Separation features of multicomponent gas mixtures at the border of regime change diffusion – concentration gravitational convection

V N Kossov 1,2, O V Fedorenko 2, S A Krasikov 2 and A B Kalimov 1

1 Abai Kazakh National Pedagogical University, Kazakhstan, 050010 Almaty, Dostyk Ave., 13
2 Institute of Experimental and Theoretical Physics at al-Farabi Kazakh National University, Kazakhstan, 050040 Almaty, al-Farabi Ave., 71

Abstract. The mixing of carbon dioxide dissolved in multicomponent gas mixtures at various pressures was studied. It was found that at a certain pressure the diffusion separation of components is violated and structured flows arise in the system. The pressure regions are fixed at which the conditions of priority transfer of the component with the highest molecular weight in the mixture are realized in the system. To analyze the effect of pressure on the process of changing the diffusion – convection modes, a mathematical model has been proposed that takes into account the kinetic features of multicomponent mixing. It is shown that the change in mass transfer modes is associated with a significant difference in the diffusion abilities of the components.

1. Introduction
Interest in the processes of priority transfer of substances, separation of liquid and gas mixtures into fractions or components with desired properties is dictated by modern approaches in the petrochemical and energy industries. With an optimal combination of factors such as productivity and selectivity in separation technologies, one should expect not only a deeper and more rational processing of multicomponent substances, but also a reduction in capital and operating costs, as well as a decrease in the environmental impact of the anthropogenic factor. Therefore, it is no coincidence that traditional and sufficiently costly technologies such as low-temperature gas separation, absorption and desorption purification methods [1, 2] use combined approaches related to increasing the selective features of a given component [3-5]. For gas mixtures containing vapors of hydrocarbon components, carbon dioxide, an increase in transfer selectivity is associated with approaches based on membrane separation mechanisms [6, 7]. The key transport parameters related to gas permeability presented for such technologies are traditionally determined on the basis of representations of Fick's classical diffusion [8].

However, for multicomponent gas mixtures, the approach to assessing partial diffusion fluxes and transport characteristics defined in the framework of [8] can lead to a distortion of the expected results associated with mass transfer, since it does not take into account a number of features of multicomponent mixing that is not typical for binary systems. First of all, these are special mixing modes during multicomponent diffusion, which include the diffusion barrier, reverse diffusion, and osmotic diffusion
The calculations presented in this work show that other diffusing gases influence the partial flow of the component. As a result, nonlinear distributions of component concentrations and mixture densities, which differ significantly from the distributions expected with the traditional approach [8], appear in a given channel. In experiments on the study of mixing in three-component systems at various pressures and compositions [13], diffusion of a mixture of solution vapors into an inert gas [14], convective flows, which lead to a synergistic effect associated with a significant increase in the rate of mixing of system components, were recorded. Moreover, the preferential transfer of the component with the highest molecular weight, which is not typical for diffusion, was noted in [13]. Therefore, the solution of issues related to the study and refinement of separation mechanisms in multicomponent gas mixtures, including in systems containing greenhouse gases, the correct estimation of the parameters determining the occurrence of special and convective mixing modes, seems important for applied problems of combined mass transfer.

The aim of the work is an experimental study of diffusion and combined mass transfer in a three- and four-component gas mixture containing carbon dioxide at various pressures and isothermal conditions. A computational model is proposed for determining the thermophysical parameters of the mixture at which the transport characteristics of the mixture will correspond to the diffusion representation. The results of a numerical study are compared with experimental data.

2. Experimental study

The following gases were used for research: helium B (purity 0.9999), nitrogen (purity 0.9999), argon (purity 0.99993), and carbon dioxide (purity 0.9998). Gas mixtures were compiled using partial pressures, followed by adjustments according to the results of measurements of the obtained composition on a chromatograph. The error in determining the concentration of a given component in the initial mixture was ± 1%.

An analysis of the initial compositions of the studied mixtures and the concentrations of the mixing components was carried out on a Chrom 5 gas chromatograph with katharometers as detectors, helium carrier gas, a capillary column 1 of 3 m long and 2 mm in diameter filled with a Hayeser D solid support with a fraction of 80/100 mesh and capillary column 2 with a length of 1.5 m and a diameter of 3 mm filled with a 5A solid support with a fraction of 60/80 mesh.

