Peculiarities of occurrence of concentration gravitational currents caused by mechanical equilibrium loss of a multicomponent system containing greenhouse gases

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Abstract. Rayleigh-Bénard convection in single-component media arises due to the instability of mechanical equilibrium. In mixtures, convective flow depends on density distribution in given geometries. For isothermal binary mixtures, Rayleigh-Taylor convection occurs with unstable stratification, while stable stratification limits transport to diffusion. Adding a third component can destabilize equilibrium, leading to convective currents. Understanding concentration field formation is crucial for analyzing convective structures of varying intensity. This work presents experimental data on "diffusion-convection" mode transitions in isothermal ternary mixtures with greenhouse gases under decreasing density conditions in vertical channels. Calculations identify regions of damped and increasing perturbations, while numerical simulations explore the early stages of convection. Results are compared with experiments and previous studies, incorporating artificial intelligence for generalization.

1.Introduction

At present, there are a large number of studies related to the study of transport phenomena in mixtures containing greenhouse gases [1], calculation of greenhouse gas distributions in the atmosphere [2, 3], modeling of greenhouse gas flows in multiphase media [4, 5] and other features of combined mixing [6, 7]. Among the above diversity, let us pay attention to the results obtained in the study of diffusive and convective characteristics in binary and multicomponent mixtures containing carbon dioxide and other greenhouse gases.

In particular, generalization of the results [1, 8, 9] on the study of mutual diffusion of methane, propane and carbon dioxide in the region of temperatures close to normal (293 – 313 K) and pressures higher than atmospheric (0.05 – 0.5 MPa) MPa showed a significant difference between the experimental and calculated in the kinetic approximation [10] diffusion coefficient of CO_2. It was also noted that in mixtures with CO_2, the baric dependence of diffusion coefficients in the region of elevated pressures cannot be described within the framework of traditional kinetic representations [10] and it is necessary to apply correlating coefficients to harmonize experimental data with calculated ones.

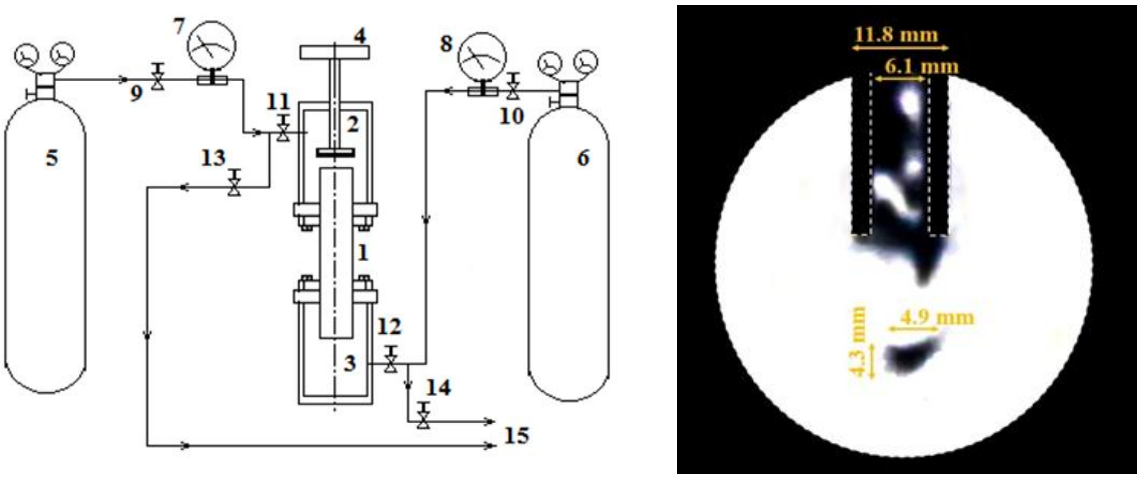
Another reason for the existence of discrepancies between the experimental data and the expected at diffusive mixing of partial fluxes of components is the presence of convective perturbations in the system, which were not taken into account for consideration. Experiments on studying diffusion in multicomponent gas mixtures [11,12] have shown that for the systems whose mutual diffusion coefficients differ considerably from each other there is a violation of mechanical equilibrium with the subsequent occurrence of currents, essentially intensifying the total mass transfer. There are conditions under which the priority transfer of the component with the highest molecular weight is fixed, which is not typical for diffusion [13]. The parameters of the transition from the diffusive state to the convective state can be predicted in the framework of stability theory [14], the extension of which to the case of isothermal ternary mixtures showed a satisfactory correlation between experimental and calculated data

[15]. In [16], it was shown that as the pressure increases, the density and thermophysical properties of CO_2 change significantly compared to those calculated in the ideal approximation.

