Diffusion and convective mixing modes of binary gas mixtures dissolved in the third component

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Abstract. The numerical investigation of the mixing of an isothermal binary gas mixture dissolved in the third component has been carried out. The boundary relation that determines the change of “diffusion – concentration convection” modes is obtained in the framework of a linear stability analysis for a flat vertical channel with mass-impermeable walls. Diffusion and convection regimes were studied for a mixture of a pair of gases H₂ and Ar, which was diluted first with a light and then with a heavier component. It is shown that the nature of the ballast gas has a significant effect on the diffusion and convective mixing regimes of the main diffusing components.

1. Introduction

The mutual influence of the components on each other in multicomponent gas mixtures can lead to phenomena that do not occur in ordinary binary diffusion. This is evidenced by the results given in the experimental works [1-4], as well as the analysis of the Stefan-Maxwell equations [5-9]. Features of multicomponent mass transfer, such as reverse diffusion, osmotic diffusion, diffusion barrier, and diffusion instability can occur at certain ratios of concentrations and interdiffusion coefficient of the components [1, 5]. The physical mechanism of these phenomena is due to the fact that the observed transfer of the component is conditioned by the “synergistic effect”, which consists in the superposition of the hydrodynamic (convective) flow on the molecular transfer [9].

One example of the Toor’s effects, for example, osmotic diffusion, is the diffusion of two gases uniformly diluted by a third (ballast) gas, the concentration gradient of which is equal to zero (the diffusion of two main gases through the layer of third immobile gas). This task is of great practical interest, since when various diluent gases with different properties are used in the diffusion, it becomes possible to control the nature of the mass transfer [3].

Depending on the direction of the mixture density gradient, various mechanisms of the mixing, i.e. both diffusion and convection caused mixing, occur. In [10], it was shown that during diffusion of a binary system equally diluted by the third component, there are nonlinear partial concentration dependences on the coordinate leading to the formation of a non-monotonic distribution of the mixture density, which can cause gravitational convective instability.
The mathematical descriptions of the processes occurring in multicomponent gas mixtures employ methods based on both linear stability analysis [4, 11–14] and numerical approaches [15–21] that simulate complex mass transfer. At the same time, the study of diffusion and convective mixing of multicomponent systems dissolved in a diluent gas is fragmented both experimentally and theoretically [20, 21]. Therefore, the investigation of the features of multicomponent mixing, which leads to isothermal convective transfer of components during binary mixture diffusion in a third solvent gas, seems interesting from the point of view of interpreting separation processes.

In this work, the numerical investigation based on a linear stability analysis of the influence of the diluent gas nature on the transport of the main miscible components is conducted.

2. Problem formulation

The mathematical description is based on the analysis of the system of equations of continuum mechanics for multicomponent systems with respect to small perturbations [22]. The macroscopic motion of an isothermal ternary gas mixture is described by the general system of hydrodynamic equations, which includes the Navier-Stokes equations, the conservation of the number of particles of the mixture and components.

With the condition of independent component diffusion, for an isothermal gas mixture \( \sum_{i=1}^{3} j_i = 0 \); \( \sum_{i=1}^{3} c_i = 1 \), and the system of equation to be solved has the form [22, 23]:

\[
\begin{align*}
\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \nabla \mathbf{u}) \right] &= -\nabla p + \eta \nabla^2 \mathbf{u} + \left( \frac{\eta}{3} + \zeta \right) \nabla \text{div} \mathbf{u} + \rho g \\
\frac{\partial n}{\partial t} + \text{div}(n \mathbf{v}) &= 0 \\
\frac{\partial c_i}{\partial t} + \mathbf{v} \nabla c_i &= -\text{div} j_i \\
j_i &= -(D_{11}^* \nabla c_1 + D_{12}^* \nabla c_2) \\
j_j &= -(D_{21}^* \nabla c_1 + D_{22}^* \nabla c_2)
\end{align*}
\]

Here \( \mathbf{u} \) is the mass-average velocity; \( \mathbf{v} \) is the number-average velocity; \( \rho \) is the density; \( p \) is the pressure; \( \eta \) and \( \zeta \) are the coefficients for the shearing and volume viscosities, respectively; \( g \) is the acceleration of gravity; \( n \) is the numerical density; \( t \) is the time; \( c_i \) is the concentration of the \( i \)th component; \( j_i \) is the diffusion flux density of the \( i \)th component; and \( D_{ij}^* \) is the practical diffusion coefficient, defined using interdiffusion coefficients \( D_{ij} \):

\[
\begin{align*}
D_{11}^* &= D_{13} \left[ c_1 D_{32} + (c_2 + c_3) D_{12} \right] \\
D_{12}^* &= -\frac{c_1 D_{21} (D_{12} - D_{13})}{D} \\
D_{22}^* &= D_{23} \left[ c_2 D_{31} + (c_1 + c_3) D_{21} \right] \\
D_{21}^* &= -\frac{c_2 D_{13} (D_{21} - D_{23})}{D} \\
D &= c_1 D_{21} + c_2 D_{13} + c_3 D_{12}
\end{align*}
\]

