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

V. G. Chernyak and E. A. Vilisova

A. M. Gor'kiĭ Ural State University, 620083 Ekaterinburg, Russia

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 gas-transport equation. The theory is compared with experimental data. © *1996 American Institute of Physics.* [S1063-7761(96)01207-3]

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 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:

$$\mathbf{J}_i = n_i(\mathbf{U}_i - \mathbf{U}) = -nD\nabla x_i, \quad \mathbf{N}_i = n_i\mathbf{U} + \mathbf{J}_i, \quad i = 1,2, \tag{1}$$

$$\mathbf{U} = x_1\mathbf{U}_1 + x_2\mathbf{U}_2 = \sigma_{12}D\nabla x_1,$$

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 ith kind per unit volume, $\mathbf{U}_i$ is the macroscopic velocity of the ith component in a stationary coordinate system, and σ_{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_0 of the capillary) must be small (Kn≪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:

$$\mathbf{J}_i = -S_i nD\nabla x_i, \quad i = 1,2, \tag{2}$$

where the correction factor S_i (diffusion factor) depends on Kn, the accommodation coefficients ε_1 and ε_2 of molecules of each component and the concentration x_1 ($x_2 = 1 - x_1$). Moreover, S_i depends on the mass ratio m_1/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 σ_{12}.

The calculation of S_i and σ_{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 ≤ 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_1 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 $x_1 \ll 1$ 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 ≤ 0.25. Only a small number of experimental points falls within this range of Kn.[5]

The calculation of S_i and σ_{12} as a function of Kn and the accommodation coefficients ε_1 and ε_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 $(\tilde{r}, \varphi, z)$ 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.,

$$f_i(\tilde{\mathbf{r}}, z, \mathbf{v}_i) = f_{i0}[1 + \mu_i z + h_i(\tilde{\mathbf{r}}, \mathbf{v}_i)], \qquad (3)$$

where

$$f_{i0} = n_{i0} \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{v_i^2}{\bar{v}_i^2} \right),$$

$$\bar{v}_i = \left(\frac{2 k_B T}{m_i} \right)^{1/2}, \qquad \mu_i = \frac{1}{x_i} \frac{dx_i}{dz},$$

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 $\tilde{r}$ 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

$$\mathbf{v}_{i\perp} \cdot \frac{\partial h_i}{\partial \tilde{\mathbf{r}}} + v_{iz} \mu_i = L_{ii} + L_{ij}, \quad (i,j) = 1,2, \qquad (4)$$

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

As boundary conditions, we choose the model of specular–diffuse reflection. The fraction ε_i 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 $(1 - \varepsilon_i)$ is reflected specularly. Then the perturbations h_i satisfy the following boundary conditions:

$$h_i(\mathbf{v}_i) = (1 - \varepsilon_i) h_i(\mathbf{v}_i - 2(\mathbf{v}_i \cdot \mathbf{n})\mathbf{n}), \quad (\mathbf{v}_i \cdot \mathbf{n}) > 0, \quad \tilde{r} = R_0, \qquad (5)$$

where $\mathbf{n}$ is the inner normal to the surface of the capillary.

For the linearized collision integrals, we employ their second-order approximations,[6] 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

$$\mathbf{c}_{1\perp} \cdot \frac{\partial h_1}{\partial \mathbf{r}} + \frac{n_2}{n_1} R_0 \mu c_{1z} = R_1 [-h_1 + 2 c_{1z}(1 - \varphi_{12}^{(1)}) u_1$$
$$+ 4 c_{1r} c_{1z}(1 - \varphi_{12}^{(3)}) \pi_{1rz}], \qquad (6)$$

$$\mathbf{c}_{2\perp} \cdot \frac{\partial h_2}{\partial \mathbf{r}} - R_0 \mu c_{2z} = R_2 \left[-h_2 + 2 c_{2z}\left(u_2 + \sqrt{\frac{m_1 n_1}{m_2 n_2}} \psi_{12}^{(1)} u_1 \right) \right.$$
$$+ 4 c_{2r} c_{2z}\left((1 - \psi_{22}^{(3)} + \psi_{22}^{(4)}) \pi_{2rz} \right.$$
$$\left. + \frac{n_1}{n_2} \psi_{12}^{(4)} \pi_{1rz} \right) \Bigg],$$

