# MUTUAL-DIFFUSION COEFFICIENTS OF SOME BINARY GAS MIXTURES

L. A. Pozhar and V. N. Shchelkunov

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In the temperature range 100-300°K, at a pressure of $1.013 \cdot 10^5$ Pa, on the basis of the classical kinetic theory of gases, the mutual-diffusion coefficients of binary mixtures of the gases He, Ar, $CO_2$, $O_2$, and $N_2$ are calculated.

In solving a series of practical problems of cryogenic technology associated with mass-transfer processes, it is necessary to know, as well as all the other thermodynamic and transfer properties of the gas mixtures, the mutual-diffusion coefficients of these mixtures in the temperature range 100-300°K.

It is also known that classical kinetic theory of gases is applicable for the description of transfer processes in mixtures of the gases He, Ar, $CO_2$, $O_2$, $N_2$ in the given temperature range, at pressures up to $10^6$ Pa [1, 2]. However, systematic investigation of the question of the accuracy with which the mutual-diffusion coefficients of binary mixtures of the gases He, Ar, $CO_2$, $O_2$, $N_2$ may be calculated in the first Chapman—Cowling approximation is not a feature of the current literature.

In the first Chapman—Cowling approximation, the mutual-diffusion coefficients of binary mixtures of simple gases satisfy the relation

$$[D_{12}]_1 = \frac{3\,(2\pi m_{12}kT)^{1/2}}{16 n m_{12}\pi\sigma_{12}^2\Omega_{12}^{(1,1)*}\,(T_{12}^*)}, \tag{1}$$

where $m_{12} = m_1m_2/(m_1 + m_2)$, and the integral $\Omega_{12}^{(1,1)*}\,(T_{12}^*)$ depends on the form of the potential describing the interaction of the molecules of components 1 and 2 of the gas mixture, and is a function only of $T_{12}^*$. This model potential was taken in the form of the Lennard-Jones (6-12) potential

$$\varphi(r) = 4\varepsilon_{12}\left[\left(\frac{\sigma_{12}}{r}\right)^{12} - \left(\frac{\sigma_{12}}{r}\right)^{6}\right] \tag{2}$$

together with the combinatorial relations

$$\varepsilon_{12}\sigma_{12}^6 = (\varepsilon_{11}\sigma_{11}^6\varepsilon_{22}\sigma_{22}^6)^{1/2},\ \sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}. \tag{3}$$

According to classical kinetic theory of gases, Eq. (1) more accurately describes the mutual diffusion of monoatomic gases. However, in those cases where the process of pair collision of multiatomic molecules is similar to the analogous process for monoatomic molecules, Eq. (1) will also be a good approximation for the mutual-diffusion coefficients of binary mixtures of multiatomic gases.

## 1. Calculation of Mutual-Diffusion Coefficients of Binary Gas Mixtures of He, Ar, $CO_2$, $O_2$, $N_2$

In the temperature range 100-300°K, Eq. (1) is used to calculate the mutual-diffusion coefficients of binary gas mixtures of He, Ar, $CO_2$, $O_2$, $N_2$. The parameters of the poten-

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TABLE 1. Parameters of the Lennard-Jones (6-12) Potential Used in the Calculations

| Gas mixture | $\varepsilon_{12}/k$, K | $\sigma_{12}$, Å |
|---|---|---|
| He—Ar | 33,5 | 2,997 |
| He—$N_2$ | 33,6 | 3,096 |
| He—$O_2$ | 38,7 | 2,972 |
| Ar—$O_2$ | 114,4 | 3,426 |
| $O_2$—$CO_2$ | 128,0 | 3,768 |
| Ar—$CO_2$ | 138,0 | 3,673 |
| $N_2$—Ar | 91,1 | 3,599 |
| $O_2$—$N_2$ | 101,3 | 3,557 |
| He—$CO_2$ | 46,1 | 3,253 |
| $N_2$—$CO_2$ | 139,2 | 3,789 |

