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MASS TRANSPORT IN A NONUNIFORM ISOTHERMAL MIXTURE OF REAL GASES

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A method of describing mass transport in a nonuniform isothermal mixture of real gases is given. The computed results are compared with experimental data.

It has been reliably established that for isothermal diffusion in gas mixtures in the absence of external forces, there is a loss of mechanical equilibrium [1, 2]. Therefore, even in a nonuniform mixture of ideal gases, the process of mass transport is composed of two physically distinct components. The first is due to the random migration of molecules in a mixture that is nonuniform in composition (self diffusion [2]), while the second component is due to pressure nonuniformities, which are practically unavoidable, and which lead to the transport of all of the components of the mixture in a given volume element as a whole (convective transport). The existence of two physically distinct transport mechanisms whose contributions to the total mass transport process can be of the same order of magnitude [2] means that both components must be taken into account in a theory of mass transport.

The usual method of taking into account the convective component of mass transport is to impose certain conditions on the fluxes, which are characteristic of the device in which the diffusion is observed. An example of a restriction of this kind is the assumption that the mean velocity is equal to zero in the diffusion of ideal gases in a two-bulb device [3]. When restrictions are introduced, mass transport can be described sufficiently accurately in the particular device under consideration. For example, in the two-bulb device the above restriction allows one to describe the quasistationary stage of the mass transport and to obtain a unique characteristic of the process — the coefficient of mutual diffusion [3].

However, there are at least two reasons why an approach of this kind cannot be considered completely satisfactory. The first is that if we want to describe diffusion in a device with a different geometric shape or with different conditions on the boundary of the device, the applicability of the restrictions must be re-examined because the characteristics of the process (such as the coefficient of mutual diffusion) are partly determined by these restrictions [2] and the same characteristics cannot be used to describe diffusion in a different device unless exactly the same restrictions are introduced. Here it should also be noted that the nature of the restrictions can change significantly when we go from ideal gases to real gases. For example, in the diffusion of real gases in a two-bulb device, the average velocity will not be zero even in the quasistationary case since the number densities of different real gases are not equal at equal pressure.

The second reason is that the introduction of restrictions reduces the description of a complicated mass transport process to a form natural for only one of the components. For example, the convective component is automatically included in the flux given by Fick's first law of diffusion. Such a reduction of two physically different processes into a single description leads to doubts about its validity (especially for real gases) and to difficulties in the interpretation of the experimental data [4].
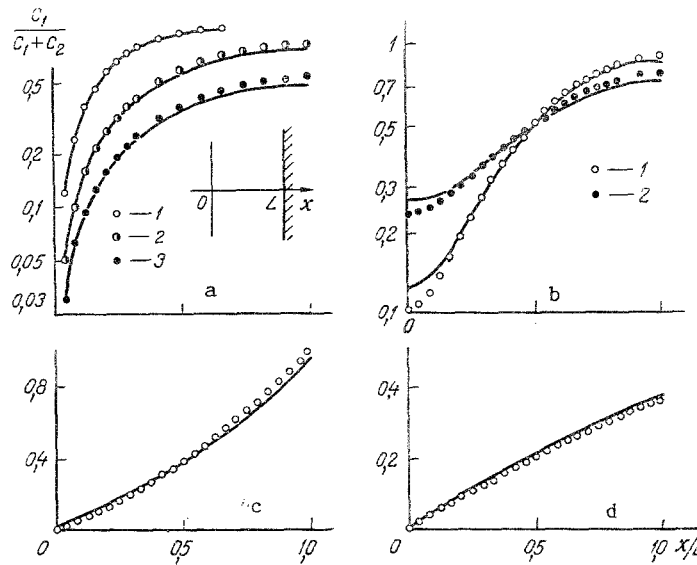
Fig. 1. Distribution of the molar fraction along
the length of the channel. a) Capillary method,
argon—helium mixture, $\tau = \pi^2 D_{12} t/4L^2$, 1) $\tau = 0.1$,
2) 0.5, 3) 1; b) Loshmidt method, argon—helium mix-
ture, $\tau = \pi^2 D_{12} t/L^2$, 1) $\tau = 0.52$, 2) 1; c) station-
ary flow-through method, argon—helium mixture,
steady-state distribution; d) Stefan method, ace-
tone—nitrogen mixture, steady-state distribution.
Points represent solution of (10)-(12). Solid
lines: solution of second Fick equation with
constant D_{12} (a, b); approximation of experi-
mental data of [1, 12] (c and d).

