DIFFUSION BAROEFFECT IN A CAPILLARY IN A BROAD RANGE OF KNUDSEN NUMBERS

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The magnitude of the diffusion baroeffect in a capillary is calculated in the entire range of Knudsen numbers based on a solution of BGK equations for a binary gas equation. The theoretical magnitudes of the baroeffect agree well with the experimental results obtained in a broad range of Knudsen numbers. The thermodynamic coefficients are calculated, and the Onsager reciprocal relation is demonstrated, from which in the limit of a viscous system it follows that the barodiffusion constant is equal to the coefficient of diffusion slippage.

The flow of a binary gas mixture in a broad range of Knudsen numbers is examined in [1-3]. A comparison with experimental data is absent in these articles. This deficiency is aggravated by the fact that there is no exact solution for the problem either for BGK (Bhatnagar, Gross, and Krook [1]) equations or for the Boltzmann equation. The present report is devoted to a calculation of the magnitude of the diffusion baroeffect and the time in which its maximum value is reached, which can be determined directly in an experiment. During the solution of this problem and the comparison with experimental data, the authors encountered contradictions in certain parameters of the collisions.

Thermodynamic flows produced by pressure and concentration gradients are studied in Sec. 3. The equality of the coefficient of diffusion slippage and the barodiffusion constant is demonstrated. The latter quantity can be calculated by the classical methods of Chapman and Enskog and of Grad in a problem without boundaries. This fact is proof that the coefficient of diffusion slippage cannot depend on the details of the interaction of the molecules with the surface.

1. Let us examine a system of two bulbs of volumes V_1 and V_2 joined by a capillary of radius R and length L. If the bulbs are filled with different gases to the same pressure p at the same temperature T and the channel is opened, then as a result of the mutual diffusion of the gases a pressure difference arises in the bulbs which after a time t_m reaches a maximum value Δp_m. To determine the latter two values, one must know the average velocities of the components of the mixture which are produced by the pressure and concentration gradients.

The average velocities can be determined from a solution of a system of BGK equations describing the isothermal flow of a binary gas mixture in a long capillary:

$$\begin{gathered}
\mathbf{v}_i \nabla f_i = \nu_{ii}(M_i - f_i) + \nu_{ij}(M_{ij} - f_i) \\
\mathbf{v}_j \nabla f_j = \nu_{jj}(M_j - f_j) + \nu_{ji}(M_{ji} - f_j) \\
M_i = M_{0i}\left[1 - k_i z - \frac{m_i}{kT} u_{iz} v_{iz}\right] \\
M_{ij} = M_{0i}\left[1 - k_i z - \frac{m_i}{kT} u_{ijz} v_{iz}\right] \\
M_{0i} = n_{0i}(m_i/2\pi kT)^{3/2} \exp(-m_i v_i^2/2kT)
\end{gathered} \tag{1.1}$$

where M_i is a linear expansion of the local Maxwell distribution function, M_{ij} are functions describing the distribution of molecules of the i-th component which have collided with molecules of the j-th component, M_{0i} is the Maxwell distribution function, ν_{ii} and ν_{ij} are the frequencies of self- and cross-collisions, f_i is the distribution function of the i-th component, and n_i is the density of the i-th component.

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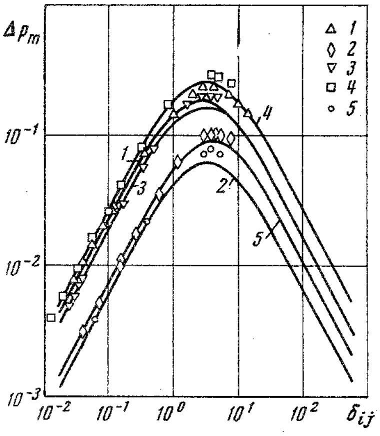

Fig. 1

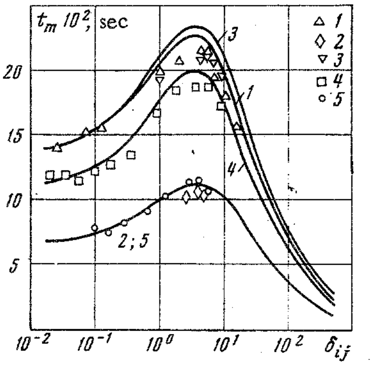

Fig. 2

Let us assume a linear variation in density of each component along the capillary axis

$$n_i(z) = n_{0i}(1 - k_i z)$$

where n_{0i} is the density of molecules at the origin of the coordinate system which is located at the center of the capillary.