where

$$\mathbf{c}_i = \frac{\mathbf{v}_i}{\bar{v}_i}, \quad \mu = \frac{dx_1}{dz}, \quad \mathbf{r} = \frac{\tilde{\mathbf{r}}}{R_0}, \quad R_i = \frac{\gamma_{i2}}{\bar{v}_i} R_0,$$

$$u_i = \frac{U_i}{\bar{v}_i} = \int c_{iz} E_i h_i d\mathbf{c}_i, \quad \pi_{irz} = \frac{P_{irz}}{2 p_i} = \int c_{ir} c_{iz} E_i h_i d\mathbf{c}_i, \qquad (7)$$

$$E_i = \pi^{-3/2} e^{-c_i^2}, \quad \varphi_{12}^{(k)} = \frac{\nu_{12}^{(k)}}{\gamma_{12}}, \quad \psi_{i2}^{(k)} = \frac{\nu_{i2}^{(k)}}{\gamma_{22}}, \quad i = 1,2.$$

Here P_{irz} and p_i are, respectively, the partial tensor of tangential stresses and the pressure of the i-th component and γ_{ij} is the effective collision frequency between molecules of the i- and j-th kinds. The expressions for the frequencies $\nu_{ij}^{(k)}$ in terms of the masses, the concentrations, and the Chapman–Cowling Ω-integrals are presented in Ref. 6; R_i is the rarefaction parameter for the i-th component of the gas mixture and is inversely proportional to Kn [see Eq. (18)].

We note that on account of the assumption that the concentration of the first component is low, the transport equation for this component is not coupled to the equation for the second component and can be solved independently. In turn, the equation for the second component includes macroscopic quantities of both components of the mixture.

Equations (6) and (7), together with the boundary conditions (5), uniquely determine the distribution function (3).

Ultimately, the quantities S_i and σ_{12} are of interest. In the first Chapman–Enskog approximation for the diffusion coefficient[7] $[D]_1 = \bar{v}_1^2/2\nu_{12}^{(1)}$ these quantities have the following form in the case $n_1 \ll n_2$:

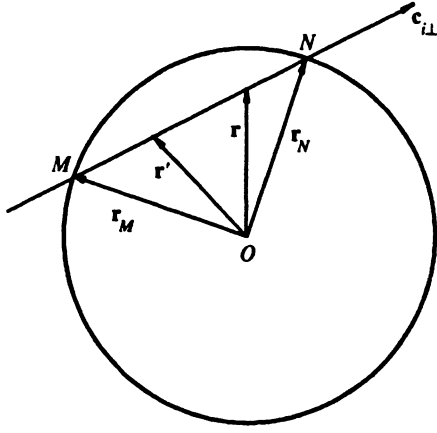$$S_1 = -S_2 = -\frac{2R}{R_0 \mu} \frac{n_1}{n_2} \langle u_1 \rangle, \quad R \equiv R_1, \qquad (8)$$

V. G. Chernyak and E. A. Vilisova   81

FIG. 1. Scheme of integration along the direcion $c_\perp$.

$$\sigma_{12} = \frac{2R}{R_0\mu}\left(\frac{n_1}{n_2}\langle u_1\rangle + \sqrt{\frac{m_1}{m_2}}\langle u_2\rangle\right), \qquad (9)$$

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

$$\langle u_i\rangle = 2\int_0^1 u_i(r)r\,dr. \qquad (10)$$

We note that the diffusion factor S_i is completely determined by the macroscopic velocity of the first component, while the diffusion slipping coefficient σ_{12} 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 $\pi_{irz}(r)$ 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 $c_{i\perp}$ (Fig. 1).[8] 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 π_{irz} of the components of the gas mixture ($i = 1,2$):

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

$$u_1(r) = \frac{R_1}{\pi}\int_\Sigma\left[-\frac{1}{2}\frac{n_2}{n_1}\frac{\mu R_0}{R_1}A_{01} + (1 - \varphi_{12}^{(1)})u_1(r')A_{01}\right.$$
$$\left. + 2(1 - \varphi_{12}^{(3)})\pi_{1rz}(r')\mathbf{B}_{11}\cdot\frac{\mathbf{r}'}{r'}\right]d\mathbf{r}', \qquad (11)$$

$$\pi_{1rz}(r) = \frac{R_1}{\pi}\int_\Sigma\left[-\frac{1}{2}\frac{n_2}{n_1}\frac{\mu R_0}{R_1}A_{11} + (1 - \varphi_{12}^{(1)})u_1(r')A_{11}\right.$$
$$\left. + 2(1 - \varphi_{12}^{(3)})\pi_{1rz}(r')\mathbf{B}_{21}\cdot\frac{\mathbf{r}'}{r'}\right]\frac{\mathbf{e}\cdot\mathbf{r}}{r}d\mathbf{r}'; \qquad (12)$$

