Journal of Engineering Physics and Thermophysics, Vol. 70, No. 1, 1997

CALCULATION OF THERMAL-DIFFUSION SEPARATION IN A MIXTURE OF GASES

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UDC 533.735

A method for calculating thermal-diffusion separation in a multicomponent mixture of gases is presented that does not require the application of either a thermal-diffusion coefficient or other quantities associated with it (a thermal-diffusion ratio, a factor of thermal diffusion). A comparison of the calculated results with experimental data for binary mixtures is given.

The proposed method is based on extension of a model, described in [1], for mass transfer in inhomogeneous gases to nonisothermal mixtures. Accounting for the nonisothermicity of a mixture does not affect the basic principles of the model, but only calls for modification of the form of an expression for the diffusion component of a flow.

We will consider a nonisothermal gaseous mixture which is inhomogeneous in composition and which consists of n components. We will write the density of the total mole flux of the i-th component of the mixture in the same way as in the isothermal case [1]:

$$\mathbf{N}_i = \mathbf{N}_{id} + \mathbf{N}_{ic}\,. \tag{1}$$

We will also leave unchanged the expression for the convective component of the mole flux density of the i-th component of the mixture:

$$\mathbf{N}_{ic} = c_i \mathbf{v}\,. \tag{2}$$

We will write the relationship for the diffusion component of the mole flux density of the i-th component of the mixture just as in [2], but without two free-path lengths:

$$\mathbf{N}_{id} = -\frac{1}{3} l_i u_i \nabla c_i - \frac{1}{3} l_i c_i \nabla u_i\,. \tag{3}$$

The second term in formula (3) reflects the contribution to the diffusion flux attributable to the inhomogeneity of the mixture temperature.

Comparing expression (3) with the relationship used in [1] for the diffusion component in the isothermal case, we can write:

$$\frac{1}{3} l_i u_i = D_i\,. \tag{4}$$

Substituting D_i into the first term in expression (3) and replacing u_i in the second term of expression (3) from formula (4), after transformations, we obtain

$$\mathbf{N}_{id} = -\nabla (D_i c_i) + D_i c_i \nabla (\ln l_i)\,. \tag{5}$$

According to [3], the expression for l_i in a model of solid spheres has the form

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Ural State University, Ekaterinburg, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 70, No. 1, pp. 60-63, January-February, 1997. Original article submitted February 17, 1994.

$$l_i = \left(c \sum_{j=1}^{n} x_j K_{ij} \right)^{-1} , \tag{6}$$

where

$$c = \sum_{j=1}^{n} c_j ; \quad x_j = c_j / c ;$$

K_{ij} are constants that depend on the masses and diameters of the molecules.

Changes in the mole fractions of the components observed in the process of thermodiffusion separation are small; therefore, ignoring them, formula (6) yields

$$\nabla (\ln l_i) = - \nabla (\ln c) . \tag{7}$$

Restricting the further consideration to mixtures that obey the equation of state of an ideal gas and assuming the pressure to be uniform, we obtain

$$\nabla (\ln c) = - \nabla (\ln T) . \tag{8}$$

With Eqs. (7) and (8) expression (5) takes the form

$$\mathbf{N}_{id} = - \nabla (D_i c_i) + \frac{D_i c_i}{T} \nabla T . \tag{9}$$

Taking account of Eqs. (2) and (9), we rewrite Eq. (1) as

$$\mathbf{N}_i = - \nabla (D_i c_i) + \frac{D_i c_i}{T} \nabla T + c_i \mathbf{v} . \tag{10}$$

Substitution of expression (10) into the continuity equation for the i-th component of the mixture [4] gives

$$\frac{\partial c_i}{\partial t} + \nabla \left[- \nabla (D_i c_i) + \frac{D_i c_i}{T} \nabla T + c_i \mathbf{v} \right] = 0 . \tag{11}$$

In order to obtain a closed system of equations from which it is possible to determine all the unknown functions (n functions $c_i(\mathbf{r}, t)$ and three velocity components $\mathbf{v}(\mathbf{r}, t)$), we must add the Navier-Stokes equations (the temperature distribution is assumed to be prescribed) to the n equations of the type of Eq. (11). The pressure, mass density, mixture viscosity, and coefficients D_i, entering into the equations of the system must be substituted in the form of explicit dependences on the mole densities and temperature:

$$p = cRT , \quad \rho = \sum_{j=1}^{n} c_j M_j , \quad \mu = \mu (c_1, c_2, \ldots, c_n, T) . \tag{12}$$

The coefficient of self-diffusion in a mixture D_i is calculated by the Blank formula [1]:

$$D_i = \left(\sum_{j=1}^{n} \frac{c_j}{c D_{ij}} \right)^{-1} . \tag{13}$$

When $j \neq i$, D_{ij} is the trace coefficient of mutual diffusion of type-i molecules in a gas of type-j molecules at a mole density equal to c; D_{ii} is the coefficient of self- diffusion of type-i molecules at a mole density equal to c.

