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EXACT SOLUTION OF THE CAPILLARY DIFFUSION EQUATION FOR A THREE-COMPONENT MIXTURE

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The paper gives an exact solution of the steady system of equations for stable three-component diffusion in the entire range of concentrations for a long capillary under a controlled capillary pressure differential. The solution allows one to calculate the distributions of component concentrations and mixture density along the capillary. It is shown that if the diffusion coefficients are markedly different, an extremum of mixture density can arise inside the capillary. In particular, if the density of the mixture in the upper flask is higher than that in the lower flask and the stratification of the system is generally stable, a region with a reverse density gradient that is unstable against gravity convection can appear inside the capillary. A comparison with experimental results shows that the resistance to gravity convection is disturbed when an extremum of mixture density arises in the channel during steady diffusion.

Free convection in a heterogeneous three-component gas medium in a gravitational field for the case where the mixture density is smaller in the upper flask than in the lower flask was discovered in 1966. Studies of [1–3] and subsequent experimental investigations [4, 5] demonstrated that convection has a number of interesting features.

To establish the causes of abnormal convection, Kosov and Seleznev [4] attempted to solve the system of equations of steady three-component capillary diffusion for the case of lower concentration of one of the components. However, for finite concentrations of all mixture components, this solution gives a non-physical result — a concentration extremum inside the capillary for one of the components.

The present paper gives an exact solution of the equations of steady three-component diffusion over the entire range of concentrations for a long capillary under conditions of a controlled capillary pressure difference, i. e., in the presence of a hydrodynamic capillary flow of the mixture.

We consider the problem of steady diffusion of a three-component mixture of ideal gases through a long ($L \gg R$) capillary (L and R are the capillary length and radius, respectively). Figure 1 shows a diagram of the capillary diffusion.

Below, the superscript $i = 1, 2, 3$ corresponds to the mixture component number (the mixture components are arranged so that $m_1 < m_2 < m_3$, where m_i is the molecular weight of the ith component).

Let the concentration and pressure in the flasks (see Fig. 1) be constant. The stable steady three-component capillary diffusion is described by the equations

$$\begin{gathered} P_1 = \text{const}, \qquad P_2 = \text{const}, \qquad T = \text{const}, \\ \sum_i c_i = 1, \qquad \operatorname{div}(n c_i \boldsymbol{u}_i) = 0 \quad (i = 1,\ 2), \qquad \sum_{j=1}^{3} \frac{c_i c_j}{D_{ij}} (\boldsymbol{u}_i - \boldsymbol{u}_j) = -\operatorname{grad}(c_i) \quad (i = 1,\ 2), \end{gathered} \tag{1}$$

where P is the gas pressure, T is the gas temperature, n is the number density of the gas, which changes along the capillary because of the pressure difference and gravity, c_i is the molar concentration of the ith component, $\boldsymbol{u}_i$ is the average-number velocity of the ith component, and D_{ij} is the interdiffusion coefficient of the ith and $j$the components. The last equation in (1) is a Stefan–Maxwell equation.

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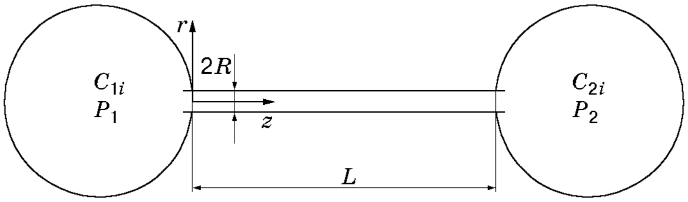

Fig. 1. A diagram of capillary diffusion of the gas mixture.

The pressure difference gives rise to a nonzero average-number molecular flux through the capillary. For a closed system of flasks, the number averaged molecular flux is equal to zero although in this case, the pressure difference is nonzero due to the barodiffusion effect. More precisely, a number averaged molecular flux arises when the channel pressure difference differs from the barodiffusion value. We consider the case of a small pressure difference, i.e., a slow gas flow. For large pressure differences, it is difficult to specify boundary conditions for diffusion because it is necessary to obtain a solution for the concentration field in the vicinity of the capillary ends; however, the solution type remains the same as for laminar flows.

