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ON THE CALCULATION OF THE BARODIFFUSION CONSTANTS OF BINARY GAS MIXTURES (McCORMACK MODEL)

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An expression for the barodiffusion constant is obtained on the basis of the McCormack model equations in the approximation of a continuous medium.

The barodiffusion constant is an important physical quantity characterizing such phenomena as diffusiophoresis, separation of a mixture during flow, etc. Expressions for it are obtained in a number of reports using the Boltzmann equation [1,2] or model kinetic equations in the Hamel form [3,4]. When the values of the barodiffusion constant obtained from the solution of equations in the Hamel form are compared with experimental data [5,6] it turns out that they differ rather considerably from each other for a number of binary mixtures. The most important disagreement is observed for binary mixtures with molecules of markedly differing masses (Ar—H_2, Ar—He, Ar—Ne, etc.). Evidently, the reason for the noncorrespondence between the theoretical results and experimental data consists in the fact that the Hamel model does not describe sufficiently correctly the flow of a binary mixture in the mode of a continuous medium; in particular, an adequate description of the diffusion and viscosity of the mixture cannot be provided simultaneously within its framework. Thus, the necessity arises of using more refined models of a binary gas mixture. Such models include McCormack's model [7]. It is based on matching the moments of order N from exact and model collision integrals and provides a correct description of the flow of a mixture in the mode of a continuous medium. In [8] the method of half-space moments is used to solve model equations in the McCormack form with N = 2. Usually when this method is used difficulties develop in estimating the accuracy of the results obtained. Since even the second approximation of the method of half-space moments leads to very cumbersome expressions, it is practically impossible to find the third approximation, which would permit an estimation of the rate of convergence of the results obtained to numerical results. In the present report the method of asymptotic joining, which is free of the defects inherent to the method of half-space moments, is used to solve model equations in the McCormack form.

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Let us consider the slow flow of a binary gas mixture in a cylindrical channel of radius R in the approximation of a continuous medium. A density gradient $dn_i/dz = n_iK_i$ of a component exists in the direction of the z axis, which coincides with the axis of the channel; the temperature T of the mixture is assumed to be constant. Then we have the following equation for the difference between the velocities of the components averaged over a cross section of the channel:

$$\langle v_1 \rangle - \langle v_2 \rangle = -D \frac{p^2}{p_1p_2}\left[\frac{\partial (p_1/p)}{\partial z} + \frac{p_1p_2}{p^2}\sigma \frac{\partial \ln p}{\partial z}\right]. \tag{1}$$

Here D is the coefficient of interdiffusion; p_i, partial pressure of component i; p, total pressure of the mixture; σ, barodiffusion constant. Thus, to calculate σ one must know the velocities of the components of the mixture.

We represent the unknown distribution function of molecules of component i in the form

$$f_i = n_i(z)(h_i/\pi)^{3/2}\exp\{-h_iu_i^2\}(1+\Phi_i),\ h_i = m_i/2kT,$$

where $\Phi_i \ll 1$.

Within the framework of the McCormack model Φ_i satisfies the following linearized equation [7]:

$$\begin{aligned} u_{iz}K_i + u_{ix}\frac{\partial \Phi_i}{\partial x} + u_{iy}\frac{\partial \Phi_i}{\partial y} &= -(\gamma_{ii}+\gamma_{ij})\Phi_i + \\ &+ 2\left\{(\gamma_{ii}+\gamma_{ij})q_{iz} - \left[q_{iz} - \left(\frac{m_i}{m_j}\right)^{1/2} q_{jz}\right]\nu_{ij}^{(1)}\right\}c_{iz} + \\ &+ 2\left[(\gamma_{ii}+\gamma_{ij}-\nu_{ii}^{(3)}-\nu_{ij}^{(3)}+\nu_{ii}^{(4)})\frac{\Pi_{ixz}}{p_i} + \nu_{ij}^{(4)}\frac{\Pi_{jxz}}{p_j}\right]\times \\ &\times c_{ix}c_{iz} - \left[q_{iz} - \left(\frac{m_i}{m_j}\right)^{1/2} q_{jz}\right]\nu_{ij}^{(2)}c_{iz}\left(c_i^2 - \frac{5}{2}\right),\ i,\ j = 1,\ 2,\ i \neq j, \end{aligned} \tag{2}$$

where $c_i = h_i^{1/2}u_i$; $q_{iz} = h_i^{1/2}v_{iz}$, dimensionless macroscopic velocity of component i; Π_{ixz}, partial tensor of viscous stresses, while the expressions for γ_{ii}, γ_{ij}, and $\nu_{ij}^{(k)}$, which depend on the Chapman–Cowling integrals, are given in [7]. By definition,

$$q_{iz} = q_i = \pi^{-3/2}\int_{-\infty}^{+\infty} c_{iz}\exp\{-c_i^2\}\Phi_i dc_i,$$

$$\Pi_{ixz} = \Pi_i = 2p_i\pi^{-3/2}\int_{-\infty}^{+\infty} c_{ix}c_{iz}\exp\{-c_i^2\}\Phi_i dc_i.$$

