

Let us consider the influence of the Mach number and the angle of attack on the location of the center of pressure of models of blunted bodies of small length. In subsonic flow over a model of a segmental body with $R/D = 1.46$ the center of pressure c_p moves from 2-5 calibers ahead of the model at $\alpha = 5^\circ$ to 2.5-20 calibers behind the model at $\alpha = 10^\circ$ as a result of a change in the sign of the normal force. In supersonic flow over segments both the angle of attack and the Mach number have a weak effect on the location of the center of pressure, which is located behind the model (by 3-5 calibers for a model with $R/D = 1.46$, for example). For blunted cones the location of the center of pressure is at a distance of 0.3-1.5 calibers behind the model and depends little on the blunting radius. With an increase in the Mach number the center of pressure approaches the model (see Fig. 2c).

In the case of flow over cones having a beveled base the value of c_p grows as the angle of attack increases. Edges cut off parallel have little effect on the location of the center of pressure of a blunted cone in the investigated range of Mach numbers and angles of attack.

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DIFFUSION SLIP AND BARODIFFUSION OF A GASEOUS MIXTURE IN PLANE AND CYLINDRICAL CHANNELS

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In the forced flow of a gaseous mixture in a capillary or a porous medium in a field of partial-pressure gradients, a number of effects occur (the diffusion baroeffect [1, 2], the mixture-separation effect [3, 4], etc.), a rigorous analysis of which requires the inclusion of Boltzmann's kinetic equation. The main object of the kinetic consideration in this case is to obtain expressions for the flows of the mixture components, averaged over the cross section of the channel or referred to unit surface of the porous medium. This problem has been solved in a number of papers [5-7] for channels of correct geometry (a plane slit or a circular cylindrical capillary) using the linearized kinetic equation with the model BGK integral of the collisions in the Hamel form [8]. In [9] the flow of a mixture in a plane channel was considered using the accurate linearized collision operator, but subsequent use of the moment method of solution was confined to the solid-sphere model of the molecules. The limitation of the models used does not enable the accuracy of the results obtained to be guaranteed, particularly with regard to such kinetic quantities as the diffusion slip coefficient or the barodiffusion constant of the gaseous mixture in the channel. It is well known, in particular [8], that no matter how the parameters of the slip in the BGK model for the mixture are chosen, it is not possible to ensure an adequate description of the diffusion and the viscosity of the mixture simultaneously even for normal hydrodynamic flow. Below we solve the problem of the flow of a mixture in a channel using the linearized kinetic equation with the collision operator in the model form proposed by McCormack [10]. The advantage of this model, based on the equivalence of the N-order mo-

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ments of the accurate and the model integrals, is the fact that it automatically gives a correct description of the mixture in the hydrodynamic limit for an arbitrary interaction between the molecules. For the case of isothermal flow of the mixture considered here, satisfactory approximation is obtained for $N=2$, when the diffusion velocity and the partial tensor of the viscous stresses are defined by the moments of the distribution function, in addition to the density, the mean-mass velocity, and the temperature. The method of solution used is limited to the region small Knudsen numbers ($Kn=\lambda/d$, where λ is the effective mean free path of the molecules and d is the characteristic transverse dimension of the channel). In this case the region of mixture flow in the channel can be divided into two: the region far from the walls where the usual hydrodynamic approximations hold, and a thin region close to the walls (the Knudsen layer), the solution in which must be considered taking into account the true boundary conditions for the distribution function on the walls of the channel and the asymptotic conditions on the external boundary of the layer. The solution of the problem in the external region gives an expression for the velocities of each of the components of the mixture in the channel with certain fictional macroscopic boundary conditions on its walls. These conditions are found by solving the kinetic equation in the Knudsen layer, for which the method of total moments is used. This formulation of the problem is closely connected with the problem of determining the diffusion slip velocity of a mixture [11-14], in view of the fact that the consideration begins with precisely this case. The problem is then generalized to the case of the flow of a mixture in plane and cylindrical channels when there are both concentration gradients and a gradient of the total pressure of the mixture present. It is known in this case, in particular, that the baro-diffusion constant in the expression for the difference in the velocity components averaged over the cross section is equal to (with opposite sign) the diffusion slip coefficient, which agrees with the general conclusions of the thermodynamics of irreversible processes [15].

1. Diffusion Slip. Suppose the gaseous mixture occupies the half-space $x > 0$ above the plane $x=0$. There is a gradient of the partial density of the component $k_\alpha = n_\alpha^{-1} dn_\alpha/dz$ in the z direction, the total pressure of the mixture p and the temperature T being assumed constant. Far from the walls there is a constant gradient of the longitudinal mean-mass velocity of the mixture $\partial u_z^{as}(x)/\partial x$, normal to the surface of the walls. For small values of the gradients, the solution for the distribution function of the particles of the α -sort, can be sought in the form

$$f_\alpha = f_\alpha^{(0)}(1 + \Phi_\alpha),$$

$$f_\alpha^{(0)} = n_\alpha(z) \left(\frac{\beta_\alpha}{\pi}\right)^{3/2} \exp(-\beta_\alpha v^2), \quad \beta_\alpha = m_\alpha/2kT,$$

where $\Phi_\alpha(v, x)$ satisfies the linearized kinetic equation [14]

$$v_z k_\alpha + v_x \frac{\partial \Phi_\alpha}{\partial x} = \sum_\beta \widehat{L}_{\alpha\beta}^{(N)} \Phi_\alpha \quad (1.1)$$

with the collision operator specified in the form [10]

$$\widehat{L}_{\alpha\beta}^{(2)} \Phi_\alpha = -\gamma_{\alpha\beta} \Phi_\alpha + 2 \left\{ \gamma_{\alpha\beta} q_{\alpha z} - \left[q_{\alpha z} - \left(\frac{m_\alpha}{m_\beta}\right)^{1/2} q_{\beta z} \right] v_{\alpha\beta}^{(1)} c_{\alpha z} + 2 \left\{ (\gamma_{\alpha\beta} - v_{\alpha\beta}^{(2)}) \frac{\Pi_{\alpha xz}}{p_\alpha} + v_{\alpha\beta}^{(3)} \frac{\Pi_{\beta xz}}{p_\beta} \right\} c_{\alpha x} c_{\alpha z} \right\} \Phi_\alpha, \quad (1.2)$$