To check the proposed method, the above-mentioned system of equations was solved numerically for binary mixtures of gases with initial and boundary conditions corresponding to a one-dimensional model of the method

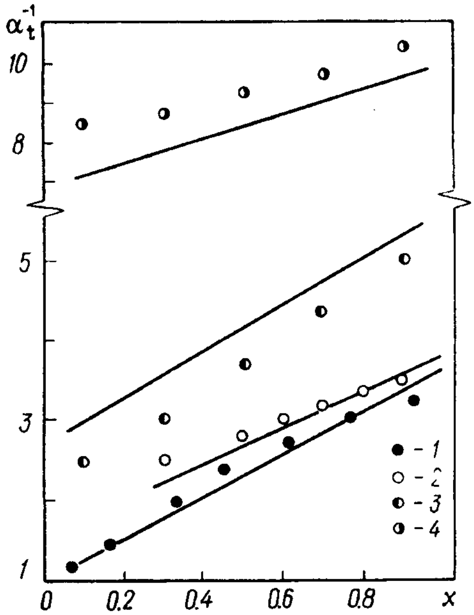


Fig. 1. The dependences of α_t^{-1} on the mole fraction of heavy component calculated from the results of the solution of system (14): 1) Xe–He mixture. $T_{\text{cold}} = 315$ K, $T_{\text{hot}} = 365$ K; 2) Ar–He, 288 and 373; 3) Kr–Ne, 225 and 275; 4) Kr–Ar, 425 and 475. Curves denote approximations of the experimental data of [6] and a linear approximation of the data from [7] for the Ar–He mixture.

of two-volumes and with a given linear temperature distribution along the channel that connects the volumes. In this case the system consists of three equations:

$$\frac{\partial c_1}{\partial t} + \frac{\partial}{\partial z}\left[-\frac{\partial}{\partial z}(D_1 c_1) + \frac{D_1 c_1}{T}\frac{\partial T}{\partial z} + c_1 v\right] = 0,$$

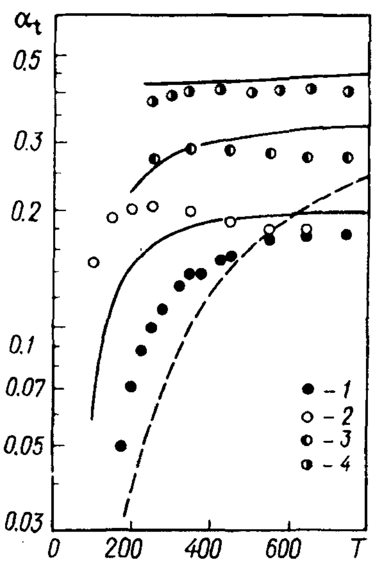
$$\frac{\partial c_2}{\partial t} + \frac{\partial}{\partial z}\left[-\frac{\partial}{\partial z}(D_2 c_2) + \frac{D_2 c_2}{T}\frac{\partial T}{\partial z} + c_2 v\right] = 0, \qquad (14)$$

$$\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial z}\left(\rho v^2 + p - \frac{4}{3}\mu\frac{\partial v}{\partial z}\right) = 0$$

(the z axis is directed along the channel, μ = const).

To obtain a numerical solution of system (14), each equation was approximated following McCormack's explicit scheme [5]. The temperatures of the hot and cold volumes T_{hot} and T_{cold} were assigned and, proceeding from these values, the temperatures were calculated at grid nodes located along the channel. The values of cD_{ij} in expression (13) depend only on the temperature and properties of the gases in the mixture. In all the calculations, whose results are presented below in graphs, to compute cD_{ij} we use the formulas for a first approximation of the Chapman–Enskog theory, the Lennard–Jones (12-6) potential, the parameters of the potential for pure gases from [4], and the parameters of the potential calculated by ordinary combination rules for interaction between heterogeneous molecules.

The initial conditions $c_1(z, 0)$ and $c_2(z, 0)$ were assigned from the condition of constancy of pressure and mole fractions of components along the channel and in the volumes; $v(z, 0) = 0$. The boundary conditions – the velocities v at fictitious nodes located inside the volumes at a distance of one grid spacing from the edges of the channel – were assumed to be equal to the velocities at the channel edges; c_1 and c_2 at the channel edges were taken to be equal to their values in the volumes and were calculated at each time step from the balance condition of the number of molecules. In calculations we used grids with 7 and 13 nodes along the channel length.



