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Direct statistical simulation of gas mixture mass transfer in a porous layer with condensation of one of the components and absorption of another

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Abstract

Based on the method of direct statistical simulation, a physical–mathematical model has been developed for gas mixture mass transfer in a highly porous body under the conditions of condensation of one of the components and trapping of a non-condensable admixture. Distributions of gas velocities and densities in a porous layer and in the space above it are found, as well as distributions of flows of a condensable component and absorbable admixture along the depth of the porous layer. The efficiencies of the absorption of the admixture in a porous layer and on a plane surface are compared. © 1998 Elsevier Science Ltd. All rights reserved.

Key words: Mass transfer; Porous body; Direct statistical simulation; Condensation; Trapping of molecules

Nomenclature

f velocity distribution function of molecules
I density of resultant flow of molecules
I_a density of flow of molecules incident on unit surface of model spheres
k Boltzmann constant
Kn Knudsen number
L dimension of computational domain along the x coordinate
L_ε thickness of a porous layer
m mass of a molecule
n numerical density of gas
n_ε number of immovable particles per unit volume of a porous body
Q evaporation heat (per 1 atom)
r radius of immovable particle
S surface area of immovable particles per unit volume of a porous body
T_0 temperature of evaporation surface
T_ε temperature of a porous layer
v mean numerical velocity of gas
x, y, z Cartesian coordinates.

Greek symbols
ε porosity
λ_g mean gas-dynamic free path of molecules of Component 1
λ_ε mean free path of gas molecules with respect to immovable particles
ξ velocity of gas molecules.

Subscripts
$i = 1, 2$ evaporating component and non-condensing gas, respectively
e saturated vapour
$0, \infty$ boundaries of computational domain.

1. Introduction

In investigation of the problems connected with substance condensation from a gas mixture, when one of its components is non-condensable under given thermodynamic conditions, it is usually assumed that the

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molecules of this component do not enter the condensate [1–5]. However, in cryogenic engineering, a phenomenon of cryotrapping is often utilized, when the molecules of a non-condensable component enter the condensate (they are 'trapped' by a growing condensate layer) in condensation of an easily condensable component [6, 7]. The presence of cryogenic temperatures is not important in this case. Low temperatures are required only to realize a sufficiently large flow of a condensing substance. It is precisely this flow that determines the probability of the trapping of the molecules of a non-condensable component. The phenomenon of the trapping of admixture molecules in condensation of a basic component can prove to be highly essential in many fields of modern technology (production of especially pure substances, doping of a forming condensate by specific molecules in creation of microelectronics elements, separation of gas mixtures during their pumping through porous bodies, purification of a gas phase from ecologically injurious admixtures, etc.).

In [8, 9] a simple model is suggested allowing one to take into account the effect of the trapping of admixture molecules (including those which do not condense under given thermodynamic conditions) during condensation of an easily condensing substance. In this model both the concentration of admixture molecules in a condensate and the trapping coefficient of these molecules depend substantially on the condensation rate. It also follows from the expressions obtained that under definite conditions the condensation of one component can increase the concentration of another component [10]. In [8–10] the case of a free molecular regime of gas flow was considered for simplicity. It should be noted that an approach similar to that of [8–10] was also applied in work [11], in which the growth of an aerosol particle was investigated in condensation from a gas mixture in the regime of a continuous medium.

In the present work we investigate the flow of a two-component gas mixture in a model highly porous body on the basis of direct statistical simulation, which allows one to take into account both the interaction of components in a gas phase and their interaction with the walls of pores, as well as to analyze an influence of mass transfer in the porous body on the processes of condensation and trapping. Note that in [12] a kinetic problem was considered for flow of a one-component gas with condensation in a highly porous body and escape into a vacuum.

2. Formulation of the problem

Let us consider the problem of mass transfer for a mixture of two gases in a model porous body with condensation of one component and trapping of the other component, which is a non-condensing gas. The geometric scheme of the problem is presented in Fig. 1.

Component 1 evaporates (sublimes) from the surface $x = 0$. Above this surface there is a highly porous layer of thickness L_ε, which is modelled by a homogeneous system of randomly distributed immovable spherical particles of radius r (a 'dusty gas' model) [13, 14, 9].