where $c_\alpha = \beta_\alpha^{1/2} v$; $\gamma_{\alpha\beta}$ is a certain effective collision frequency; $q_{\alpha z} = \beta_\alpha^{1/2} v_z$ is the dimensionless macroscopic velocity of the α -component; $\Pi_{\alpha xz}$ is the partial tensor of the viscous stresses; $p_\alpha = n_\alpha kT$, and by definition

$$q_{\alpha z} = \pi^{-3/2} \int c_{\alpha z} \exp(-c_\alpha^2) \Phi_\alpha dc_\alpha,$$

$$\Pi_{\alpha xz} = 2p_\alpha \pi^{-3/2} \int c_{\alpha x} c_{\alpha z} \exp(-c_\alpha^2) \Phi_\alpha dc_\alpha.$$

The quantities $v_{\alpha\beta}^{(1)}$, $v_{\alpha\beta}^{(2)}$, and $v_{\alpha\beta}^{(3)}$ are given by the expressions

$$v_{\alpha\beta}^{(1)} = \frac{16}{3} \frac{\mu_{\alpha\beta}}{m_\alpha} n_\beta \Omega_{\alpha\beta}^{(11)} = \frac{n_\beta kT}{m_\alpha n [D_{\alpha\beta}]_1},$$

$$v_{\alpha\beta}^{(2)} = \frac{16}{5} \frac{\mu_{\alpha\beta}}{m_\alpha + m_\beta} n_\beta \left[\frac{10}{3} \Omega_{\alpha\beta}^{11} + \frac{m_\beta}{m_\alpha} \Omega_{\alpha\beta}^{22} \right],$$

$$v_{\alpha\beta}^{(3)} = \frac{16}{5} \frac{\mu_{\alpha\beta}}{m_\alpha + m_\beta} n_\beta \left[\frac{10}{3} \Omega_{\alpha\beta}^{11} - \Omega_{\alpha\beta}^{22} \right],$$

where $\Omega_{\alpha\beta}^{lr}$ are well-known Chapman-Cowling integrals [16]; $[D_{\alpha\beta}]_1$ is the coefficient of mutual diffusion of the α and β molecules (the first Chapman-Enskog approximation [16]); $\mu_{\alpha\beta}$ is the reduced mass of the molecules.

Multiplying Eq. (1.1) successively by $c_z \exp(-c_\alpha^2)$ and $c_x c_z \exp(-c_\alpha^2)$ and integrating with respect to the velocities, we obtain the following equations for the moments:

$$p_\alpha k_\alpha + \frac{\partial \Pi_{\alpha xz}}{\partial x} = \sum_{\beta} \frac{n_\alpha n_\beta kT}{n [D_{\alpha\beta}]_1} (u_{\beta z} - u_{\alpha z}); \quad (1.3)$$

$$\sum_{\beta} a_{\alpha\beta} \frac{\Pi_{\beta xz}}{y_\beta} = -y_\beta \beta_\alpha^{-1/2} \frac{\partial Q_{\alpha z}}{\partial x}, \quad (1.4)$$

where

$$a_{\alpha\alpha} = \frac{y_\alpha}{p} \left(v_{\alpha\alpha}^{(2)} - v_{\alpha\alpha}^{(3)} + \sum_{\beta \neq \alpha} v_{\alpha\beta}^{(2)} \right); \quad a_{\alpha\beta} = -\frac{y_\alpha}{p} v_{\alpha\beta}^{(3)}, \quad \beta \neq \alpha.$$

Here $y_\alpha = p_\alpha/p$ is the relative concentration of the α component and the quantity $Q_{\alpha z}$ is defined by the expression

$$Q_{\alpha z} = 2\pi^{-3/2} \int c_{\alpha x} c_{\alpha z} \exp(-c_\alpha^2) \Phi_\alpha d\mathbf{c}_\alpha. \quad (1.5)$$

Far from the walls the distribution function of the α -component must satisfy the well-known Chapman-Enskog [16] or Gred [17] expansions. When choosing the model collision integral in the form (1.2), an adequate description of the gaseous mixture in this region is ensured by specifying f_α in the form of the ten-moment Gred approximation [17]

$$f_\alpha = n_\alpha \left(\frac{\beta_\alpha^{3/2}}{\pi} \right) \exp[-\beta_\alpha (\mathbf{v} - \mathbf{u})^2] \left[1 + \frac{m_\alpha}{kT} \mathbf{w}_\alpha (\mathbf{v} - \mathbf{u}) + \frac{m_\alpha}{kT} \frac{\Pi_{\alpha rs}}{p_\alpha} (v_r - u_r)(v_s - u_s) \right], \quad (1.6)$$

where $\mathbf{w}_\alpha = \mathbf{u}_\alpha - \mathbf{u}$ (\mathbf{u} is the mean-mass velocity of the mixture). For the case of slow flow of the mixture considered, here the linearization (1.6), taking into account the smallness of the quantities $\beta_\alpha^{1/2} u_z, \beta_\alpha^{1/2} \mathbf{w}_{\alpha z}, \Pi_{\alpha xz}/p_\alpha$, leads to the following result:

$$f_\alpha^{\text{as}} = f_\alpha^{(0)} (1 + \Phi_\alpha^{\text{as}}), \quad \Phi_\alpha^{\text{as}} = 2c_{\alpha z} q_{\alpha z}^{\text{as}} + 2 \frac{\Pi_{\alpha xz}^{\text{as}}}{p_\alpha} c_{\alpha x} c_{\alpha z}. \quad (1.7)$$

Substituting (1.7) into (1.5) and integrating we obtain $Q_{\alpha z} = q_{\alpha z}^{\text{as}}$, i.e., in this region, instead of (1.4), the following equation holds:

$$\sum_{\beta} a_{\alpha\beta} \frac{\Pi_{\beta xz}^{\text{as}}}{y_\beta} = -y_\alpha \frac{\partial u_{\alpha z}^{\text{as}}}{\partial x}. \quad (1.8)$$