This paper presents experimental results on the study of multicomponent mixtures containing greenhouse gases on the stability of equilibrium of isothermal ternary gas systems at different pressures for the situation in which the density of the mixture decreases with altitude. The calculation on determination of the boundary of change of kinetic modes "diffusion - convection" and concentration distributions of mixture components at the initial stage of mixing are presented. The obtained results of the numerical study are compared with the experimental data.

2. Experimental studies

Let us present the experimental values of separation of the gas mixture 0.4163 H_2 (1) + 0.5837 CO_2 (2) – N_2 (3) at different pressures. Let us assume that the numbers before the chemical element correspond to the initial concentration in mole fractions, and the numbers in brackets define the component numbering. The mixing of components was carried out on a device representing a variation of the two-bell method, which is widely used in experimental studies at various pressures and temperatures [1]. Let us briefly describe the experimental setup and the methodology of the experiment. Flasks 2 and 3 connected by a vertical channel 1 represent a diffusion cell (figure 1).

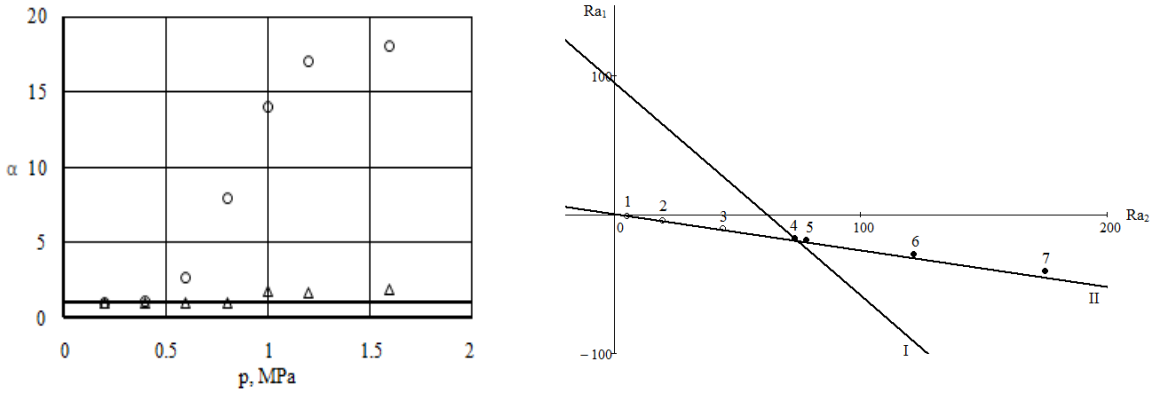


(a) (b)

Figure 1. Diffusion cell: (a) Principal scheme of the experimental stand [15]: 1 – diffusion channel; 2, 3 – upper and lower chambers of the diffusion cell; 4 – valve; 5, 6 – gas cylinders; 7 – 12 – the system of cocks and manometers; 13, 14 – pipelines that supply experimental mixtures for subsequent chromatographic analysis 15; (b) Convective flows observed at change of "diffusion – concentration gravitational convection" modes.

Geometric characteristics of the diffusion cell are as follows: the volumes of the upper and lower flasks are equal and are $V_u = V_l = (55.0 \pm 0.5) \cdot 10^{-6}$ m^3; diameter and length of the vertical cylindrical channel are: $d = (4.00 \pm 0.05)\, 10^{-3}$ m, $L = (70.00 \pm 0.05) \cdot 10^{-3}$ m. The temperature in all experiments was constant and equal to $T = 298.0$ K. The experimental condition assumed that the density of nitrogen in the lower flask 3 would be greater than the density of the mixture of hydrogen and carbon dioxide, which was located in flask 2. The region of investigated pressures is 0.2 – 1.7 MPa. The concentration of components was measured by gas chromatography. For the investigated mixture the error in determining the concentration of the component is ± 1%. The methodology of the experiment implied the fulfillment of certain procedures. The gases under study were supplied into flasks 2 and 3 with connecting channel 1 and closed valve 4. Upon completion of the filling procedure, valve 4 was

