Special modes of diffusion mass transfer in isothermal triple gas mixtures

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Abstract. In isothermal three-component gas mixtures in quasi-stationary conditions the procedure of numerical solution of Stefan-Maxwell diffusion equations using the software package “MathCad” is considered. It is shown that one of the specific features of multicomponent diffusion is the appearance of nonlinear concentration distributions of components in vertical channels. Due to the difference in the coefficients of mutual diffusion of gases in some systems under certain conditions, nonlinear distributions of component concentrations lead to a non-monotonic distribution of the density of the gas mixture. By the example of hydrogen – nitrogen – methane and methane – n-butane – nitrogen systems at a constant temperature $T = 298$ K, the influence of the content of the component with the highest molecular weight in the triple gas mixture on the degree of nonlinearity of the density distribution in the diffusion channel is analyzed. It is suggested that the inversion of the density distribution of the mixture may be the cause of convective instability in triple gas systems. The results of calculations are compared with experimental data.

1. Introduction

In a complex multicomponent multiphase transfer, the heat-mass transfer intensity is determined by both molecular and convective mixing mechanisms [1]. However, this practically does not take into account the fact that the process of molecular diffusion can create conditions for breaking the stability of mechanical equilibrium even in stationary media, which determines the occurrence of concentration gravitational convection, which significantly changes the rate of mixing of the components of the system [2, 3]. Experiments on the study of isothermal diffusion in three-component mixtures have shown that in systems with significantly different coefficients of mutual diffusion of gases (CMD) there are convective flows that significantly intensify the total mass transfer [4]. It is established that certain values of pressure and concentration of components contribute to the transition from the diffusion region to the convective one [4, 5]. Convective mixing causes a synergistic interaction of the components in which the transport intensity significantly exceeds the intensity of Stefan flows, which were observed in the evaporation of liquid mixtures into an inert gas at a high elastic value of saturated vapors [3, 6, 7].

The features of the convective transport of system components observed in [2, 3] can be described in the framework of the theory of convective instability [8], which allows determining the critical parameters under which structured flows occur under thermal gravitation conditions [9-11].
difference between isothermal convective mixing is that it occurs at the initial hydrostatically stable stratification, which involves a decrease in the density of the mixture with a height [12]. For different diffusion channel geometries, boundary relations for isothermal triple mixtures were obtained in [12-14]. At the same time, it should be noted that the possibilities of the approach [8], extended to the case of isothermal gas mixtures, are limited, since it assumes a linear distribution of component concentrations in the diffusion channel [15]. Therefore, it is necessary to increase the accuracy in determining the concentration profiles in the diffusion channels.

The study of diffusion mixing mechanisms in multicomponent mixtures is numerically related to the Stefan-Maxwell equations [1]. The authors of [16] confirmed the satisfactory agreement between the values of partial flows of the components that were measured experimentally and calculated by equations the Stefan-Maxwell. For the case of low content of the component with the highest molecular weight in the system, the possibility of inversion of the gas mixture density was shown by Kosov and co-authors in [17]. It was noted in [17-20] that multicomponent diffusion has a number of features that are absent in binary systems. These include, first of all, the existence of non-monotonic distributions of component concentrations that can cause anomalous diffusion regimes with complex interaction of molecular and convective components of mass transfer.

The mentioned features of multicomponent diffusion depend on physical and chemical parameters in a complex way, and their analysis is of interest from the point of view of interpretation of separation processes in gas mixtures. Therefore, the aim of this work was to apply the methodology described in [17] for determining the partial values of component concentrations to the case of an arbitrary content in the ternary gas mixtures with highest molecular weight. The presented modification of the solution of Stefan-Maxwell equations allows us to determine the concentration profiles of the components and the density distribution in the diffusion channel for different initial composition of the ternary mixture.

2. Quasi-stationary diffusion in isothermal three-component gas mixtures

Let us consider the diffusion of a three-component mixture in a system of two flasks I and II connected by a long vertical channel \((L \gg r, L \text{ and } r - \text{the length and radius of the channel})\). Here and further the index “1” corresponds to the component with the minimum molecular weight \(M_1\).

Index “2” refers to the component with the highest molecular weight \(M_2\), and index “3” refers to the component with an intermediate weight \(M_3\). Constant values of component concentrations \(c_i\) and pressure \(p\) are maintained in the diffusion cell flasks. The temperature \(T\) in the flasks is the same.