The average velocity of molecules of the i-th component which have undergone collisions with molecules of the j-th component depends on the average velocities of the components in the following way:

$$u_{ijz} = u_{iz} + \delta m_j m_0^{-1}(u_{jz} - u_{iz})$$

where $m_0 = m_i + m_j$, while the collision parameter δ is, in general, a function of the masses of the molecules and their diameters.

Determinations of all the enumerated values (as well as those which will be encountered later for the j-th component) are obtained by exchanging the indices $i \rightleftharpoons j$ in the respective equations. In selecting the parameters ν_{jj}, ν_{ii}, ν_{ij}, and δ of the collisions from the condition of correspondence of the moments of the Boltzmann collision integral and its BGK model [4], no conditions are set on the value of δ. Morse [5] suggested taking $\delta = 1$, which leads to an incorrect Schmidt number and the impossibility of a correct description of diffusion and viscous flow simultaneously. The requirement of a correct Schmidt number in the limit of identical molecules of the i-th and j-th components leads to $\delta = 5/3$. The value $\delta = 5/3$ can be used only in the case of close masses and molecule diameters.

Another well-known approach to the selection of the collision parameters is as follows: $\delta = 1$, while ν_{ii}, ν_{jj}, and ν_{ij} are determined from a comparison of the solution of the system of equations (1.1) by the Chapman–Enskog method with the experimental values of the coefficients of viscosity η_i and η_j of the pure components and the diffusion coefficient D_{ij}. With such a selection of the collision parameters, the coefficient of viscosity η of the mixture differs by 1.5-2 times from the experimental value for many pairs of gases.

In the present work, the collision parameters ν_{ii}, ν_{jj}, ν_{ij}, and δ were determined from the condition of obtaining the correct values of all four coefficients: η_i, η_j, η, D_{ij}.

As shown in [1], the solution of the system of equations (1.1) leads to the following equations for the average velocities of the components:

$$u_{iz} = b_i(A_i r^2 + B_i - 1)$$

where the coefficients A_i, A_j, B_i, and B_j, which depend on the Knudsen numbers of the components, are a solution of an algebraic system of equations written in matrix form

$$\begin{bmatrix} Y_i & M_i & P_i & G_i \\ W_i & Y_i & H_i & P_i \\ P_j & G_j & Y_j & M_j \\ H_j & P_j & W_j & Y_j \end{bmatrix} \times \begin{bmatrix} A_i \\ B_i \\ A_j \\ B_j \end{bmatrix} = \begin{bmatrix} \pi \\ \pi/2 \\ \pi \\ \pi/2 \end{bmatrix} \tag{1.2}$$

where the following designations are introduced:

$$Y_i = C_{12}{}^i + \alpha_i(\pi/2 - C_{12}{}^i), \quad W_i = C_{11}{}^i + \alpha_i(\pi/3 - C_{11}{}^i)$$

$$M_i = C_{22}{}^i + \alpha_i(\pi - C_{22}{}^i), \quad H_i = -\alpha_i b_j b_i^{-1}(\pi/3 - C_{11}{}^i)$$

$$P_i = -\alpha_i b_j b_i^{-1}(\pi/2 - C_{12}{}^i), \quad G_i = -\alpha_i b_j b_i^{-1}(\pi - C_{22}{}^i)$$

$$C_{11}{}^i = I_1^2[{}^{64}/_3 + 160/\delta_i^2] + 48/\delta_i I_0^1 - I_1^0[40/3 + 32/\delta_i^2] - \pi/\delta_i^2 + 8\sqrt{\pi}/3\delta_i$$

$$C_{12}{}^i = I_1^0[8/\delta_i^2 - {}^8/_3] + {}^{32}/_3 I_1^2 + \frac{8}{\delta_i} I_0^1 - \pi/\delta_i^2 + 4\sqrt{\pi}/3\delta_i$$

$$C_{22}{}^i = 8I_1^0, \quad I_n^m(\delta) = \int_0^1\int_0^\infty x^m(1 - x^2)^{1/2} y^n \exp(-y^2 - 2\delta x/y)\,dx\,dy$$

$$\alpha_i = \delta m_j \nu_{ij}/m_0\nu_i, \quad \nu_i = \nu_{ii} + \nu_{ij}$$
$$b_i = [\Delta_i(1-\alpha_j) - \Delta_j\alpha_i]/(1-\alpha_i-\alpha_j), \ \Delta_i = {}^1/_2\,(2kT/m_i)^{1/2}\,Rk_i/\delta_i,$$
$$\delta_i = (m_i/2kT)^{1/2}\nu_i R$$

(δ_i is the inverse Knudsen number).

