STABLE DIFFUSION BOUNDARIES IN THREE-COMPONENT GAS MIXTURES

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Within the framework of the Boussinesq approximation, as a function of the relationship between the partial diffusion factors, we have investigated an isothermal three-component gas mixture with respect to linear stability. In the stable diffusion region the process of isothermal mass transfer is described by standard Fick equations. We have determined the regions of increasing (diminishing) monotonic and oscillatory perturbations. We have investigated the relationship between the Rayleigh numbers and the parameters of the mixture.

A study of convective flows in multicomponent media showed that under certain conditions a rather slight change in the physical characteristics leads to a qualitative change in the behavior of the system. A clear illustration of this assertion is offered by formation of Bénard structures in thermal convection [1]. In binary systems, owing to the competition between the concentration gradients of the components and temperatures near the diffusion boundary of separation density-stratified regions are formed, and in the gravitational field this leads to the onset of convective flows [2-4]. As an example we can cite the storage of liquefied natural gas in a closed container, when owing to temperature and concentration nonuniformities two diverse layers are formed, with a diffusion separation surface between them. As the light gas fractions are vaporized, the density of the liquid in the upper portion of the container will be higher than in the lower portion. The system becomes hydrostatically unstable, mixing takes place, and here a sharp increase in pressure may lead to an uncontrollable release of gas [5]. A similar result may come about in isothermal diffusion in certain three-component gas mixtures [6-8]. The onset of concentration convection is associated with a number of unique features [7-9], the main one being the difference in the partial diffusion factors for the components [10]. The physical pattern of instability onset for the diffusion process in such systems involves the fact that the difference in the diffusion capacities of the components leads to density stratification of the gas mixture, with the subsequent onset of convection in the gravitational field.

The present study presents an analysis of the influence exerted by isothermal mass transfer in three-component gas mixtures on linear stability, and we determine the regions in which stable diffusion exists, the latter being described by Fick equations, and finally, we determine areas of diffusional instability.

Let us examine an ideal incompressible isothermal three-component gas mixture at constant pressure, contained between two parallel planes. In the derivation of the three-convection equations we usually resort to the small perturbation method [1] in which the thermodynamic variables c_1, c_2, and P are represented by added factors calculated from certain constant mean values c_1^0, c_2^0, and P_0. We will assume that the density nonuniformities generated by nonuniformity in pressure are negligibly small. As regards the density nonuniformities generated by concentration nonuniformity, the latter is assumed to be small in comparison with the mean density ρ_0 and disappears at the boundaries of the planes. When we take into consideration the condition of independent diffusion, which presumes the description of the mass component transfer by partial coefficients which in the center-of-mass system [11] are identical with the effective diffusion factors (EDF) [12, 13], and assuming these to be constant for the given mixture composition, in the Boussinesq approximation (the density nonuniformities are taken into consideration in the term containing the lift force in the Navier—Stokes equation of motion) the following system of equations to describe mass transfer as follows:

$$\frac{\partial c_1}{\partial t} + \mathbf{u}\nabla c_1 = D_1\nabla^2 c_1, \quad \frac{\partial c_2}{\partial t} + \mathbf{u}\nabla c_2 = D_2\nabla^2 c_2,$$
$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\nabla)\,\mathbf{u} = -\frac{1}{\rho_0}\nabla P + \nu\Delta\mathbf{u} + g\,(\beta_1 c_1 + \beta_2 c_2)\,\gamma, \tag{1}$$

where $\beta_k = 1/\rho_0(\partial\rho/\partial c_k)$, while γ is the unit vector directed vertically upward.

Let us formulate the boundary conditions. Following [1, 3, 14-16], we will assume that the tangential stresses disappear at the boundary, with the zero-valued normal flow component and the convective fluctuations that arise not leading to any strains at the boundaries. The concentration value has been fixed at the boundaries and, consequently, the perturbation of this value disappears at the boundaries. When we take all of this into consideration, we find that

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$$z = 0,\ d;\ c_1 = c_2 = 0,\ \mathbf{u} = 0;\ \frac{\partial c_1}{\partial n} = \frac{\partial c_2}{\partial n} = 0. \tag{2}$$

The condition of mechanical equilibrium is written in the form

$$\mathbf{u} = 0,\ \frac{\partial c_1^0}{\partial t} = \frac{\partial c_2^0}{\partial t} = 0,\ (\beta_1 \nabla c_1^0 + \beta_2 \nabla c_2^0)\,\boldsymbol{\gamma} = 0. \tag{3}$$