The mean free path of gas molecules with respect to fixed particles of the porous body skeleton is equal to

$$\lambda_\varepsilon = \frac{4}{3}\frac{\varepsilon}{1-\varepsilon}r \tag{1}$$

and the number of immovable particles per unit volume and the area of their surface are, respectively, equal to

$$n_\varepsilon = 3(1-\varepsilon)/4\pi r^3 \tag{2}$$

$$S = 3(1-\varepsilon)/r. \tag{3}$$

Let us formulate this problem as a boundary problem of the kinetic theory of mass transfer of a mixture of gases in a domain consisting of a porous layer and a part of the space above it. The dimensions of the computational domain are the following: $L = 500\lambda_g$ along the x-coordinate, $500\lambda_g$ along the y-coordinate, $100\lambda_g$ along the z-coordinate. In this case the thickness of the porous layer is equal to $L_\varepsilon = 350\lambda_g$. On the evaporation surface ($x = 0$) we prescribe the Maxwell distribution function for the molecules of Component 1 entering the computational domain

$$x = 0;\quad f_1^+(\xi_x > 0) = n_{1e}(T_0)\left(\frac{h_0}{\pi}\right)^{3/2}\exp\{-h_0\xi^2\} \tag{4}$$

and the condition of diffuse reflection of molecules of Component 2:

$$x = 0;\quad f_2^+(\xi_x > 0) = n_{2r}\left(\frac{h_0}{\pi}\right)^{3/2}\exp\{-h_0\xi^2\} \tag{5}$$

where $h_0 = m_1/2kT_0$, $n_{1e}(T_0)$ is the density of the saturated vapour of Component 1 at the temperature T_0 and n_{2r} is determined from the non-leakage condition for Component 2.

On the upper boundary of the computational domain ($x = L$) we prescribe the following conditions for the distribution functions of the components (conditions at infinity):

$$x = L;\quad f_1(\xi_x < 0) = 0;$$

$$f_2(\xi_x < 0) = n_{2\infty}\left(\frac{h_0}{\pi}\right)^{3/2}\exp\{-h_0\xi^2\} \tag{6}$$

with the assigned parameters $n_{2\infty}$ and $T_\infty = T_0$. The quantities $n_{1\infty}$ and $v_{i\infty}$, as well as v_∞ should be determined from the solution of the problem.

As scales for dimensionless density, temperature, velocity, flow density and length, we select, respectively, the following quantities: n_{1e}, T_0, $h_0^{-1/2}$, $n_{1e}h_0^{-1/2}$, λ_g, where

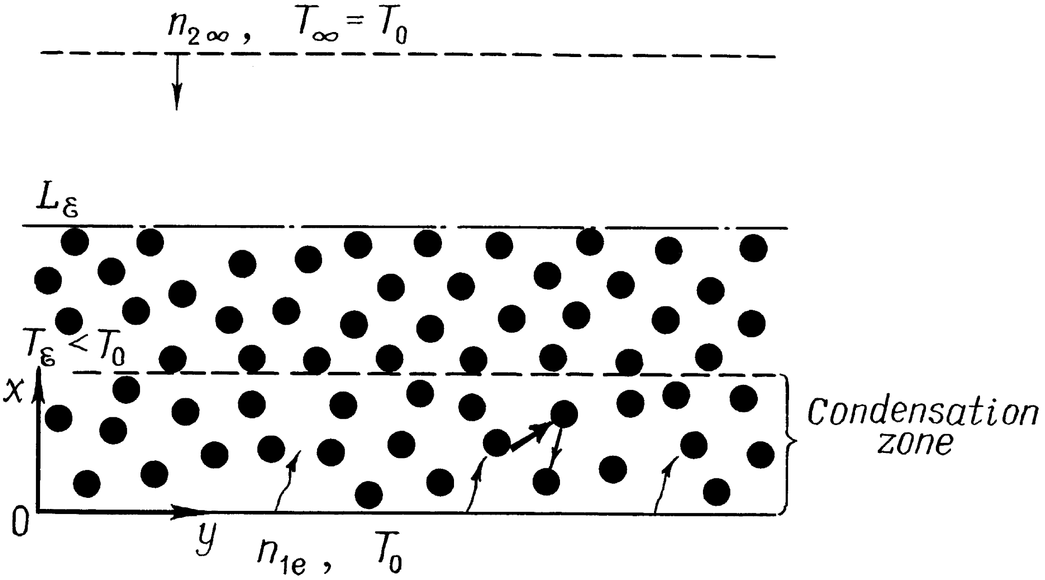

Fig. 1. Geometric scheme of the problem.