We discuss a method of describing mass transport in an isothermal mixture of real gases.
It is based on the concept that there are two components of the process and does not require
restrictions of any kind on the fluxes. It will be shown below that this method gives a
complete description of mass transport in moderately dense gas mixtures with a minimum of
information about the properties of the gases making up the mixture.

We consider a nonuniform isothermal mixture of real gases consisting of n components.
According to the two-component model of mass transport [2], the total molar flux density
of the i-th component of the mixture N_i can be written as

$$N_i = N_{id} + N_{ic},\tag{1}$$

where N_{id} is the flux density of the i-th component due only to random migration of molec-
ules of type i in the gas mixture (the diffusive flux density); N_{ic} is the flux density of
the i-th component due to motion of a volume element of the mixture as a whole (convective
flux density). Using Fick's first law of diffusion, we can write

$$N_{id} = -D_i \nabla c_i,\tag{2}$$

where D_i is the coefficient of self-diffusion in the mixture [5], and describes the trans-
port of molecules of the i-th component due only to their random migration in the gas mix-
ture. The quantity N_{ic} can be written as

$$N_{ic} = c_i v,\tag{3}$$

v is the velocity of the volume element as a whole due to a pressure nonuniformity. Sub-
stituting (2) and (3) into (1), we obtain

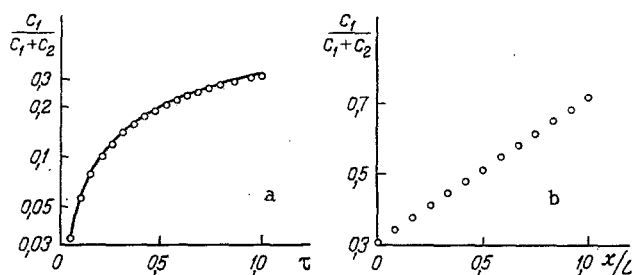$$N_i = -D_i \nabla c_i + c_i v.\tag{4}$$

Fig. 2. Results of the calculation for the two-bulb method. Argon—helium mixture: a) time dependence of the molar fraction of argon in the bulb initially filled with pure helium, $\tau = 0.04 \cdot D_{12}t/L^2$; b) distribution of the molar fraction of argon with channel length, $\tau = 1$. The points represent the solution of (10) through (12). The solid line is the solution of the second Fick equation with constant D_{12}.

Using the Blank formula [5], the coefficient D_i can be written as:

$$D_i = \left(\sum_{j=1}^{n} \frac{c_j}{cD_{ij}} \right)^{-1}, \tag{5}$$

where $c = \sum_{j=1}^{n} c_j$.

Here D_{ij} ($j \neq i$) is the trace coefficient of mutual diffusion of type i molecules in a gas of type j molecules for a molar density c; D_{ii} is the coefficient of self-diffusion of type i molecules for a molar density c. Equation (5) is supported experimentally for binary mixtures of dense gases and even certain liquid mixtures [5], and also for trinary mixtures of dense gases [6]. In addition, it has been shown experimentally [6, 7] that the products cD_{ij} do not depend on the molar density c (they are constants for a given temperature) up to densities of the order of the critical density. The constancy of these quantities indicates that the density dependence of the coefficients of mutual and self-diffusion corresponds to the theory of a rarefied gas over a wide interval of densities.