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

$$u_2(r) = \frac{R_2}{\pi}\int_\Sigma\left[\frac{1}{2}\frac{\mu R_0}{R_2}A_{02} + \left(u_2(r')\right.\right.$$
$$\left. + \sqrt{\frac{m_1}{m_2}\frac{n_1}{n_2}}\psi_{12}^{(1)}u_1(r')\right)A_{02} + 2\left((1 - \psi_{22}^{(3)})\right.$$
$$\left.\left. + \psi_{22}^{(4)})\pi_{2rz}(r') + \frac{n_1}{n_2}\psi_{12}^{(4)}\pi_{1rz}(r')\right)\mathbf{B}_{12}\cdot\frac{\mathbf{r}'}{r'}\right]d\mathbf{r}', \qquad (13)$$

$$\pi_{2rz}(r) = \frac{R_2}{\pi}\int_\Sigma\left[\frac{1}{2}\frac{\mu R_0}{R_2}A_{12} + \left(u_2(r')\right.\right.$$
$$\left. + \sqrt{\frac{m_1}{m_2}\frac{n_1}{n_2}}\psi_{12}^{(1)}u_1(r')\right)A_{12} + 2\left((1 - \psi_{22}^{(3)})\right.$$
$$\left. + \psi_{22}^{(4)})\pi_{2rz}(r') + \frac{n_1}{n_2}\psi_{12}^{(4)}\pi_{1rz}(r')\right)$$
$$\left.\times\mathbf{B}_{22}\cdot\frac{\mathbf{r}'}{r'}\right]\frac{\mathbf{e}\cdot\mathbf{r}}{r}d\mathbf{r}', \qquad (14)$$

where

$$\mathbf{e} = \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad \mathbf{e}_0 = \frac{\mathbf{r}_N - \mathbf{r}'}{|\mathbf{r}_N - \mathbf{r}'|}, \quad A_{mi} = \frac{T_m}{|\mathbf{r} - \mathbf{r}'|} - \frac{K_{mi}}{|\mathbf{r}_N - \mathbf{r}'|},$$

$$\mathbf{B}_{mi} = \frac{T_m\mathbf{e}}{|\mathbf{r} - \mathbf{r}'|} - \frac{K_{mi}\mathbf{e}_0}{|\mathbf{r}_N - \mathbf{r}'|},$$

$$T_m(t) = \int_0^\infty x^m\exp\left(-x^2 - \frac{t}{x}\right)dx,$$

$$K_{mi} = \frac{\mathbf{r}_M\cdot\mathbf{r}}{r^2}\sum_{k=1}^\infty (1 - \varepsilon_i)^k T_m[R_i((k-1)|\mathbf{r}_N - \mathbf{r}_M|$$
$$+ |\mathbf{r} - \mathbf{r}_M| + |\mathbf{r}_N - \mathbf{r}'|)], \quad i = 1,2$$

The integration extends over the transverse cross-sectional area Σ of the capillary. The argument t of the functions T_m is $t = R_1|\mathbf{r} - \mathbf{r}'|$ in Eqs. (11) and (12) and $t = R_2|\mathbf{r} - \mathbf{r}'|$ in Eqs. (13) and (14).

The Eqs. (11)–(14) are Fredholm integral equations of the second kind. We employ the Bubnov–Galerkin method to solve them.[9] The advantage of this method is that it makes it possible to determine with the required degree of accuracy the quantities $\langle u_i\rangle$ and $\langle\pi_{irz}\rangle$, averaged over the cross section of the channel, without calculating their profiles $u_i(r)$ and $\pi_{irz}(r)$. The rate of convergence of the Bubnov–Galerkin method depends on the choice of approximating expressions for the macroscopic parameters. It has been established[8] that approximations of the form

$$\tilde{u}_1(r) = \frac{n_2}{n_1}\mu R_0(a_1 + a_2r^2), \quad \tilde{\pi}_{1rz}(r) = \frac{n_2}{n_1}\mu R_0 a_5 r,$$

