Journal of Engineering Physics and Thermophysics, Vol. 69, No. 6, 1996

SOME FEATURES OF CONVECTIVE HEAT AND MASS TRANSFER IN MULTICOMPONENT GASEOUS MIXTURES

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UDC 536.25

Unstable diffusive mass transfer in a three-component gaseous mixture under nonisothermal conditions is investigated experimentally. Using linear analysis of the mixture for stability, the critical Rayleigh numbers are determined.

Introduction. The study of mass transfer in some multicomponent gaseous mixtures under isothermal conditions has shown that a difference in the diffusion powers of the components leads to stratification of the gaseous mixture in density with the subsequent appearance of powerful convective flows in the gravity field that exceed by an order of magnitude or more the molecular transfer proper [1]. The superposition of hydrodynamic flows that are due to the action of Archimedes forces on molecular transfer makes the diffusion process unstable [1, 2]. In [1-4], parameters (the concentration, pressure, temperature, viscosity of the mixture, dimensions of the diffusion channel) are given for which the transition from a stable state (the description is given within the framework of Fick's laws) to an unstable state is possible. Clearly, the process will be greatly complicated if it occurs in a nonuniform temperature field. This can be judged by analyzing investigations devoted to the study of binary diffusion of gases under nonisothermal conditions (as a rule the aim was to determine the temperature dependence of diffusion characteristics) [5-7] as well as multicomponent unstable mass transfer [4, 8] in which the stabilizing action of temperature, including that in heating from above, was shown. In the case of the opposite direction of a temperature gradient, the intensity of the overall unstable mass transfer is affected by two oppositely acting factors: on the one hand, the increase in temperature leads to enhancement of the diffusion powers of the components, thus "washing out" the stratified gaseous regions and stabilizing the transfer; on the other, the density of the diffusing component decreases, which leads to hydrodynamic disturbances and is a destabilizing factor.

In the present investigation, an attempt was made to show the picture of multicomponent diffusion when heating was performed at the site of the gas lying below and to assess the action of the aforementioned factors on mass transfer.

Experimental Investigations. For the experiment, we took a binary mixture of hydrogen and nitrous oxide with a component concentration (molar fractions) of $0.4505H_2 + 0.5495N_2O$ that diffused into pure argon.

The experiments were carried out on an installation with a two-flask diffusion apparatus [8, 9] with the following geometric parameters: volumes of the upper and lower flasks $V_{up} = V_{low} = 62.0 \pm 0.6$ cm^3; channel length and diameter 6.3 ± 0.05 and 0.400 ± 0.001 cm, respectively. The temperature of the upper flask was maintained at 293.0 ± 0.3, and that of the lower flask at 363.0 ± 1 K. The pressure in the experiments was 1.96 MPa. The initial composition of the binary mixture was determined on an ITR-1 interferometer with a total error of no more than 0.1%, and after diffusion, that of the three-component mixture was determined on a KhROM-4 chromatograph with a total error of 0.3%. Each experiment under these conditions was carried out several times and the resultant values of the concentrations were determined as the arithmetic mean of the result.

Since the density of the binary mixture is lower than the density of the pure gas it was placed in the upper flask, and the argon in the lower one. The initial gases, their concentrations, and the pressure were selected so that in isothermal diffusion ($T = 293$ K) an unstable low-intensity diffusion process is observed in the system. This

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Al' Farabi Kazakh National State University, Almaty. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 6, pp. 977-981, November-December, 1996. Original article submitted June 6, 1996.

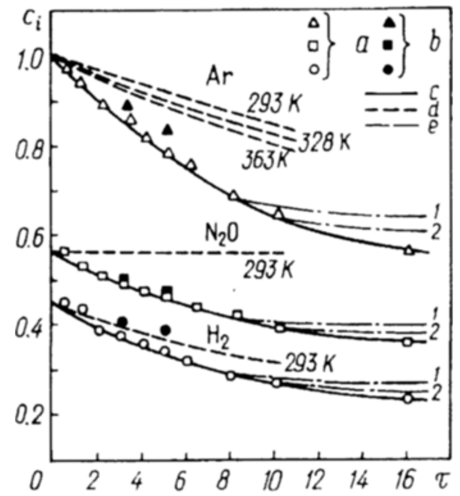

Fig. 1. Hydrogen, nitrous oxide (upper flask), and argon (lower flask) concentrations in diffusion in the system of $0.4505H_2 + 0.5495N_2O$ and Ar versus duration of the experiment. The points are experimental data for unstable nonisothermal (a) and isothermal ($T = 293$ K) (b) processes for argon, nitrous oxide, and hydrogen, respectively; c) approximation of experimental data by polynomials; the remaining lines are a calculation according to [10] under the assumption of stable diffusion (d) for the initial and (e) for 8-h (1), 10- (2) distributions of component concentrations, respectively. c_i, molar fraction; τ, h.