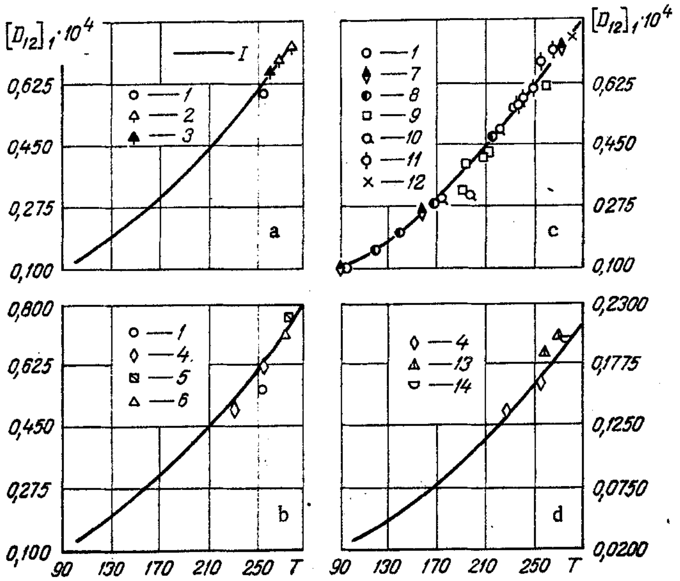

Fig. 1. Dependence of the mutual-diffusion coefficients $[D_{12}]$ ($m^2$/sec) on the temperature: a) for the gas mixture He—$N_2$; b) He—$O_2$; c) He—Ar; d) Ar—$O_2$; I) theoretical curves according to Eq. (1); the points correspond to the experimental results of [4] (1), [5] (2), [6] (3), [7] (4), [8] (5), [9] (6), [10] (7), [11] (8), [12] (9), [13] (10), [14] (11), [15] (12), [16] (13), [17] (14).

tial function in Eq. (2) are taken in the form of the quantities $\varepsilon_{12}$, $\sigma_{12}$ shown in Table 1, which are calculated inaccordance with Eq. (3) for sets of parameters $\varepsilon_{11}$, $\sigma_{11}$, $\varepsilon_{22}$, $\sigma_{22}$ which lead to the best agreement between the calculated and experimental values of the mutual-diffusion coefficients for binary mixtures of the gases He, Ar, $CO_2$, $O_2$, $N_2$ [1-3].

The results of calculating these coefficients are shown in Figs. 1-3, together with literature data on their experimental values at $p = 1.013 \cdot 10^5$ Pa. Everywhere below, the deviation of the calculated values from the experimental results is expressed as a percentage of the experimental results.

Comparison of the mutual-diffusion coefficients of the gas mixtures He—$N_2$, He—$O_2$, and He—Ar calculated according to Eq. (1) with the experimental values reveals a discrepancy of no more than 3%, which is within the limits of the experimental error. This means, on the one hand, that the accuracy of the first Chapman—Cowling approximation for the mu-