For a two-component mixture simultaneous solution of Eqs. (1.3) and (1.8) leads to the result ($\alpha, \beta = 1, 2$; $\alpha \neq \beta$)

$$u_{\alpha z}^{\text{as}} = u_{\alpha z}^{\text{as}}(0) + \frac{\eta_\beta}{\eta} [U_{\alpha\beta}^0 - U_{\alpha\beta}^{\text{as}}(0)] [1 - \exp(-sx)] + \frac{\partial u_z^{\text{as}}(x)}{\partial x} x. \quad (1.9)$$

Here $u_{\alpha z}^{\text{as}}(0)$ are fictional values of the macroscopic velocities of the components on the wall $U_{\alpha\beta}^{\text{as}}(x) = u_{\alpha z}^{\text{as}}(x) - u_{\beta z}^{\text{as}}(x)$, and in addition

$$U_{\alpha\beta}^0 = -\frac{[D_{\alpha\beta}]_1}{y_\alpha y_\beta} \frac{dy_\alpha}{dz}, \quad s^{-2} = \frac{y_\alpha y_\beta [D_{\alpha\beta}]_1}{p |a| \eta}, \quad (1.10)$$

$$\eta_\alpha = y_\alpha \sum_{\beta=1}^2 y_\beta \frac{|a|_{\beta\alpha}}{|a|}, \quad \eta = \sum_{\alpha} \eta_\alpha,$$

where $|a|$ is the determinant of system (1.8), and $|a|_{\beta\alpha}$ is the cofactor of the element $a_{\beta\alpha}$ of the determinant. Note that the quantities η_α agree by definition with the partial viscosities introduced in [17].

TABLE 1

Coeff.	Method of calc.	Elementary consideration [1]	13-moment approx. [12]	Variational method [14, 19]		Semispace-moments method [9, 15]	Present paper		BGK model			Empirical formula [22]
				first approx.	second approx.		first approx.	second approx.	total-moments method [7]	semispace-moments method [5, 13, 20]	variational method [6, 21]	
a	1,00	1,14	1,07	1,29	0,946	1,06	1,05	0,735 0,688	0,700 0,651	0,750 0,688	1,05	
b	0	0,068	0,750	0,598	1,0	0,753	0,850	1,06 0,753	1,18 0,838	1,00 0,750		
c	2,00	1,93	2,00	1,90	2,0	0,995	0,924	0,940 0,995	0,667 0,717	1,00 1,00		

TABLE 2

Mixture	Exptl. data	Variational method [19] ($b_1 = b_2 = 1$)	Present paper			
			$b_1 = b_2 = 1$		$b_1 \neq b_2$	
			first approx.	second approx.	first approx.	second approx.
$N_2-C_2H_4$	0,073 [22] 0,04 [2]	0,10	0,11	0,12	0,093	0,10
$CO_2-C_3H_8$	0,11 [22]	0,11	0,12	0,13	—	—
$Ar-CO_2$	0,026 [2]	0,031	0,040	0,050	0,034	0,044

Below we also require an expression for $\Pi_{\alpha XZ}^{as}$, which follows from (1.8) and (1.9)

$$\Pi_{\alpha XZ}^{as} = -\eta_{\alpha} \frac{\partial u_z^{as}(x)}{\partial x} - \frac{v_{\alpha\beta}^2}{|\alpha|\eta} s [U_{\alpha\beta}^0 - U_{\alpha\beta}^{as}(0)] \exp(-sx). \quad (1.11)$$

The relations obtained determine the behavior of the fundamental macroscopic quantities of the mixture outside the Knudsen layer. They simultaneously completely define the form of the asymptotic distribution function (1.7) on the external boundary of this layer. Note that in the traditional approach to determining the velocity of diffusion slip [11-14] the usual well-known Chapman-Enskog [16] or Gred [17] solutions are used as the asymptotic distribution function, in which the viscous stresses are independent of the diffusion velocities of the components. In fact, this corresponds to the determination of $\Pi_{\alpha XZ}$ from equations of form (1.8) in which instead of $\partial u_z^{as}/\partial x$ we have the derivative of the mean-mass velocity of the mixture $\partial u_z^{as}/\partial x$. It can be shown that in this case it follows from Eqs. (1.3) that $U_{\alpha\beta}^{as} = U_{\alpha\beta}^0 = U_{\alpha\beta}^{as}(0)$. Since $U_{\alpha\beta}^{as}(0)$ is known, the problem reduces to determining the values of the mean-mass (or mean-molar) velocity of the mixture on the walls $u_z^{as}(0)$, which is also called the slip velocity. In our case $U_{\alpha\beta}^{as} = u_{\alpha Z}^{as} - u_{\beta Z}^{as}$ varies over the cross section of the channel, i.e., besides $u_z^{as}(0)$ or, which is the same thing, to determine independently the quantities $u_{1Z}^{as}(0)$ and $u_{2Z}^{as}(0)$. The derivation of relations of form (1.8) is considered in [18], where the occurrence of a dependence of the viscous stresses on the diffusion velocities of the components was associated with the use (within the framework of the 13-moment approximation) of the expansion of the distribution function in terms of Maxwellian quantities for the mean partial velocity of the mixture component. It is easy to show, however, that these relations follow from the usual 10-moment (or 13-moment) Gred approximation if, in the equations for $\Pi_{\alpha XZ}$ in [17], we keep together with $\partial u_z/\partial x$ the term of the form $(2/5)\partial q_{\alpha Z}/\partial x$. In fact, since when there is no temperature gradient (and neglecting small thermodiffusion corrections) $q_{\alpha Z} = (5/2)p_{\alpha} w_{\alpha Z}$ [17], consideration of this term quickly leads to (1.8).

