On the theory of the isothermal motion of a binary gas mixture in a capillary

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The isothermal motion of a binary gas mixture in capillaries under the action of a concentration gradient is studied theoretically. The diffusion fluxes of the mixture components and the diffusion slipping velocity of the mixture as a whole are calculated for arbitrary Knudsen number on the basis of a solution of the transport equation. The theory is compared with experimental data.

1. INTRODUCTION

We study a binary gas mixture in which a concentration gradient is present, the pressure and temperature are spatially uniform, and there are no external forces. Then the fluxes \( \mathbf{J}_i \) and \( N_i \) of the molecules of the \( i \)-th component relative to the number-average velocity \( U \) of the entire mixture in a stationary coordinate system are correspondingly determined according to Fick's first law by the following expressions:

\[
\mathbf{J}_i = n_i (U_i - U) = -D \nabla x_i, \quad N_i = n_i U + \mathbf{J}_i, \quad i = 1, 2,
\]

where

\[
x_i = n_i / n, \quad n = n_1 + n_2,
\]

\( D \) is the interdiffusion coefficient, \( n_i \) and \( n \) are the partial and total number of molecules per unit volume, \( x_i \) is the fraction of molecules of the \( i \)-th kind per unit volume, \( U_i \) is the macroscopic velocity of the \( i \)-th component in a stationary coordinate system, and \( \alpha_{12} \) is the diffusion slipping coefficient.

It is known that the expressions (1), which were obtained on the basis of linear transport theory for an unbounded gas, can be used to describe the diffusion of gases in capillaries only under certain conditions. The flow must be averaged over the transverse cross section of the capillary. The Knudsen number (\( Kn \) is the ratio of the average mean-free path length \( l \) of the molecules to the radius \( R \) of the capillary) must be small (\( Kn \ll 1 \)). The reflection of molecules from the capillary surface should not be completely specular.

It is convenient to extend Fick's law to arbitrary \( Kn \) as follows:

\[
\mathbf{J}_i = -S_i D \nabla x_i, \quad i = 1, 2,
\]

where the correction factor \( S_i \) (diffusion factor) depends on \( Kn \), the accommodation coefficients \( e_i \) and \( e_2 \) of molecules of each component and the concentration \( x_i (x_2 = 1 - x_i) \). Moreover, \( S_i \) depends on the mass ratio \( m_i / m_2 \) and the ratio \( d_1 / d_2 \) of the effective diameters of the molecules.

The form of the expression (1) for the number-average velocity \( U \) of the mixture remains unchanged. The extension to arbitrary \( Kn \) refers only to the diffusion slipping coefficient \( \alpha_{12} \).

The calculation of \( S_i \) and \( \alpha_{12} \) is a problem in the kinetic theory of gases. There are a large number of works which are devoted to solving this problem. The main works are briefly discussed in Refs. 1–3. In Ref. 1, the motion of a binary gas mixture in a capillary with intermediate values of \( Kn \) is described on the basis of a solution of the transport equation with an approximate collision integral. The scattering of the molecules by the capillary surface is assumed to be completely diffuse. In Ref. 2, the model of specular–diffuse scattering is used for the boundary conditions, but the results are valid only for small \( Kn \) (\( Kn \ll 0.25 \)).

In the present paper, we describe the isothermal isobaric motion of a binary gas mixture in a capillary for arbitrary values of \( Kn \) in the approximation of specular–diffuse gas-surface interaction. Our interest in this problem arose in connection with the need to compare the theory of light-induced drift of gas mixtures in capillaries \(^4\) with the experimental data. \( ^5 \) The experimental methods are based on the action of resonance laser radiation on one component of a gas mixture followed by measurement of the difference of the concentrations of the absorbing gas established along the capillary. In Ref. 5 a theoretical model relating the displacement of the concentration to the velocity of light-induced drift in the capillary is proposed. This model assumes that the diffusion flux of the absorbing gas is known. Since in the experiment of Ref. 5 the pressure of the buffer gas and mixture as a whole varied over quite a wide range, the generalized Fick's law (2) should be used for the diffusion flux.