Equations (1) are complemented by equations of state

\[
p = nkT \quad T = \text{const}
\]

The system of equations (1) is solved by using the small perturbation approach [22], in which the concentration of the \( i \)th component \( c_i \) and the pressure \( p \) can be written as:

\[
c_i = \langle c_i \rangle + c_i' \quad p = \langle p \rangle + p'
\]
where \( <c_i>, \langle p \rangle \) are the constant averaged values of the respective quantities, taken as their initial values.

Assuming that at \( L \gg r \) (\( L \) and \( r \) are the length and radius of the diffusion channel, respectively) the difference between the perturbations of the number-average \( \mathbf{v} \) and the mass-average \( \mathbf{u} \) velocities in the Navier-Stokes equations are negligible [23], as well as suggesting that nonstationary perturbations of mechanical equilibrium are small, neglecting the terms quadratic in perturbations, and selecting the appropriate scale of measuring units (\( d \) for distance, \( d^2/\nu \) for time, \( D^*/d \) for velocity, \( \rho_0/D^*_{22}/d^2 \) for pressure), we obtain a system of equations of gravitational concentration convection for the perturbed values in dimensionless quantities (dashed marks are omitted):

\[
\begin{align*}
\text{Pr}_{22} \frac{\partial c_1}{\partial t} - (\mathbf{u} e_z c_1) &= \tau_{11} \nabla^2 c_1 + \frac{A_2}{A_1} \tau_{12} \nabla^2 c_2 \\
\text{Pr}_{22} \frac{\partial c_2}{\partial t} - (\mathbf{u} e_z c_2) &= \frac{A_1}{A_2} \tau_{21} \nabla^2 c_1 + \nabla^2 c_2 \\
\frac{\partial \mathbf{u}}{\partial t} &= -\nabla p + \nabla \cdot \mathbf{u} + (\text{Ra}_i \tau_{11} c_1 + \text{Ra}_i c_2) e_z
\end{align*}
\]

(2)

\[
\text{div} \mathbf{u} = 0
\]

where \( e_z \) is the unit vector in the direction of the \( z \) axis; \( \text{Pr}_g = \nu \left( D^*_g \right)^{-1} \) is the diffusive Prandtl number; \( \text{Ra}_g = g \beta \Delta A d^4 \left( \nu D^*_g \right)^{-1} \) is the partial Rayleigh number; \( \tau_g = D^*_g \left( D^*_{22} \right)^{-1} \) are the parameters that determine the relationship between the practical diffusion coefficients; \( \beta_i = -\frac{1}{\rho_0} \left( \frac{\partial \rho}{\partial c_i} \right)_{\rho,T} \); \( A_i e_z = -\nabla c_{i0} \) (subscript 0 corresponds to the mean values).

The system of equations (2) is solved under the following boundary conditions for a flat vertical channel:

\[
\begin{align*}
\mathbf{u} &= 0 \quad \frac{\partial c_1}{\partial t} = 0 \quad \frac{\partial c_2}{\partial t} = 0 \quad x = \pm 1
\end{align*}
\]

where \( x = 0 \) corresponds to the middle of the channel and on the solid surface \( x = 1 \) and \( x = -1 \).

The problem of stability (2) can be reduced to determining the sequence of critical relations for partial Rayleigh numbers \( \text{Ra}_i \) and critical motions. For odd perturbations, solution (2) will take the form [24]:

\[
\begin{align*}
\mathbf{u} &= \left( \frac{\sin \gamma x}{\sin \gamma} - \frac{\sin \gamma x}{\sin \gamma} \right) \exp[-\lambda t] \quad c_i = -\frac{K_i}{\gamma^4} \left( \frac{\sin \gamma x}{\sin \gamma} - \frac{\sin \gamma x}{\sin \gamma} \right) \exp[-\lambda t]
\end{align*}
\]

(3)

where \( \gamma = \text{Ra}^{1/4} \), i.e. \( \gamma = (\text{Ra}_1 \tau_{11} K_1 + \text{Ra}_2 K_2)^{1/4} \); \( K_1 = \frac{1 - A_2}{A_1} \tau_{12}, \quad K_2 = \frac{\tau_{11} - A_2}{\tau_{21}} \tau_{12} \); \( A_i \) is the partial concentration gradient of the \( i \)th component; and \( \lambda \) is the perturbation decrement.