The equation of state within the scope of an ideal gas will be presented in the following form:

$$\rho = \rho_0 (1 + \beta_1 c_1 + \beta_2 c_2). \tag{4}$$

Let us make dimensionless the initial system of differential equations relative to the time scale d^2/D_3, the linear dimension d, the distance between the plates, and relative to the original physical characteristics: D_3, the partial diffusion factor for the third component (used as one of the scale units for the diffusion factor of the third component, whose flow is defined in terms of the linear combination of the two remaining components, thus making it possible, in explicit form, to account for its influence as well) and ν, while for the concentration gradient we will use the scale $-\Delta c_i/d$. We will introduce the stream function for velocity perturbations $\psi(x, z)$. With the diffusion model [12, 13] and the Boussinesq approximation [1, 14, 15] satisfied, following linearization, we derive a system of equations for the dimensionless perturbations in c_1 and c_2:

$$\frac{\partial c_1}{\partial t} - \tau_1 \nabla^2 c_1 = -\frac{\partial \psi}{\partial x},\ \frac{\partial c_2}{\partial t} - \tau_2 \nabla^2 c_2 = -\frac{\partial \psi}{\partial x},$$
$$\left(\frac{1}{\Pr}\frac{\partial}{\partial t} - \nabla^2\right)\nabla^2 \psi = \left(\tau_1 R_1 \frac{\partial c_1}{\partial x} + \tau_2 R_2 \frac{\partial c_2}{\partial x}\right) \tag{5}$$

when

$$z = 0,\ 1;\ c_1 = c_2 = \psi = 0. \tag{6}$$

The similarity parameters in the problem are $\Pr = \nu/D_3$, the diffusion Prandtl number, $R_1 = g\beta_1\Delta c_1 d^3/\nu D_1$ and $R_2 = g\beta_2\Delta c_2 d^3/\nu D_2$, the diffusion Rayleigh numbers for the first and second components of the gas mixture, respectively; $\tau_1 = D_1/D_3$ and $\tau_2 = D_2/D_3$, quantities characterizing the relationship between the EDF. The mutual direction of the concentration gradients for the components is determined through a specific formulation of the problem and will be dealt with later on. Introduction of the parameters τ_1 and τ_2 allows us to determine the contribution of each component to the phenomenon of diffusion instability, which distinguishes isothermal concentration convection from instability in a binary mixture in the presence of a temperature gradient such as the one dealt with by Nield [16]. For a binary system the concentration characteristics of the components govern one of the diffusion factors, while in the case of a three-component mixture these characteristics determine three diffusion factors as a minimum (when described by partial factors). In this connection, the introduction of the parameters τ_i and a slight change in the solution of system of equations (5) make it possible, in our opinion, more fully to account for the unique features of mass transfer in three-component gas systems.

We will look for the solution of the boundary-value problem (5), (6) in the following form:

$$\psi = \psi_1 \sin(\pi a x) \sin(\pi n z) \exp[-\lambda t],$$
$$\begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} = \begin{Bmatrix} c_1^1 \\ c_2^1 \end{Bmatrix} \cos(\pi a x) \sin(\pi n z) \exp[-\lambda t]. \tag{7}$$

After we have substituted (7) into system of equations (5), and eliminating the constants c_1^1, c_2^1, and ψ_1 sequentially, we derive the following cubic equation for the perturbation decrement λ:

$$\lambda^3 + r\lambda^2 + s\lambda + q = 0, \tag{8}$$

where

$$r = -k^2(\tau_1 + \tau_2 + \Pr);\ s = k^4\tau_1\tau_2 + \Pr\left[(\tau_1 + \tau_2)k^4 + \left(\frac{\pi a}{k}\right)^2 (\tau_1 R_1 + \tau_2 R_2)\right];\ q = -\Pr\,\tau_1\tau_2\,[k^6 + (\pi a)^2(R_1 + R_2)];$$

$$k^2 = \pi^2(n^2 + a^2),\ n = 1,\ a = \frac{1}{\sqrt{2}}.$$

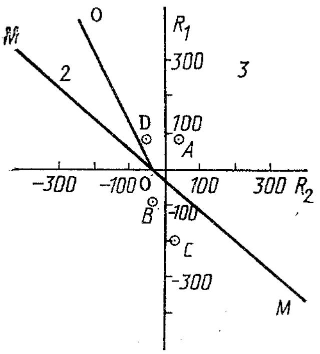

Fig. 1. Neutral lines and regions in which monotonic and oscillatory disturbances exist: 1) region of stable diffusion; 2) region of monotonic instability; 3) region of oscillatory instability; MM and OO) neutral lines of monotonic and oscillatory perturbations at points A, B, C, while D corresponds to the experimental data from [7-10, 17, 19].