$$\tilde{u}_2(r) = -\mu R_0(a_3 + a_4r^2), \quad \tilde{\pi}_{2rz}(r) = -\mu R_0 a_6 r \qquad (15)$$

give satisfactory accuracy (the error does not exceed $\sim 3\%$) with arbitrary Kn for the average quantities $\langle u_i\rangle$. Here a_k are unknown constants, which depend on Kn, the accommodation coefficients ε_i, and the molecular param-

eters. In addition, from the conservation of momentum for the mixture as a whole $n_1 \pi_{1rz} + n_2 \pi_{2rz} = 0$ it follows that $a_5 = a_6$.

In the Bubnov–Galerkin method the coefficients a_k are determined by requiring that the expressions obtained by substituting the approximations (15) for $u_i(r)$ and $\pi_{irz}(r)$ 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

$$(f,g) = 2\pi \int_0^1 f(r)g(r) r \, dr = 0. \tag{16}$$

In this manner we obtain the following system of linear algebraic equations:

$$\sum_{i=1}^{6} \alpha_{kl} a_l = \alpha_k, \quad k = 1,2,3,4,5,6. \tag{17}$$

The expressions for α_{kl} and α_k are complicated and are not presented here.

We choose the effective collision frequency γ_{12} in the form $\gamma_{12} = \nu_{12}^{(1)}$ and the frequency γ_{22} in the form $\gamma_{22} = \nu_{22}^{(3)} - \nu_{22}^{(4)}$. 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 $n_1 \ll n_2$ 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:

$$R_1 = \frac{8}{3\sqrt{\pi}} \left(\frac{m_2}{m_1 + m_2} \right) \frac{1}{\text{Kn}}, \quad \text{Kn} = \frac{l_1}{R_0},$$

$$l_1 = \frac{1}{\pi n_2 d_{12}^2} \sqrt{\frac{m_2}{m_1 + m_2}}, \tag{18}$$

$$\frac{R_2}{R_1} = \frac{3}{5} \left(\frac{d_2}{d_{12}} \right)^2 \sqrt{\frac{2(m_1 + m_2)}{m_2}}, \quad d_{12} = \frac{d_1 + d_2}{2}.$$

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:

$$1 - \varepsilon_i \ll 1, \quad i = 1, 2. \tag{19}$$

Linearizing the problem with respect to the small parameters $1 - \varepsilon_i$ gives

$$S_1 = S_1^{(0)} + S_1^{(1)}(1 - \varepsilon_1),$$

$$\sigma_{12} = \sigma_{12}^{(0)} + \sigma_{12}^{(1)}(1 - \varepsilon_1) + \sigma_{12}^{(2)}(1 - \varepsilon_2). \tag{20}$$

The quantities $S_1^{(0)}$ and $\sigma_{12}^{(0)}$ 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 $n_1 \ll n_2$, S_1 does not depend on the nature of the interaction between molecules of the second component and the wall.

Analytic expressions for $S_1^{(k)}$ and $\sigma_{12}^{(l)}$ can be obtained only for large and small values of Kn.

1. Almost free-molecular regime (Kn $\gg 1$ or $R \ll 1$):

Up to terms of order R^2 the kinetic coefficients have the form

$$S_1^{(0)} = 1.505R + R^2 \ln R - (0.25\Phi_1 + 0.384)R^2 + \dots , \tag{21}$$

$$S_1^{(1)} = 3.009R + 6R^2 \ln R + 3.240R^2 + \dots , \tag{22}$$

$$\sigma_{12}^{(0)} = 1.505 \left(\sqrt{\frac{m_1}{m_2}} - 1 \right) R + \left(\sqrt{\frac{m_1}{m_2}} \Phi_2 - 1 \right) R^2 \ln R$$
$$+ \left[0.25\Phi_1 + 0.384 - \sqrt{\frac{m_1}{m_2}}(2.264 - 0.25\Phi_3 \right.$$
$$\left. - 1.879\Phi_2 - \Phi_2 \ln \Phi_2) \right] R^2 + \dots , \tag{23}$$

$$\sigma_{12}^{(1)} = -3.009R - 6R^2 \ln R - \left(3.240 + 4.527\sqrt{\frac{m_1}{m_2}} \right) R^2$$
$$+ \dots , \tag{24}$$