Since the capillary is long and thin and the flow is slow, the transverse concentration distribution is ignored, i.e., the system is considered one-dimensional. Averaging system (1) over the channel cross section, we obtain the following system (the trivial equation for temperature is omitted):

$$\begin{gathered}\sum_i c_i = 1, \qquad n\sum_i c_i u_i = j = \frac{J}{S}, \qquad n c_i u_i = j_i = \frac{J_i}{S} = \gamma_i \quad (i = 1,\, 2),\\ \sum_{j=1}^{3} \frac{c_i c_j}{D_{ij}}\,(u_i - u_j) = -\frac{dc_i}{dz} \quad (i = 1,\, 2).\end{gathered} \tag{2}$$

Here J is the total number flux through the capillary, J_i is the total number flux of the ith component through the capillary, S is the cross-section area of the capillary, j and j_i are the densities of the number flux and the ith component, respectively, and γ_i is a constant.

It should be noted that we do not solve the problem of the relationship between the flux J and the pressure difference ΔP, restricting ourselves to the statement that J is constant along the channel. The value of J must be found from the solution of the hydrodynamic problem.

The boundary conditions for system (2) are

$$c_1(0) = C_{11}, \qquad c_2(0) = C_{21}, \qquad c_1(L) = C_{12}, \qquad c_2(L) = C_{22}, \tag{3}$$

where C_{ik} are the concentrations of the components in the flasks, $i = 1$ and 2 is the component number, and $k = 1$ and 2 is the flask number.

In the notation of (2), the Stefan–Maxwell equations reduce to

$$\sum_{j=1}^{3} \frac{1}{nD_{ij}}\,(c_j j_i - c_i j_j) = -\frac{dc_i}{dz} \qquad (i = 1,\, 2).$$

Since $j_i = \text{const}$ and $c_3 = 1 - c_1 - c_2$, for two independent concentrations (the solution can be easily extended to an N-component mixture), we have a closed system of two heterogeneous linear equations with constant coefficients.

We introduce the following notation: $\varphi_i = j_i/j$ is the dimensionless flux, $\zeta = jz/(nD_{12})$ is the dimensionless coordinate, and $\delta_{i3} = D_{i3}/D_{12}$ $(i = 1,\, 2)$ are the dimensionless diffusion coefficients ($\delta_{12} = 1$). Then,

$$\sum_{j=1}^{3} \frac{1}{\delta_{ij}}\,(c_j\varphi_i - c_i\varphi_j) = -\frac{dc_i}{d\zeta} \quad (i = 1,\, 2), \qquad \sum_{i=1}^{3} \varphi_i = 1. \tag{4}$$

Expressing c_3 and φ_3 in (4) in terms of c_i and φ_i ($i = 1$ and 2), we have the equations

$$\begin{gathered} c_2 j_1\Big(\frac{1}{\delta_{12}} - \frac{1}{\delta_{13}}\Big) - c_1\Big(\frac{\varphi_2}{\delta_{12}} - \frac{1-\varphi_2}{\delta_{13}}\Big) + \frac{dc_1}{d\zeta} = -\frac{\varphi_1}{\delta_{13}},\\ c_1 j_2\Big(\frac{1}{\delta_{12}} - \frac{1}{\delta_{23}}\Big) - c_2\Big(\frac{\varphi_1}{\delta_{12}} - \frac{1-\varphi_1}{\delta_{23}}\Big) + \frac{dc_2}{d\zeta} = -\frac{\varphi_2}{\delta_{23}}, \end{gathered} \tag{5}$$