Gases for which the products cD_{ij} do not depend on density will be called moderately dense gases. (We note that the equation of state of such a gas can differ significantly from the ideal gas law). We introduce the constant quantities $A_{ij} = cD_{ij}$ and substitute in (5):

$$D_i = \left(\sum_{j=1}^{n} \frac{c_j}{A_{ij}} \right)^{-1}. \tag{6}$$

Substituting D_i from (6) into (4), we obtain an expression for N_i:

$$\mathbf{N}_i = -\left(\sum_{j=1}^{n} \frac{c_j}{A_{ij}} \right)^{-1} \nabla c_i + c_i \mathbf{v}. \tag{7}$$

Substitution of this expression in the equation of continuity for the i-th component of the mixture (in the absence of chemical transformations [8]) gives

$$\frac{\partial c_i}{\partial t} + \nabla \left[-\left(\sum_{j=1}^{n} \frac{c_j}{A_{ij}} \right)^{-1} \nabla c_i + c_i \mathbf{v} \right] = 0. \tag{8}$$

Three additional equations must be added to the n equations of the form (8) in order to have a closed system of equations from which all of the unknown functions can be determined (the n functions $c_i(r, t)$ and the three components of the velocity $v(r, t)$). Since v is defined as the velocity of a volume element in the mixture as a whole due to a pressure nonuniformity, one can take the Navier—Stokes equations as the needed equations. For a compressible fluid in the absence of body forces we have

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\nabla)\mathbf{v} \right] = -\nabla p + \mu \left[\Delta \mathbf{v} + \frac{1}{3} \nabla (\nabla \mathbf{v}) \right], \tag{9}$$
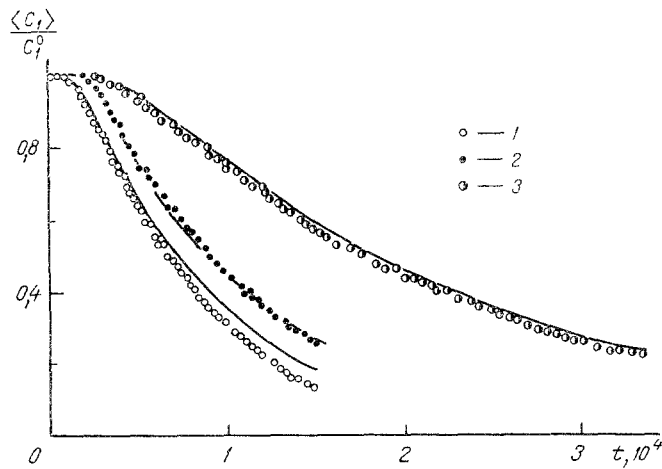
Fig. 3. Time dependence of $\langle c_1 \rangle / c_1{}^0$. Experimental data: 1) sulfur hexafluoride — methane, $p = 3.79$ MPa, $c_1{}^0 = 2.832$ kmole/m³, $c_2{}^0 = 1.481$ kmole/m³; 2) sulfur hexafluoride — argon, $p = 4.10$ MPa, $c_1{}^0 = 4.163$ kmole/m³; $c_2{}^0 = 1.546$ kmole/m³; 3) sulfur hexafluoride — xenon, $p = 3.90$ MPa, $c_1{}^0 = 3.148$ kmole/m³, $c_2{}^0 = 1.776$ kmole/m³. The temperature was 323°K for all runs. Solid curves: solution of (10) through (12) for the corresponding conditions. t, 10^4 sec.

where

$$\rho = \sum_{j=1}^{n} c_j M_j.$$

The pressure p in (9) must have the explicit functional dependence $p = p(c_1, c_2, \ldots, c_n)$ which can be obtained by using the equation of state of the mixture, for example. The viscosity μ of the mixture will also be of the form $\mu = \mu(c_1, c_2, \ldots, c_n)$. Its explicit form can be obtained following the suggestions in [8]. Hence the n equations of the form (8) and equation (9) form a system of n + 3 equations for the n + 3 unknown functions mentioned above. The solution of this system of equations (for specified initial and boundary conditions) gives a complete description of the mass transport process in an isothermal mixture of moderately dense gases.