We will now determine $u_{\alpha Z}^{as}(0)$. We will seek a solution for Φ_{α} in the form

$$\Phi_{\alpha} = c_{\alpha x} h_{\alpha}(c_{\alpha x}, x)$$

and we introduce a distribution function for the incident and reflected molecules such that $h_{\alpha} = h_{\alpha}^{+}$ for $c_{\alpha x} > 0$ and $h_{\alpha} = h_{\alpha}^{-}$ for $c_{\alpha x} < 0$.

Assigning the usual Maxwellian conditions for the reflection of the molecules on the walls, we have

$$h_{\alpha}^{+}(c_{\alpha x}, 0) = (1 - \kappa_{\alpha}) h_{\alpha}^{-}(-c_{\alpha x}, 0), \quad c_{\alpha x} > 0, \quad (1.12)$$

where κ_{α} is the fraction of the particles of the α -sort, which suffer diffuse reflection at the walls.

The solution for h_{α}^{\pm} will be sought in the form of the expansion

$$h_{\alpha}^{\pm} = 2 \sum_{k=0}^{\infty} a_{k\alpha}^{\pm}(x) c_{\alpha x}^k,$$

the coefficients of which satisfy the system of moment equations obtained by multiplying (1.1) by $c_{\alpha x}^n \exp(-c_{\alpha x}^2)$, and integrating over the whole of velocity space.

We will first consider the approximation ($k=0$), for which $h_{\alpha}^{\pm} = 2a_{0\alpha}^{\pm}$. In this case

$$q_{\alpha z} = \frac{1}{2}(a_{0\alpha}^+ + a_{0\alpha}^-), \quad \Pi_{\alpha xz} = \frac{p_{\alpha}}{\sqrt{\pi}}(a_{0\alpha}^+ - a_{0\alpha}^-), \quad Q_{\alpha z} = q_{\alpha z}.$$

The condition on the wall $a_{0\alpha}^+ = (1 - \kappa_{\alpha}) a_{0\alpha}^-$ takes the form

$$q_{\alpha z}(0) = -\frac{\pi^{1/2} 2 - \kappa_{\alpha}}{2} \frac{\Pi_{\alpha xz}(0)}{p_{\alpha}}. \quad (1.13)$$

It is easy to show that the system of moment equations ($n=0.1$) reduces in this case to equations of the form (1.3) and (1.8), i.e., we can use the solutions (1.9) and (1.11), assuming $u_{\alpha}^{\text{as}}(0) = u_{\alpha}(0)$ and $\Pi_{\alpha xz}^{\text{as}}(0) = \Pi_{\alpha xz}(0)$. Then, condition (1.13) reduces to a system of two algebraic equations for $u_1^{\text{as}}(0)$ and $u_2^{\text{as}}(0)$, by expanding which we obtain

$$u_{\alpha}^{\text{as}}(0) = b_{\alpha} \left[\frac{m_{\beta}^{1/2} y_{\beta}}{(m^{1/2} b)_y} \frac{\Lambda}{1 + \Lambda} U_{\alpha\beta}^0 + \left(\frac{\pi k T}{2} \right)^{1/2} \frac{1}{1 + \Lambda} \left(\frac{\eta_{\alpha}}{m_{\alpha}^{1/2} p_{\alpha}} + b_{\beta} \frac{\eta}{p} \frac{\Lambda}{(m^{1/2} b)_y} \right) \frac{\partial u_z^{\text{a}}(x)}{\partial x} \right] \quad (1.14)$$

$$(\alpha, \beta = 1, 2; \alpha \neq \beta),$$

where

$$\Lambda = \left(\frac{\pi k T}{2} \right)^{1/2} \frac{(m^{1/2} b)_y}{m_1^{1/2} m_2^{1/2}} \frac{1}{s [D_{121}]}; \quad (m^{1/2} b)_y = b_2 m_1^{1/2} y_1 + b_1 m_2^{1/2} y_2;$$

$$b_{\alpha} = \frac{2 - \kappa_{\alpha}}{\kappa_{\alpha}} \quad (\alpha = 1, 2).$$

We will define the diffusion slip velocity u_D as the value of the mean-molar velocity of the mixture $u_Z^{\text{m}} = \sum_{\alpha} y_{\alpha} u_{\alpha z}^{\text{as}}$ as $x \rightarrow \infty$, assuming in this case that $\partial u_Z^{\text{as}}(x)/\partial x = 0$. We then have

$$u_D = y_1 u_1^{\text{as}}(0) + y_2 u_2^{\text{as}}(0) + \frac{\eta_2 y_1 - \eta_1 y_2}{\eta} [U_{12}^0 - U_{12}^{\text{as}}(0)].$$

Using (1.14), we obtain after simple reduction

$$u_D = -\sigma_{12} y_1 y_2 U_{12}^0 = \sigma_{12} D_{12} \frac{dc_1}{dz}, \quad \sigma_{12} = \frac{\Lambda}{1 + \Lambda} \sigma_{12}^k + \frac{1}{1 + \Lambda} \sigma_{12}^b, \quad \sigma_{12}^k = \frac{m_1^{1/2} b_2 - m_2^{1/2} b_1}{(m^{1/2} b)_y}, \quad \sigma_{12}^b = \frac{1}{\eta} \left(\frac{\eta_1}{y_1} - \frac{\eta_2}{y_2} \right). \quad (1.15)$$

Note that σ_{12}^k when $b_1 = b_2 = 1$ (total diffuse reflection) corresponds to the diffusion slip coefficient obtained in [1, 11], and σ_{12}^b is equal to (with opposite sign) the barodiffusion constant in viscous flow obtained in [17].

The calculation of the velocity u_D in the second approximation ($k=0,1$) is considered in the appendix.