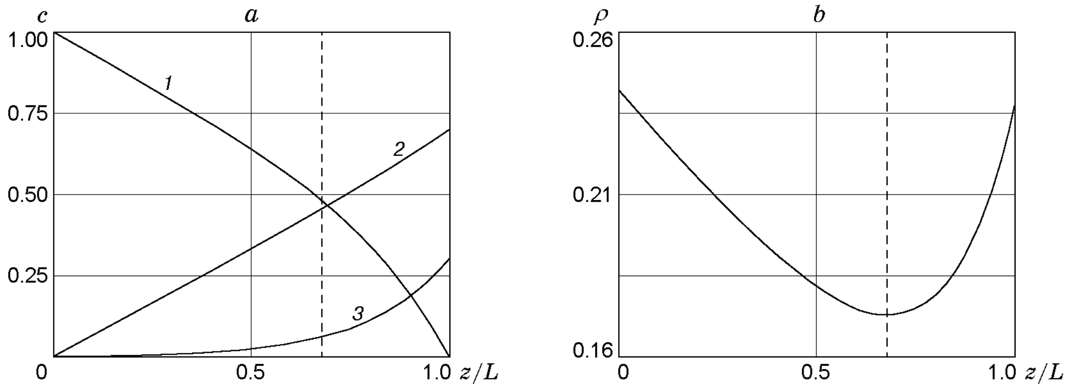

Fig. 2. Distributions of Ar, He, and R12 concentrations (a, curves 1–3, respectively) and density (b) for a (30% R12 + 70% He)–Ar mixture for $j = 0$ ($C_{\mathrm{Ar},1} = 1$, $C_{\mathrm{He},2} = 0.7$, $C_{\mathrm{R12},2} = 0.3$, $m_{\mathrm{Ar}} = 0.0399$ kg/mole, $m_{\mathrm{He}} = 0.004026$ kg/mole, $m_{\mathrm{R12}} = 0.121$ kg/mole, $D_{\mathrm{He-Ar}} = 6.39 \cdot 10^5$ m^2/sec, $D_{\mathrm{He-R12}} = 3.3 \cdot 10^5$ m^2/sec, $D_{\mathrm{Ar-R12}} = 0.69 \cdot 10^5$ m^2/sec, $j_{\mathrm{He}} = -4.238 \cdot 10^5$ m/sec, and $j_{\mathrm{Ar}} = 4.247 \cdot 10^5$ m/sec).

where φ_i are the arbitrary constants of integration determined from the boundary conditions. It is the independence of the component flux through the channel cross section that makes this problem solvable exactly without additional assumptions on the smallness of the concentration of one of the components [4].

The solution of the system of inhomogeneous linear equations is the sum of the particular solution of the homogeneous system c_{Fi} and the general solution of the uniform system c_{0i}: $c_i = c_{Fi} + c_{0i}$.

Denoting

$$A = \frac{1-\varphi_1}{\delta_{23}} + \frac{1-\varphi_2}{\delta_{13}} + \frac{1-\varphi_3}{\delta_{12}}, \qquad B = \frac{\varphi_1}{\delta_{12}\delta_{13}} + \frac{\varphi_2}{\delta_{12}\delta_{23}} + \frac{\varphi_3}{\delta_{13}\delta_{23}},$$

we can express c_2 in terms of c_1 from the first equation in (7) and obtain the following equation for c_1:

$$\frac{d^2 c_1}{d\zeta^2} - A\,\frac{dc_1}{d\zeta} + Bc_1 = B\varphi_1.$$

The general solution of the homogeneous system (5) has the form

$$c_{0i} = \sum_{k=1}^{2} X_{li} \exp{(\lambda_k \zeta)}, \tag{6}$$

and a particular solution of the inhomogeneous system (5) has the form $c_{Fi} = \varphi_i$. In the exponent (6), the constants λ_k are calculated from the formula

$$\lambda_k = (A + (-1)^k \sqrt{A^2 - 4B}\,)/2 \qquad (k = 1,\, 2).$$

Introducing the additional notation

$$K_i = \frac{1-\delta_{13}\lambda_i}{\delta_{13}-1} + \varphi_2, \quad x_1 = \frac{K_2 C_{11} - C_{12} + \varphi_2 - K_2\varphi_1}{K_2 - K_1}, \quad x_2 = \frac{K_1 C_{11} - C_{12} + \varphi_2 - K_1\varphi_1}{K_1 - K_2},$$

where explicit boundary conditions (3) for $z = 0$ are taken into account, we finally have

$$c_1(\zeta) = \varphi_1 + x_1 \exp{(\lambda_1\zeta)} + x_2 \exp{(\lambda_2\zeta)}, \quad c_2(\zeta) = \varphi_2 + K_1 x_1 \exp{(\lambda_1\zeta)} + K_2 x_2 \exp{(\lambda_2\zeta)}. \tag{7}$$

It is impossible to express explicitly the constants φ_i from boundary conditions (3) for $z = L$ but we can calculate φ_i numerically for specified concentrations C_{2i}.