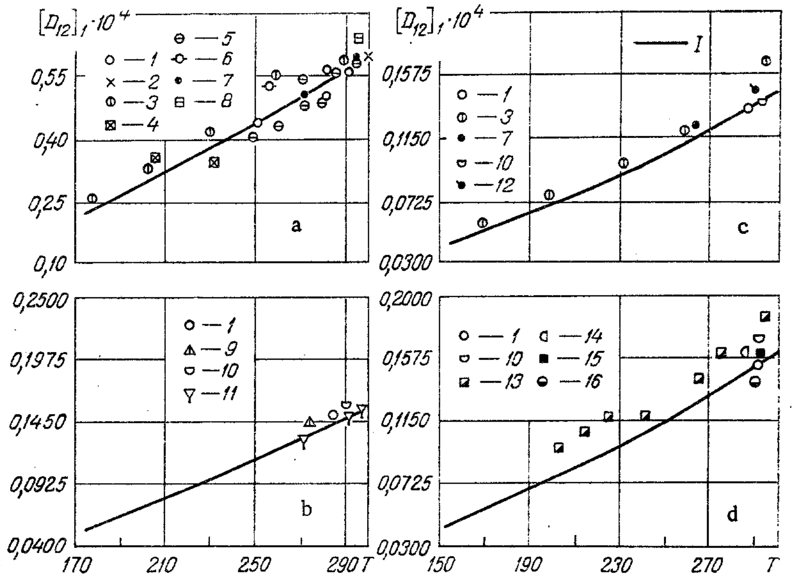

Fig. 2. Dependence of the mutual-diffusion coefficient $[D_{12}]_1$ (m$^2$/sec) on the temperature: a) for the gas mixture He—CO$_2$; b) O$_2$—CO$_2$; c) Ar—CO$_2$; d) N$_2$—CO$_2$; I) theoretical curves according to Eq. (1); the points correspond to the experimental values of [4] (1), [15] (2), [18] (3), [19] (4), [20] (5), [21] (6), [22] (7), [23] (8), [16] (9), [17] (10), [24] (11), [25] (12), [26] (13), [27] (14), [28] (15), [29] (16).

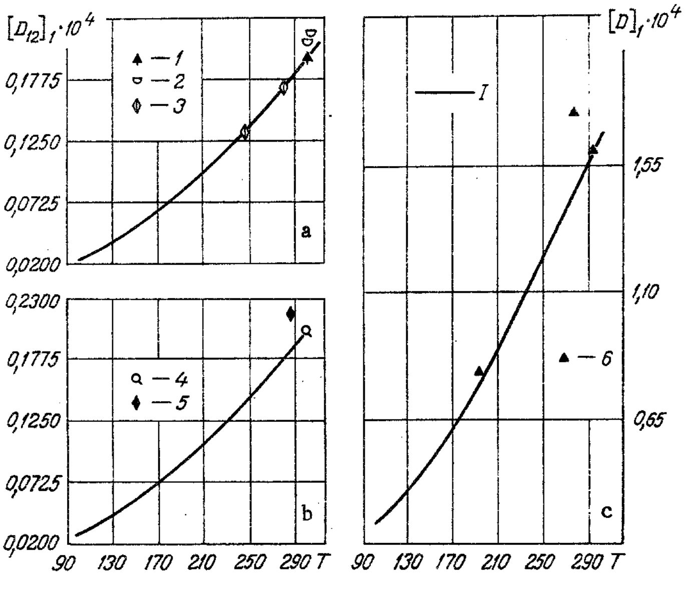

Fig. 3. Dependence of the mutual-diffusion coefficient $[D_{12}]_1$ (m$^2$/sec) and the self-diffusion coefficient $[D]_1$ (m$^2$/sec) of gaseous He on the temperature: a) for the gas mixture N$_2$—Ar; b) O$_2$—N$_2$; c) He; I) theoretical curves according to Eqs. (1) and (4) the points correspond to the experimental data of [6] (1), [17] (2), [30] (3), [13] (4), [31] (5), and [32] (6).

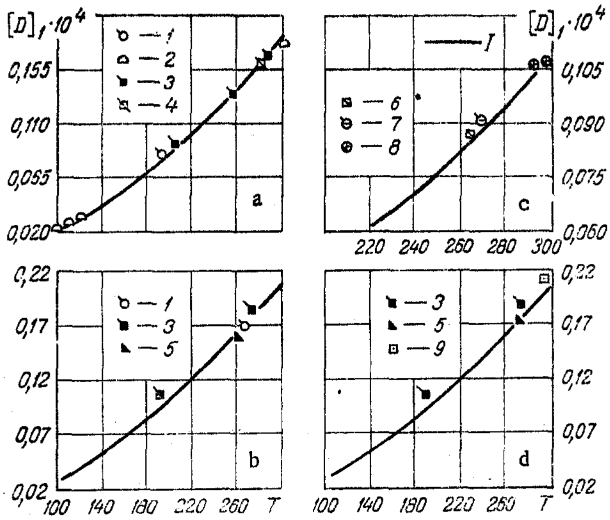

Fig. 4. Dependence of the self-diffusion coefficients $[D]_1$ ($m^2/sec$) on the temperature for gases: a) Ar, b) $O_2$; c) $CO_2$; d) $N_2$; I) theoretical curves according to Eq. (4); the points correspond to the experimental values of [13] (1), [33] (2), [34] (3), [35] (4), (36) [5], [8] (6), [37] (7), [38] (8), [39] (9).

tual-diffusion coefficients of simple gases predicted by the classical kinetic theory of gases is attained in the case of the mixtures $He-N_2$, $He-O_2$, and He–Ar, while in the others the error in determining these coefficients is in the range 3-6%, which complicates the interpretation of the results of calculation.