We consider the solution of the system (8) and (9) for the case of a binary mixture only. In addition, we consider only the one-dimensional case, when all unknown functions depend on a single coordinate x ($c_j = c_j(x, t)$, for example), and the velocity v lies along the x axis and $v = v(x, t)$. The use of one-dimensional models of the experimental methods (in which the data is obtained which will be compared with the solution of the system (8) and (9)) should not lead to significant errors in the description of mass transport. (It is well-known that one-dimensional models are used in the theoretical description of practically all experimental methods of studying diffusion).

For binary mixtures of moderately dense gases in the one-dimensional case, (8) and (9) can be written in the form

$$\frac{\partial c_1}{\partial t} - \frac{A_{11}A_{12}}{c_1A_{12}+c_2A_{11}}\left[\frac{\partial^2 c_1}{\partial x^2} - \frac{\frac{\partial c_1}{\partial x}}{c_1A_{12}+c_2A_{11}}\left(A_{12}\frac{\partial c_1}{\partial x}+A_{11}\frac{\partial c_2}{\partial x}\right)\right] + c_1\frac{\partial v}{\partial x} + v\frac{\partial c_1}{\partial x} = 0, \quad (10)$$

$$\frac{\partial c_2}{\partial t} - \frac{A_{22}A_{21}}{c_1A_{22}+c_2A_{21}}\left[\frac{\partial^2 c_2}{\partial x^2} - \frac{\frac{\partial c_2}{\partial x}}{c_1A_{22}+c_2A_{21}}\left(A_{21}\frac{\partial c_2}{\partial x}+A_{22}\frac{\partial c_1}{\partial x}\right)\right] + c_2\frac{\partial v}{\partial x} + v\frac{\partial c_2}{\partial x} = 0, \quad (11)$$

$$\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x} = \frac{1}{c_1M_1+c_2M_2}\left(-\frac{\partial p}{\partial x}+\frac{4\mu}{3}\frac{\partial^2 v}{\partial x^2}\right). \quad (12)$$

In (10) through (12) the viscosity μ is assumed to be constant and equal to the average value of the viscosities of the pure components. In addition we assume $A_{21} = A_{12}$ so that the trace-coefficients of mutual diffusion are given either by experimentally measured values, or calculated from the formulas of the first approximation of the Chapman−Enskog theory. In an ideal gas mixture the equation of state of an ideal gas is used in the form $p = (c_1 + c_2)$. RT, while for dense gas mixtures we use the virial equation of state of the mixture, including the third virial coefficient:

$$p = (c_1 + c_2) RT \left[1 + B_{mix}(c_1 + c_2) + C_{mix}(c_1 + c_2)^2 \right], \tag{13}$$

where B_{mix} and C_{mix} are the second and third virial coefficients of the mixture. The coefficients B_{mix} and C_{mix} were obtained using the methods of [9], which give the explicit dependence of B_{mix} and C_{mix} on c_1, c_2, and the virial coefficients of the pure components. We note that all constants needed in order to solve (10)-(12) (A_{11}, A_{12}, A_{22}, the virial coefficients of the pure components, the viscosity) can be obtained either from experimental data or calculated from expressions relating these parameters to the molecular interaction potential [10].

The method was tested by applying the system of equations (10) through (12) to mass transport in ideal and real binary gas mixtures. We used initial and boundary conditions appropriate for the one-dimensional models of five well-known and accepted experimental methods of studying diffusion in gases (the capillary method, Loshmidt method, two-bulb method, method of Stefan, stationary flow-through method). The system (10)-(12) was solved numerically using finite differences on a grid of 25 points (13 points for the two-bulb method). All derivatives were approximated to first order accuracy. Equations (10) and (11) were solved using an explicit scheme with velocities obtained from the preceding time step, while (12) was solved with an implicit scheme using only the values of c_1 and c_2. Since the time step was always less than 10^{-4} times the characteristic diffusion time, this method leads only to an insignificant error in the time for which the solution is determined.