The diffusion factor \( S_i \) should not be calculated on the basis of the theory of Ref. 1 for two reasons. First, in the theory of Ref. 1 the concentration \( x_i \) is a variable parameter, while in experiments on light-induced separation of mixtures the concentration of the absorbing gas is low. The assumption that the concentration is low in the formulation of the problem greatly simplifies the mathematical operations and decreases the volume of computational work, since for \( x_i \ll 1 \) the quantity \( S_i \) does not depend on \( x_i \). Second, and this is the main point, the theory of Ref. 1, which presupposes diffuse scattering of molecules by the capillary surface, does not permit reconstructing the values of the accommodation coefficients of the excited particles by comparing theory with experiment. The calculation of \( S_i \) on the basis of the results of Ref. 2 makes sense only for \( Kn \ll 0.25 \).

Only a small number of experimental points falls within this range of \( Kn \).
The calculation of $S_1$ and $\sigma_{ij}$ as a function of $Kn$ and the accommodation coefficients $e_1$ and $e_2$ on the basis of the solution of the gas-transport equation under the condition that the concentration of one component of a binary mixture is low is the main objective of the present paper.

2. FORMULATION OF THE PROBLEM

We study steady-state mass-transfer processes in a binary gas mixture in a capillary with radius $R_0$. The state of the gas is perturbed by a longitudinal concentration gradient. The total pressure $p$ and the temperature $T$ of the mixture are uniform and no external forces are present. We choose a cylindrical coordinate system $(r, \varphi, z)$ with origin at the center of the capillary so that the $z$ axis is oriented along the concentration gradient. As always in linear transport theory, we assume that the relative concentrations $x_i = n_i / n$ of the components change very little over distances of the order of the molecular mean free path. The weakly nonequilibrium state of the gas is described by distribution functions which can be represented in the form of perturbed Maxwellian distributions, i.e.,

$$f_i(r, \varphi, v_i) = f_{i0}[1 + \mu_i z + h_i(r, \varphi, v_i)],$$

where

$$f_{i0} = n_i V_i \left( \frac{m_i \beta}{2\pi k_B T} \right)^{1/2} \exp \left( -\frac{m_i v_i^2}{2k_B T} \right),$$

$n_{i0}$ is the equilibrium number density of the $i$-th component, $m_i$ is the mass of a molecule of the $i$-th kind, $k_B$ is Boltzmann’s constant, and $V_i$ is the radius vector in a plane perpendicular to the $z$ axis. The expression (3) takes account of the fact that the length of the capillary is much greater than its radius, so that the end distortions in the flow profiles can be neglected. For this reason, the disturbances $h_i$ do not depend on the longitudinal coordinate $z$.

The $h_i$ satisfy the linearized transport equations

$$v_j \frac{\partial h_i}{\partial z} + v_i \mu_i \frac{\partial n_j}{\partial z} + L_{ij} h_i, \quad (i, j) = 1, 2,$$

where $L_{ij}$ and $L_{ij}$ are the linearized collision integrals of type $i-j$ and $j-i$, respectively, and $v_i \mu_i$ is the component of the molecular velocity vector $v_i$ in a plane perpendicular to the $z$ axis.

As boundary conditions, we choose the model of specular–diffuse reflection. The fraction $e_1$ of particles of the $i$-th kind is scattered diffusely at each point of the capillary surface with a Maxwellian velocity distribution corresponding to the local number density, and the fraction $(1-e_1)$ is reflected specularly. Then the perturbations $h_i$ satisfy the following boundary conditions:

$$h_i(v_i) = 1 - e_1 h_i(v_i - 2v_i n_i), \quad (v_i, n_i) > 0, \quad \varphi = \varphi_0,$$

where $n_i$ is the inner normal to the surface of the capillary.

For the linearized collision integrals, we employ their second-order approximations,5 for which the first ten moments of the total and approximate collision integrals are equal, and which make it possible to obtain accurate results in describing isothermal mass transfer. Isothermal heat transfer, which is a subtle effect, will be neglected.