The separation of multicomponent gas mixtures containing carbon dioxide was studied using a device that is a variation of the two-flask method, which is widely used in experimental studies at various pressures and temperatures [15]. Two flasks connected by a vertical rectangular channel and a blocking device represent a diffusion cell, which is connected to the transport communications block providing delivery of the studied gases under given conditions for subsequent mixing (figure 1). The geometric characteristics of the diffusion cell are as follows: the volume of the upper flask \( V_u = (185.0 \pm 0.5) \times 10^{-6} \) m\(^3\); the volume of the lower flask \( V_l = (186.0 \pm 0.5) \times 10^{-6} \) m\(^3\); the dimensions of the rectangular vertical channel \( a \times b \times L = (30.00 \pm 0.05 \times 6.00 \pm 0.05 \times 165 \pm 0.05) \times 10^{-3} \) m (figure 1). The temperature in all experiments was constant and equal to \( T = 298.0 \) K.

The experimental technique involved the execution of certain procedures described, for example, in [16]. To study the separation of gas mixtures containing carbon dioxide, it was assumed at the initial stage that the internal cavities of the experimental stand including the main elements of the diffusion cell, i.e. the upper 2 and lower 3 flasks with channel 1 connecting them, were evacuated. Valve 4 should be closed. The upper flask 2 must be filled with a gas mixture for separation from the cylinder 5 through the open valves 9 and 11. The valve 13 must be closed. The pressurization of the upper flask 2 is carried out to the pressure of the experiment and is controlled by a pressure gauge 7. After refilling of the upper flask 2, valves 9 and 11 are closed. Similarly, the lower flask 3 is charged with process gas (in this case nitrogen) from the cylinder 6 through the open valves 10 and 12. Valve 14 must be closed. The gas supply to the lower flask 3 is carried out to the pressure of the experiment and is controlled by a pressure gauge 8. After filling the lower flask 2, valves 10 and 12 are closed.

During the experiment, valve 4 is opened and closed after the experiment time. The measurement of the resulting concentrations is carried out by supplying gas mixtures to the chromatograph through the outputs 15 when opening valves 11, 13 and 12, 15 for the upper or lower flasks of the diffusion cell.
In ternary gas mixtures, the concentrations of carbon dioxide and nitrogen were directly measured. The concentration for helium can be obtained from the condition of conservation of the number of particles \( \sum_{i=1}^{n} c_i = 1 \), where \( c_i \) is the concentration of the \( i \)-th component. The experiment was repeated several times and averaging the measured values determined the specific value of the concentration of the components. In all experiments with ternary gas systems for any pressure, the density of the mixture of helium and carbon dioxide in the upper flask was lower than the density of nitrogen, which was located in the lower flask.

In the four-component mixtures, the experimental procedure was almost similar to the previous description. The only difference was that in the upper flask of the diffusion cell there was a mixture of helium and carbon dioxide diluted with argon, and in the lower flask was nitrogen. In this case, the concentrations of nitrogen, argon, and carbon dioxide were directly measured, and the concentration of helium was recalculated from the condition of conservation of the number of particles. As for the case of ternary systems, it was assumed that the initial mixing stage is realized under conditions of decreasing mixture density with height.

3. Discussion of results
Figure 2 shows concentrations \( c_i \) of carbon dioxide, nitrogen, and helium at various pressures. In the 0.45 He + 0.55 CO\(_2\) – N\(_2\) system (hereinafter, we agree that the numbers in front of the chemical element correspond to the initial composition of the component in mole rates in the mixture), a nonlinear pressure dependence is observed (figure 2). There is a significant difference between the experimental data and those calculated under the assumption of diffusion. Diffusion calculations for the selected experimental conditions and the geometric parameters of the channel of the experimental cell were carried out using the FlowSimulation calculation module of the SolidWorks package [17]. The concentration dependences shown are not typical for diffusion, in which, according to calculations, the mixing intensity decreases with increasing pressure. The recorded maxima in the concentration of carbon dioxide and nitrogen do not correspond to the diffusion representation of mixing. The peak value of the concentration of the component with the highest molecular weight may be due to the manifestation of convective mixing mechanisms caused by the instability of the mechanical equilibrium of the mixture at given pressure values [18]. With increasing pressure, the mixing intensity of carbon dioxide and nitrogen decreases, but the difference between the convective and diffusion components is still large. As for helium, at pressures exceeding 1.0 MPa or more, the coincidence of the experimental and calculated values of concentrations under the assumption of diffusion is recorded. In this regard, its transfer can be described by Fick's traditional ideas.
Figure 2. Component concentrations at various pressures in a flat vertical channel at \( T = 298.0 \, \text{K} \) for the 0.45 He + 0.55 CO\(_2\) – N\(_2\) system: 1 is the carbon dioxide concentration (experiment); 2 is the nitrogen concentration (experiment); 3 is the helium concentration (experiment); 4 is the calculation for carbon dioxide in the assumption of diffusion; 5 is the diffusion calculation for helium.