On solution of Eqs. (8), depending on the parameters r, s, and q, we can obtain either three real roots (monotonic perturbations), or one real and two complex-conjugate roots, which describe the oscillation perturbations. Assuming that $\lambda = \alpha + i\omega$, according to (8) we can derive a system of equations for the real and imaginary parts of the decrement:

$$\alpha^3 - 3\alpha\omega^2 + r(\alpha^2 - \omega^2) + s\alpha + q = 0, \tag{9}$$

$$\omega[3\alpha^2 - \omega^2 + 2\alpha r + s] = 0. \tag{10}$$

We will determine the boundary of instability for the monotonic and oscillatory perturbations. At the stability boundary we have $\alpha = 0$. It then follows from (9) and (10) that

$$q - r\omega^2 = 0, \tag{11}$$

$$\omega(s - \omega^2) = 0. \tag{12}$$

In the case of monotonic perturbation we have $\omega = 0$ (the neutral perturbation is steady) and from (12) we have q = 0, which gives us

$$R_1 = -\frac{k^6}{(\pi a)^2} - R_2. \tag{13}$$

If the perturbation oscillates at a frequency ω at the boundary of stability, and this frequency is different from zero, it then follows from (12) that $\omega^2 = s$, i.e., the frequency of the neutral oscillations has the form

$$\omega^2 = k^4\tau_1\tau_2 + \mathrm{Pr}\left[(\tau_1 + \tau_2)k^4 + \left(\frac{\pi a}{k}\right)^2(\tau_1 R_1 + \tau_2 R_2)\right]. \tag{14}$$

The complex consisting of the critical Rayleigh numbers characterizing oscillatory instability is found from expression (10), according to which rs − q = 0, i.e.,

$$R_1 = -\frac{k^6\{(\tau_1 + \tau_2 + \mathrm{Pr})[\tau_1\tau_2 + \mathrm{Pr}(\tau_1 + \tau_2)] - \tau_1\tau_2\mathrm{Pr}\}}{(\pi a)^2(\tau_1 + \mathrm{Pr})\tau_1\mathrm{Pr}} - \frac{\tau_2(\tau_2 + \mathrm{Pr})}{\tau_1(\tau_1 + \mathrm{Pr})}R_2. \tag{15}$$

Expressions (13)-(15) characterize the areas of stable (unstable) diffusion.

Three-component gas mixtures were analyzed for stability with the aid of (13) and (15) and we will illustrate this analysis on the example of the ideal gas system Ar (1)—N_2 (2)—He (3) (the numbering of the components is indicated in parentheses), which may be located in any of the three areas (see Fig. 1), classified as follows in analogy with [1]: 1) the area of stable diffusion (the process is described by standard Fick equations); 2) the area of monotonic disturbances; 3) the area of oscillatory disturbances. It is obvious that if $R_1 > 0$ and $R_2 > 0$, the system is hydrostatically unstable, which corresponds to a situation in which a heavier mixture such as, for example argon with nitrogen, is located in the upper portion of the diffusion mechanism, while helium is located in the lower portion. Experimental data [8, 17] showed that mixtures similar to $0.5N_2$ (2) + 0.5Ar (1)—He (3) (the component concentrations are given in mole fractions) generate hydrodynamic-type instability (the point A is located in the first quadrant).

When $R_1 < 0$ and $R_2 < 0$, the mixture being tested is in the stable state, i.e., the density of the gas in the upper portion of the diffusion channel is lower than the density of the mixture in the lower part. For the triple system He (3)—0.5Ar (1) + $0.5N_2$ (2) in the case of a two-column device [18] (this will be the case when the binary argon—nitrogen mixture is in the lower portion of the diffusion apparatus, while helium is in the upper portion) experimental studies [19] demonstrated the stable nature of the diffusion process in various temperature regimes (the point B is situated in the third quadrant).

The three-component mixture 0.5He (3) + $0.5N_2$ (2)—Ar (1), corresponding to the case $R_1 < 0$ and $R_2 > 0$, will be stable when the components are ideal gases. Results from [6] show that this system is stable from the standpoint of diffusion (the point C is in the fourth quadrant). If we assume that one of the components of the binary mixture is a real gas (for example, methane, carbon dioxide, halogen-derivative carbohydrates), it may turn out with a change in the conditions (we have reference here to a different compressibility z for the original components) in terms of density the mixture may surpass a pure component, and hydrodynamic flows may therefore be set up within the system. However, this question must subsequently be studied on its own, both experimentally and theoretically.

Of greatest interest, in our opinion, is the problem related to research into the stability of equilibrium systems in the Rayleigh number range $R_1 > 0$ and $R_2 < 0$, where gas mixtures analogous, for example, to He (3) + Ar (1)—N_2 (2), will be unstable from the standpoint of diffusion. Experimental data from [7-10, 17] showed that in triple mixtures with markedly diverse values for the diffusion factors of components under specific conditions convective flows are generated, and these significantly distort the process of isothermal diffusion mass transfer. Starting from a specific critical parameter (pressure, the diameter of the diffusion channel, temperature) a system in the stable state turns unstable, and here complex oscillation regimes are observed, these related to the change in the composition of the mixture.