Solution (7) can be used to calculate the distribution of the mixture density inside the channel:

$$\rho(z) = \sum_i n m_i c_i(z).$$

As follows from the curves of $\rho = \sum\limits_i n m_i c_i(z) \Big/ \sum\limits_i n m_i$ versus z/L shown in Figs. 2–5, an extremum of mixture density is observed inside the channel for some combinations of gases (C_i and m_i are the concentration and molecular

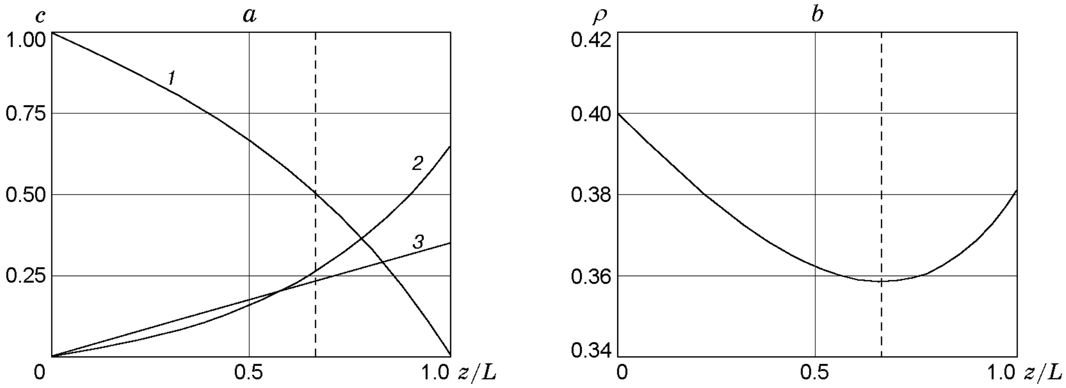

Fig. 3. Distributions of N_2, Ar, and H_2 concentrations (a, curves 1–3, respectively) and density (b) for a N_2–(35% H_2 + 65% Ar) mixture for $j = 0$ ($C_{N_2,1} = 1$, $C_{H_2,2} = 0.35$, $C_{Ar,2} = 0.65$, $m_{N_2} = 0.028$ kg/mole, $m_{H_2} = 0.0020158$ kg/mole, $m_{Ar} = 0.0399$ kg/mole, $D_{H_2-N_2} = 6.89 \cdot 10^5$ m^2/sec, $D_{H_2-Ar} = 7.25 \cdot 10^5$ m^2/sec, $D_{N_2-Ar} = 0.9 \cdot 10^5$ m^2/sec, $j_{H_2} = -2.436 \cdot 10^5$ m/sec, and $j_{N_2} = 2.594 \cdot 10^5$ m/sec).