Figure 3. Pressure dependence of the transfer of Ar + CO\(_2\) from the upper flask for the composition of the 0.3 Ar + 0.28 CO\(_2\) + 0.42 He mixture: 1 is the argon concentration (experiment); 2 is the carbon dioxide concentration (experiment); 3 is the helium concentration (experiment); 4 is the calculation under the assumption of diffusion for argon; 5 is the calculation under the assumption of diffusion for carbon dioxide; 6 is the calculation under the assumption of diffusion for helium.

The transfer is somewhat different for a four-component mixture containing CO\(_2\) at different pressures. The initial mixture of helium and carbon dioxide was diluted with argon. Moreover, in the sum of the concentrations of Ar and CO\(_2\) in the four-component mixture 0.42 He + 0.30 Ar + 0.28 CO\(_2\) – N\(_2\) are approximately equal to the carbon dioxide content in the studied early ternary system 0.45 He
+ 0.55 CO₂ - N₂. Figure 3 shows concentrations cᵢ of carbon dioxide, argon, nitrogen, and helium at various pressures. As in the previous case with ternary systems, a significant discrepancy is observed between the experimental data and those calculated under the assumption of diffusion for all components of the studied four-component mixture. The maximum discrepancy is recorded for the components with the highest molecular weights, i.e., for carbon dioxide and argon. However, a nonlinear dependence of the concentrations on pressure was not noted for these components.

![Figure 3](image.png)

**Figure 3.** Concentrations of carbon dioxide, argon, nitrogen, and helium at various pressures.

In technological schemes associated with the purification of the main component from unwanted impurities, the efficiency of the process is associated with the part of the retained fractions (or particles with desired properties), that is, with the separation coefficient [19]. We define it by analogy with [19] as the ratio of the separated component of a given density to the total content of the heavy component in the mixture measured in percent. Figure 4 shows a generalized separation coefficient for heavy components (argon and carbon dioxide) and a leakage factor of helium. For these experimental conditions, in the pressure range 0.3 MPa – 1.3 MPa, the separation coefficient for components with the highest molecular weights is several tens of percent decreasing monotonously with increasing pressure. While the leakage factor of helium practically does not change, and its losses in the upper flask are determined by diffusion mechanisms. For the practical use of these features, it is very important to calculate at what thermophysical and geometric parameters the separation effect will manifest itself in the maximum way.

To determine the parameters at which the separation effect is possible, an approach based on the theory of stability [20] can be used, which allows to define the boundary of the “diffusion – concentration gravitational convection” transition in terms of the partial Rayleigh numbers of the heavy and light components. Extending the approach [20] to the macroscopic motion of an isothermal ternary gas mixture, we write the system of equations of hydrodynamics, which includes the Navier-Stokes equations, the conservation of the number of particles in the mixture and components, taking into account the conditions \( \sum_{j=1}^{n_j} j_i = 0 \) and \( \sum_{i=1}^{n_i} c_i = 1 \) as follows [18]:

\[
\begin{align*}
\sum_{j=1}^{n_j} j_i &= 0 \\
\sum_{i=1}^{n_i} c_i &= 1
\end{align*}
\]
The system of equations (1) and (3) was solved in several stages. At the first stage, a system of concentration convection equations for perturbed quantities was obtained based on the small parameter method. At the second stage, the considered system of equations was written in dimensionless quantities by appropriate selection of the scale of units of measure. At the third stage, the shape of the diffusion channel (in our case, a flat vertical channel) and boundary conditions (in the case under consideration, the boundary conditions suggest that the perturbations of velocity and flow of matter at the borders vanish) are selected. The final system of equations is solved analytically. The complete solution of the resulting system of equations was obtained by the authors of [22].