We confine our attention to the case in which the concentration of one component of the mixture is low ($n_1 \ll n_2$). Then, after being rendered dimensionless and linearized with respect to the small parameter $n_1 / n_2$, retaining only terms of leading order in this ratio, the transport equations (4) assume the form

$$e_{11} \frac{\partial h_{11}}{\partial z} + e_{12} \frac{\partial h_{12}}{\partial z} + \frac{\partial \pi_{11}}{\partial z} + \frac{\partial \pi_{12}}{\partial z} = 0,$$

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FIG. 1. Scheme of integration along the direction $e_i$.

$$\sigma_{i2} = 2 R \frac{n_1(u_1) + \frac{m_1}{m_2} n_2(u_2)}{n_1 + \frac{m_1}{m_2} n_2},$$

where the angular brackets denote averaging over the transverse cross section of the capillary

$$\langle u_i \rangle = \frac{1}{2} \int u_i(r) r dr.$$

We note that the diffusion factor $S_i$ is completely determined by the macroscopic velocity of the first component, while the diffusion slipping coefficient $\sigma_{i2}$ includes the velocity of both components of the gas mixture.

3. SOLUTION OF THE TRANSPORT EQUATIONS

We employ the integral–moment method, based on the transformation of the integrodifferential transport equation for the distribution function into a system of integral equations for its moments.

We assume temporarily that the quantities $u_i(r)$ and $\pi_{ij}(r)$ on the right-hand side of Eqs. (6) are known. Then the transport Eqs. (6), taking account of the boundary conditions (5), can be integrated along an arbitrarily chosen direction of molecular velocity $e_i$ (Fig. 1). Using the integral form of the kinetic equations and the definitions (7) of the macroscopic quantities, we obtain two systems of integral equations for the dimensionless velocities $u_i$ and stress tensors $\pi_{ij}$ of the components of the gas mixture ($i=1,2$):

1) for the first component ($i=1$)

$$u_1(r) = R \frac{1}{\pi} \int \left[ \frac{1}{2} \frac{n_1}{n_2} \frac{\mu R_0}{R} A_{01} + \frac{1}{2} (1 - \psi_{11}^{(1)}) u_1(r') B_{11} r' \right] dr',$$

$$\pi_{12}(r) = R \frac{1}{\pi} \int \left[ \frac{1}{2} \frac{n_1}{n_2} \frac{\mu R_0}{R} A_{12} + \frac{1}{2} (1 - \psi_{11}^{(1)}) \pi_{12}(r') B_{12} r' \right] r' dr',$$

2) for the second component ($i=2$)

$$u_2(r) = R \frac{1}{\pi} \int \left[ \frac{1}{2} \frac{n_1}{n_2} \frac{\mu R_0}{R} A_{02} + \frac{1}{2} (1 - \psi_{11}^{(1)}) u_2(r') \right] dr',$$

$$\pi_{22}(r) = R \frac{1}{\pi} \int \left[ \frac{1}{2} \frac{n_1}{n_2} \frac{\mu R_0}{R} A_{12} + \frac{1}{2} (1 - \psi_{11}^{(1)}) \pi_{22}(r') B_{12} r' \right] r' dr',$$

where

$$\psi_{11}(r) = \frac{r - r'}{|r - r'|}, \quad \psi_{12}(r) = \frac{r - r'}{|r - r'|}, \quad A_{ij} = \frac{\pi}{r - r'}, \quad B_{ij} = \frac{\pi}{r - r'}, \quad T_{ij}(t) = \int_0^t \exp \left( -\frac{x^2 - t}{x} \right) dx,$$