As a result of the solution (2) the following equations were obtained in [8] for the velocities V_i of the components and the tensor $\overline{\Pi}_i$ of viscous stresses outside the Knudsen boundary layer:

$$p_iK_i + \frac{1}{r}\frac{\partial}{\partial r}(r\overline{\Pi}_i) = \frac{n_in_j}{nD}kT(V_j - V_i), \tag{3}$$

$$a_{ii}\frac{\overline{\Pi}_i}{y_i} + a_{ij}\frac{\overline{\Pi}_j}{y_j} = -y_i\frac{\partial V_i}{\partial r}, \tag{4}$$

where

$$a_{ii} = \frac{y_i}{p}(\nu_{ii}^{(3)} - \nu_{ii}^{(4)} + \nu_{ij}^{(3)});\quad a_{ij} = -\frac{y_i}{p}\nu_{ij}^{(4)};\quad y_i = \frac{p_i}{p}.$$

It is easy to show that the solution of this system of equations has the form

$$V_i = A_i\alpha_i\left(1 - \frac{r^2}{R^2}\right) + B_i + M_i, \tag{5}$$

$$\overline{\Pi}_i = 2y_iA_i\alpha_i\frac{a_{jj} - (y_j/y_i)a_{ij}}{a_{ii}a_{jj} - a_{ij}a_{ji}}\frac{r}{R^2}. \tag{6}$$

Here

$$A_i = -\frac{(a_{ij}a_{ji} - a_{ii}a_{jj})(p_iK_i + p_jK_j)}{4\delta_iy_iy_j^2\alpha_i}R^2;$$

$$B_i = \frac{D}{\delta_i y_i y_j kT}\left\{p_i K_i\left[\frac{a_{ii}}{y_i} - \frac{1}{\delta_i y_j^2}(a_{ij}a_{ji} - a_{ii}a_{jj})\right]\right.$$
$$\left. + p_j K_j\left[\frac{a_{ij}}{y_j} - \frac{1}{\delta_i y_j^2}(a_{ij}a_{ji} - a_{ii}a_{jj})\right]\right\};$$
$$\delta_i = \left(\frac{a_{ji}}{y_i} - \frac{a_{jj}}{y_j}\right)\frac{y_i}{y_j} - \left(\frac{a_{ii}}{y_i} - \frac{a_{ij}}{y_j}\right); \quad \alpha_i = (\gamma_{ii} + \gamma_{ij})\, h_i^{1/2} R \sim \frac{1}{\mathrm{Kn}}$$

(in the mode of a continuous medium $\alpha_i \to \infty$); M_i are integration constants, which are determined through the solution (2) in the Knudsen boundary layer.

Using (5) we can calculate the difference between the velocities of the components of a mixture outside the Knudsen layer:

$$V_1 - V_2 = B_1 - B_2 + M_1 - M_2 = \frac{D}{\delta_1 y_2}\left[K_1\left(\frac{a_{11}}{y_1} - \frac{a_{21}}{y_2}\right) + K_2\left(\frac{a_{12}}{y_1} - \frac{a_{22}}{y_2}\right)\right] + M_1 - M_2. \tag{7}$$

Keeping in mind that

$$D(K_1 - K_2) = -D\frac{p^2}{p_1 p_2}\frac{\partial(p_1/p)}{\partial z},$$

Eq. (7) can be written in the form

$$V_1 - V_2 = -D\frac{p^2}{p_1 p_2}\frac{\partial(p_1/p)}{\partial z} + D\frac{\varepsilon - 1}{(1 + \varepsilon y_1/y_2)\, y_2}\frac{1}{p}\frac{\partial p}{\partial z} + M_1 - M_2, \tag{8}$$

where

$$\varepsilon = \frac{a_{12}y_2 - a_{22}y_1}{a_{12}y_1 - a_{11}y_2}.$$

Then we obtain the expressions for the velocities of the components of the mixture and the partial tensor of viscous stresses in the Knudsen boundary layer. We assume that the reflection of gas molecules from the channel wall is diffusional. Multiplying both sides of (2) successively by $c_{iz} \exp\{-c_i^2\}$ and $c_{iz}c_{ix} \exp\{-c_i^2\}$ and integrating over c_i and along the characteristic curve s, we obtain the system of integral equations