2. Diffusion and Barodiffusion of a Mixture in a Channel. A Plane Channel. Consider the flow of a mixture in a channel bounded at $y = \pm d/2$ by two infinite parallel planes. In the z direction, as previously, there is a gradient of the partial density of the component k_{α} , and $\sum_{\alpha} p_{\alpha} k_{\alpha} = dp/dz \neq 0$. The linearized kinetic equation for this case keeps the form (1.1), and the equations of moments (1.3) and (1.4) remain true. For small Knudsen numbers the solution of Eqs. (1.3) and (1.8), which holds in the region far from the walls at a distance of the order of several mean free paths, leads to the relations

$$u_{1z} = -\frac{1}{2\eta} \left(\frac{d^2}{4} - y^2 \right) \frac{dp}{dz} + u_1 \left(\frac{d}{2} \right) + \frac{\eta_2}{\eta} \left[U_{12}^0 - U_{12}^{\text{as}} \left(\frac{d}{2} \right) \right] \left[1 - \frac{\text{ch } sy}{\text{ch } (sd/2)} \right], \quad (2.1)$$

$$U_{12} = u_1 - u_2 = U_{12}^0 \left[1 - \frac{\text{ch } sy}{\text{ch } (sd/2)} \right] + U_{12}^{\text{as}} \left(\frac{d}{2} \right) \frac{\text{ch } sy}{\text{ch } (sd/2)};$$

$$\Pi_{1xz} = -y \frac{\eta_1}{\eta} \frac{dp}{dz} - \frac{y_1^2 y_2^2}{|a| \eta} s \left[U_{12}^0 - U_{12}^{\text{as}} \left(\frac{d}{2} \right) \right] \frac{\text{sh } sy}{\text{ch } (sd/2)}, \quad (2.2)$$

$$\Pi_{xz} = \Pi_{1xz} + \Pi_{2xz} = -y \frac{dp}{dz},$$

where

$$U_{12}^{as}\left(\frac{d}{2}\right) = u_1^{as}\left(\frac{d}{2}\right) - u_2^{as}\left(\frac{d}{2}\right);$$

$$U_{12}^0 = -\frac{[D_{12}]_1}{y_1 y_2} \left[\frac{dy_1}{dz} + \alpha_p^b y_1 y_2 \frac{1}{p} \frac{dp}{dz} \right]; \quad \alpha_p^b = -\sigma_{12}^b.$$

We will introduce the variable $x = y + d/2$ and consider the behavior of the quantities (2.1) and (2.2) close to the lower wall for $x \sim \delta$, where δ is the effective thickness of the Knudsen layer. Note that the quantity s is of the order of the inverse mean free path, i.e., $sd \gg 1$. Using the condition $\delta/d \gg 1$, we obtain that the expressions (2.1) and (2.2) on the external boundary of the Knudsen layer reduce to the expressions (1.9) and (1.11), which were used in the slip problem, with $(-d/2\eta) dp/dz$ replaced by $\partial u_Z^{as}(x)/\partial x$. Then, the problem of determining $u_{\alpha Z}^{as}(d/2)$ reduces to that considered above, and we can use the results already obtained.

We will find an expression for the mean-molar velocity in the channel. Averaging u_{1Z} and u_{2Z} over the cross section of the channel, we have

$$\langle u \rangle_z^M = -\frac{d^2}{12\eta} \frac{dp}{dz} + y_1 u_{1z}^{as}\left(\frac{d}{2}\right) + y_2 u_{2z}^{as}\left(\frac{d}{2}\right) + \frac{\eta_2 y_1 - \eta_1 y_2}{\eta} \left[U_{12}^0 - U_{12}^{as}\left(\frac{d}{2}\right) \right].$$

Using the results corresponding to the first approximation of the moment method (expression (1.14)), we obtain after simple reduction

$$\langle u \rangle_z^M = -\left(\frac{d^2}{12\eta} + Bd \right) \frac{dp}{dz} - \sigma_{12} y_1 y_2 U_{12}^0,$$

where

$$B = \frac{1}{2\eta^2} \left(\frac{\pi kT}{2} \right)^{1/2} \frac{1}{1+\Lambda} \left(b_1 \frac{\eta_1^2}{m_1^{1/2} p_1} + b_2 \frac{\eta_2^2}{m_2^{1/2} p_2} + b_1 b_2 \frac{\eta^2}{p} \frac{\Lambda}{(m^{1/2} b)} \right),$$

and σ_{12} is found from expression (1.15). Here, in the final expression we have omitted terms $\sim (sd)^{-1}$ compared with unity.

It is also of interest to have an expression for the difference between the velocities of the components of the mixture averaged over the cross section. Using (2.1) and neglecting terms $\sim (sd)^{-1}$ compared with unity, after averaging, we obtain

$$\langle u \rangle_{1z} - \langle u \rangle_{2z} = U_{12}^0 + U_{12}^{as}\left(\frac{d}{2}\right) \frac{2}{sd}.$$

Using (1.14) with $\partial u_Z^{as}(x)/\partial x$ replaced by $(-d/2\eta) \frac{dp}{dz}$ we obtain

$$U_{12}^{as}\left(\frac{d}{2}\right) = \frac{\Lambda}{1+\Lambda} \left[U_{12}^0 + \frac{sd}{2} [D_{12}]_1 \alpha_p^* \frac{1}{p} \frac{dp}{dz} \right],$$

where

$$\alpha_p^* = \alpha_p^b + \alpha_p^h, \quad \alpha_p^h = -\sigma_{12}^h.$$

As a result, we have

$$\langle u \rangle_{1z} - \langle u \rangle_{2z} = U_{12}^0 + \frac{\Lambda}{1+\Lambda} [D_{12}]_1 \alpha_p^* \frac{1}{p} \frac{dp}{dz} = -\frac{[D_{12}]_1}{y_1 y_2} \left[\frac{dy_1}{dz} + \alpha_p y_1 y_2 \frac{1}{p} \frac{dp}{dz} \right], \quad (2.3)$$

where

$$\alpha_p = \frac{\Lambda}{1+\Lambda} \alpha_p^h + \frac{1}{1+\Lambda} \alpha_p^b.$$