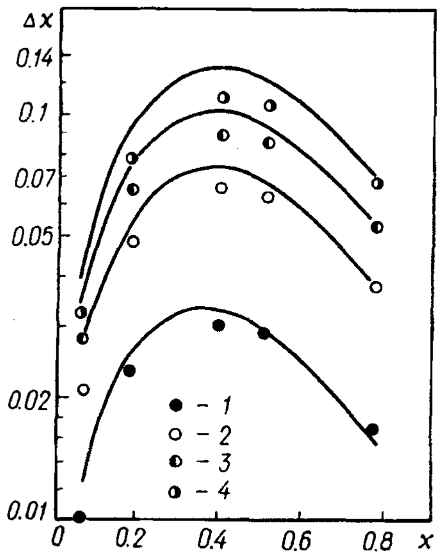


Fig. 2. The dependences of α_t on temperature calculated for equimolar mixtures from the results of the solution of system (14) (in all of the calculations $T_{hot} - T_{cold} = 50$ K): 1) Xe–Ar mixture; 2) Ar–Ne; 3) Kr–Ne; 4) Xe–He. Curves denote approximations of the experimental data of [6]; the dashed curve denotes approximations for Xe–Ar mixture. T, K.

Fig. 3. Thermal-diffusion separation in Ar–He mixture. (Δx, difference in the mole fractions of argon in the cold and hot volumes; x, mole fraction of argon at the initial moment): 1) $T_{cold} = 290$ K, $T_{hot} = 400$ K; 2) 293 and 596.2; 3) 294 and 795.4; 4) 291.5 and 1010.8. Curves denote approximations of the experimental data of [8].

The numerical solution was continued until c_1, c_2, and ν had nearly stationary distributions. The stationary values of c_1 and c_2 in the hot and cold volumes were used to calculate α_t by the formula from [6], if it was necessary for comparison with experimental data.

We can see from Fig. 1 that the form of the concentration dependences does not contradict the kinetic theory of gases (the dependences are close to linear ones), and the deviation from experimental data lies within the usual limits [6].

Figure 2 shows that for the two mixtures there is a rather good quantitative agreement with experimental data, but for argon–neon and xenon–argon mixtures a noticeable difference in the region of low temperatures is observed. It can be noted that for the xenon–argon mixture the character of disagreement with experimental data is similar to the deviation given in [6] of the values of α_t calculated according to the Chapman–Enskog theory for the Lennard–Jones (12-6) potential from those obtained experimentally.

Figure 3 presents the results of the solution of system (14) at considerable differences between the temperatures of the hot and cold volumes and, consequently, at rather large values of separation. In spite of the fact that in deriving expression (9) we used the smallness condition for the change in mole fractions, the difference from experimental data does not exceed 20%. It can be seen that the traditional mode of description of thermal-diffusion separation for large temperature differences could have caused difficulties associated with the selection of a mean temperature. For example, for the data denoted by number 4 in Fig. 3 the assignment temperature calculated according to [6] is equal to 509 K, while that calculated according to [9] is equal to 579 K. Calculations by the method proposed do not cause such difficulties, since the initial data used (the coefficients D_{ij}) refer to strictly defined temperatures and concentrations.

In addition to the above-given results obtained using the Lennard–Jones (12-6) potential, we carried out calculations for Maxwell molecules and for the potential of solid spheres. In solving system (14) for Maxwell molecules, the prescribed initial state remains unchanged, i.e., thermal-diffusion separation is absent. Using the model of solid spheres, we obtained almost linear dependences of α_t^{-1} on concentration and values of α_t that were independent of the temperatures of the hot and cold volumes. All these results agree with the inferences of the kinetic theory of gases.

NOTATION

n, number of components in the mixture; i, j, subscripts numbering the mixture components; $\mathbf{N}_i$, density of the total mole flux of the i-th component; $\mathbf{N}_{id}$, density of the diffusion mole flux of the i-th component; $\mathbf{N}_{ic}$, density of the convective mole flux of the i-th component; c_i, partial mole density of the i-th component; c, total mole density of the mixture; v, local velocity of the mixture motion as a whole (v is the same in a one-dimensional case); l_i, mean free path of type-i molecules; u_i, average thermal velocity of type-i molecules; D_i, self-diffusion coefficient of molecules of the i-th mixture component; D_{ij}, trace coefficient of mutual diffusion of type-i molecules in gas j; D_{ii}, self-diffusion coefficient in gas i; K_{ij}, constants entering into formula (6); T, temperature; p, pressure; ρ, mass density of mixture; μ, mixture viscosity; M_i, molecular mass of i-th component; x_i, mole fraction of i-th component; t, time; z, coordinate; R, universal gas constant; T_{hot}, temperature of hot volume; T_{cold}, temperature of cold volume; α_t, factor of thermal diffusion.

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