$$v_i = \frac{\alpha_i}{2\pi}\int_0^{2\pi}\int_0^b \left\{T_0(\alpha_i s)\left[2\left(1 - \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i}\right)v_i(x', y') + \right.\right.$$
$$\left. + 2\frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i}v_j(x', y')\right] - \left[T_2(\alpha_i s) + \frac{3}{2}T_0(\alpha_i s)\right]\times$$
$$\times\frac{\nu_{ij}^{(2)}}{\gamma_i}(v_i(x', y') - v_j(x', y')) + \frac{2}{h_i^{1/2}}T_1(\alpha_i s)\cos\theta\times$$
$$\left.\times\left[\left(1 - \frac{\nu_{ii}^{(3)} - \nu_{ii}^{(4)} + \nu_{ij}^{(3)}}{\gamma_i}\right)\frac{\Pi_i(x', y')}{p_i} + \frac{\nu_{ij}^{(4)}}{\gamma_i}\frac{\Pi_j(x', y')}{p_j}\right]\right\} ds\,d\theta - \frac{K_i}{2\pi h_i^{1/2}}\int_0^{2\pi}\int_0^b T_0(\alpha_i s)\, ds\,d\theta,$$

$$\frac{\Pi_i}{p_i} = \frac{\alpha_i}{\pi}\int_0^{2\pi}\int_0^b \left\{2h_i^{1/2}T_1(\alpha_i s)\cos\theta\left[\left(1 - \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i}\right)\times\right.\right.$$
$$\left.\times v_i(x', y') + \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i}v_j(x', y')\right] - h_i^{1/2}\left[T_3(\alpha_i s) + \right.$$
$$\left. + \frac{3}{2}T_1(\alpha_i s)\right]\cos\theta\,[v_i(x', y') - v_j(x', y')]\frac{\nu_{ij}^{(2)}}{\gamma_i} + 2T_2(\alpha_i s)\times$$
$$\left.\times\cos^2\theta\left[\left(1 - \frac{\nu_{ii}^{(3)} - \nu_{ii}^{(4)} + \nu_{ij}^{(3)}}{\gamma_i}\right)\frac{\Pi_i(x', y')}{p_i} + \frac{\nu_{ij}^{(4)}}{\gamma_i}\frac{\Pi_j(x', y')}{p_j}\right]\right\} ds\,d\theta - \frac{K_i}{2\pi}\int_0^{2\pi}\int_0^b T_1(\alpha_i s)\cos\theta\, ds\,d\theta. \tag{9}$$

Here $\gamma_i = \gamma_{ii} + \gamma_{ij}$; $x' = r + s \cdot \cos\theta$; $y' = s \cdot \sin\theta$; $b = (1/R)[r \cos\theta + (R^2 - r^2 \sin^2\theta)^{1/2}]$ is the length of the segment of the characteristic curve from the channel wall to the point r.

We use the method of asymptotic joining [9,10] to solve (9) in the Knudsen boundary layer. We introduce the new variables $\eta_i = \alpha_i[1 - (r/R)]$, while we represent the velocities of the components of the mixture and the tensor of viscous stresses in the form

$$v_i = V_i + 2A_i F_i(\eta_i), \quad \Pi_i = \overline{\Pi}_i + 2A_i h_i^{1/2} \Psi_i(\eta_i), \tag{10}$$

where F_i and Ψ_i are correction functions which possess the following properties:

$$\lim_{\eta_i \to \infty} \eta_i^m F_i(\eta_i) = 0, \quad \lim_{\eta_i \to \infty} \eta_i^m \Psi_i(\eta_i) = 0, \quad m > 0. \tag{11}$$

With allowance for (5), (6), and (10), Eqs. (9) take the form

$$\pi^{1/2} F_i(\eta_i) = y_i^2 \frac{\gamma_i (a_{jj} - y_j a_{ij}/y_i)}{p_i (a_{ii} a_{jj} - a_{ij} a_{ji})} T_1(\eta_i) - \frac{M_i}{2A_i} T_0(\eta_i) - \frac{M_i - M_j}{2A_i} \times$$

$$\times \left[\frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} (\pi^{1/2} - T_0(\eta_i)) + \frac{\nu_{ij}^{(2)}}{\gamma_i} \left(\pi^{1/2} - \frac{1}{2} T_2(\eta_i) - \frac{3}{4} T_0(\eta_i) \right) \right] + \left(1 - \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} \right) \times$$