An analytical solution of the system of equations of concentration convection for a vertical channel with boundary conditions assuming that the velocity and substance flow perturbations at the boundaries vanish, allowed to obtain in terms of the Rayleigh numbers $Ra_i$ a boundary relation determining the change of “diffusion – convection” modes in the form [22]:

$$
\tau_{11}\left(1 - \frac{A_1}{A_i}\tau_{12}\right)Ra_1 + \left(\tau_{11} - \frac{A_1}{A_i}\tau_{21}\right)Ra_2 = \gamma^4\left(\tau_{11} - \tau_{12}\tau_{21}\right)
$$

(4)

where $\gamma = Ra^{1/4}$, i.e., $\gamma = (Ra, \tau_{11}K_1 + Ra_2 K_2)^{1/4}$, $Ra_i = \left(\frac{g\beta_i d^4}{\rho_0} \right)^{1/4}$, $K_1 = \left(1 - \frac{A_1}{A_i}\tau_{12}\right)\left(\tau_{11} - \tau_{12}\tau_{21}\right)^{-1}$, $K_2 = \left(\tau_{11} - \frac{A_1}{A_i}\tau_{21}\right)\left(\tau_{11} - \tau_{12}\tau_{21}\right)^{-1}$, $A_i$ is the partial concentration gradient of the $i$-th component, $\beta_i = -\frac{1}{\rho_0}\left(\frac{\partial \rho}{\partial c_i}\right)_{\rho, T}$, where $\rho_0$ is the average density, $v$ is the kinematic viscosity, $d$ is the characteristic size of the diffusion channel. The parameters $\tau_{ij} = \frac{D_{ij}^*}{D_{22}^*}$ were calculated...
using the PDC found by formulas (2) and the IDC of gas pairs, which at \( p = 0.101 \) MPa and \( T = 298.0 \) K have the following values: \( D_{\text{He-N2}} = 7.3 \times 10^{-5} \) m\(^2\)·s\(^{-1}\), \( D_{\text{CO2-N2}} = 1.65 \times 10^{-5} \) m\(^2\)·s\(^{-1}\), \( D_{\text{He-CO2}} = 6.2 \times 10^{-5} \) m\(^2\)·s\(^{-1}\). The expression for the partial concentration gradient of the \( i \)-th component \( A_i \) was obtained using the expressions for the concentration distributions of the \( i \)-th component according to [23]. The numerical value of \( A_i \) depends on the initial composition of the mixture under consideration. In order to identify the area where the separation of the heavy component is possible on the plane of the partial Rayleigh numbers, it is necessary to determine the location of the line of the zero density gradient by the formula:

\[
\tau_{11} \cdot Ra_1 = -Ra_2
\]

The mutual arrangement of the boundary lines (4) and (5) shows the existence of a region (the sector between lines \( I \) and \( II \) in figure 5) when convection takes place in the system, although the density in the upper part of the channel is lower than in the lower one, which is at the first glance corresponds only to diffusion.

Figure 5. Diffusion and convection regions for the 0.45 He + 0.55 CO\(_2\) – N\(_2\) system: 
\( I \) is the neutral line of monotonic perturbations; \( II \) is the line of zero density gradient; 
\( I \) – numerical calculation at a pressure of 0.05 MPa; \( 2 \) – 7 – numerical data for various values of \( p \): \( 2 \) – 0.1; \( 3 \) – 0.2; \( 4 \) – 0.3; \( 5 \) – 0.4; \( 6 \) – 0.5; \( 7 \) – 0.6 MPa.

Based on the obtained solution (4), a program was compiled in the Mathcad system that allows to obtain a stability map and partial Rayleigh numbers in coordinates (\( Ra_1, Ra_2 \)). The experimental data are reconstructed through the partial Rayleigh numbers, for example, according to the formulas given in [18], and then displayed on the coordinate plane (\( Ra_1, Ra_2 \)).

The considered approach was used to numerically study the 0.45 He + 0.55 CO\(_2\) – N\(_2\) system, the results of which are shown in figure 5. In the pressure range from 0.2 MPa onwards, the system under consideration is in the convective region, which is consistent with the experimental data shown in figure 2. Numerical calculation has shown that the transition to the convective region, where the separation of the heavy component is possible, occurs at a pressure of about 0.1 MPa. Up to this pressure, diffusion is realized in the system. No experiments were carried out at these pressures due to the characteristics of the bench equipment used, which does not allow studies at pressures below 0.2 MPa. Thus, the boundary of the “diffusion – concentration gravitational convection” regime change can be obtained as part of the stability analysis of the mechanical equilibrium of the gas mixture.
The position of the boundary lines (4) and (5) depends on the partial Rayleigh numbers Ra, which in turn depend on the physicochemical properties of the studied components and the geometric characteristics of the diffusion channel. For example, for this system, the transition from the diffusion region to the sector of combined mass transfer can be carried out by varying the radius and length of the connecting channel, its angle of inclination, and the initial composition of the gas mixture. Therefore, the proposed approach can be used not only to study the effect of pressure on the location of the region where the separation process takes place, but also to study the effect of other thermophysical characteristics.