By solving the system of equations (1.2) one can obtain equations for the velocities of the components averaged over the cross section of the capillary

$$\langle u_{iz}\rangle = b_i\Phi_i + b_jF_i$$

where the following designations are introduced:

$$\Phi_i = \Delta^{-1}\{\pi\theta(1-\alpha_j)\beta_j\gamma_i - {}^1/_{12}\pi^2x_i(1-\alpha_j)\beta_j + \pi^2\alpha_j\theta\gamma_j'\gamma_i - {}^1/_{12}\pi^3\alpha_j[x_i\gamma_j + \alpha_j\gamma_i] - {}^1/_{12}\pi^2x_i\alpha_j\varkappa_j\} - 1 \tag{1.3}$$

$$F_i = \Delta^{-1}\{-\pi\theta x_i\beta_i\gamma_j + \pi^2x_i\theta\gamma_i'\gamma_j + {}^1/_{12}\pi^2\alpha_i\alpha_j\beta_i - {}^1/_{12}\pi^3\alpha_i[\alpha_i\gamma_j + \alpha_j\gamma_i] + {}^1/_{12}\pi^2x_i(1-\alpha_j)\varkappa_i\} \tag{1.4}$$

$$\Delta = \theta^2\beta_i\beta_j + \pi\alpha_i\theta\beta_j\gamma_i' + \pi\alpha_j\theta\beta_i\gamma_j' - {}^1/_{12}\pi^2x_i\alpha_j(\varkappa_i + \varkappa_j) - {}^1/_{12}\pi^2(\alpha_i^2\beta_j + \alpha_j^2\beta_i) \tag{1.5}$$

$$\gamma_i = C_{12}{}^i - C_{11}{}^i - {}^1/_4C_{22}{}^i, \quad \gamma_i' = \gamma_i - {}^1/_{12}C_{22}{}^i$$
$$\theta = 1 - \alpha_i - \alpha_j, \quad \beta_i = (C_{12}{}^i)^2 - C_{11}{}^iC_{22}{}^i$$
$$\varkappa_i = C_{22}{}^i({}^1/_2C_{12}{}^j - C_{11}{}^j) - C_{12}{}^i({}^1/_2C_{22}{}^j - C_{12}{}^j)$$

2. Assuming that the time it takes to establish stationary flow in the capillary is negligibly small compared with the relaxation time in the bulbs, one can write equations of conservation of the number of molecules of each component

$$\frac{\partial n_{i1}}{\partial t} = -\frac{\pi R^2}{V_1}\langle u_{iz}\rangle = D_in_{i1} + C_in_{jz} + K_i$$
$$\frac{\partial n_{j2}}{\partial t} = \frac{\pi R^2}{V_2}\langle u_{jz}\rangle = C_jn_{i1} + D_jn_{j2} + K_j \tag{2.1}$$
$$D_i = \frac{\varphi}{\nu_im_i}[\alpha_j(\Phi_i + F_i) - \Phi_i], \quad C_i = \frac{V_j\varphi}{V_im_j\nu_j}[F_i - \alpha_i(\Phi_i + F_i)]$$
$$\varphi = \pi R^2kT/V\theta L, \quad V = V_1V_2/(V_1 + V_2)$$

where $n_{i1}(t)$ is the density of molecules of the i-th component in the first bulb and $n_{j2}(t)$ is the density of molecules of the j-th component in the second bulb.