Hence, the barodiffusion constant in the expression for the difference between the velocities of the components averaged over the cross section turns out to be equal to (with opposite sign) the diffusion slip coefficient (or the coefficient of the concentration gradient in the expression for the mean-molar velocity of the mixture). Note that this result agrees with the conclusions of the thermodynamics of irreversible processes [15], where σ_{12} and α_p are cross coefficients satisfying Onsager's relations. The analysis given above also explains why the value of α_p differs from the barodiffusion constant in viscous flow α_p^b , calculated in [17]. Although the 13-moment Grad approximation used in this paper has enabled us to take into account the effect of viscous momentum transfer in diffusion (which leads to α_p^b differing from the values given by the first approximation of the Chapman-Enskog method [16]) the relations for $\Pi_{\alpha XZ}$ take their usual form irrespective of the diffusion velocities of the components. As already mentioned, this leads to the condition $U_{12} = U_{12}^{as}\left(\frac{d}{2}\right) = U_{12}^0$.

and subsequent averaging over the cross section of the channel does not change the result. The expression obtained above for the difference between the averaged velocities contains, together with U_{12}^0 , the term $\sim (sd)^{-1}U_{12}^{as}\left(\frac{d}{2}\right)$. When there is no total pressure gradient $U_{12}^{as}\left(\frac{d}{2}\right) \sim U_{12}^0$, and this term can be neglected. However, in general, $U_{12}^{as}\left(\frac{d}{2}\right)$ contains a term proportional to $\langle u \rangle_{1z} - \langle u \rangle_{2z}$, which makes a contribution to the difference $\text{sd}p^{-1}(dp/dz)$, comparable with the contribution from the barodiffusion term to U_{12}^0 .

A Cylindrical Channel. Consider the flow of a mixture in a circular cylindrical channel of radius R (the z axis is directed along the axis of the cylinder). The equations of moments in a cylindrical system of coordinates take the form

$$p_{\alpha}k_{\alpha} + \frac{1}{r} \frac{\partial}{\partial r} (r\Pi_{\alpha rz}) = \sum_{\beta} \frac{n_{\alpha}n_{\beta}kT}{n[D_{\alpha\beta 11}]} (u_{\beta z} - u_{\alpha z}); \quad (2.4)$$

$$\sum_{\beta} a_{\alpha\beta} \frac{\Pi_{\beta rz}}{y_{\beta}} = -y_{\alpha}\beta_{\alpha}^{-1/2} \left[\frac{1}{r} \frac{\partial}{\partial r} (rQ_{\alpha z}) - \frac{1}{r} q_{\alpha z} \right]. \quad (2.5)$$

Far from the walls $Q_{\alpha z} = q_{\alpha z}$, and Eq. (2.5) becomes

$$\sum_{\beta} a_{\alpha\beta} \frac{\Pi_{\beta rz}}{y_{\beta}} = -y_{\alpha} \frac{\partial}{\partial r} (ru_{\alpha z}). \quad (2.6)$$

For a two-component mixture simultaneous solution of Eqs. (2.4) and (2.6) gives

$$u_{1z} = -\frac{1}{4\eta} \frac{dp}{dz} (R^2 - r^2) + u_{1z}^{as}(R) + \frac{\eta_2}{\eta_1} [U_{12}^0 - U_{12}^{as}(R)] \left[1 - \frac{I_0(sr)}{I_0(sR)} \right], \quad (2.7)$$

$$\begin{aligned} U_{12} &= U_{12}^0 \left[1 - \frac{I_0(sr)}{I_0(sR)} \right] + U_{12}^{as}(R) \frac{I_0(sr)}{I_0(sR)}; \\ \Pi_{1xz} &= -\frac{r}{2} \frac{\eta_1}{\eta} \frac{dp}{dz} - \frac{y_1^2 y_2^2}{|a|\eta} s [U_{12}^0 - U_{12}^{as}(R)] \frac{I_1(sr)}{I_0(sR)}, \\ \Pi_{xz} &= \Pi_{1xz} + \Pi_{2xz} = -\frac{r}{2} \frac{dp}{dz}, \end{aligned} \quad (2.8)$$

where $I_n(x)$ are the modified Bessel functions.

In the layer close to the wall of thickness $\delta \ll R$, Eqs. (2.4) and (2.5) can be replaced by Eqs. (1.3) and (1.4). It can also be shown that Eqs. (2.7) and (2.8) on the external boundary of the Knudsen layer reduce to Eqs. (1.9)-(1.11). Hence, in this case also the problems of determining $U_{12}^{as}(R)$ reduces to the problem considered above of the slip of a mixture on a plane wall. Averaging the expressions for $u_{1z}(r)$ and $u_{2z}(r)$ over the cross section of the channel, and using for $u_{\alpha z}^{as}(R)$ the quantities (1.14) with $\partial u_{\alpha z}^{as}(x)/\partial x$ replaced by $(R/2\eta)dp/dz$ we obtain

$$\langle u \rangle_z^M = -\left(\frac{R^2}{8\eta} + BR \right) \frac{dp}{dz} - \sigma_{12} y_1 y_2 U_{12}^0.$$

The expression for $\langle u_{1z} \rangle - \langle u_{2z} \rangle$ has the same form as (2.3) in the problem of the flow in a plane channel, i.e., the barodiffusion constant $\alpha_p = -\sigma_{12}$ is independent of the channel geometry.

3. Discussion of the Results and Comparison with Experiment. It is convenient to compare the values of σ_{12} (or α_p) obtained above with the results obtained by other methods using the example of a mixture with a small relative difference between the masses and the scattering cross sections of the molecules of the components. For the solid-sphere molecular model the expression for σ_{12} can be represented in the form

$$\sigma_{12} = a \frac{m_1 - m_2}{m_1 + m_2} - b \frac{d_1 - d_2}{d_1 + d_2} - c \frac{b_1 - b_2}{b_1 + b_2}, \quad (3.1)$$

where m_{α} and d_{α} are the mass and effective diameter of the molecules of the α -sort. In (3.1) we have also taken into account the possibility of small differences in the nature of the interaction between molecules of different sorts and the walls. In Table 1 we give values of a , b , and c calculated using the general expressions for σ_{12} obtained by the different methods. For the case of the BGK model the effective collision frequencies $\gamma_{\alpha\alpha}$ and $\gamma_{\alpha\beta}$ were specified in the form