$$\sigma_{12}^{(2)} = \sqrt{\frac{m_1}{m_2}} [3.009R + 6\Phi_2 R^2 \ln R - (4.527 - 12.294\Phi_2$$
$$- 6\Phi_2 \ln \Phi_2) R^2] + \dots , \tag{25}$$

where

$$\Phi_1 = \frac{4m_2}{5(m_1 + m_2)} - 1, \quad \Phi_2 = \frac{12}{5} \frac{\sqrt{2(1 + m_1/m_2)}}{(1 + d_1/d_2)^2},$$

$$\Phi_3 = \frac{4}{5} \frac{\sqrt{m_1/m_2}}{1 + m_1/m_2}.$$

2. Hydrodynamic regime with slipping (Kn $\ll 1$ or $R \gg 1$):

Up to terms of zeroth order the kinetic coefficients have the form

$$S_1^{(0)} = 1 + \dots , \quad S_1^{(1)} = O\left(\frac{1}{R} \right), \tag{26}$$

$$\sigma_{12}^{(0)} = \frac{1}{2} \sqrt{\frac{m_1}{m_2}} \left(1 + \frac{\Phi_2 + \Phi_3}{1 - \Phi_1} \right) - 1 + \dots , \tag{27}$$

$$\sigma_{12}^{(1)} = -\frac{1}{2} \sqrt{\frac{m_1}{m_2}} \left(1 + \frac{\Phi_2 + \Phi_3}{1 - \Phi_1} \right) + \dots , \tag{28}$$

$$\sigma_{12}^{(2)} = \sqrt{\frac{m_1}{m_2}} + \dots . \tag{29}$$

The numerical results for intermediate values of Kn for He–Ar and Na–He mixtures displayed in Figs. 2–4.

FIG. 3. Comparison of theory (solid lines) and experiment:[5] Curve 1 corresponds to $\varepsilon_{Ar} = \varepsilon_{He} = 1$, and curve 2 to $\varepsilon_{Ar} = 0.98$, $\varepsilon_{He} = 0.92$.
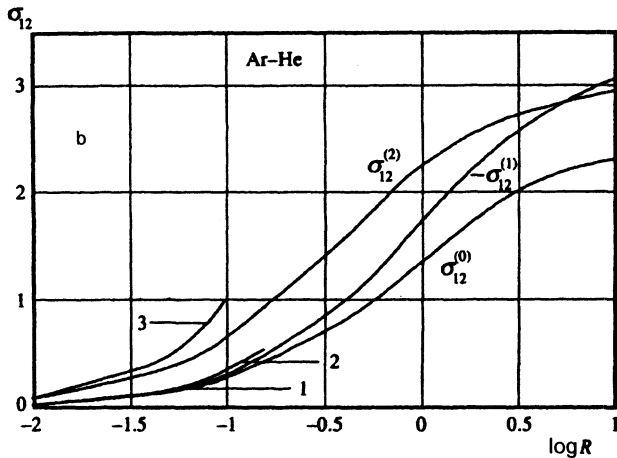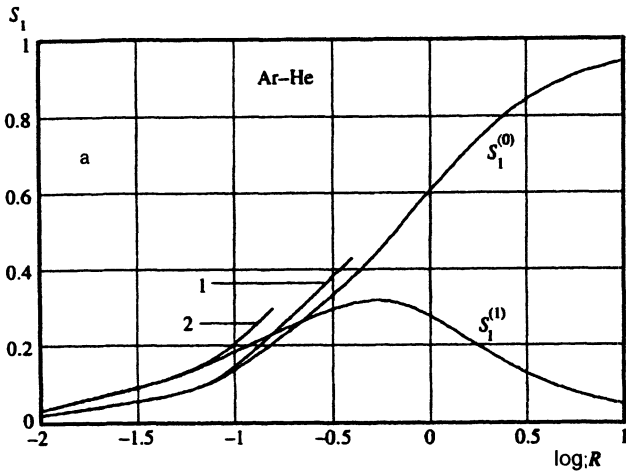

FIG. 2. $S_1^{(0)}$ and $S_1^{(1)}$ components of the diffusion factor (a) and $\sigma_{12}^{(0)}$, $\sigma_{12}^{(1)}$, and $\sigma_{12}^{(2)}$ components of the diffusion slipping coefficient (b) as a function of the rarefaction parameter R for an Ar–He gas mixture: a) 1—Eq. (21), 2—Eq. (22); b) 1—Eq. (23), 2—Eq. (24), 3—Eq. (25).

4. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

The results of the model calculation of the quantities $S_i^{(k)}$ and $\sigma_{12}^{(k)}$ 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 $S_i^{(0)}$ 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 $S_i^{(0)}$ is ~4%. This dependence is incorporated in the parameter R itself [see Eq. (18)].

The diffusion slipping coefficient σ_{12} in the limit of small Kn (27)–(29) is of interest in its own right. In this limit σ_{12} 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 simi-
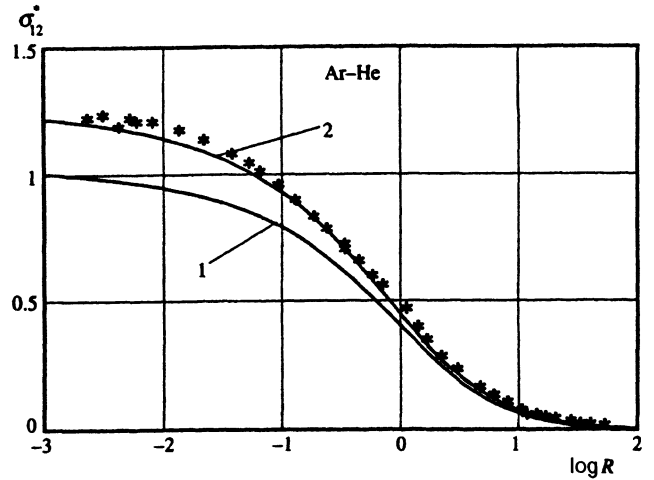
lar masses and effective diameters of the molecules. We also assume that the partial accommodation coefficients differ by a small amount. In this case the expression for σ_{12} can be written in the form
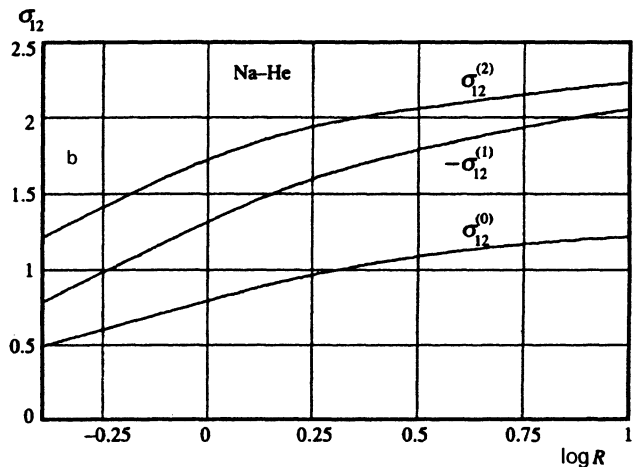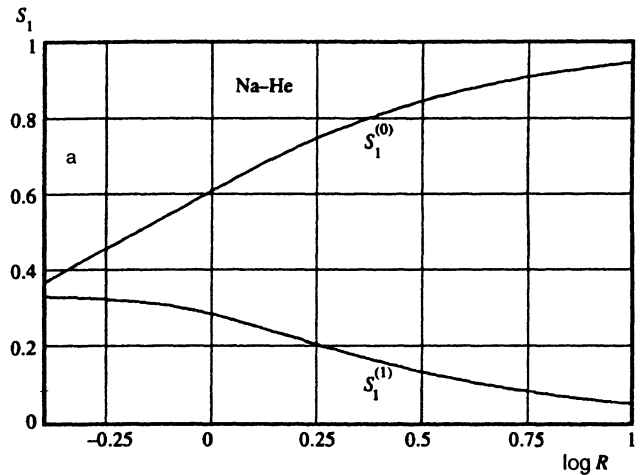

FIG. 4. $S_1^{(0)}$ and $S_1^{(1)}$ components of the diffusion factor (a) and $\sigma_{12}^{(0)}$, $\sigma_{12}^{(1)}$, and $\sigma_{12}^{(2)}$ components of the diffusion slipping coefficient (b) as a function of the rarefaction parameter R for a Na–He gas mixture.

