Multicomponent mixing on the “diffusion – convection” transition boundary at elevated pressures

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Abstract. An experimental and theoretical study of three-component mixing at the “diffusion – convection” boundary at elevated pressures is carried out. It is shown that the pressure dependence of the dimensionless parameter \( \alpha \), defined as the ratio of the experimental values of the component concentrations to those calculated by the Stefan-Maxwell equations, has characteristic regions due to the interaction of structural formations moving towards each other, in which a transition from one critical motion to another occurs. Within the framework of a linear analysis of the stability of a ternary gas mixture for a vertical circular cylinder channel, it is shown that scale perturbations determining the transition from one type of flow to another correspond to a certain value of the perturbation mode \( n \) and the critical Rayleigh numbers.

1. Introduction

Significant increase in the rate of partial mixing of the components is observed when the system passes from the mode of molecular diffusion to the area of concentration gravitational convection, under certain conditions [1, 2]. This feature is associated with the occurrence of instability of the mechanical equilibrium of the mixture and subsequent development of convective flows. Various types of convective motions in one-component medium with a monotonic dependence of density on temperature are described in detail in [3, 4]. In these works, approaches related to studies of natural gravitational convection in vertical channels are generalized for non-isothermal conditions. In addition, recommendations are presented for determining the main parameters of heat and mass transfer, related to the properties of the substance under study, which allows predicting the mixing modes under specific conditions. Moreover, it is noted that, depending on the direction of the density gradient of the mixture, various mechanisms of mixing of the components, both diffusional and caused by convection, can occur. However, propagation of the above approaches to describe the “diffusion – convection” transition in multicomponent systems in the presence of several concentration and temperature gradients requires a certain correction, since the features that are absent in binary systems are not taken into account. First of all, these include the fact of destabilizing effect of diffusion on the development of convective flows in mixtures [5-7]. The resulting movement is an important mechanism for intensifying heat and mass transfer and selective separation of components. Experimental research carried out in [8, 9] shows that even in the case of isothermal multicomponent mixing, there may be convective separation effects associated with the difference in the diffusion coefficients of the components, pressure and composition. An important feature of this type of mixing is its realizability...
under conditions of a decrease in density of the mixture with height. Therefore, solutions related to separation mechanisms in multicomponent gas mixtures are relevant, since they allow obtaining new information on the problems of combined mixing.

The aim of the work is to experimentally and numerically determine the boundary of changes in the “diffusion – concentration gravitational convection” modes in an isothermal three-component gas mixture. In terms of the diffusion Rayleigh numbers, it is supposed to obtain a family of boundary lines of changes in kinetic regimes for different modes of perturbations. The obtained results of the numerical study are compared with the experimental data.

2. Experimental data
Partial transfer of components is studied on an experimental device implementing the method of two flasks connected by a vertical cylindrical channel under isothermal conditions. The cylindrical channel has the following characteristics: \( V_1 = V_2 = (76.2 \pm 0.5) \times 10^{-6} \text{ m}^3 \), \( L = (70.00 \pm 0.05) \times 10^{-3} \text{ m} \), and \( d = (4.00 \pm 0.02) \times 10^{-3} \text{ m} \). Experiments are carried out in the pressure range from 0.2 to 6.0 MPa at a temperature of 298.0 K. Experimental stand and working procedure were described in detail in [10], so only the main stages of the research will be explained in detail below. The upper and lower flasks of the apparatus are filled with the studied gas mixtures up to the pressure of the experiment. Then, with the special device connecting the flasks, the channel is opened and at the same time the start time of the mixing process is fixed. At the end of experiment, the channel is blocked and the end time of mixing is fixed. Analysis of gas mixtures from each flask is carried out on a chromatograph. Experimental concentrations are normalized to the values calculated under the assumption of diffusion according to the Stefan-Maxwell equations [11]. Dimensionless parameters \( \alpha \) obtained in this way characterize the corresponding type of mixing. If \( \alpha \approx 1 \), diffusion occurs. Analysis of the functional dependence of \( \alpha \) on \( p \) shows, that for the system of 0.5143 He + 0.4857 Ar – 0.5148 CH\(_4\) + 0.4852 Ar, diffusion occurs in the area of pressure \( p^* \approx 1.0 \text{ MPa} \) (figure 1).

![Figure 1](image-url)  
Figure 1. Dependence of the parameter \( \alpha \) on pressure: 1 – methane, 2 – helium, 3 – argon, 4 – calculation assuming diffusion.

Further increase of pressure shows, that the parameter \( \alpha \) increases. In the system under research gravitational concentration convection arises due to the instability of the mechanical equilibrium of the mixture and the pressure \( p^* \) determines the change of the “diffusion – concentration gravitational convection” regimes. At pressures significantly exceeding \( p^* \), the linear dependence is violated.