The calculated values of the mutual-diffusion coefficients are found to be somewhat underestimated in the case of the mixtures $Ar-O_2$, $O_2-CO_2$, $Ar-CO_2$, $N_2-Ar$, for which the mean-square deviation of the calculated values of these coefficients from the experimental values varies in the range 1.4-3.3%, depending on the form of the mixture, while the arithmetic mean deviation is negative. For the $He-CO_2$ mixture, the mean-square deviation of the results of calculating the mutual-diffusion coefficients from the experimental values is small, while the maximum relative deviation reaches ± 7%. Because there is practically a complete lack of data on the mutual-diffusion coefficients of the mixture $N_2-O_2$, it is impossible to derive final conclusions on the agreement between the calculated and experimental values of these coefficients (the maximum relative deviation from the known experimental data amounts to 10%).

Finally, in the case of the mixture $N_2-CO_2$, the mean-square deviation of the results of calculating the mutual-diffusion coefficients from the experimental values in the temperature range 280-300°K is 5.4%. However, comparision with the experimental data from [26] for the temperature range 100-300°K reveals a maximum relative deviation of $-25\%$, with an arithmetic mean deviation of $-15\%$. The mutual-diffusion coefficients of the gas mixture $N_2-CO_2$ in the temperature range 100-280°K and at $p = 1.013 \cdot 10^5$ Pa have not been extensively studied experimentally. This again prevents correct interpretation of the results of calculation.

## 2. Self-Diffusion Coefficients of the Gases He, Ar, $CO_2$, $O_2$, $N_2$

In the first Chapman–Cowling approximation, the expression for the self-diffusion coefficients of simple gases, including gaseous He, Ar, $CO_2$, $O_2$, $N_2$ takes the form

$$[D]_1 = \frac{3\,(2\pi mkT)^{1/2}}{16 n m \pi \sigma^2 \Omega^{(1,1)*}(T^*)}. \tag{4}$$

On the basis of Eq. (4), for the Lennard-Jones (6-12) potential [3], the self-diffusion coefficients of the gases He, Ar, $O_2$, $N_2$ in the temperature range 100-300°K and $CO_2$ in the range 220-300°K at $p = 1.013 \cdot 10^5$ Pa were calculated. Although there has been much experimental and theoretical study of these coefficients in the temperature range 280-300°K [2], there has been little experimental study in the range 100-280°K, which hinders the analysis of the data obtained. The results of calculating the self-diffusion coefficients of the gases He, Ar, $CO_2$, $O_2$, and $N_2$ are shown in Figs. 3 and 4. Comparison of these results with experimental data shows that the mean square deviation of the calculated and experimental results is a maximum for helium (10%); it amounts to 1.2% for carbon dioxide, while for nitrogen and oxygen it is 4.5%. In the case of argon, the agreement between calculation and experiment is practically complete (the mean square deviation is 1% and lies within the limits of experimental error).

## 3. Discussion of the Results

In view of the simplicity of the model potential in Eq. (2), and also the considerations underlying Eq. (1) [1], the discrepancy between the calculated and experimental values of the mutual-diffusion coefficients of binary gas mixtures and the self-diffusion coefficients of the gases He, Ar, $CO_2$, $O_2$, $N_2$ seems perfectly natural. In the case of a mixture of monoatomic gases, it is determined by the imprecise knowledge both of the form of the interaction potential of molecules of different kinds and of its parameters [3], in connection with which any model of this potential is used; in the cases considered here, the "realistic" model seems to the Lennard-Jones (6-12) potential [1]. For mixtures of multiatomic gases, there is an additional reason for discrepancy, associated with the different character of the pair collisions between monoatomic and multiatomic molecules [40].