$$K_{mi} = R_{ij} \sum_{j=1} \left( 1 - e_j \right) T_{ij} \left( R_{ij} (k - 1) |x_i - r| \right) + |r - r'| |x_i - r|.$$
eters. In addition, from the conservation of momentum for the mixture as a whole, it follows that
\[ n_1 \dot{v}_1 + n_2 \dot{v}_2 = 0 \]
In the Bubnov–Galerkin method the coefficients \( a_k \) are determined by requiring that the expressions obtained by substituting the approximations (15) for \( u(r) \) and \( \pi_{ij}(r) \) into the integral equations (11) and (13) be orthogonal to the functions \( 1 \) and \( r^2 \), and that the expressions obtained by substituting the approximations (15) into Eqs. (12) and (14) be orthogonal to the function \( r \). Here the condition of orthogonality of any two functions \( f(r) \) and \( g(r) \) has the form
\[
(f,g) = 2 \pi \int_0^1 f(r)g(r)dr = 0. \tag{16}
\]
In this manner we obtain the following system of linear algebraic equations:
\[
\sum_{k=1}^{4} a_k a_k = a_k, \quad k = 1,2,3,4,5,6. \tag{17}
\]
The expressions for \( a_{10} \) and \( a_{20} \) are complicated and are not presented here.
We choose the effective collision frequency \( \gamma_{12} \) in the form \( \gamma_{12} = \beta_{12}^{(1)} \) and the frequency \( \gamma_{22} \) in the form \( \gamma_{22} = \beta_{22}^{(2)} \). This choice relates the frequency of collisions between different kinds of molecules to the diffusion coefficient, and the frequency of collisions between molecules of the same kind to the viscosity coefficient of the second component, which for \( n_1 < n_2 \) determines the viscosity of the mixture as whole.
We model the gas particles as hard elastic spheres with diameters \( d_i (i=1,2) \). Then the rarefaction parameter \( R_1 \) is related to \( Kn \) by the following relation:
\[
R_1 = \frac{8}{3} \sqrt{\frac{m_2}{m_1 + m_2}} \frac{1}{Kn}, \quad Kn = \frac{l_1}{R_2}, \tag{18}
\]
\[
l_1 = \frac{1}{\pi n_2 \beta_{12}^{(1)}}, \quad R_2 = \frac{3}{5} \frac{d_1}{d_2}, \quad \frac{d_1}{d_2} = \frac{d_1}{d_2}, \tag{19}
\]
Here \( l_1 \) is the mean free path of particles of the first component.
To reduce the number of free parameters and to simplify the numerical calculations, we assume that the scattering of particles at the surface of the capillary is almost diffuse:
\[
1 - e_i < 1, \quad i=1,2. \tag{20}
\]
Linearizing the problem with respect to the small parameters \( 1 - e_i \) gives
\[
\sigma_{12} = \sigma_{12}^{(0)} + \sigma_{12}^{(1)} (1 - e_1) + \sigma_{12}^{(2)} (1 - e_2). \tag{21}
\]
The quantities \( \sigma_{12}^{(0)} \) and \( \sigma_{12}^{(1)} \) characterize the diffusion factor and the diffusion slipping coefficient with total accommodation of the molecules at the surface of the capillary. We note that in the approximation \( n_1 < n_2 \), \( S_1 \) does not depend on the nature of the interaction between molecules of the second component and the wall.
Analytic expressions for \( S_1^{(0)} \) and \( \sigma_{12}^{(0)} \) can be obtained only for large and small values of \( Kn \).