enabled us to observe its influence on mass transfer without imposing a significant temperature gradient. The performance of the experiments differed only in duration. Figure 1 presents results of measuring the concentrations of the diffusing gases in the flasks of the apparatus at a certain instant and of calculations by the Stefan–Maxwell equations [10] for a nonisothermal process at $T = 328$ K and three isothermal processes at $T = 293$, 328, and 363 K. So as not to complicate the figure we will consider only the change in the concentration of the argon in the lower flask and the hydrogen and nitrous oxide in the upper flask of the apparatus (the concentrations of these gases in the other flask can easily be determined by subtracting the data in Fig. 1 from the initial data). The nonisothermal mass transfer was calculated for the arithmetic mean temperature of the hot and cold flasks of the apparatus ($\overline{T} = 328$ K). The use of the arithmetic mean temperature in the calculations was based on results of investigations of [6] as well as on the small magnitude of the temperature gradient. To this we should add that special calculations showed that flows caused by cross effects can be disregarded as compared to diffusive transfer and convection [5].

The fact that the observed process under isothermal conditions at $T = 293$ K is unstable in character was demonstrated by two control experiments with a duration of 3 and 5 h, respectively, whose results were compared with calculations. The comparison shows that the transfer of the components in the case of instability is much greater than it should be in the case of stable diffusion. This is particularly evident for the nitrous oxide, whose transfer in stable diffusion is virtually absent, since one of the special features of multicomponent mass transfer – a "diffusion lock" – manifests itself for this component [11]. At the same time, in unstable diffusion, its concentration in the lower flask increases even more than for such a mobile gas as hydrogen.

The imposition of a temperature gradient on this unstable system when the lower flask of the apparatus is heated to 363 K while the upper one remains at $T = 293$ K will not lead to a change in gas orientation in the experiment and, hence, in the gradient of the overall density of the mixture, since the argon density will exceed by just as much the density of the hydrogen-nitrous oxide mixture.

In Fig. 1, the dots are the experimental values of the concentration that was attained by one or another component of the mixture at a certain instant. The solid lines are an approximation of the results of the experiment using polynomials. As is evident from the above data, the intensity of the unstable process in heating the lower flask is enhanced compared to isothermal unstable transfer, and all the more compared to the stable nonisothermal process ($\overline{T} = 328$ K).

It was already shown earlier that convection is most intense at the initial moment (about 1–1.5 h), then decays, and is present in a very weak form for a considerable time. By a calculation similar to [12] we made an attempt to reproduce the time beginning with which a stable diffusion process is observed in the system. For this purpose, we took experimental values of the concentrations of the components at this instant, which was considered as "zero" (in Fig. 1 – the concentrations at 8 and 10 h) and, assuming that the diffusion is stable, we calculated the change in the composition in the flasks of the apparatus. It turned out that the results of the calculation are very far from the experimental data (see, for example, the data for the point that corresponds to 16 h). This indicates the presence of convective flows in the system in addition to molecular transfer.

It can be assumed that the system selected for the investigation will not reach the normal stable diffusion process under the conditions of the experiment. Indeed, turning to the concentrations of the components that were attained at 16 h it turns out that the hydrogen concentration is practically equilibrium, but then in the upper flask there will be a mixture with a predominance of the heavy component, namely, nitrous oxide, and in the lower flask of argon (and what is more, heated argon), which, in the gravity field, will lead to the process of normal mixing. This will persist until the concentrations of the gases become completely equilibrium in both flasks of the apparatus.

We note another special feature that accompanies unstable mass transfer: this is the development of an oscillating regime of change in the overall concentration of the components [2]. A similar character of the change in the component concentration should also be present in our system but studying it in greater detail seems diffult and calls for special investigations.