$$\gamma_{\alpha\alpha} = Ad_{\alpha}^2 \left(\frac{\pi kT}{m_{\alpha}} \right)^{1/2} n_{\alpha}, \quad \gamma_{\alpha\beta} = \frac{8}{3} d_{\alpha\beta}^2 \left(\frac{2\pi kT}{\mu_{\alpha\beta}} \right)^{1/2} n_{\beta}, \quad d_{\alpha\beta} = (d_{\alpha} + d_{\beta})/2,$$

where $A = 16/3$ and $16/5$ (the first and second rows, respectively), which corresponds to the usually employed choice of these quantities [13, 7]. For $A = 16/3$ the values of a , b , and c are practically independent of the concentration, and for $A = 16/5$ in Table 1 we give the values corresponding to $y_1 = y_2 = 0.5$. The use of the same model parameters to calculate the second approximation for the McCormack model (the present paper *) showed that for a 50% mixture the results are practically insensitive to the choice of the model parameters. This is also confirmed by calculations for the case when $\gamma_{\alpha\alpha}$ and $\gamma_{\alpha\beta}$ are specified in the form described in [10] for the third-order model. Two approximations of the variational method correspond to the results in [14] considering and ignoring corrections of the order of the thermodiffusion constant (taking these corrections into account in our scheme would correspond to the use of the McCormack model with $N=3$). In the last column of Table 1 we give empirical values of a and b obtained by processing experimental data on the diffusion-phoresis of oil drops in gaseous mixtures of nonuniform concentration [22].

It follows from the results that the different methods of calculation give fairly close values of the coefficient a , but the BGK model seems to be less satisfactory in this respect. The coefficient b is more sensitive to the chosen approximation, and methods which do not take into account the variation in the distribution function in the Knudsen layer [1, 12] give quite different results.

Note that the results of the present paper and the calculations based on the BGK model lead to a weaker dependence on the differences between the reflection coefficients at the wall.

The closeness of the results of the first approximation of the present paper and of the variational method is noteworthy. An analysis of the general expression for $\sigma_{12}^{(v)}$ in [14] shows that when the thermodiffusion corrections are neglected the corresponding expression for σ_{12} (for $b_1 = b_2 = 1$) in our notation has the form

$$\sigma_{12} = \sigma_{12}^{(v)} + \frac{m_1 - m_2}{(m)_y} = \frac{1}{2} (\sigma_{12}^h + \sigma_{12}^b).$$

On the other hand, the parameter Λ in Eq. (1.15) varies in the range 0.88-1.15 for arbitrary ratios of the masses and the concentrations of the components. For an isotopic mixture $\Lambda = (5\pi)^{1/2}/4 = 0.99$, which also demonstrates the above-mentioned closeness of the results.

It should be noted that for actual interaction potentials of the molecules the thermal-diffusion corrections, as a rule, are considerably less than for the sphere model, so that the use of the second approximation of the method of moments may be more important in some cases than taking these corrections into account.

A wide-ranging comparison of the experimental and theoretical values of σ_{12} for a number of mixtures has been made in [19, 21]. These mainly use the results on diffusion-phoresis of suspended particles [22] and measurements of the diffusion baroeffect [2, 20]. Within the limits of the accuracy of the experimental data the theoretical results for σ_{12} (like calculations based on the variational method [14]) are in satisfactory agreement with experiment. Mixtures with very close molecular masses of the components ($N_2 - C_2H_4$, $CO_2 - C_3H_8$, $Ar - CO_2$) are of particular interest. For these mixtures the direction of motion of the particles in diffusion-phoresis and also the diffusion baroeffect (the occurrence of a difference in pressure for flow through a capillary of a gaseous mixture of nonuniform concentration) have a sign which is opposite to that which is predicted by elementary theory [1]. Table 2 shows that the results of calculations of the values of σ_{12} for three mixtures are in satisfactory agreement with experimental data. In the calculations we used the molecular interaction parameters described by the Lennard-Jones potential. The quantitative agreement with experiment can be improved by assuming that the nature of the reflection of the molecules from the walls is different. In the last two rows of Table 2 we give values of σ_{12} in the first and second approximations for which we used experimental values of $K = b_1/b_2$ obtained in [4] from the results of measurements of the separation of mixtures of $N_2 - C_2H_4$ ($K = 1.035$) and $Ar - CO_2$ ($K = 1.011$) for molecular flow of these mixtures in circular cylindrical capillaries ($Kn \gg 1$).

Experiments on the separation of a mixture in another limiting region ($Kn \ll 1$) can also be used in principle to determine the barodiffusion constant α_p [12, 23]. Unfortunately, the results obtained in [4] cannot be extended into the region of fairly small Knudsen numbers. Nevertheless, the observed change in sign of the effect for an $N_2 - C_2H_4$ mixture for $Kn \sim 1$ and the order of magnitude of the effect for $Kn < 1$ are in satisfactory agreement with calculations using the value $\alpha_p = -\sigma_{12}$. A similar change in sign, not observed in [4], would be expected for $Kn < 1$ in an $Ar - CO_2$ mixture, to which attention has already been drawn in [23].

Appendix. We will calculate the rate of diffusion slip in the second approximation ($k=0.1$), when $h_{\alpha}^{\pm} = 2(a_{0\alpha}^{\pm} + a_{1\alpha}^{\pm} c_{\alpha X})$. Instead of the equations for the coefficients $a_{0\alpha}^{\pm}$ and $a_{1\alpha}^{\pm}$ is more convenient first of all to deal with a system of equations for the moments $M_{\alpha}^{(n)}$, which are defined in the form

*The results of the first approximation, as is seen from (1.15), generally are independent of the arbitrary parameters of the model.

$$M_{\alpha}^{(n)} = \pi^{-1/2} \left[\int_{-\infty}^0 c_{\alpha x}^n h_{\alpha}^{-}(x, c_{\alpha x}) \exp(-c_{\alpha x}^2) dc_{\alpha x} + \int_0^{\infty} c_{\alpha x}^n h_{\alpha}^{+}(x, c_{\alpha x}) \exp(-c_{\alpha x}^2) dc_{\alpha x} \right].$$