V. G. Chernyak and E. A. Vilisova   84

TABLE I. $S_1^{(0)}$ and $S_1^{(1)}$ components of the diffusion factor as a function of m_1/m_2.

| | $S_1^{(0)}$ | | | $S_1^{(1)}$ | | |
| | m_1/m_2 | | | m_1/m_2 | | |
R	0.1	1	10	0.1	1	10
0.01	0.0146	0.0146	0.0146	0.0276	0.0276	0.0276
0.1	0.123	0.124	0.125	0.185	0.185	0.185
0.4	0.357	0.361	0.366	0.339	0.334	0.329
1	0.591	0.600	0.609	0.314	0.299	0.285
4	0.868	0.873	0.877	0.124	0.114	0.107
10	0.945	0.947	0.948	0.0530	0.0506	0.0489

$$\sigma_{12}=a\frac{m_1-m_2}{m_1+m_2}-b\frac{d_1-d_2}{d_1+d_2}+c(\varepsilon_1-\varepsilon_2). \qquad (30)$$

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:

$$a=0.7-1.29, \quad b=0-1.18, \quad c=0.667-2.$$

According to experiments[11] on diffusiophoresis of oil drops in binary gas mixtures $a=0.95$ and $b=1.05$.

Table III gives the computational results for σ_{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 $m_1=m_2$, $\varepsilon_1=\varepsilon_2$, 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$_2$,[12] N$_2$–C$_2$H$_4$,[11,12] C$_2$H$_4$–Ne,[13] and He–D$_2$.[14]

In the case of physically indistinguishable molecules $(m_1=m_2, d_1=d_2, \varepsilon_1=\varepsilon_2)$, a relative fraction x_i of which is tagged, there exist diffusion fluxes of the components (self-diffusion) and a molar flux of the mixture as a whole. The functional dependence of the fluxes on Kn changes. In

the almost free-molecular regime (Kn$\gg$1) $S_i\sim R$ and $\sigma_{12}\sim R^2\ln R$, and in an almost continuous medium (Kn $\ll$1) $S_i\sim 1$ and $\sigma_{12}\sim 1/R$. Obviously, the latter results for Kn$\ll$1 cannot be obtained on the basis of the standard Knudsen layer theory, where the motion of a gas along a flat wall in the half-space is studied.

The quantities $S_i^{(0)}$, $S_i^{(1)}$, $\sigma_{12}^{(0)}$, $\sigma_{12}^{(1)}$, and $\sigma_{12}^{(2)}$ are displayed in Figs. 2(a) and (b) as functions of the rarefaction parameter R for the Ar–He mixture. One can see that in the hydrodynamic regime with slipping $(R\geqslant 10)$, the contribution of the accommodation component $S_1^{(1)}$ to the diffusion factor S_1 is negligible. This means that for $R\geqslant 10$ and $(1-\varepsilon_i)\ll 1$ the diffusion fluxes are essentially independent of the character of the interaction between the molecules and the capillary surface. The accommodation components $\sigma_{12}^{(1)}$ and $\sigma_{12}^{(2)}$ of diffusion slipping coefficient σ_{12} are important for any regime of motion of the gas.

The diffusion factors $S_i^{(0)}$ 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 $S_i=1$ 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 II. $\sigma_{12}^{(0)}$, $\sigma_{12}^{(1)}$, and $\sigma_{12}^{(2)}$ components of the diffusion slipping coefficient as a function of m_1/m_2 for $d_1/d_2=1$.

| | $\sigma_{12}^{(0)}, 10^{-3}$ | | | $-\sigma_{12}^{(1)}, 10^{-2}$ | | | $\sigma_{12}^{(2)}, 10^{-2}$ | | |
| | m_1/m_2 | | | m_1/m_2 | | | m_1/m_2 | | |
R	0.1	1	10	0.1	1	10	0.1	1	10
0.01	-9.94	-0.0411	30.6	2.78	2.81	2.89	0.891	2.78	8.41
0.1	-84.3	-1.030	257	19.4	21.1	26.6	6.77	20.7	59.4
0.4	-244	-36.2	813	39.9	52.3	94.9	16.9	51.5	151
1	-407	-5.20	1520	45.6	74.8	186	24.6	74.4	225
4	-606	-2.76	2589	37.0	89.7	311	29.7	90.1	278
10	-663	-0.758	2892	32.6	94.1	359	30.5	94.4	296

TABLE III. $\sigma_{12}^{(0)}$, $\sigma_{12}^{(1)}$, and $\sigma_{12}^{(2)}$ components of the diffusion slipping coefficient as a function of d_1/d_2 for $m_1/m_2=1$.