Linear Analysis for Stability. The state of an ideal three-component gaseous mixture in a nonuniform temperature field without allowance for barodiffusion is described by the hydrodynamic approximation in the following manner [5, 13]:

$$\begin{gathered}
\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\nabla)\,\mathbf{u} = -\frac{1}{\rho}\nabla p + \nu\nabla^2\mathbf{u} + g\boldsymbol{\gamma}\,, \\
\operatorname{div}\,(\rho\mathbf{u}) = 0 \quad \frac{\partial c_i}{\partial t} + (\mathbf{u}\nabla)\,c_i = \operatorname{div}\mathbf{j}_i\,, \\
\mathbf{j}_i = \frac{n^2}{\rho}\sum_{j=1}^{\nu} m_i m_j D_{ij}\nabla c_j - D_i^T\nabla\ln T\,, \\
\frac{\partial T}{\partial t} + (\mathbf{u}\nabla)\,T = \operatorname{div}\mathbf{q}\,, \quad \mathbf{q} = -\Lambda_\infty\nabla T\,,
\end{gathered} \tag{1}$$

where **u** is the rate of convection; p is the pressure; ρ and ν are the density and kinematic viscosity of the mixture; c_i and m_i are the concentration and mass of the molecule of the i-th component; T is the temperature; D_{ij}, D_i^T, and Λ_∞ are the diffusion, thermal diffusion, and thermal conductivity coefficients for the mixture in the steady state; γ is the unit vector pointing vertically upward.

We simplify the problem. We consider a horizontal layer that is bounded by two parallel plates, the distance between which is d (the z axis points upward and is perpendicular to the plane determined by x and y). We disregard cross effects (thermal diffusion and diffusive heat conduction). Let us use linear analysis for stability [13, 14] that proposes representing (1) in the Boussinesq approximation for disturbed quantities. Making (1) dimensionless by means of the scales of length d, time d^2/D_{11}^*, velocity D_{11}^*/d, gradients of concentration $\delta c_i/d$ and temperature $\delta T/d$, and pressure $\rho_0\nu D_{11}^*/d$ and using the current function ψ for the disturbance of the rate, we obtain the equations for critical motions:

$$\frac{\partial c_1}{\partial t} - \nabla^2 c_1 - A\nabla^2 c_{22} = -\frac{\partial\psi}{\partial x}\,, \quad \frac{\partial c_2}{\partial t} - B\nabla^2 c_1 - \tau_{22}\nabla^2 c_2 = -\frac{\partial\psi}{\partial x}\,,$$

$$\frac{\partial T}{\partial t} - \mathrm{Le}_1 \nabla^2 T = - \frac{\partial \psi}{\partial x} , \qquad (2)$$

$$\left(\frac{1}{\mathrm{Pr}_1} \frac{\partial}{\partial t} - \nabla^2 \right) \nabla^2 \psi = \mathrm{R}_1 \frac{\partial c_1}{\partial x} + \tau_{22} \mathrm{R}_2 \frac{\partial c_2}{\partial x} + \mathrm{Le}_1 \mathrm{R} \frac{\partial T}{\partial x} ,$$

where $\mathrm{R} = g\beta\delta T d^3/\nu a$ and $\mathrm{R}_i = g\beta_c \delta c_i d^3/\nu D^*_{ii}$ are the thermal and concentration Rayleigh numbers; $\mathrm{Pr}_i = \nu/D^*_{ii}$ is the diffusion Prandtl number; $\mathrm{Le}_i = a/D^*_{ii}$ is the Lewis number; $\tau_{ij} = D^*_{ij}/D^*_{ii}$ characterizes the ratio between the diffusion coefficients, $A = \tau_{ij}\delta c_j/\delta c_i$, $B = \tau_{ij}\delta c_i/\delta c_j$.

At the boundaries of the layer, the conditions

$$\mathrm{u} = 0 , \quad T = T_m , \quad \Lambda \frac{\partial T}{\partial n} = \Lambda_m \frac{\partial T_m}{\partial n} ; \quad \frac{\partial T}{\partial n} = \frac{\partial c_1}{\partial n} = \frac{\partial c_2}{\partial n} = 0 \qquad (3)$$

are satisfied for the velocity, temperature, and concentration of the components.