$\lambda_g = (\sqrt{2}n_{1e}\pi d_1^2)^{-1}$, d_1 is the diameter of molecule 1. By definition,

$$n_1 = \int f_i(\xi)\,\mathrm{d}\xi, \quad n = n_1 + n_2 \tag{7}$$

$$v_i = \frac{1}{n_i}\int \xi f_i(\xi)\,\mathrm{d}\xi, \quad v = (v_1 n_1 + v_2 n_2)/(n_1 + n_2). \tag{8}$$

The temperature of the porous body skeleton is supposed to be $T_\varepsilon < T_0$, i.e., condensation of Component 1 on the particles of the porous body is possible during the process of mass transfer. We will also take into account the process which is analogous to cryotrapping [6, 7] and which consists in the fact that when a condensing gas and a gas not condensing at a given temperature are supplied simultaneously to the surface, the latter gas is absorbed. Mathematically the process of trapping can be described by means of the expressions for the densities of the net flows of each component into the condensate which is supposed to be solid [8, 9]:

$$I_i = I_{ia} - \frac{I_i}{I_1 + I_2} j_i = I_{ia} - \frac{I_i}{I_1 + I_2} n_s \sqrt{\frac{kT_\varepsilon}{2\pi m_i}} \exp\left\{-\frac{Q_i}{kT_\varepsilon}\right\} \tag{9}$$

where n_s is the resultant density of molecules in the condensate which is supposed to be a constant quantity, I_{ia} is the density of the flow of molecules incident on the condensate surface.

Note that for the trapping of admixture to be a quantitatively noticeable process, i.e., for the resultant admixture flux

$$I_2 = \frac{I_{2a}}{1 + j_2/I_1} \quad (I_2 \ll I_1) \tag{10}$$

not to be negligible, the process of phase transition should be substantially non-equilibrium. For this purpose, as follows from equation (10), it is necessary to increase the net flux of the condensing component and to decrease the value of j_2, which characterizes the re-evaporation probability for the admixture molecules. Besides, in the case of a porous layer, the characteristics of this layer (its thickness L_ε and specific surface S), as well as the conditions of mass transfer are of importance.

It is assumed that the thickness of the condensate layer on the particles of the porous body is negligibly small throughout the process. The boundary of the condensation zone (Fig. 1) is determined from the condition $I_1 = 0$; in a dry zone (where $I_1 < 0$) we assume in calculations that $I_1 = 0$ and consider diffuse reflection from the surface of model spheres.

The formulated problem (4)–(6) and (9) has a stationary solution.

3. Method of solution and input data

The present problem of the kinetic theory of gases (4)–(6) and (9) was solved by means of direct statistical Monte Carlo simulation [15, 4]. The numerical procedure includes two stages. At the first stage, mutual collisions of gas molecules are calculated both inside and outside of the porous body without account for the movement of molecules. At the second stage of free flow, in contrast to the usually applied method, we include the collisions of molecules with the porous body skeleton [12, 16]. The dimensions of a calculating cell along the directions x, y, z were selected to be $2.5 \times 500 \times 1\lambda_g$, i.e., the number of calculating cells in the present computational domain was equal to $200 \times 1 \times 100$. Note that in calculations the movement of molecules is considered in three directions (i.e., along x, y and z), but macroscopic parameters change in the main along the direction x, with the periodicity condition being used along the z-axis. The problem was solved by a stationarity-approach technique.

We assume that there are 1247 model spheres in the computational domain of the porous layer with the dimensions $350 \times 500 \times 100\lambda_g$. Then on the basis of these data, prescribed porosity $\varepsilon = 0.9$ and expression (2) we determine the radius of a sphere: $r = 1.01872 \cdot 10^{-4}$ m and from the correlation (3) we find the surface area of spheres per unit volume: $S = 3 \cdot 10^3\ \mathrm{m}^{-1}$.

We select naphthaline ($C_{10}H_8$) as evaporating (subliming) substance and consider the temperature of the evaporation surface to be equal to $T_0 = 325$ K. Then at a given temperature the pressure of saturated vapour is equal to $p_{1e} = 1$ mmHg [17], i.e., $n_{1e} = 2.96 \cdot 10^{22}\ \mathrm{m}^{-3}$. The other data necessary for Component 1 are: $m_1 = 2.1278 \cdot 10^{-25}$ kg, $d_1 = 7.2 \cdot 10^{-10}$ m, $Q_1 = 6.68 \cdot 10^{-20}$ J atom^{-1}, $\lambda_g = 1.4668 \cdot 10^{-5}$ m, $n_s = 1 \cdot 10^{29}\ \mathrm{m}^{-3}$.