As an example, Fig. 1a shows a one-dimensional model of the capillary method. The region of space $0 < x \leq L$ represents the "capillary" and it is filled initially with a pure gas of type 1 whose molar density is c_1^0. The region $x \leq 0$ is filled with a gas of type 2 with molar density c_2^0. For mass transport in ideal gases we have $c_2^0 = c_1^0$. For real gases c_2^0 was calculated from the equation of state of the pure type 2 gas with the condition that the pressures in the "volume" $x \leq 0$ and "capillary" be equal at the initial time. The initial condition on the velocity was $v = 0$ at all points of the grid. The boundary conditions on the open end of the capillary ($x = 0$) were $c_1 = 0$, $c_2 = c_2^0$ (the volume of the capillary is much smaller than the volume with the type 2 gas). The boundary condition $v(-h, t) = v(0, t)$ was used for the velocity at the open end of the capillary. That is, the velocity at the fictitious grid point to the left of $x = 0$ was assumed equal to the value at $x = 0$. The numerical results show that the distributions of c_1 and c_2 along the length of the capillary de-depend very weakly on this boundary condition (one could also use $v(-h, t) = 0$). At the closed end of the capillary ($x = L$): $\partial c_1 / \partial x = 0$, $\partial c_2 / \partial x = 0$, and $v = 0$ (from the condition that the gas cannot penetrate through the closed end). One-dimensional models of the other experimental methods and the appropriate boundary conditions are constructed in a similar way.

The solution of the system (10)-(12) is shown in Figs. 1 and 2 for ideal gas mixtures. In all of the calculations (except for the Loshmidt method) the channel was initially filled with the heavier gas (type 1). In the Loshmidt method each of the gases initially occupy half of the channel.

The results of Figs. 1 and 2 show good agreement between our method and the usual method, and also the experimental data for ideal gases. We note the small (of order 10%) difference observed in Fig. 1 near the closed end of the channel. The difference apparently occurs because for the coarse grid used here the zero boundary condition for the velocity v at the closed end of the channel significantly affects the velocity at neighboring grid points and distorts the solution somewhat. Calculations for the capillary method using a coarser grid (8 lattice points) show that the difference near the closed end of the capillary increases by about a factor of two.

Figure 3 shows the experimental results and the solution of the system (10) through (12) for mass transport in the capillary method for three significantly nonideal gas mixtures. In all cases the capillary was initially filled with pure sulfur hexafluoride of known initial molar density c_1^0. The volume joined with the capillary (about 100 times larger than
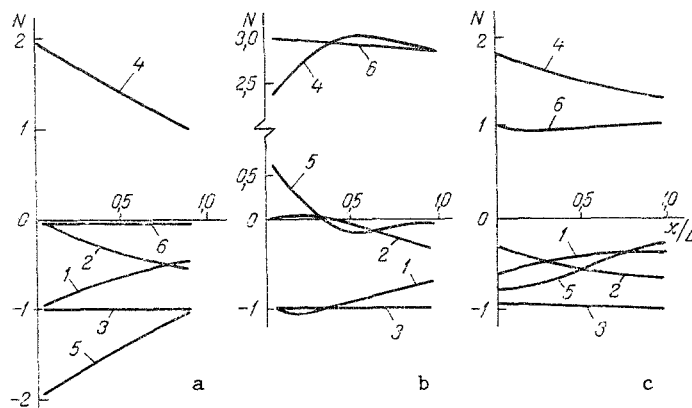
Fig. 4. Distribution of the molar flux densities along the length of the channel (in relative units): a) Stefan method (conditions as in Fig. 1d); b) stationary flow-through method (conditions as in Fig. 1c); c) two-bulb method (conditions as in Fig. 2b); 1) N_{1d}; 2) N_{1c}; 3) N_1; 4) N_{2d}; 5) N_{2c}; 6) N_2.

the capillary volume) was filled with a different pure gas with a density c_2^0 such that its pressure was equal to that of the sulfur hexafluoride in the capillary. The mass transport process was followed by measuring the mean molar density of the sulfur hexafluoride $<c_1>$ over a short portion of the capillary ($\sim 0.14L$) using the NMR method described in [13].