1. Almost free-molecular regime (\( Kn \gg 1 \) or \( R \rightarrow 1 \)):
Up to terms of order \( R^2 \) the kinetic coefficients have the form
\[
S_1^{(0)} = 1.505R + R^2 \ln R - \frac{0.25 \Phi_1 + 0.384 R^2}{2}, \tag{22}
\]
\[
\sigma_{12}^{(0)} = 1.505 \left( \frac{m_1}{m_2} \right) \frac{1}{1 + \frac{m_1}{m_2}} R^2 \ln R - \frac{0.25 \Phi_1 + 0.384 \left( \frac{m_1}{m_2} \right)^2}{2} R^2, \tag{23}
\]
\[
\sigma_{12}^{(1)} = -3.009R - 6m_2 \ln R + \left( 3.240 + 4.527 \frac{m_1}{m_2} \right) R^2 + \ldots, \tag{24}
\]
\[
\sigma_{12}^{(2)} = \frac{m_1}{m_2} \left( 3.009R + \frac{6m_2}{m_1} \right) \ln R - (4.527 - 12.294\Phi_2 - 6\Phi_2 \ln R^2 + \ldots, \tag{25}
\]
where
\[
\Phi_1 = \frac{4m_2}{3(m_1 + m_2)} - 1, \quad \Phi_2 = \frac{12 \sqrt{2(1 + m_1/m_2)}}{5 \left( 1 + d_1/d_2 \right)^2}, \tag{26}
\]
\[
\Phi_3 = \frac{4}{5} \frac{m_1/m_2}{1 + m_1/m_2}, \tag{27}
\]2. Hydrodynamic regime with slipping (\( Kn \ll 1 \) or \( R \gg 1 \)):
Up to terms of zeroth order the kinetic coefficients have the form
\[
S_1^{(0)} = 1 + \ldots, \quad S_1^{(1)} = O \left( \frac{1}{R} \right), \tag{28}
\]
\[
\sigma_{12}^{(0)} = 1 - 2 \sqrt{\frac{m_1}{m_2}} \frac{1 + \Phi_2 + \Phi_2}{1 - \Phi_1} - 1 + \ldots, \tag{29}
\]
\[
\sigma_{12}^{(1)} = -2 \sqrt{\frac{m_1}{m_2}} \frac{1 + \Phi_2 + \Phi_2}{1 - \Phi_1} + \ldots, \tag{30}
\]
\[
\sigma_{12}^{(2)} = \frac{m_1}{m_2} + \ldots. \tag{31}
\]
The numerical results for intermediate values of \( Kn \) for He–Ar and Na–He mixtures displayed in Figs. 2–4.
and components of the diffusion factor (a) and $a_\gamma$, $a_\alpha$, $a_\beta$, $a_\delta$, and components of the diffusion slipping coefficient (b) as a function of the rarefaction parameter $R$ for an Ar-He gas mixture: a) 1—Eq. (21), 2—Eq. (22); b) 1—Eq. (23), 2—Eq. (24), 3—Eq. (25).

4. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

The results of the model calculation of the quantities $S^{(1)}$, $S^{(2)}$, $a^{(1)}$, and $a^{(2)}$ for a mixture of gases, in which the effective diameters of the molecules are equal ($d_1 = d_2$) but the masses can be different, are presented in Tables I and II. One can see that for a fixed value of the rarefaction parameter $R$ the diffusion factor $S^{(2)}$ is essentially independent of the ratio of the molecular masses $m_1/m_2$. When the ratio $m_1/m_2$ is varied, the maximum change in $S^{(2)}$ is ~4%. This dependence is incorporated in the parameter $R$ itself [see Eq. (18)].

The diffusion slipping coefficient $a^{(2)}$ in the limit of small Kn (27)—(29) is of interest in its own right. In this limit $a^{(2)}$ does not depend on the geometry of the surface bounding the flow and can be calculated independently by solving the Knudsen layer problem. A detailed review of these works is given in Ref. 10.

It is convenient to compare the results (27)—(29) of the present work with other theories for a gas mixture with similar masses and effective diameters of the molecules. We also assume that the partial accommodation coefficients differ by a small amount. In this case the expression for $a^{(2)}$ can be written in the form

\[ a^{(2)} = \frac{1}{2} \left( \frac{m_1}{m_2} \right) a^{(1)} \]

This expression is in good agreement with the results of the present work.
From the expressions (27)–(29) we have \( a = 1.063, \) \( b = 0.750, \) and \( c = 1.0. \) According to the data of Ref. 10, the different methods for solving the Boltzmann equation in the case of an equimolar mixture \((x_1 = x_2 = 0.5)\) give the following values:

\[
\begin{align*}
  a &= 0.7 - 1.29, \\
  b &= 0 - 1.18, \\
  c &= 0.667 - 2.
\end{align*}
\]

According to experiments \(11\) on diffusiophoresis of oil drops in binary gas mixtures \( a = 0.95 \) and \( b = 1.05. \)

Table I gives the computational results for \( a_{12} \) in isotopic mixtures of molecules with identical masses and different effective diameters. In this case, for intermediate values of \( Kn, \) according to the theory, the direction of the diffusion slipping velocity is reversed. If \( m_1 = m_2, \) \( e_1 = e_2, \) and \( d_1 < d_2, \) then the number-average flux of the gas mixture is directed opposite the concentration gradient of the first component for large \( Kn \) and along the concentration gradient for small \( Kn. \) If \( d_1 > d_2, \) the opposite is true. We note that reversal of the diffusion slipping velocity for intermediate \( Kn \) in the case of equimolar mixtures \((x_1 = x_2)\) has been recorded experimentally in measurements of the diffusion baroeffect and barodiffusion separation of mixtures for the gases \( Ar-CO_2, N_2-C_2H_4, Cl_2H_4-Ne, \) and \( He-D_2.\)

The quantities \( a_{1}^{(0)}, a_{1}^{(1)}, a_{1}^{(2)}, \) and \( a_{1}^{(3)} \) of the diffusion slipping coefficient \( a_{12} \) are important for any regime of motion of the gas.