opened and the mixing time was recorded. Its closing occurs at the end of the experiment. Then the investigated mixtures through the outlets 15 are fed to the chromatograph and the experimental values of concentrations are determined. The defining moment of the experimental study is the registration of the transition from one state to another. Obviously, this can be done by comparing the experimental data (concentrations of components) with those calculated by the Stefan-Maxwell equations [10] assuming diffusion in ternary mixtures. If the experimental concentrations c_{exp} and calculated according to the Stefan-Maxwell equations c_{theor} are close to each other, this indicates a diffusion mode of mixing. The significant difference between the concentrations in experience and theory shows the presence of other mixing mechanisms. The transition boundary can be fixed if we follow the ratio of the diffused experimental and calculated concentrations of components $\alpha = c_{exp}/c_{theor}$. Figure 2 (a) shows the functional dependence of the dimensionless parameter α on pressure for the analyzed system obtained in [13].



(a) (b)

Figure 2. Experimental and calculated data of diffusive and convective mixing in the mixture 0.4163 H_2 (1) + 0.5837 CO_2 (2) – N_2 (3) at different pressures and temperature T = 298.0 K. The mixing time is τ = 30 minutes: (a) Dependence of α on pressure. The line is the calculation on the assumption of diffusion. The points correspond to: Δ – hydrogen; ○ – carbon dioxide; (b) Stability cartogram: I – neutral line of monotonic perturbations; II – line of zero density gradient; 1 – 7 – numerical data at different values of p: 1 – 0.2; 2 – 0.4; 3 – 0.6; 4 – 0.7; 5 – 0.8; 6 – 1.0; 7 – 1.2 MPa.

The data analysis shows that in the pressure region 0.1 – 0.6 MPa diffusion is realized in the system. This is evidenced by the equality to unity of the dimensionless parameter α_i for all three components of the studied mixture. Starting from the pressure of 0.6 MPa the growth of α_i for each component of the mixture is fixed. Especially significant increase is noted for CO_2 and to a lesser extent for the most diffusively mobile H_2. Apparently, the pressure $p^* \geq 0.7$ MPa provides a change of transport modes from diffusive to convective (figure 1(b)). Such mixing is not typical for diffusion. The highest values of α_i for CO_2 at pressures higher than the transition pressure indicate that under the given conditions there is a preferential transport of CO_2. At further pressure increase the linear dependence is broken. A similar situation is observed for most systems with greenhouse gases (Freon-12, carbon dioxide, diazote oxide, methane) dissolved mainly in nitrogen with admixtures of hydrogen, helium, water vapor, and other components.

3. Sustainability analysis

The description of multicomponent mixing is reduced to the joint solution of the Navier-Stokes equations, convective diffusion and conservation of the number of particles of components. Due to the detailed consideration of various simplifications of the basic equations of hydrodynamics presented in

[14-19], they can be omitted and we can immediately pass to the system of perturbed dimensionless equations, which for a ternary mixture take the form:

$$Pr_{22}\frac{\partial c_1}{\partial t}-(\vec{u}\vec{\gamma})=\tau_{11}\nabla^2 c_1+\frac{A_2}{A_1}\tau_{12}\nabla^2 c_2,\qquad Pr_{22}\frac{\partial c_2}{\partial t}-(\vec{u}\vec{\gamma})=\frac{A_1}{A_2}\tau_{21}\nabla^2 c_1+\nabla^2 c_2 \tag{1}$$
$$\frac{\partial \vec{u}}{\partial t}=-\nabla p+\nabla^2\vec{u}+(Ra_1\tau_{11}c_1+Ra_2c_2)\vec{\gamma},$$
$$div\vec{u}=0,$$

where $Pr_{ii}=\frac{v}{D_{ii}^*}$ is the diffusion Prandtl number, $Ra_i=g\beta_i A_i d^4/vD_{ii}^*$ is the diffusion Rayleigh number, v is the kinematic viscosity coefficient, $\beta_i=-\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial c_1}\right)_{p,T}$, $\tau_{ij}=\frac{D_{ij}^*}{D_{22}^*}$ are the parameters determining the relationship between practical diffusion coefficients, $\vec{\gamma}$ is the unit vector directed vertically upwards. The parameters $\tau_{ij}=D_{ij}^*/(D_{22}^*)$ are calculated through D_{ij}^*, which are recovered through the pairwise diffusion coefficients [11].