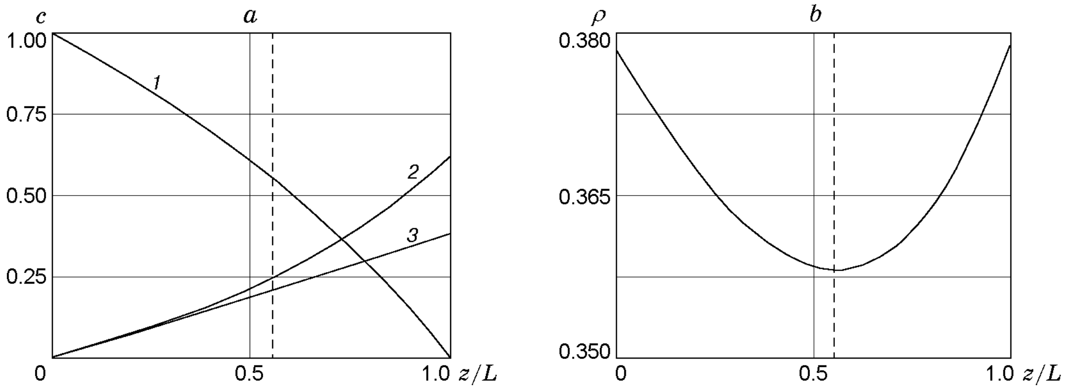

Fig. 4. Distributions of N_2, CO_2, and H_2 concentrations (a, curves 1–3, respectively) and density (b) for a (38% H_2+62% CO_2)–N_2 mixture for $j = 0$ ($C_{H_2,1} = 0.38$, $C_{CO_2,1} = 0.62$, $C_{N_2,2} = 1$, $m_{H_2} = 0.0020158$ kg/mole, $m_{CO_2} = 0.044$ kg/mole, $m_{N_2} = 0.028$ kg/mole, $D_{H_2-N_2} = 6.89 \cdot 10^5$ m^2/sec, $D_{H_2-CO_2} = 5.75 \cdot 10^5$ m^2/sec, $D_{N_2-CO_2} = 1.29 \cdot 10^5$ m^2/sec, $j_{H_2} = -2.512 \cdot 10^5$ m/sec, and $j_{N_2} = 2.896 \cdot 10^5$ m/sec).

weight of the components, respectively, D_i are the diffusion coefficients of the components under normal conditions, and j_i are the densities of the component fluxes). In Figs. 2–4, the vertical dashed curve shows the cross section in which the extremum is observed. Under conditions of an external gravitational field (diffusion in a vertical capillary), the existence of an extremum of mixture density inside the channel can lead to convective instability of the diffusion even if a less dense mixture is in the upper flask.

For $j = 0$, Figs. 2–4 show calculation results for several mixtures studied in [4]. All cases of disturbance of diffusion stability observed in [4] are characterized by the appearance of a density extremum in the channel. We note that for $j = 0$, solution (7) gives the desired concentration distribution only as the limit for $j \to 0$. For $j = 0$, we can modify the above solution and obtain a simpler explicit relation [6].

The concentration and density distributions were calculated for several values of the flux density, and the results are shown in Fig. 5. From this figure it follows that the position and value (even the change of sign) of the density inversion in the channel can be controlled by varying the flux j.

Since the concentration and density distributions along the capillary do not depend on the channel length L, all calculations are performed for unit length. For the same reason, the concentration and density distributions can be realized experimentally for any section of the axis Oz by maintaining the corresponding concentrations in the flasks.

It can be stated that during diffusion of a three-component mixture, gravity convection (instability) is due to the appearance of a minimum of mixture density inside the capillary.