Diffusion (one-dimensional case) in such a system is described by the following system of equations:

\[
\sum_{i=1}^{3} C_i = 1, \quad p = \text{const}, \quad T = \text{const}
\]

\[
n \sum_{i=1}^{3} C_i \cdot u_i = 0 \quad \quad \quad n \cdot c_i \cdot u_i = \frac{J_i}{S} = \text{const}, \quad i = 1, 2; \quad (1)
\]

\[
\sum_{j \neq i} c_i \cdot c_j \frac{d}{dz}(u_i - u_j) = -\frac{d}{dz} c_i, \quad i = 1, 2; \quad j = 1, 2, 3
\]

where \(n\) is the number density, \(u_i\) is the vector of average speed of molecules of the \(i\)-th component; \(D_i\) is the coefficient of mutual diffusion [21], \(J_i\) is the full numerical flux of the \(i\)-th component through the capillary; \(S\) is the cross-sectional area of capillary; \(j\) and \(j_i\) are the total and partial density of numeric flow, respectively.

The boundary conditions have the following form:

\[
Z = L, C_1 = C_{1I}, C_2 = C_{2I}, \quad C_3 = C_{3I}
\]

\[
Z = L, C_1 = C_{1II}, C_2 = C_{2II}, \quad C_3 = C_{3II} \quad (2)
\]
Taking into account equation (2), we transform the diffusion equations to the traditional form:

\[
\sum_{j=0}^{n} \frac{1}{D_j} (c_j \cdot \frac{d}{dz} c_j - c_j) = -\frac{dc_i}{dz}
\]  

(3)

Taking into account the condition of independent diffusion \( j_1 + j_2 + j_3 = 0 \), the Stefan-Maxwell equations (3) are written as follows:

\[
\frac{dc_1}{dz} - c_i \cdot \left( \frac{1}{D_{12}} - \frac{1}{D_{13}} \right) + c_j \cdot \left( \frac{1}{D_{21}} - \frac{1}{D_{23}} \right) = -\frac{j_1}{D_{13}}
\]

\[
\frac{dc_2}{dz} - c_i \cdot \left( \frac{1}{D_{12}} - \frac{1}{D_{23}} \right) + c_j \cdot \left( \frac{1}{D_{21}} - \frac{1}{D_{13}} \right) = -\frac{j_2}{D_{23}}
\]  

(4)

System (4) has a solution for \( c_i \) in the form of superposition of a particular solution of inhomogeneous system of equation and a general solution of equations. The values of \( j_n \), the computational complexes depending on the composition, are determined by substituting the numerical values of the problem parameters for the corresponding boundary conditions (2) and are calculated using the “MathCad” computing package. As a result, \( c_i \) concentrations can be defined as a function of the coordinate and the numerical values of \( j \),

\[
c_i(z) = -B \left[ j_i \cdot \left( X_i \cdot z - X_i \cdot \frac{A}{B} \right) + X_i \cdot K_i \cdot \exp \left( \frac{z}{B} \right) \right]
\]  

(5)

where \( K_i, X_i, A, B \), are the computational complexes depending on the concentration of components, CMD and geometric characteristics of the diffusion channel.

The density distribution of the mixture and the value of its gradient are determined by the ratios

\[
\frac{1}{n} \rho(z) = m_{c_1} + m_{c_2} + m_{c_3}
\]

\[
\frac{1}{n} \frac{d\rho}{dz} = (m_i - m_3) \cdot \frac{dc_i}{dz} + (m_i - m_2) \cdot \frac{dc_j}{dz} =
\]

\[
= -B \cdot X_3 \cdot \left( m_i \cdot j_i + m_j \cdot j_j \right) + X_2 \cdot e^{\frac{z}{B}} \cdot \left( \Delta m_i \cdot K_i - \Delta m_j \cdot K_j \right) \quad \Delta m_l = m_l - m_2
\]  

(6)

where \( m_i \) is the mass of the molecule of the \( i \)-th component.

3. Results

The validity of the calculations according to methods (5) – (6) was verified with mixtures of \( \text{CH}_4 + \text{Ar} - \text{N}_2, \text{CH}_4 + \text{C}_2\text{H}_6 - \text{N}_2, \text{H}_2 + \text{N}_2 - \text{CH}_4 \), which were studied experimentally in [4, 12]. From experience it is known what type of mixing takes place in the studied system: diffusion or convection. Therefore, comparing the distribution profiles of concentration (density) in the channel, we can notice the agreement between the obtained calculations with the actual situation observed in the experiment. Figures 1 and 2 show the concentration profiles of the components and the density distribution of the mixture for some triple mixtures, containing hydrocarbon components in the diffusion channels of real...
experimental devices, corresponding to the conditions of experiments in which diffusion and convective mixing was studied.