Having determined $n_{i1}(t)$ and $n_{j2}(t)$ from the system of equations (2.1), one can find the maximum value Δp_m of the baroeffect and the time t_m when it is reached, by time differentiation of the solution obtained:

$$t_m = \frac{1}{S_1 - S_2}\ln\frac{S_2}{S_1} \tag{2.2}$$
$$\frac{\Delta p_m}{p} = \frac{(D_i + C_i - S_2)(S_1 - D_i - C_i)}{C_i(S_2 - S_1)}\left(e^{S_1t_m} - e^{S_2t_m}\right) \tag{2.3}$$
$$S_{1,2} = (D_i + D_j)^{1/2} \pm {}^1/_2\sqrt{(D_i - D_j)^2 + 4C_iC_j}$$

Let us examine the free-molecular limit ($\delta_{ij} \to 0$) of Eqs. (2.2) and (2.3). Having used the well-known series expansion of the integrals I_n^m, we obtain

$$t_m = \frac{3LV}{4R^3\sqrt{2\pi kT}}\,\frac{\sqrt{m_im_j}}{(\sqrt{m_i} - \sqrt{m_j})}\ln\sqrt{\frac{m_i}{m_j}}$$
$$\frac{\Delta p_m}{p} = \exp\left(-\frac{\sqrt{m_i}}{\sqrt{m_i} - \sqrt{m_j}}\ln\sqrt{\frac{m_i}{m_j}}\right) - \exp\left(-\frac{\sqrt{m_j}}{\sqrt{m_i} - \sqrt{m_j}}\ln\sqrt{\frac{m_i}{m_j}}\right)$$

which coincides with the equations for these values obtained on the basis of Knudsen's equation for the flow rate of a gas in a free-molecular process.

Let us examine the viscous limit of Eqs. (2.2) and (2.3)

$$t_m = \frac{8VL\eta}{p\pi R^4}\ln\frac{R^2p}{8D_{ij}\eta}, \quad \frac{\Delta p_m}{p} = \frac{8D_{ij}\eta}{R^2p}\sigma$$

where σ is the coefficient of diffusion slippage, while the viscosity of the mixture is

$$\eta = p(\nu_i c_j + \nu_j c_i)/\nu_i \nu_j, \quad c_i = n_i/n, \quad D_{ij} = kTc_j/\mu\delta\nu_{ij}, \quad \mu = m_1 m_2/m_0$$

Calculations were conducted according to Eqs. (2.2) and (2.3) in the entire range of Knudsen numbers for five pairs of gases. The integrals I_1^0, I_0^1, and I_1^2 needed for the calculations were determined on an electronic computer. The collision parameters were determined from experimental coefficients by the following equations:

$$\nu_{ii} = p/2\eta_i, \quad \nu_{jj} = p/2\eta_j, \quad \delta = kT/2\mu\nu_{ij}D_{ij}$$

$$\nu_{ij} = \frac{p}{2}\left[\frac{1}{\eta} - \frac{1}{2\eta_i} - \frac{1}{2\eta_j}\right] + \frac{p}{2}\sqrt{\frac{1}{\eta^2} + \left(\frac{1}{2\eta_i} - \frac{1}{2\eta_j}\right)^2}$$

The calculated curves and experimental values of $t_m(\delta_{ij})$ and $\Delta p_m(\delta_{ij})$ are presented in Figs. 1 and 2. The terms are as follows: Δp_m in mm Hg, t_m in 10^2 sec, $\delta_{ij} = 2\delta_i\delta_j/(\delta_i + \delta_j)$. The curves and points correspond to: 1) He−Ar, 2) H_2−D_2, 3) D_2−Ar, 4) H_2−Ar, 5) H_2−He.

With good agreement of the theoretical and experimental results with respect to Δp_m, an increase in the disagreement to 20% is observed in the intermediate process for the viscous and free-molecular limits. The excess of the experimental values of Δp_m over the theoretical values in the free-molecular region is explained by the fact that the lighter gases have the principal share of the specular reflection.

The disagreement in the region of the viscous process with slippage apparently must be attributed to the insufficiently accurate calculation of the coefficient of diffusion slippage, which is very sensitive to the parameters of the interaction potentials of the molecules. Since only the ratio of fluxes of the components enters into Δp_m, it is of special interest to compare the theoretical calculations and experimental results on the time it takes to reach the maximum baroeffect. It is seen from Fig. 2 that the agreement is good – the disagreement not exceeding 10%. Thus, the comparison shows that the model BGK equations for the most part describe the experimental data well. For better agreement in the region of the nearly free-molecular process, it is necessary to adopt more realistic boundary conditions than completely diffuse reflection. In order to achieve a correct description of the viscous limit either the model must be improved or the Boltzmann equation must be solved directly with the actual interaction potential of the molecules.