4. Conclusions
The obtained experimental data showed that complex combined mass transfer associated with the appearance of convective perturbations can occur at certain pressures during diffusion in three- and four-component gas mixtures containing carbon dioxide. In this case, priority transfer of the component with the highest molecular weight, which is not typical for diffusion, is noted. In some cases, the pressure dependence of the intensity of partial mixing of the components is non-linear. The proposed computational mathematical model allows to analyze the influence of diffusion and hydrodynamic factors on the process of combined mass transfer in isothermal gas mixtures. The obtained boundary relation allows to identify the spectrum of physicochemical and geometric parameters that determine the transition of the mixture under study from the diffusion to convective state. In this regard, when using various technologies for cleaning gas systems, extracting and utilizing carbon dioxide, it is necessary to recommend an analysis of the stability of mechanical equilibrium of the studied gas mixture.

Acknowledgments
This research has been funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP05130712) and the grant of Abai Kazakh National Pedagogical University (Grant No. 03-05/360).

References
[1] Alekperov V Yu, Maganov R U, Nekrasov V I, Gimaletdinov R R, Usmanov M R, Ozhegin A V and Chernyshev A N 2018 Chemical Technologies and Products 1 5
[2] Yarkeeva N R and Ishbulatov I A 2019 Oil and Gas Business 17(1) 11
[3] Kudinov A N, Kurchatov I M and Laguntsov N I 2014 Theor. Found. Chem. Eng. 48(4) 352
[4] Semenov A P, Viktorov A S, Berberov A B, Volkov A S and Vinokurov V A 2012 Technologies of oil and gas 582(24)
[5] Bishimbaev V and Ermahanova F 2010 Perspectives of innovations, economics and business 6(3) 134
[6] Zhmakin V V and Tepyakov V V 2016 Petroleum Chemistry 56(4) 335
[7] Liu S L, Shao L, Chua M L, Lau C H, Wang H and Quan S 2013 Progress in Polymer Science 38(7) 1089
[8] Ismail A F, Khulbe K C and Matsuura T 2015 Fundamentals of gas permeation through membranes Gas Separation Membranes (Springer, Cham) pp. 11-35
[9] Brunetti A, Tocci E, Cersosimo M, Kim J S, Lee W H, Seong J G, Lee Y M, Drioli E and Barbieri G J. 2019 Membrane Science 580 202
[10] Wohlrab S, Meyer T, Stöhr M, Hecker C, Lubenua U and Böhmann A 2011 J. Membrane Science 369(1–2) 96
[11] Bastani D, Esmaeili N and Asadollahi M 2013 J. Indust. and Engin. Chem. 19(2) 375
[12] Kaminskii V A 2011 Russ. J. Phys. Chem. A 85(12) 2203
[13] Kossov V, Fedorenko O and Zhakebayev D 2019 Chem. Engin. and Technol. 42(4) 896
[14] Dilʼman V V and Lotkho V A 2015 Theor. Found. Chem. Eng. 49(1) 102
[15] Nezovitina N A, Bogatyrev A F and Makeenko A O 2016 J. Eng. Phys. and Thermophys. 89(3) 733
[16] Asembaeva M K, Kosov V N, Krasikov S A and Fedorenko O V 2019 Tech. Phys. Letters 45(21)
[17] Alyamovsky A A, Sobachkin A A, Odintsov E V, Kharitonovich A I and Ponomarev N B 2008 SolidWorks 2007/2008. Computer Modeling in Engineering Practice (St. Petersburg: BHV-Petersburg)

[18] Kosov V N, Fedorenko O V, Zhavrin Y I and Mukamedenkyzy V 2014 Tech. Phys. 59(4) 482

[19] Antipina N A, Kaplan A L and Pesherenko S N 2011 Drilling and Oil 12 40

[20] Gershuni G Z and Zhukhovitsky E M 1972 Convective Stability of an Incompressible Fluid (Moscow: Nauka)

[21] Bird R B, Stewart W E and Lightfoot E N 2007 Transport Phenomena (New York: John Wiley & Sons)

[22] Zhavrin Y I, Kosov V N, Fedorenko O V and Akzholova A A 2016 Theor. Found. Chem. Eng. 50 171

[23] Aleksandrov O E 2001 Tech. Phys. 46(11) 1367