In the system 0.55 CH\textsubscript{4} + 0.45 Ar – N\textsubscript{2} under the given conditions of the experiment, the CMD components are approximately the same (here and further we agree that the numbers before the chemical element correspond to the concentration of the component in the initial mixture). The calculation results fix the linear character of the concentration profiles of the components along the length of the diffusion channel, which corresponds to diffusion experimentally observed in [4]. The density distribution of the mixture is also linear. The type of dependences and other initial compositions of components in the mixture do not change.

However, for the ternary mixture CH\textsubscript{4} + C\textsubscript{4}H\textsubscript{10} – N\textsubscript{2}, in which the condition is satisfied for the components of the CMD, \( D_{12} = D_{23} < D_{13} \) there is a different picture of distribution of concentrations along the length of the channel. Figure 1 shows the concentration profiles of the components.

![Figure 1](image.png)

**Figure 1.** Distribution of concentrations of components for the mixture CH\textsubscript{4} + C\textsubscript{4}H\textsubscript{10} – N\textsubscript{2} at \( T = 298.0 \text{ K}, p = 1.5 \text{ MPa} \). Content of butane in the mixture corresponds to: (a) – 0.1, (b) – 0.2, (c) – 0.3, (d) – 0.4 molar fractions. Lines correspond to: 1 – CH\textsubscript{4}, 2 – N\textsubscript{2}, 3 – C\textsubscript{4}H\textsubscript{10}.

In a triple gas mixture CH\textsubscript{4} (1) + C\textsubscript{4}H\textsubscript{10} (2) – N\textsubscript{2} (3) the linearity in the distribution of the concentration of the component with the highest molecular weight is violated already at a low butane content. With an increase of its content in the initial composition of the mixture, the disturbance becomes more significant.
Figure 2. Distribution of concentrations of components for the mixture $\text{H}_2 + \text{N}_2 – \text{CH}_4$ at $T = 298.0 \text{ K}, \rho = 1.5 \text{ MPa}$. The nitrogen content of the mixture corresponds to: (a) – 0.7, (b) – 0.6, (c) – 0.5, (d) – 0.4 molar fractions. Lines correspond to: 1 – $\text{H}_2$, 2 – $\text{CH}_4$, 3 – $\text{N}_2$.

Figure 3. Density distributions for the mixtures $0.7 \text{ CH}_4 + 0.3 \text{ C}_4\text{H}_{10} – \text{N}_2$ (a) and $0.5 \text{ H}_2 + 0.5 \text{ N}_2 – \text{CH}_4$ (b) at $T = 298.0 \text{ K}, \rho = 1.5 \text{ MPa}$. 
Finally, for the mixture \( \text{H}_2 + \text{N}_2 – \text{CH}_4 \) (figure 2) for which the difference in the CMD components becomes more significant \( (D_{12} = D_{23} \neq D_{13}) \) the nonlinear distribution of the component concentration is manifested not only in the component with the highest molecular weight (i.e. nitrogen), but also in that with an intermediate partial density (methane). Nonlinearities in concentration distributions shown in figures (1) and (2) are associated with the appearance of special mixing regimes during diffusion revealed by Kaminskii in [20].

Figure 3 shows the density distributions in the diffusion channel for the mixtures 0.7 CH\(_4\) + 0.3 C\(_4\)H\(_{10}\) – N\(_2\) and 0.5 H\(_2\) + 0.5 N\(_2\) – CH\(_4\) calculated by ratios (5), (6).

The nonlinear density distribution is atypical in terms of traditional diffusion representations and is absent in binary gas mixtures. In ternary gas mixtures in the gravity field, this distribution can lead to instability of the mechanical equilibrium of the system under study, followed by turbulence of the gas mixture on a scale significantly exceeding the characteristic size of the separation zone of the gas mixture, which has a size of the order of the diameter of the connecting channel. Therefore, in these mixtures we should expect a significant increase in the intensity of the total mass transfer of the components observed in the experiments [2, 3], which confirms the assumptions.