3. Let us examine the flow, produced by pressure and concentration gradients, of a binary mixture in a capillary from the point of view of the thermodynamics of irreversible processes. The fluxes of particle number and mass are written as

$$J_1 = n_i \langle u_{iz}\rangle + n_j \langle u_{jz}\rangle = L_{11}X_1 + L_{12}X_2$$

$$J_2 = \rho\,[\langle u_{iz}\rangle - \langle u_{jz}\rangle] = L_{21}X_1 + L_{22}X_2$$

respectively, where ρ is the density of the mixture, while

$$X_1 = -\rho\frac{1}{\rho}\frac{\partial p}{\partial z}, \quad X_2 = -n\frac{\partial c_i}{\partial z}$$

emerge in the role of thermodynamic forces, where, according to Onsager's interaction principle, the cross kinetic coefficients are equal to $L_{12} = L_{21}$. Having made use of the equations for the average velocities of the components, we find the kinetic coefficients

$$L_{11} = \frac{nkT}{\theta m_j \nu_j \rho}\left[\frac{c_i}{c_j}\alpha_i(\Phi_i + F_i) - c_iF_i - \frac{c_i^2\alpha_i}{c_j\alpha_j}\Phi_i + c_i(\Phi_j + F_j) - c_i\frac{\alpha_i}{\alpha_j}F_j - c_j\Phi_j\right]$$

$$L_{12} = \frac{kT}{\theta m_j \nu_j}\left[\frac{c_i}{c_j}F_i - \frac{c_i\alpha_i}{c_j\alpha_j}\Phi_i + \Phi_j - \frac{\alpha_i}{\alpha_j}F_j\right]$$

$$L_{21} = \frac{kT}{\theta m_j \nu_j}\left[\frac{\alpha_i}{c_j}(\Phi_i + F_i - \Phi_j - F_j) + \frac{c_i\alpha_i}{c_j\alpha_j}F_j - F_i + \Phi_j - \frac{c_i\alpha_i}{c_j\alpha_j}\Phi_i\right]$$

$$L_{22} = \frac{\rho kT}{n\theta m_j \nu_j c_j}\left[F_i + \frac{\alpha_i}{\alpha_j}F_i - \left(\Phi_j + \frac{\alpha_i}{\alpha_j}\Phi_i\right)\right]$$

The difference between the cross kinetic coefficients has the form

$$L_{21} - L_{12} = \frac{kT}{\theta m_j \nu_j}\left[\frac{\alpha_i}{c_j}(\Phi_i + F_i - \Phi_j - F_j) + \frac{c_i\alpha_i}{c_j\alpha_j}F_j - F_i - \frac{c_i}{c_j}F_i + \frac{\alpha_i}{\alpha_j}F_j\right] \tag{3.1}$$

By substituting Eqs. (1.4) and (1.5) into (3.1), one can show that $L_{21} - L_{12} = 0$ for arbitrary Knudsen numbers. In the limit ($\delta_{i,j} \to \infty$) of the viscous process we have

$$L_{12} = D_{ij}\sigma, \quad L_{11} = R^2pn/8\eta\rho$$

$$L_{22} = \rho n^{-1}D_{ij}, \quad L_{21} = \alpha_p D_{ij}$$

for the kinetic coefficients, where α_p is the barodiffusion constant, with

$$\alpha_p = \sigma = \frac{(2c_i - 1)(v_j\sqrt{m_j} + v_i\sqrt{m_i}) + c_j v_i\sqrt{m_j} - c_i v_j\sqrt{m_i}}{(c_j\sqrt{m_j} + c_i\sqrt{m_i})(c_j v_i + c_i v_j)}$$

The following conclusions can be drawn from the equality of the cross coefficients. The coefficient L_{21}, characterizing the "separation effect" of the mixture in the entire range of Knudsen numbers, which is of practical importance, is more conveniently studied experimentally by measuring L_{12} in experiments on the diffusion baroeffect. The simplicity and completely attainable sufficient accuracy of the measurement of the coefficient of diffusion slippage from experiments on the baroeffect permit one to recommend its application for the determination and control of parameters of the interaction potentials of molecules. An exact expression for the coefficient of diffusion slippage did not exist before. The barodiffusion constant is calculated exactly by Grad's method in [6] for any interaction potential.

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