$$\times \int_0^\infty F_i(\eta_i') T_{-1}(|\eta_i - \eta_i'|)\, d\eta_i' + \frac{\alpha_i}{\alpha_j} \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} \times$$

$$\times \int_0^\infty F_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) T_{-1}(|\eta_i - \eta_i'|)\, d\eta_i' - \frac{1}{2} \frac{\nu_{ij}^{(2)}}{\gamma_i} \int_0^\infty \left[F_i(\eta_i') - \right.$$

$$\left. - \frac{\alpha_i}{\alpha_j} F_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) \right] [T_1(|\eta_i - \eta_i'|) + 2T_{-1}(|\eta_i - \eta_i'|)]\, d\eta_i' -$$

$$- \left(1 - \frac{\nu_{ii}^{(3)} - \nu_{ii}^{(4)} + \nu_{ij}^{(3)}}{\gamma_i} \right) \int_0^\infty \operatorname{sign}(\eta_i - \eta_i') T_0(|\eta_i - \eta_i'|) \Psi_i(\eta_i')\, d\eta_i' -$$

$$- \frac{\nu_{ij}^{(4)}}{\gamma_i} \frac{\alpha_i}{\alpha_j} \left(\frac{h_j}{h_i} \right)^{1/2} \int_0^\infty \operatorname{sign}(\eta_i - \eta_i') T_0(|\eta_i - \eta_i'|) \Psi_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) d\eta_i',$$

$$\pi^{1/2} \Psi_i(\eta_i) = -2y_i^2 \frac{\gamma_i (a_{jj} - y_j a_{ij}/y_i)}{p_i (a_{ii} a_{jj} - a_{ij} a_{ji})} \frac{1}{R^2} T_2(\eta_i) + \frac{M_i}{A_i} T_1(\eta_i) -$$

$$- \frac{M_i - M_j}{A_i} \left[\frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} T_1(\eta_i) + \frac{\nu_{ij}^{(2)}}{\gamma_i} (T_3(\eta_i) + 2T_1(\eta_i)) \right] -$$

$$- 2\left(1 - \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} \right) \int_0^\infty F_i(\eta_i') \operatorname{sign}(\eta_i - \eta_i') T_0(|\eta_i - \eta_i'|)\, d\eta_i' -$$

$$- 2\frac{\alpha_i}{\alpha_j} \frac{\nu_{ij}^{(1)} - \frac{5}{4}\nu_{ij}^{(2)}}{\gamma_i} \int_0^\infty F_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) \operatorname{sign}(\eta_i - \eta_i') T_0(|\eta_i - \eta_i'|)\, d\eta_i' +$$

$$+ \frac{\nu_{ij}^{(2)}}{\gamma_i} \int_0^\infty \left[F_i(\eta_i') - \frac{\alpha_i}{\alpha_j} F_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) \right] [T_2(|\eta_i - \eta_i'|) + 2T_0(|\eta_i - \eta_i'|)]\, d\eta_i' +$$

$$+ 2\left(1 - \frac{\nu_{ii}^{(3)} - \nu_{ii}^{(4)} + \nu_{ij}^{(3)}}{\gamma_i} \right) \int_0^\infty \Psi_i(\eta_i') T_{-1}(|\eta_i - \eta_i'|)\, d\eta_i' + 2\frac{\alpha_i}{\alpha_j} \left(\frac{h_j}{h_i} \right)^{1/2} \int_0^\infty \Psi_j\left(\frac{\alpha_j}{\alpha_i} \eta_i' \right) T_{-1}(|\eta_i - \eta_i'|)\, d\eta_i'. \tag{12}$$

TABLE 1. Values of Barodiffusion Constant σ for Different Binary Mixtures

Mixture	He—N₂	He—Ar	H₂—Ar	N₂—O₂
Hamel model [3, 5]	0,59	0,55	0,94	0,06
McCormack model(15)	0,79	0,97	1,33	0,09
Experimental σ	0,80 [6]	1,04 [5]	1,36 [5]	0,10 [6]

Terms of order $1/\alpha_i$ are omitted in writing (12). Taking (11) into account, in Eqs. (12) one must set $M_i = M_j$, while the expression for the difference between the velocities of the components of the mixture averaged over the channel cross section are written in the form

$$\langle v_1 \rangle - \langle v_2 \rangle = \frac{2}{R^2} \int_0^R \left\{ V_1 - V_2 + 2A_1 \left[F_1(\eta_1) - \frac{\alpha_1}{\alpha_2} F_2(\eta_2) \right] \right\} r dr. \tag{13}$$