The neutral lines of the monotonic and oscillatory disturbances form the systems H_2 + Ar—N_2, He + Ar—N_2, He + N_2—CH_4, H_2 + N_2—CH_4, H_2 + N_2—Ne, depending on the mixture parameters τ_1, τ_2, and Pr, can be seen in Fig. 2. It might be noted that an increase in the parameter τ_2 leads to a reduction in the critical Rayleigh number, which suggests destabilization of the system. For example, for a 0.5He (3) + 0.5Ar (1)—N_2 (2) mixture when $\tau_2 = D_2/D_3 \to 1$, in the place of the nitrogen in the system being tested we should have a lighter gas (helium, at the very least). In other words, the system exhibits hydrodynamic disturbances. As demonstrated by special studied such as those conducted in [8], when a denser gas is mixed with one that is less dense, convective currents arise considerably earlier than is the case with diffusion unstable systems. Conversely, when $\tau_1 = D_1/D_3 \to 1$, the unstable

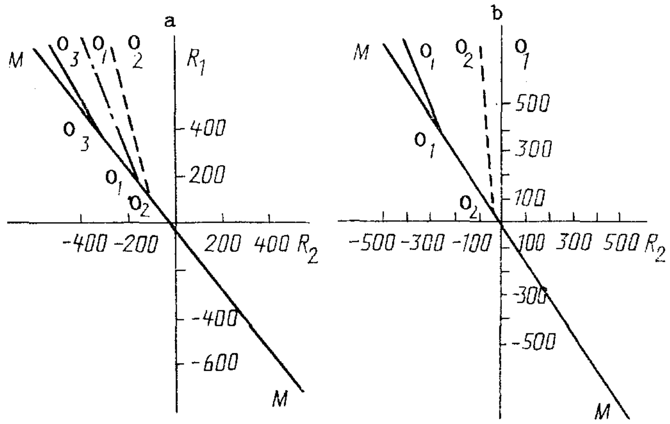

Fig. 2. Mutual position of the MM monotonic perturbation and OO oscillatory perturbation lines, corresponding to the following mixtures: a) O_1O_1: 0.5He + 0.5Ar—N_2;O_2O_2: $0.5H_2$ + 0.5Ar—N_2; O_3O_3: 0.5He + $0.5N_2$—CH_4; b) O_1O_1: $0.5H_2$ + $0.5N_2$—CH_4;O_2O_2: $0.5H_2$ + $0.5N_2$—Ne; P = 0.1 MPa, T = 300 K.

process undergoes stabilization. Then, for a given mixture, the place of argon must be occupied by a lighter gas and in the limit case the triple mixture degenerates into a stable binary He—N_2 system. Analysis of this triple gas mixture in terms of stability, depending on the viscosity of the mixture (Fig. 2b), shows that the critical Rayleigh numbers corresponding to monotonic disturbances remain constant. With an increase in viscosity, the onset of an oscillatory regime is more likely in systems in which the viscosity is lower. This conclusion apparently requires more detailed verification which, unfortunately, could not be undertaken owing to a lack of published data. Let us note that it is exceedingly complex in the experiment to determine the boundaries of stable diffusion, of monotonic and oscillatory disturbances for three-component systems, and we can therefore speak only of qualitative agreement of the analysis with respect to linear stability within the scope of a plane layer exhibiting a true pattern of diffusion instability, such as that observed in the vertical cylindrical tubing of closed diffusion equipment [7-10, 16].

Thus, the onset of isothermal diffusion instability in multicomponent gas systems significantly distorts the normal course of the exchange of mass. Diffusion, which exerts a stabilizing role in the case of binary systems, for three and more components will lead, in certain gas mixtures, to the onset of density stratification in specific areas and to the appearance of dissipative convection structures. This must necessarily be taken into consideration in the designing of chemical-engineering equipment and in measuring the constants of heat and mass transfer.

NOTATION

c_i, excess (in terms of the average) concentration of the i-th component; t, time; u, velocity; D_i, partial diffusion factor for the i-th component; P, convective addition to the hydrostatic pressure P_0, corresponding to the average values of concentration for the components and the average density ρ_0; ν, viscosity of the gas mixture; g, gravitational acceleration; γ, unit vector directed upward along the vertical; $\psi(x, z)$, stream function; x and z, axes of the Cartesian coordinate system; $Pr = \nu/D_3$, partial diffusion Prandtl number; $Ri = g\beta_i \Delta c_i d^3/\nu D_i$, partial diffusion Rayleigh number of the i-th component; d, thickness of layer, identical to the diameter of the diffusion channel; τ, dimensionless parameter characterizing the relationship between the partial diffusion factors; λ, decrement, defining the course of the disturbance; ω, frequency of neutral oscillations; z, compressibility of the component.

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