In this case the equations of moments (1.3) and (1.4), in which $q_{\alpha z} = \frac{1}{2} M_{\alpha}^{(0)}$, $\Pi_{\alpha z} = p_{\alpha} M_{\alpha}^{(1)}$, and $Q_{\alpha z} = M_{\alpha}^{(2)}$, must be supplemented by two equations of the form

$$\begin{aligned} \frac{\partial}{\partial x} \left(M_{\alpha} - \frac{\Pi_{\alpha xz}}{p_{\alpha}} \right) &= 2\beta_{\alpha}^{1/2} \gamma_{\alpha} (q_{\alpha z} - Q_{\alpha z}), \\ \frac{\partial}{\partial x} (q_{\alpha z} - Q_{\alpha z}) &= \frac{1}{2} \beta_{\alpha}^{1/2} \gamma_{\alpha} \left(M_{\alpha} - 3 \frac{\Pi_{\alpha xz}}{p_{\alpha}} \right), \end{aligned}$$

where $M_{\alpha} = 2M_{\alpha}^{(3)}$; $\gamma_{\alpha} = \gamma_{\alpha\alpha} + \gamma_{\alpha\beta}$ ($\alpha, \beta = 1, 2$).

Condition (1.12) leads to the following relations for the moments on the wall ($x=0$):

$$\begin{aligned} (4 - \pi) q_{\alpha z}(0) + b_{\alpha} \pi^{1/2} \frac{\Pi_{\alpha xz}(0)}{p_{\alpha}} - (2 - \pi) Q_{\alpha z}(0) &= 0, \\ 2\pi^{1/2} q_{\alpha z}(0) - b_{\alpha} (4 - 3\pi) \frac{\Pi_{\alpha xz}(0)}{p_{\alpha}} + b_{\alpha} (2 - \pi) M_{\alpha}(0) &= 0. \end{aligned} \quad (A.1)$$

As a result, to determine $q_{\alpha z}$, $Q_{\alpha z}$, $Q_{\alpha z}$, $\Pi_{\alpha xz}$, and M_{α} ($\alpha = 1, 2$) we have a system of eight equations with boundary conditions (A.1), and the conditions that the required functions should be bounded as $x \rightarrow \infty$. This system is solved by reducing it to an eight-order equation in $Q_{\alpha z}$. The results obtained for the case when $\partial u_z^{as}(x)/\partial x = 0$ can be represented in the form

$$\begin{aligned} Q_{1z} &= \beta_1^{1/2} \eta_2 \sum_{k=1}^3 C_k \exp(-\lambda_k x) + \beta_1^{1/2} A^* U_{1z}^0, \\ Q_{2z} &= -\beta_2^{1/2} \eta_1 \sum_{k=1}^3 C_k \exp(-\lambda_k x) + \beta_2^{1/2} (A^* - 1) U_{1z}^0, \\ \Pi_{1xz} &= -\Pi_{2xz} = g\eta \sum_{k=1}^2 C_k \lambda_k \exp(-\lambda_k x), \\ q_{\alpha z} &= Q_{\alpha z} - \frac{D^* \eta}{\beta_{\alpha} \gamma_{\alpha}^2} \sum_{k=1}^3 C_k \lambda_k^2 f_{\alpha k} \exp(-\lambda_k x), \\ M_{\alpha} &= \sum_{k=1}^3 \left(\frac{2D^* \eta}{\beta_{\alpha} \gamma_{\alpha}^3} \lambda_k^2 f_{\alpha k} - (-1)^{\alpha} \frac{3g\eta}{p_{\alpha}} \right) C_k \lambda_k \exp(-\lambda_k x), \quad \alpha = 1, 2, \end{aligned} \quad (A.2)$$

where $g = s^{-2}D$; $D^* = \frac{1}{s^2(\beta_2 \gamma_2^2 - \beta_1 \gamma_1^2)}$; $D = \frac{p_1 p_2}{p[D_{12}]}_1$;

$$\begin{aligned} f_{\alpha k} &= \lambda_k^4 - \beta_{\beta} \gamma_{\beta}^2 \lambda_k^2 - D \left[\gamma^* \lambda_k^2 + \left(\frac{\beta_{\alpha} \gamma_{\alpha}^3}{p_{\alpha}} + \frac{\beta_{\beta} \gamma_{\beta}^3}{p_{\beta}} - \gamma^* \beta_{\beta} \gamma_{\beta}^2 \right) \right], \\ \lambda^* &= \gamma_{\alpha}/p_{\alpha} + \gamma_{\beta}/p_{\beta} + 1/g \quad (\alpha, \beta = 1, 2; \beta \neq \alpha). \end{aligned}$$

In this case λ_k are the positive roots of the equation

$$\lambda^6 - Z_1 \lambda^4 + Z_2 \lambda^2 - Z_3 = 0,$$

where

$$Z_1 = D\gamma^* + \beta_1 \gamma_1^2 + \beta_2 \gamma_2^2, \quad Z_2 = D \left[\frac{\beta_1 \gamma_1^2 \gamma_2}{p_2} + \frac{\beta_2 \gamma_2^2 \gamma_1}{p_1} \right] + s^2 (\beta_2 \gamma_2^2 + \beta_1 \gamma_1^2) + \beta_1^2 \beta_2^2 \gamma_1^2 \gamma_2^2, \quad Z_3 = s^2 \beta_1 \beta_2 \gamma_1^2 \gamma_2^2.$$

Substituting the boundary conditions (A.1) into (A.2) we obtain a system of four linear algebraic equations for C_1 , C_2 , C_3 , and A^* . Note that to determine the rate of diffusion slip u_D it is sufficient to find the constant A^* . In fact

$$u_D = \lim_{x \rightarrow \infty} (\beta_1^{-1/2} y_1 q_{1z} + \beta_2^{-1/2} y_2 q_{2z}) = (A^* - y_2) U_{1z}^0$$

or

$$\sigma_{12} = \frac{y_2 - A^*}{y_1 y_2}.$$

Because of the complexity of the expression for A^* described using the corresponding fourth-order determinants, it will not be given here. The results of specific calculations of σ_{12} in the first and second approximation for certain special cases are given in Tables 1 and 2.

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