The comparison in Fig. 3 demonstrates good agreement between our method and experiment. For mixtures containing methane a significant (of order 20%) systematic overestimate of the calculations is observed at large values of the time. The most probable cause is an unfortunate choice of the virial coefficients for methane used in the calculation of the pressure from equation (13).

Figure 4 shows the molar flux density distributions along the length of the channel, calculated from the solution of the system (10)-(12) (Eqs. (2)-(5) were used).

It is clear from Fig. 4 that in spite of the fact that the quantities N_1 and N_2 are the sums of the quantities N_{1d} and N_{1c}, N_{2d} and N_{2c}, which vary significantly along the length of the channel, the fluxes N_1 and N_2 are constant along the length of the channel, as they must be for steady-state methods (for the two-bulb method this also must be true in the quasistationary stage of the process). Also for the Stefan method N_2 must be zero and therefore the fluxes N_{2d} and N_{2c} must exactly cancel one another. This is also evident from Fig. 4a (the deviation of N_2 from zero does not exceed 4% of the fluxes N_{2d} and N_{2c}, which is consistent with the accuracy of the solution for the grid used here). Finally, we must have $N_1 + N_2 = 0$ for the two-bulb method in the case of ideal gases, and this is evident from Fig. 4c. In addition to the above three facts, which follow from conservation of number of particles in a volume element, we point out two more. First, from the theoretical analysis of the stationary flow-through method [2] it follows that the ratio N_2/N_1 must be equal to $(M_1/M_2)^{1/2}$ (for the system argon—helium this quantity is 3.16). It is seen from Fig. 4b that this relation is satisfied to within the accuracy of the grid used for the calculations. Also from the theory of the two-bulb method for ideal gases [3] it follows that the molar fractions must vary linearly along the length of the channel. This is seen to be the case in Fig. 2b.

Hence the idea that the process of mass transport consists of two components leads to a good description of the process in moderately dense gases using a minimum amount of information on the properties of the gases making up the mixture. (In practice it is sufficient to know the parameters of the molecular interaction potentials for the pure gases).

Our method does not require information on the behavior of the kinetic characteristics of mass transport for arbitrary ratios of the concentrations of the components.

The possibility of extending the applicability of our method to mass transport in still denser gases is obvious. It would only be necessary to know the dependence of the quantities A_{ij} and A_{ii} on the density c.

Our approach can be extended to the case of mass transport in a system with chemical transformations. In order to do this an expression of the type (7) must be substituted into more general conservation equations including the molar rate of formation of one of the components per unit volume (see [8, Chap. 17]). Naturally, the explicit dependence of these rates on the molar densities of the components of the mixture must be known.

NOTATION

i, j, indices numbering the components of the mixture; n, number of components in the mixture; N_i, total molar flux density of the i-th component; N_{id}, diffusive molar flux density of the i-th component; N_{ic}, convective molar flux density of the i-th component; N_i, N_{id}, and N_{ic}, corresponding flux densities in the one-dimensional case; c_i, partial molar density of the i-th component: v, velocity of a volume element of the mixture as a whole, due to a pressure nonuniformity (v in the one-dimensional case); D_i, coefficient of self-diffusion of the i-th component in the mixture; c, total molar density of the mixture; D_{ij}, trace coefficient of mutual diffusion of molecules of type i in gas j; D_{ii}, coefficient of self-diffusion of gas i; $A_{ij} = cD_{ij}$; ρ, mass density; p, pressure; μ, viscosity; M_i, molecular mass of the i-th component; R, universal gas constant; T, temperature; B_{mix} and C_{mix}, second and third virial coefficients of the mixture; x, coordinate; D_{12}, coefficient of mutual diffusion; L, length of the channel in which mass transport is considered; h, grid step size; t, time; τ, dimensionless time; c_i^0, initial molar density of the i-th component; $<c_1>$, molar density of sulfur hexafluoride averaged over a short part of the channel.

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