3. Problem formulation and numerical stability analysis
Mathematical description is based on the analysis of the system of equations of continuum mechanics for multicomponent systems with respect to small perturbations [3, 4]. Macroscopic motion of an isothermal ternary gas mixture is described by a general system of hydrodynamic equations, which includes the Navier-Stokes equations, the conservation equations of the particle number of the mixture and components.
Taking into account the independent diffusion condition, under which for an isothermal gas mixture
$$\sum_{i=1}^{3} j_i = 0; \quad \sum_{i=1}^{3} c_i = 1,$$
this system of equations has the following form [12]:

$$\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \nabla) \mathbf{u} \right] = -\nabla p + \eta \nabla^2 \mathbf{u} + \left( \frac{\eta + \xi}{3} \right) \nabla \text{div} \mathbf{u} + \rho \mathbf{g},$$

$$\frac{\partial n}{\partial t} + \text{div}(n \mathbf{v}) = 0,$$

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \nabla c_i = -\nabla j_i,$$

$$j_i = -\left( D_i^1 \nabla c_1 + D_i^2 \nabla c_2 \right)$$

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

$$D_i^1 = \frac{D_{13} \left[ c_i D_{12} + (c_2 + c_3) D_{13} \right]}{D},$$

$$D_i^2 = \frac{D_{23} \left[ c_i D_{13} + (c_1 + c_2) D_{12} \right]}{D},$$

$$D = c_1 D_{13} + c_2 D_{12} + c_3 D_{12},$$

Equations (1) are supplemented by the state equation of medium

$$\rho = \rho(c_1, c_2, p) \quad T = \text{const}$$

When solving the system of equations (1), the method of small perturbations is used [3, 4], assuming the concentration of the $i$th component $c_i$ and the pressure $p$ to be represented as follows:

$$c_i = \langle c_i \rangle + c_i' \quad p = \langle p \rangle + p'$$

where $\langle c_i \rangle$, $\langle p \rangle$ are the constant average values taken as the starting point.

Considering that for $L \gg r$ ($L$ and $r$ are the length and radius of the diffusion channel, respectively), the differences between perturbations of the number-average $\mathbf{v}$ and the mass-average $\mathbf{u}$ velocities in the Navier-Stokes equation will be insignificant [12]. Assuming that the nonstationary perturbations of mechanical equilibrium are small, neglecting the quadratic terms on perturbations, and choosing the appropriate scales of the units of measurement ($d$ for distance, $d^2/\nu$ for time, $\rho_0 \nu D_{12}^* / d^2$ for pressure, $D_{22}^*/d$ for velocity and $A_i d$ for concentration of the $i$th component), one can obtain a system of equations of gravitational concentration convection for the perturbed values in dimensionless quantities (strokes are omitted):

$$\text{Pr}_{22} \frac{\partial c_1}{\partial t} - (\mathbf{ue}_z) = \tau_{11} \nabla^2 c_1 + \frac{A_1}{A_i} \tau_{12} \nabla^2 c_2,$$

$$\text{Pr}_{22} \frac{\partial c_2}{\partial t} - (\mathbf{ue}_z) = \frac{A_i}{A_2} \tau_{21} \nabla^2 c_1 + \nabla^2 c_2,$$

$$\frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \nabla^2 \mathbf{u} + (Ra_1 c_1 + Ra_2 c_2) \mathbf{e}_z.$$
\[ \text{div} \mathbf{u} = 0 \]

where \( \text{Ra}_i = g \beta_i A_i d^4 \left( \nu D_n^* \right)^{-1} \) is the Rayleigh partial number; \( \beta_i = -\frac{1}{\rho_0} \left( \frac{\partial \rho}{\partial c}_i \right) \rho_T \); \( A_i \mathbf{e}_z = -\nabla c_{i0} \) (the index 0 refers to the average values); \( \text{Pr}_n = \nu \left( D_n^* \right)^{-1} \) is the Prandtl diffusion number; \( \tau_{ij} = D_{ij}^* \left( D_{22}^* \right)^{-1} \) is the parameter that determines the ratio between the practical diffusion coefficients; and \( \mathbf{e}_z \) is the unit vector in the direction of the axis \( z \).