4. Conclusions
In the article for isothermal ternary mixtures, hydrogen – nitrogen – methane and methane – n-butane – nitrogen, where the interdiffusion coefficients differ significantly from each other, non-monotonic distributions of component concentrations can occur. The occurrence of such concentration distributions allows one to fix special regimes during diffusion. Nonlinear distributions of component concentrations in some cases lead to the emergence of conditions for a nonlinear density distribution in the diffusion channel. For a certain range of parameters, the density of the gas mixture can be inverted. In the field of gravity, such distribution can lead to instability of mechanical equilibrium with subsequent occurrence of convective currents.

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Nomenclature
- \( c_i \) – concentration of the \( i \)-th component, mole fractions
- \( D_{ij} \) – coefficient of mutual diffusion, m\(^2\)/s
- \( d \) – diameter of the diffusion channel, m
- \( j_i \) – partial density of the numerical flow of the \( i \)-th component, m/s
- \( L \) – length of the diffusion channel, m
- \( m_i \) – mass of the molecule of the \( i \)-th component, kg
- \( n \) – numerical density, m\(^{-3}\)
- \( p \) – pressure, Pa
- \( r \) – radius of the channel, m
- \( T \) – temperature, K
- \( t \) – time, s;
- \( u_i \) – average velocity vector of the \( i \)-th component, m/s
- \( z \) – coordinate, m
- \( \rho \) – density of the mixture, kg/m\(^3\)

Indexes
- \( i, j \) – numbering of components in a multicomponent mixture

References
[1] Frank-Kamenetskii D A 1955 Diffusion and Heat Exchange in Chemical Kinetic (Princeton: Princeton Univ. Press)
[2] Kosov V N, Seleznev V D and Zhavrin Yu I 1997 Tech. Phys. 42 1236
[3] Dil’man V V, Lipatov D A, Lotkhov V A and Kaminskii V A 2005 Theor. Found. Chem. Eng. 39 566
[4] Zhavrin Yu I., Kosov V N, Fedorenko O V and Akzhola A A 2016 Theor. Found. Chem. Eng. 50 171
[5] Kosov V N, Kul’zhanov D U, Zhavrin Yu I and Fedorenko O V 2017 Russ. J. Phys. Chem. A 91 984
[6] Kashirskaya O A, Lotkhov V A and Dil’man V V 2010 Theor. Found. Chem. Eng. 44 665
[7] Kashirskaya O A, Lotkhov V A and Dil’man V V 2007 Advances in chemistry and chemical technology 21 20
[8] Gershuni G Z and Zhukhovitskii E M 1976 Convective Stability of Incompressible Fluids (Jerusalem: Keter)
[9] Ingel’ L K 2013 Technical Physics 58 658
[10] Ryzhkov I I 2013 Thermal diffusion in mixtures: equations, symmetries, solutions, and their stability (Novosibirsk: Siberian Branch of the Russian Academy of Sciences)
[11] Ingel’ L K 2017 J. Engin. Phys. and Thermophys. 58 437
[12] Kossov V N, Seleznev V D. 2004 Anomalous Onset of the Free Gravitational Convection in Isothermal Ternary Gas Mixtures (Yekaterinburg, Ural Branch Russian Academy of Science)
[13] Kosov V N, Fedorenko O V, Zhavrin Yu I and Mukamedenkyzy V 2014 Techn. Phys. 59 482
[14] Kosov V N, Krasikov S A and Fedorenko O V 2017 Eur. Phys. J. Spec. Top. 226 1177
[15] Kosov V N, Zhakebaev D B and Fedorenko O V 2017 News of the National Academy of Sci. of the Rep. of Kazakhstan, Phys.- math. series 315 134
[16] Dil’man V V, Lotkhov V A and Kashirskaya O A 2009 Theor. Found. Chem. Eng. 43 288
[17] Kosov V N, Zhavrin Yu I and Seleznev V D 1998 Tech. Phys. 43 488
[18] Dil’man V V, Kashirskaya O A and Lotkhov V A 2010 Theor. Found. Chem. Eng. 44 379
[19] Kaminskii V A 2011 Russ. J. Phys. Chem. A 85 1986
[20] Kaminskii V A 2011 Russ. J. Phys. Chem. A 85 2203
[21] Bird R B, Stewart W E and Lightfoot E N 2002 Transport Phenomena (John Wiley & Sons, Inc.)