We will seek the solution of (2) with account for (3) in the form

$$\psi = \psi_0 \sin (\pi L x) \sin (\pi n z) \sin (\pi m y) \exp [- \lambda t] ,$$

$$\left\{ c_1, c_2, T \right\} = \left\{ c_1^0, c_2^0, T^0 \right\} \cos (\pi l x) \sin (\pi n z) \sin (\pi m y) \exp [- \lambda t] , \qquad (4)$$

where l, m, and n are the disturbance modes; λ is the disturbance decrement. Substituting (4) into (2) and eliminating successively the amplitude values from the current function, component concentration, and temperature, we obtain a fourth-degree equation for the disturbance decrement λ in the form (see [5, 13] for more details)

$$K\lambda^4 + L\lambda^3 + M\lambda^2 + N\lambda + S = 0 , \qquad (5)$$

where K, L, M, N, and S depend in a complicated manner on the similarity numbers, ratios between the diffusion coefficients, and disturbance modes.

Let us consider the general analysis for monotonic disturbances for which the decrements are material and the stability bound (for $\lambda = 0$) is determined by the relation (see [13, 15] for more details):

$$\frac{k^6}{(\pi l)^2} = (A - \tau_{22}) \mathrm{R}_1 - (B - 1) \tau_{22} \mathrm{R}_2 + \mathrm{R} , \quad k^2 = \pi^2 (l^2 + n^2 + m^2) . \qquad (6)$$

Limiting cases (6) presuppose two forms of instability for monotonic disturbances that are due to thermal and concentration mechanisms. In the case R = 0 (an isothermal mixture) the equilibrium crisis is due to concentration convection (see [1, 2, 4]), and instability is possible in the case

$$(A - \tau_{22}) \mathrm{R}_1 + (B - 1) \tau_{22} \mathrm{R}_2 > \frac{k^6}{(\pi l)^2} . \qquad (7)$$

We note that depending on the orientation of the mixture components relative to the diffusion channel the sign of the Rayleigh numbers should be allowed for in (6) and (7).

If $\mathrm{R}_1 = \mathrm{R}_2 = 0$, then in a homogeneous mixture the critical thermal Rayleigh number is determined by the relation

$$\mathrm{R} = \frac{k^6}{(\pi l)^2} . \qquad (8$$

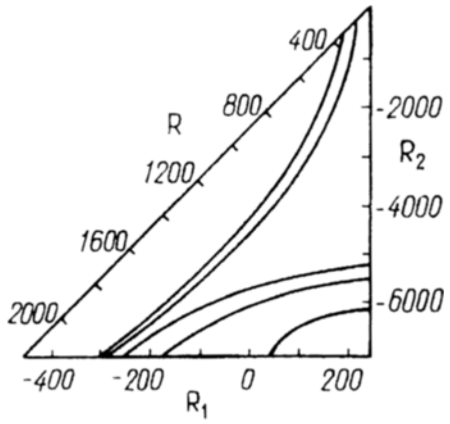

Fig. 2. Isolines of constant values of the critical R_1 number in the plane (R, R_2) for the system of 0.4505 H_2 (3) + 0.5495N_2O (1) and Ar (2) for $P = 0.1$ MPa. The figures in the parentheses denote the numbering of the components.

In the problem under consideration, what is investigated is a diffusion-unstable system whose determining factor is the competition of concentration gradients against a background of temperature nonuniformity. Therefore, prescribing R values in (6), we can obtain isolines that characterize the overall mass transfer (see Fig. 2) for the investigated system of 0.4505H_2 + 0.5495N_2O and Ar. From the results of the calculation it is evident that, in heating from below, there is a decrease in the critical concentration Rayleigh numbers. This indicates greater destabilization of the process as compared to the isothermal case, which is in qualitative agreement with experiment. In summary, we note that allowance for thermal diffusion and diffusive heat conduction, according to [13], does not alter substantially the obtained results for the critical Rayleigh numbers.

Thus, if unstable diffusion is observed in an isothermal three-component system, for nonisothermal conditions (when the gas is heated in the lower part of the diffusion apparatus) the transfer of components will be greater and the intensity of the process increases as the temperature gradient increases.

NOTATION

$\overline{T}$, average temperature, g, free-fall acceleration; j_i, density of the diffusion flow of the i-th component; q, heat flux density; δT, temperature difference; δc_i, concentration difference for the i-th component; ρ_0, average density; β, β_c, thermal expansion coefficient and its concentration analog; a, thermal diffusivity coefficient for the mixture; D^*_{ij}, diffusion matrix coefficients; n, normal, disturbance mode.

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