The solution of the system of equations (2) can be conditionally divided into several stages [20]. At the first stage, taking into account the existence of three-dimensional motions in channels of different geometry and finite length, the velocity approximation is written, considering all components of the vector $\vec{u}$ to be different from zero. Next, based on the continuity equation, a relation is written that relates the radial components of the velocity components defined through *n*-th order Bessel functions. At the second stage, from the first two equations of the system (1), the concentrations of components are determined using the Kantorovich method under boundary conditions assuming zero reversal of velocity and flux perturbations at the boundaries of the diffusion channel. At the third stage, the monotonic stability boundary is determined.

On the basis of the described approach of solving the system of equations of concentration convection (1), for example, for a vertical cylindrical channel of finite height with boundary conditions assuming zero reversal of perturbations of velocity and flow of matter at the boundaries, in [20] the boundary relation defining the change of "diffusion – convection" modes in terms of Rayleigh numbers Ra_i was obtained in the form:

$$\int \vec{u}\nabla^2\vec{u}dV+Ra_1\tau_{11}\int u_z\,c_1 dV+Ra_2\int u_z\,c_1 dV=0 \tag{2}$$

Based on the obtained solution (2), it is possible to obtain a stability map in (Ra_1, Ra_2) coordinates and map the experimental data on it. The experimental data are reconstructed through Rayleigh partial numbers

$$Ra_1=\frac{gnr^4\Delta m_1}{\rho vD_{11}^*}\cdot\frac{\partial c_1}{\partial z},\quad Ra_2=\frac{gnr^4\Delta m_2}{\rho vD_{22}^*}\cdot\frac{\partial c_2}{\partial z} \tag{3}$$

where $\Delta m_1=m_1-m_2$, $\Delta m_2=m_2-m_3$, m_i is the molecular weight of the i-th component, $n=p/k_BT$ and then displayed on the coordinate plane (Ra_1, Ra_2). The cartogram (Ra_1, Ra_2) also shows the zero-density gradient line, whose location is determined by the following equation:

$$\tau_{11}Ra_1=-Ra_2 \tag{4}$$

The intersection of the boundary line defined by equation (3) with the axes Ra_1 and Ra_2 allows us to obtain two critical Rayleigh numbers. The results of numerical investigation of the system 0.4163 H_2 + 0.5837 CO_2 – N_2 are presented in figure 2(b). It is known from experience what mixing mode is realized under the given conditions. We will use the notation in the form of brightened points "o" for diffusion.

The regime, where mixing is determined by convective perturbations, we denote by dark signs "●". The set of points on the plane (Ra_1, Ra_2) determines the correspondence of the observed mixing modes to the calculated boundary relations. The critical Rayleigh numbers defining the stability boundary have the following values: $Ra_1 = 94.4773$ and $Ra_2 = 61.6623$. In the pressure range from 0.2 to 0.6 MPa, the considered system is in the diffusion region, which is in agreement with the experimental data shown in figure 2 (a). Numerical calculation showed that the transition to the convective region occurs at a pressure of 0.775 MPa (point 4). The possibility of transition of the system from the diffusion region to the convective region is associated with the presence of density inversion in the vertical channel due to the difference in the diffusion coefficients of the components.

At the same time, it was recorded that at certain compositions of the mixture the discrepancy between the experimental and calculated data increases. This suggests that the calculation model should be corrected. Application of analysis methods based on artificial intelligence [21] has shown that within the framework of the applied formalism, the discrepancy can be significantly reduced if the following corrective actions are applied:

- the equation of state must take into account the nonlinear dependence of density on pressure;
- correct determination of cross-diffusion coefficients;
- mutual influence of pressure and composition on diffusion.

4. Conclusion

The studies have shown that for multicomponent systems containing carbon dioxide and other greenhouse gases under isothermal conditions there are areas of pressure and concentration at which there is a violation of the stability of mechanical equilibrium of the system. In this case there is a regime change from diffusion mixing process to concentration gravitational convection. The change of "diffusion – convection" modes occurs at a certain content of carbon dioxide in the mixture. Moreover, in a certain pressure range, a priority transfer of the component with the highest molecular weight is observed. In the system with CO_2, the "diffusion – convection" transition is realized at lower pressures than in mixtures where this component is absent.

For the considered ternary systems within the framework of the analysis on stability of mechanical equilibrium of a gas mixture the boundary of change of "diffusion – concentration gravitational convection" modes is determined. Comparison with experience showed a satisfactory agreement between theory and experience in determining the diffusion and convection regions.

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6. References

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