The diffusion factors \( S_{10}, S_{11}, S_{12}, \) and \( S_{13} \) calculated for the \( Ar-He \) and \( Na-He \) mixtures differ from one another by at most 0.2% for any values of the rarefaction parameter \( R. \) In the experiment of Ref. 5 on light-induced separation of a \( Na-He \) mixture, the pressure of the buffer gas \( (He) \) in the capillary varied over the range \( p = 0.021 - 12.5 \) kPa, which corresponds to rarefaction parameters \( R = 0.4 - 240. \) In Ref. 5, in the analysis of the experiment for the purpose of determining the values of the light-induced drift velocity of \( Na \) vapor, it was assumed that \( S_1 = 1 \) for arbitrary \( R. \) The error made in so doing can be estimated from Fig. 4(a). We note that when isothermal diffusion and light-induced drift problems are solved simultaneously, the transport equations include terms

<table>
<thead>
<tr>
<th>( \frac{m_1}{m_2} )</th>
<th>( \frac{m_1}{m_2} )</th>
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<tbody>
<tr>
<td>( R )</td>
<td>0.1</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
<td>4</td>
<td>0.868</td>
</tr>
<tr>
<td>10</td>
<td>0.945</td>
</tr>
</tbody>
</table>

\( \sigma_{12} = a_{1}^{(0)} \left( \frac{m_1 - m_2}{m_1 + m_2} \right) b d_1 - d_2 + c (e_1 - e_2). \) (30)
that take account of induced intramolecular transitions in a resonance interaction of the radiation with the gas as well as the radiative decay of the excited level. This results in a renormalization of the diffusion transport coefficients. As a result, the expressions for the diffusion coefficient $D$, the diffusion factor $S_i$, and diffusion slipping coefficient $\alpha_{12}$ will include corrections due to the drift motion of the gas. However, it can be shown (as done for $D$ in Ref. 5) that these corrections are of order $\Delta d/d$ — the relative difference of the effective diameters of the excited and unexcited particles. Then the corresponding corrections for the diffusion fluxes $J_i$ and the number-average velocity $U$ of the mixture will be of the same order $R_{ij} \Delta d/d$. Since $R_{ij} \leq 1$ and $\Delta d/d \ll 1$, these corrections can be neglected.

In Fig. 3 the theory is compared with an experiment on the diffusion slipping of an Ar–He mixture. The quantity $u_{Tz}$ represents the ratio of $u_{12}$ to the free-molecular value $u_1$ [the first term in the expression (23)]. In Ref. 14 the experimental values of $u_{12}$ were found from measurements of the magnitude of the barodiffusion separation of the Ar–He mixture. The measurements were performed over a wide range of values with concentration ratios $n_A/n_{He}=0.08$. One can see from Fig. 3 that the discrepancy between the theory with $E_A=1$, $E_{He}=1$ (curve 1) and the experimental data is greatest in the free-molecular regime and is $\approx 20\%$. The theoretical curve (2), corresponding to the accommodation coefficients $E_A=0.98$ and $E_{He}=0.92$, satisfactorily describes the experiment for $R_s > 1$. We note that the accommodation coefficients $E_A=0.975$ and $E_{He}=0.935$ were extracted from the experiments of Ref. 8 on Poiseuille flow in glass capillaries. The small discrepancy between theory and experiment in the intermediate regime could be due to two factors. First, the approximation $n_i \approx n_{He}$ adopted in the theory does not completely meet the conditions of the experiment. Second, the calculations were performed for a model of hard spherical molecules. It can be expected that better agreement between theory and experiment can be obtained by using the Lennard–Jones potential.

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