Solution to the system of equations (2) for the flat vertical channel has resulted in the boundary relation (in terms of the Rayleigh numbers) that determines the change of the “diffusion – convection” modes in the form [24]:

\[
\tau_{11} \left( 1 - \frac{A_2}{A_1} \tau_{12} \right) \text{Ra}_1 + \left( \tau_{11} - \frac{A_1}{A_2} \tau_{21} \right) \text{Ra}_2 = \gamma^4 \left( \tau_{11} - \tau_{12} \tau_{21} \right)
\]

(4)
In figure 1, equation (4) in the coordinates of the Rayleigh numbers \((\text{Ra}_1, \text{Ra}_2)\) determines the boundary line I that separates the area of decaying (diffusion), i.e. the area lying below the boundary line I, and rising (concentration convection), i.e. the area lying above the boundary line I, perturbations. The position of the stability line described by equation (4) depends on \(\tau_{ij}\), i.e., the ratio of practical diffusion coefficients \(D_{ij}^*\) of light and heavy components of the mixture and the partial gradients of concentrations.

3. Numerical results

Based on the obtained analytical solution (4), a program was compiled in the Mathcad system to obtain the stability map and partial Rayleigh numbers in coordinates \((\text{Ra}_1, \text{Ra}_2)\). The calculation program was verified with an exact solution to the problem of the stability of the equilibrium of a liquid layer bounded by vertical parallel infinite planes with heat-insulated boundaries [22].

For numerical investigation we chose the systems \(0.5009 \text{H}_2 + 0.4991 \text{He} – 0.4969 \text{Ar} + 0.5031 \text{He}\) and \(0.4958 \text{H}_2 + 0.5042 \text{N}_2 – 0.5106 \text{Ar} + 0.4894 \text{N}_2\), which have been experimentally studied in [3]. Studies conducted in [3] showed that that the nature of the diluent gas significantly affects the diffusion process in isobaric conditions in three-component systems with ballast gases. At the same time, this influence on the value of the diffusion coefficient can reach about 20–40%.

The results of the numerical experiment for the systems \(0.5009 \text{H}_2 + 0.4991 \text{He} – 0.4969 \text{Ar} + 0.5031 \text{He}\) and \(0.4958 \text{H}_2 + 0.5042 \text{N}_2 – 0.5106 \text{Ar} + 0.4894 \text{N}_2\) at pressure \(\rho = 0.101\) MPa and temperature \(T = 298.0\) K are shown in figure 1. Partial Rayleigh numbers in accordance with equations (2) as applied to the flat vertical channel of width \(a\), thickness \(b\) and length \(L\) can be written as follows:

\[
\text{Ra}_1 = \frac{gna^2b^2\Delta m_1}{\rho\nu D_{11}^*} \frac{\partial c_1}{\partial z} \quad \text{Ra}_2 = \frac{gna^2b^2\Delta m_2}{\rho\nu D_{22}^*} \frac{\partial c_2}{\partial z}
\]

(5)

where \(\Delta m_1 = m_1 - m_2\), \(\Delta m_2 = m_2 - m_1\), \(m_i\) is the molecular mass of \(i\)th component. The arrangement of the monotone instability line I described by equation (4) and the line of zero density gradient II defined by the equation \(\tau_{11}\text{Ra}_1 = -\text{Ra}_2\) are also shown in figure 1. The mutual arrangement of boundary lines I and the line of zero density gradient II shows the existence of the region (sector between lines I and II in figure 1) when the mixture state is unstable, although the density at the top part of the channel is smaller than at the bottom, which at first glance corresponds only to diffusion-type mixing. If the experimental conditions are known (pressure, temperature, composition of the mixtures in each of the flasks, and dimensions of the diffusion channel), then by formula (5) \(\text{Ra}_1, \text{Ra}_2\) can be found, and the point reflecting the given experiment on the plane \((\text{Ra}_1, \text{Ra}_2)\) can be determined.

From the experiment, we know the regime (diffusion or convection) that takes place under predetermined conditions. If the partial Rayleigh numbers lie below the line I, then the diffusion process is observed in the system. If the partial Rayleigh numbers are in the area between the lines I and II, then the stability paradox occurs in the system, i.e. there is an unstable diffusion mixing. If the partial Rayleigh numbers are situated above the line I, then the convective mixing is observed in the mixture. The points corresponding to the convective mode will be denoted by signs ●, and the diffusion will be determined by symbols ○.