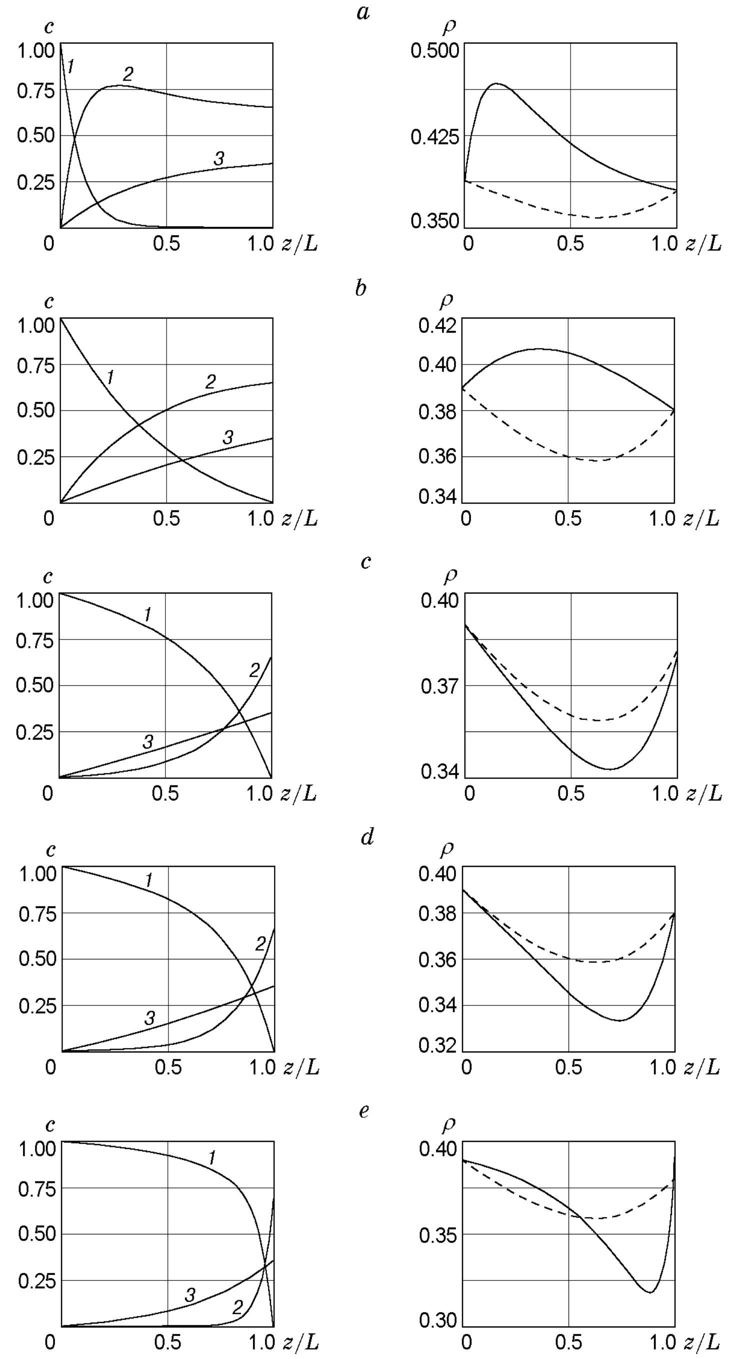

Fig. 5. Hydrodynamic flux density of an N_2–(35% He + 65% Ar) mixture versus concentration and pressure distributions for $j = -16$ (a), -4 (b), 2 (c), 4 (d), and 16 (e): curves 1–3 refer to N_2, Ar, and He, respectively; the dashed curve refers to $j = 0$ ($C_{N_2,1} = 1$, $C_{He,2} = 0.35$, $C_{Ar,2} = 0.65$, $m_{He} = 0.004026$ kg/mole, $m_{N_2} = 0.028$ kg/mole, $m_{Ar} = 0.0399$ kg/mole, $D_{He-N_2} = 6.26 \cdot 10^5$ m^2/sec, $D_{He-Ar} = 6.39 \cdot 10^5$ m^2/sec, $D_{N_2-Ar} = 0.9 \cdot 10^5$ m^2/sec; for $j = 0$, $j_{He} = -2.2 \cdot 10^5$ m/sec and $j_{N_2} = 2.391 \cdot 10^5$ m/sec).

Remark 1. The appearance of a density extremum inside the channel causes convection. After the onset of the convection, the above formulas become inapplicable. The density distribution with the extremum arises again if the convection stops.

Remark 2. As follows from the given dependences, the densities $\rho_{\min}/\rho_{\max}$ for gas mixtures change in the range of 0.72–0.94. For a vertical channel of length 1 m, the corresponding relative change in density due to gravity is defined by the Boltzmann factor: $\rho_{\min}/\rho_{\max} = \exp(-mg/(kT))$ (in the numerator of the exponent, a dimensional quantity equal to 1 m is omitted). For the heaviest gas (R12 Freon), this ratio is 0.9995. This difference in the values of the relative change in density suggests that in the vertical channel, the change in density due to three-component diffusion is dominant. The relative change in density due to gravity decreases with decrease in channel length, while the change in density due to three-component diffusion retains its value. Moreover, the explicit relation for the density (pressure) distribution in the channel was ignored in the solution of the problem; therefore, this solution can be modified for a vertical channel by adding the barometric Boltzmann multiplier. Generally, the exponent of the Boltzmann factor depends on the vertical coordinate, but because the relative change in density is small, as its value, we can use the average molecular weight of the mixture in the channel as its value with sufficient accuracy.

The appearance of a density minimum is due to the presence of the third component in the mixture, and in this case, it is necessary that the diffusion coefficients of these components differ significantly.

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