It is interesting to note that, although the interaction between helium molecules is best described by the Morse potential [1], their interaction with molecules of argon, carbon dioxide, oxygen, and nitrogen are very well described (as follows from the results of the given calculations of the mutual-diffusion coefficients of their binary mixtures) within the framework of the Lennard-Jones (6-12) potential. The limited amount of experimental data on these coefficients, as well as the relatively low accuracy of the available experimental results [41], does not allow the superiority of particular models to be established in certain cases. At the same time, the practically complete agreement between the calculated and experimental results for the mutual-diffusion coefficients studied here shows that the model of the potential used above provides a good description of the interaction of molecules of different kinds in the case of binary mixtures of the gases He, Ar, $CO_2$, $O_2$, $N_2$ and molecules of these pure gases.

The use of values of the diffusion coefficients calculated with an accuracy of 3-10% is completely acceptable for the solution of most practical problems, and the simplicity and profound physical content of Eq. (1) make it sufficiently convenient for use.

## NOTATION

$[D_{12}]_1$, mutual-diffusion coefficient in the first Chapman—Cowling approximation; $m^2/sec$; $m_1$, $m_2$, masses of molecules of types 1 and 2, kg; k, Boltzmann constant, J/K; T, temperature, °K p, pressure, Pa; n, number density of particles, $m^{-3}$; $\Omega_{12}^{(1,1)*}(T_{12}^*)$, $\Omega^{(1,1)*}(T^*)$, reduced Ω integrals of the classical kinetic theory of gases [1]; $\varphi(r)$, Lennard-Jones (6-12) potential, J; $\varepsilon_1$, $\sigma_1$; $\varepsilon_2$, $\sigma_2$; $\varepsilon_{12}$, $\sigma_{12}$; ε, σ, parameters of the Lennard Jones (6-12) potential, J and m, respectively; r, distance between the centers of mass of molecules 1 and 2, m; $T_{12}^* = kT/\varepsilon_{12}$, $T^* = kT/\varepsilon$, reduced temperature; $[D]_1$, self-diffusion coefficient in the first Chapman—Cowling approximation, $m^2/sec$; m, molecular mass, kg.

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# SURFACE-FRICTION COEFFICIENT IN TURBULENT FLOW AT A BOUNDARY LAYER

V. M. Kapinos

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Using Thompson two-parameter velocity profiles equations defining the dependence of the surface-friction coefficient on the integral characteristics of the boundary layer are obtained.

Because the initial system of differential equations is not closed, the calculation of a turbulent boundary layer requires the use of various kinds of empirical relations. In integral and quasiintegral methods of calculating turbulent friction, one of the closing equations is taken in the form of a dependence of the surface-friction coefficient on some parameters of the boundary layer. Relations of similar type are used in differential calculation methods assuming a polynomial specification of the frictional-stress distribution over the boundary-layer thickness. In most cases, it is borne in mind here that turbulent flow is described from the viewpoint of its local equilibrium, although calculation methods employing empirical data on the frictional drag and with the determination of a flow field with "inheritance" are known [1].

Numerous empirical dependences expressing the friction coefficient as a function of the Reynolds number referred to the longitudinal coordinate or the momentum-loss thickness are known. Single-parameter formulas of the form $c_f = f(\mathrm{Re})$, $c_f = f(\mathrm{Re}_\theta)$ are valid at large Reynolds numbers for boundary layers of a plane plate; sometimes, it is used, together with the assumption that H = const, in calculations of gradient flows by an integral method. It is assumed here that the influence of the pressure gradient is taken into account intrinsically by the integral momentum relation.

Two- and three-parameter dependences are of greater accuracy, reflecting more completely the features of the flow in the boundary layer — in particular, with zero pressure gradient.

The most widespread approach is the semiempirical method based on the law of the wall, the formula of [2]

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