The considered systems are stable. In the system \(0.5009 \text{H}_2 + 0.4991 \text{He} – 0.4969 \text{Ar} + 0.5031 \text{He}\), the partial Rayleigh numbers corresponding to the thermophysical conditions of the problem have the following values \(\text{Ra}_1 = -6.6364\) and \(\text{Ra}_2 = -229.1691\) (point 1). For the system \(0.4958 \text{H}_2 + 0.5042 \text{N}_2 – 0.5106 \text{Ar} + 0.4894 \text{N}_2\), the partial Rayleigh numbers have the following values \(\text{Ra}_1 = -35.214\) and \(\text{Ra}_2 = -44.9886\) (point 2). Thus, replacing a light ballast gas (helium) with a heavy (nitrogen) one leads to a decrease in the partial Rayleigh number \(\text{Ra}_1\) for the light component and an increase in the partial Rayleigh number \(\text{Ra}_2\) for the heavy component.
Figure 1. Areas of steady and unstable diffusion for the systems: 1 – 0.5009 H\textsubscript{2} + 0.4991 Ar + 0.5031 He; 2 – 0.4958 H\textsubscript{2} + 0.5042 N\textsubscript{2} – 0.5106 Ar + 0.4894 N\textsubscript{2}; 3 – 0.4969 Ar + 0.5031 He – 0.5009 H\textsubscript{2} + 0.4991 He; 4 – 0.5106 Ar + 0.4894 N\textsubscript{2} – 0.4958 H\textsubscript{2} + 0.5042 N\textsubscript{2}. I – neutral line of monotone perturbations; II – line of zero density gradient.

If the location of gases relative to the diffusion channel is changed, i.e. to consider unstable systems, then replacing light ballast gas with a heavy one causes the increase in the Rayleigh partial number $Ra_1$ for the light component and the decrease in the partial Rayleigh number $Ra_2$ for the heavy component ($Ra_1 = 2.4003$ and $Ra_2 = 52.2355$ (point 3 for the system 0.4969 Ar + 0.5031 He – 0.5009 H\textsubscript{2} + 0.4991 He); $Ra_1 = 26.2913$ and $Ra_2 = 33.4548$ (point 4 for the system 0.5106 Ar + 0.4894 N\textsubscript{2} – 0.4958 H\textsubscript{2} + 0.5042 N\textsubscript{2})). The obtained results are in a good agreement with the experimental data presented in [3].

Thus, studies have shown that ballast gas has a significant impact on the diffusion and convective mixing modes of the main diffusing components. The greater the molecular weight of the diluent gas, the greater the partial Rayleigh number $Ra_2$ for the heavy component in the diffusion mode and the smaller it is in the convective mode.

4. Conclusions
The article presents the results of a computational experiment to study the diffusion and convective regimes in the binary system equally diluted by the third component. In terms of Rayleigh numbers, a stability map for the binary mixture of H\textsubscript{2} and Ar gases diluted by the ballast gases of different nature and with different locations relative to the diffusion channel has been obtained. The increase in the molar mass of the diluent gas is found to have a significant effect on the value of the partial Rayleigh numbers of the light and the heavy components and their location relative to the stability line. Thus, by selecting the appropriate nature of the diluent gas, one can either intensify or slow down both diffusion and convective processes.

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Nomenclature
$A_i$ partial concentration gradient of the $i$th component, mol fraction/m;
$c'_i$ perturbed value of the concentration of the $i$th component, molar fraction;
$D_{ij}$ mutual diffusion coefficient, m$^2$/s;
$g$ acceleration of gravity, m$^2$/s;
$j_i$ partial density of the diffusion flow of the $i$th component, m/s;
$n$ number density, m$^{-3}$;
$p'$ perturbed pressure value, Pa;
$T$ temperature, K;
$u$ vector of mass-average velocity of ternary mixture, m/s;
$v$ vector of number-average velocity of ternary mixture, m/s;
$β_i$ coefficient of linear dependence of the density of the $i$th gas component on the concentration;
$γ$ critical numbers that define the spectrum of critical Rayleigh numbers;
$η$ coefficient of dynamic viscosity, Pa s;
$λ$ temporary decrement of perturbations, s$^{-1}$;
$ν$ kinematic viscosity of the mixture, m$^2$/s;
$ξ$ bulk viscosity, Pa s;
$ρ$ density of the mixture, kg/m$^3$.

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