| | $\sigma_{12}^{(0)}, 10^{-3}$ | | | $-\sigma_{12}^{(1)}, 10^{-2}$ | | | $\sigma_{12}^{(2)}, 10^{-2}$ | | |
| | d_1/d_2 | | | d_1/d_2 | | | d_1/d_2 | | |
R	0.5	1	1.5	0.5	1	1.5	0.5	1	1.5
0.01	-0.180	-0.0411	0.0413	2.80	2.81	2.81	2.71	2.78	2.83
0.1	-2.55	-1.03	0.464	21.1	21.1	21.1	19.4	20.7	21.7
0.4	7.65	-36.2	-5.25	52.9	52.3	52.2	49.0	51.5	54.0
1	58.3	-5.20	-28.8	79.7	74.8	73.0	73.1	74.4	76.5
4	208	-2.76	-96.1	109	89.7	81.3	90.8	90.1	89.8
10	262	-0.758	-121	119	94.1	82.9	95.0	94.4	93.9

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.[4] 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 σ_{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 $R_0\mu\Delta d/d$. Since $R_0\mu \ll 1$ and $\Delta d/d \ll 1$, these corrections can be neglected.

In Fig. 3 the theory is compared with an experiment[14] on the diffusion slipping of a Ar–He mixture. The quantity σ_{12}^* represents the ratio of σ_{12} to the free-molecular value $\sigma_{12}^{(0)}$ [the first term in the expression (23)]. In Ref. 14 the experimental values of σ_{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 $n_{Ar}/n_{He} \approx 0.08$. One can see from Fig. 3 that the discrepancy between the theory with $\varepsilon_{Ar} = \varepsilon_{He} = 1$ (curve 1) and the experimental data is greatest in the free-molecular regime and is ~20%. The theoretical curve (2), corresponding to the accommodation coefficients $\varepsilon_{Ar} = 0.98$ and $\varepsilon_{He} = 0.92$, satisfactorily describes the experiment for $R \leq 1$. We note that the accommodation coefficients $\varepsilon_{Ar} = 0.975$ and $\varepsilon_{He} = 0.935$

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 $n_1 \ll n_2$ 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.

[1] V. G. Chernyak, Prikl. Mekh. Tekh. Fiz., No. 5, 50 (1982).
[2] V. M. Zhdanov and V. A. Zaznoba, Inzh.-Fiz. Zh. **65**, 403 (1983).
[3] N. D. Pochuev, V. D. Seleznov, and P. E. Suetin, Prikl. Mekh. Tekh. Fiz., No. 5, 37 (1974).
[4] V. G. Chernyak and E. A. Vilisova, Zh. Éksp. Teor. Fiz. **107**, 125 (1995) [JETP **80**, 65 (1995)].
[5] S. N. Atutov, I. M. Ermolaev, and A. M. Shalagin, Zh. Éksp. Teor. Fiz. **92**, 1215 (1987) [Sov. Phys. JETP **65**, 679 (1987)].
[6] F. J. McCormack, Phys. Fluids **16**, 2095 (1973).
[7] S. Chapman and T. G. Cowling, *Mathematical Theory of Nonuniform Gases*, 2nd ed. Cambridge University Press, New York (1952).
[8] V. G. Chernyak, B. T. Porodnov, and P. E. Suetin, Zh. Tekh. Fiz. **43**, 2420 (1973) [Sov. Phys. Tech. Phys. **18**, 1526 (1974)].
[9] S. G. Mikhlin, *Variational Methods in Mathematical Physics*, Pergamon Press, New York (1964) [Russian original, Nauka, Moscow, 1970].
[10] V. M. Zhdanov and R. V. Smirnova, Prikl. Mekh. Tekh. Fiz., No. 5, 103 (1978).
[11] K. H. Schmitt and L. Waldmann, Z. Naturforsch. **15a**, 843 (1960).
[12] L. Waldmann and K. H. Schmitt, Z. Naturforsch **16a**, 1343 (1961).
[13] H. Lang and K. Eger, Z. Phys. Chem. Neue Folge **68**, 130 (1969).
[14] A. A. Tarin, Candidate's Dissertation in Physical-Mathematical Sciences, Ural Polytechnical Institute, Sverdlovsk (1978).

Translated by M. E. Alferieff