Solution of the system of equations (2) for the cylindrical channel with circular cross section can be conditionally divided into several stages. At the first stage, we obtain the equation for the concentrations of components. Then, the equation for the velocity is written. At the second stage, solving the equation for the velocity, one can obtain the spectrum of critical Rayleigh numbers for odd and even solutions. At the third stage, we determine the boundary of the “diffusion – convection” regime change in the form \( \gamma \):

\[
\tau_{11} \left( 1 - \frac{A_2}{A_1} \tau_{12} \right) \text{Ra}_1 + \left( \tau_{11} - \frac{A_2}{A_1} \tau_{21} \right) \text{Ra}_2 = \gamma \left( \tau_{11} - \tau_{12} \tau_{21} \right) \tag{3}
\]

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

4. Numerical results

The parameter \( \gamma \) entered into equation (3) is determined by two indices \( n \) and \( l \) [13]. Index \( n \) defines the azimuthal structure of the movement, and index \( l \) determines the radial structure. The transition from the diffusion region to the convective one is characterized by the values of indices \( n \) and \( l \) equal to unity, which corresponds to diametrically antisymmetric motion, in which the cylinder is divided into two parts, in one of which the gas rises and in the other falls. If \( n = 2 \) and \( l = 1 \), then the cylinder is divided into four parts, along two of which the gas rises, and along the other two the gas falls, etc. Thus, various schemes of critical motions are realized in the gas mixture. The transition from one critical movement to another can be recorded experimentally, which is confirmed by the data shown in figure 1.

For the system of 0.5143 He + 0.4857 Ar – 0.5148 CH\(_4\) + 0.4852 Ar, a stability analysis is performed based on equation (3). Figure 2 shows the partial Rayleigh numbers and critical lines for various disturbance modes.

The partial Rayleigh numbers in accordance with the system of equations (2) are calculated by the following formulas:

\[
\text{Ra}_1 = \frac{g n \tau_{11} \Delta m_1}{\nu D_{11}^*} \frac{\partial c_1}{\partial z} \quad \text{Ra}_2 = \frac{g n \tau_{11} \Delta m_2}{\nu D_{22}^*} \frac{\partial c_2}{\partial z} \tag{4}
\]

where \( \Delta m_1 = m_i - m_2 \), \( \Delta m_2 = m_2 - m_i \), \( m_i \) is the molecular mass of \( i \)th component.

The calculated data shown in figure 2 indicate that in the system under consideration there are pressure regions at which various types of critical motions are observed. Thus, in the pressure range from 0.98 to 1.47 MPa, a transition from the diffusion mode to the convective one is observed, which corresponds to the first mode of perturbations. For \( n = 1 \) and \( l = 1 \), the critical Rayleigh numbers have the following values: \( \text{Ra}_1 = 65.24, \text{Ra}_2 = 23.98 \) at \( \gamma_1^* = 2.871 \). In the pressure range 2.94 - 3.92 MPa, as shown in figure 1, a maximum is recorded to correspond to \( n = 2 \) and \( l = 1 \), i.e., there is a change in the type of critical motion, which corresponds to the critical Rayleigh numbers \( \text{Ra}_1 = 315.7, \text{Ra}_2 = \)
116.1 at $\gamma_2' = 4.259$. The next transition corresponding to $n = 3$ and $l = 1$ is observed in the pressure range of 4.90 - 5.89 MPa, while the cylindrical channel is divided into six parts. In the system, the scale of disturbances changes to the steady-state convective flow regime and the next convective regime arises, which corresponds to the critical Rayleigh numbers $Ra_1 = 904.8$, $Ra_2 = 332.6$ at $\gamma_3' = 5.541$.

![Figure 2. Stability map for the system of 0.5143 He + 0.4857 Ar – 0.5148 CH$_4$ + 0.4852 Ar. I is the line of zero density gradient. M$_1$, M$_2$ and M$_3$ are the lines of monotonic disturbances at $n = 1$, $n = 2$ and $n = 3$. Points are the partial Rayleigh numbers calculated at the following pressure values: 1 – $p = 0.49$; 2 – 0.98; 3 – 1.47; 4 – 1.96; 5 – 2.45; 6 – 2.94; 7 – 3.92; 8 – 4.90; 9 – 5.89 MPa.](image)

Thus, the regions associated with nonlinear changes in the process intensity correspond to new scales of disturbances. In this case, the experimental partial Rayleigh numbers $Ra_i$ are located on the plane of the Rayleigh numbers $(Ra_1, Ra_2)$ near the boundary lines corresponding to different perturbation modes $n$.

5. Conclusions
The boundary of the “diffusion – convection” transition in a three-component gas mixture, where one of the components is uniformly dissolved in the other two under isothermal conditions and elevated pressures, has been studied experimentally and theoretically. It has been found that the parameter $\alpha$, defined as the ratio of the experimental concentrations to the values of the concentrations calculated under the assumption of diffusion using the Stefan-Maxwell equations, changes nonlinearly with increasing pressure. The resulting dependence has minima and maxima, the presence of which is explained by the interaction of convective structural formations moving towards each other. For the investigated system of 0.5143 He + 0.4857 Ar – 0.5148 CH$_4$ + 0.4852 Ar, a linear stability analysis has been carried out for a vertical cylindrical channel with a circular cross section. For various perturbation modes, the critical Rayleigh numbers at which the type of critical convective motions changes have been determined. The results of numerical studies are shown to be in good agreement with experimental data.
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