Using simple transformations it is easy to show that

$$\frac{A_1}{\alpha_1} = -\frac{1}{2} Dp \frac{a_{12}a_{21} - a_{11}a_{22}}{\delta_1 y_1 y_2^3 \gamma_1^2}. \tag{14}$$

With allowance for (1), (8), (13), and (14) the expression for the barodiffusion constant takes the form

$$\sigma = \frac{1 - \varepsilon}{(1 + \varepsilon y_1/y_2) y_2} + 2 \frac{a_{12}a_{21} - a_{11}a_{22}}{\delta_1 y_1 y_2^3 \gamma_1^2} \nu_{12}^{(1)} \int_0^\infty \left[F_1(x) - \left(\frac{\alpha_1}{\alpha_2} \right)^2 F_2(x) \right] dx. \tag{15}$$

The functions $F_1(x)$ and $F_2(x)$, which are the solution of the system of equations (12), are found by the method of moments as in [9]. In Table 1 we present values of σ for several binary mixtures ($y_1 = y_2 = 0.5$) obtained through the solution of model equations in the McCormack (15) and Hamel [5] forms, as well as experimental data. As follows from Table 1, the results of a calculation by (15) and the experimental data are in good agreement.

Gas mixtures having small relative differences between the masses and collision cross sections of the component molecules are of special practical interest. For the model of molecules as solid spheres the expression for σ can be represented in the form

$$\sigma = a \frac{m_2 - m_1}{m_1 + m_2} - b \frac{d_2 - d_1}{d_1 + d_2},$$

where d_i is the effective diameter of a molecule of component i. A calculation by Eq. (15) leads to the value of $a = 1.05$ and $b = 0.84$. These values are close to the corresponding results obtained in [8] using the second-order McCormack model.

NOTATION

k, Boltzmann constant; Kn, Knudsen number; $T_n(y) = \int_0^\infty x^n \exp\{-x^2 - y/x\} dx$, special function.

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FRONTAL ISOTHERMAL SORPTION DYNAMICS FOR ISOTHERM OF NONSIMPLE FORM IN THE PRESENCE OF COMPLEX FORMATION IN THE MOVING PHASE

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Approximate analytic solutions of the equations of nonequilibrium sorption dynamics are obtained for convex—concave and concave—convex isotherms, taking into account the formation of nonsorbent complexes of the material in the mobile phase.

The isothermal sorption dynamics of a material in a porous undeformed medium with the formation of a nonsorbent complex of the material with concentration c_C, is described by the material balance equation [1]

$$\frac{\partial a}{\partial t}+\frac{\partial c}{\partial t}+\frac{\partial c_C}{\partial t}+u\,\frac{\partial (c+c_C)}{\partial x}=D\,\frac{\partial^2 (c+c_C)}{\partial x^2} \tag{1}$$

and equations expressing the relation between the concentrations a—c and c_C—c. In the case of nonequilibrium dynamics, the concentration relation a—c is specified by the kinetic equation, taken here in the form of the equation of intradiffusional kinetics, where the nonequilibrium nature of the sorption process is expressed in terms of τ [2]

$$a=f(c)-\tau\,\frac{df}{dc}\,\frac{\partial c}{\partial t}\,. \tag{2}$$

An equation of this form is used to solve a number of nonlinear problems of sorption dynamics [3-5].

If the rate of complex formation is large, then $c_C = \varphi(c)$, where the function $\varphi(c)$ may be determined as the complex-formation isotherm. The initial and boundary conditions of the equations of frontal sorption dynamics for a semiinfinite column ($0 \leqslant x < \infty$) take the form

$$c(0,\ t)=1;\quad c_C(0,\ t)=\varphi(1);\quad c(x,\ 0)=c_C(x,\ 0)=c(\infty,\ t)=c_C(\infty,\ t)=0. \tag{3}$$

For concave and convex isotherms f(c), $\varphi(c)$, use of the integral-relation method leads to an approximate solution [6] describing the sorption front, and conditions of sharpening and hollowing out of the front as a function of the ratio of curvature parameters of the isotherm are introduced. In the case of equilibrium dynamics, i.e., a = f(c), using the characteristic equation corresponding to Eq. (1) with D = 0

$$\left(\frac{dx}{dt}\right)_C=\frac{u}{1+df/dC},\quad \frac{df}{dC}=\frac{f'(c)}{1+\varphi'(c)},\quad C=c+\varphi(c),$$
$$f(C)=f(c(C)), \tag{4}$$

it is simple to show that when $d^2f/dC^2 < 0$ (i.e., f(C) is convex) the front is stationary,

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