolated from [25]. According to Fig. 3a, the theoretical curves of α_T based on inelastic collisions ($\tilde{Q}_{ij}^{00,01} = 0$ and $\tilde{Q}_{ij}^{00,10} \neq 0$) follow the test curves only qualitatively. The numerical values of α_T are, on the other hand, much higher here than its test values. This discrepancy is probably due to the inadequacy of the model used for describing the inelastic collisions in terms of loaded CO₂ spheres. The temperature characteristic of α_T (Fig. 3b) follows the theoretical curve based on inelastic collisions ($\tilde{Q}_{ij}^{00,01} = 0$) with a better accuracy.

Thus, our study concerning the coefficient of thermal diffusion for these three gas systems confirms that, when applied to polyatomic gases, the rigorous theory of thermal diffusion cannot adequately explain the test results. A systematic study of the thermal diffusion phenomenon in gas mixtures, covering a wide range of concentrations and temperatures, would greatly contribute to the development of this theory.

LITERATURE CITED

1. R. Furth, Proc. Roy. Soc., A179, 461 (1942).
2. E. Whalley and R. E. S. Winter, Trans. Faraday Soc., 4b, 517 (1950).
3. M. R. Laranjeira, Physica, 26, 417, 11 (1960).
4. M. R. Laranjeira and J. Kistenmaker, *ibid.*, 26, 431, 111 (1960).
5. K. E. Grew and T. L. Ibbs, Thermal Diffusion in Gases [Russian translation], Moscow (1956).
6. G. P. Titov, A. I. Chukharev, and P. E. Suetin, in: Heat and Mass Transfer and the Transport Characteristics of Substances [in Russian], Vol. 7, Minsk (1972).
7. B. Lous and E. A. Mason, J. Chem. Phys., 54, No. 7, 3020 (1971).
8. W. H. Taylor and S. Weissman, *ibid.*, 54, No. 7, 3013 (1971).
9. L. Monchik, R. J. Munn, and E. A. Mason, *ibid.*, 45, 3051 (1968).
10. L. Monchik, S. L. Sandler, and E. A. Mason, *ibid.*, 49, 1178 (1968).

11. A. F. Zolotukhina, in: Heat and Mass Transfer and the Transport Characteristics of Substances [in Russian], Vol. 7, Minsk (1972).
12. K. L. Grew, F. A. Johnson, and W. E. Neal, Proc. Roy. Soc., A224, 513 (1954).
13. B. P. Mathur and S. C. Saxena, Z. Naturforsch., 22a, 164 (1967).
14. J. E. Walther and H. G. Drickamer, J. Phys. Chem., 62, 421 (1958).
15. A. K. Batabyal, A. K. Chosh, and A. K. Barua, J. Chem. Phys., 47, 2 (1967).
16. L. Waldmann, Z. Naturforsch., 2a, 358 (1947).
17. L. Waldmann, *ibid.*, 4a, 105 (1949).
18. L. Waldmann, *ibid.*, 2, 124 (1947).
19. G. Hirshfelder, Ch. Curtiss, and R. Byrd, Molecular Theory of Gases and Liquids [Russian translation], IL (1961).
20. T. L. Ibbs, Proc. Roy. Soc., A107, 470 (1925).
21. T. L. Ibbs and H. Inderwood, Proc. Phys. Soc., 39, 227 (1927).
22. A. E. Humphreys and P. Gray, Proc. Roy. Soc. London, A320, 397, 1542 (1970).
23. A. K. Batabyal, A. K. Chosh, and A. K. Barua, J. Chem. Phys., 48, 11 (1968).
24. J. R. Gozen and K. E. Grew, Phys. of Fluids, 7, 7, 1395 (1964).
25. S. Acharyya and A. K. Barua, J. Phys. B. (Atom. Molec. Phys.), 3, 8, 1052 (1970).