As the substance is non-condensing under the given thermodynamic conditions (Component 2) we select carbon dioxide (CO_2) with the following characteristics: $m_2 = 7.31 \cdot 10^{-26}$ kg, $d_2 = 3.2 \cdot 10^{-10}$ m, $Q_2 = 4.0 \cdot 10^{-20}$ J atom^{-1} [17, 18]. Here we will consider two cases: Case A, when $n_{2\infty} = 0.5n_{1e}$ and Case B, when $n_{2\infty} = 0.05n_{1e}$. The Knudsen number defined as $Kn = \lambda_g/\lambda_\varepsilon$ [where λ_ε is calculated according to equation (1)] is equal to $Kn = 1.2 \cdot 10^{-2}$. However, it must be kept in mind that intermolecular collisions outside of the porous body are determined mainly by the density of the second component n_2. The temperature of the porous layer is assumed to be equal to $T_\varepsilon = 290$ K.

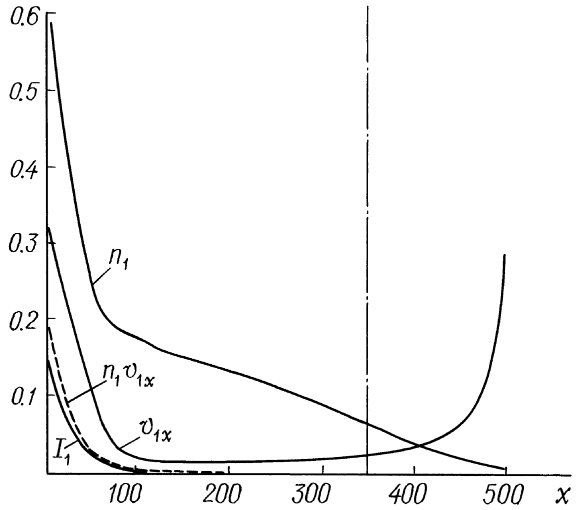

Fig. 2. Distributions of the macroscopic quantities of Component 1 in Case A (the vertical dash–dotted line in this and other figures denotes the boundary of the porous layer).

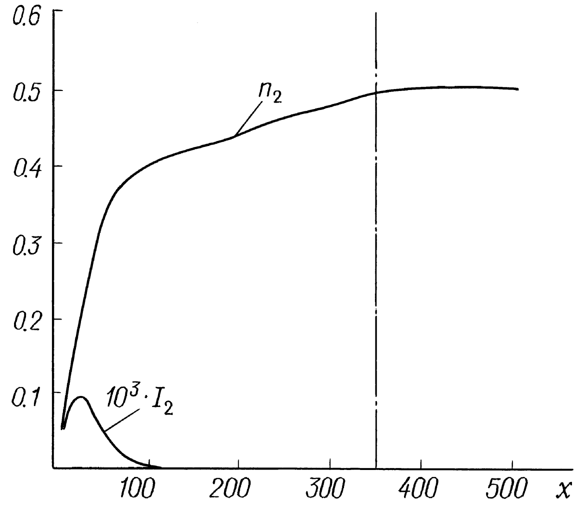

Fig. 3. Distributions of the density and flux density of absorbed molecules for Component 2 in Case A.

4. Discussion of results

Case A. The distributions of the macroscopic flow parameters determined according to equations (7) and (8) are presented in Figs 2–4. The thickness of the condensation (and trapping) zone corresponds approximately to $100\lambda_g$. The density n_1 in the porous layer decreases with an increase in x, with the sharpest decrease being observed in the condensation zone where not only the resistance of the porous body, but also the condensation induced depletion of Component 1 influence the profile of $n_1(x)$. Moreover, absorption of Component 2 in this zone causes the appearance of the gradient $n_2(x)$ and consequently, the transfer of this component to the zone of trapping (Fig. 3). Since the mixture density n changes weakly in the porous layer (Fig. 4), diffusion resistance increases for Component 1. For this very reason the velocity v_{1x} decreases in the condensation zone (Fig. 3), as well as the mean mixture velocity v_x (Fig. 4), because $n_2 v_{2x}$ is a small quantity. On the boundary of the porous layer $n_2 v_{2x} < 0$, i.e., the resultant flow of Component 2 is directed into the porous body. Note that in this case $v_{1y} \ll v_{1x}$.

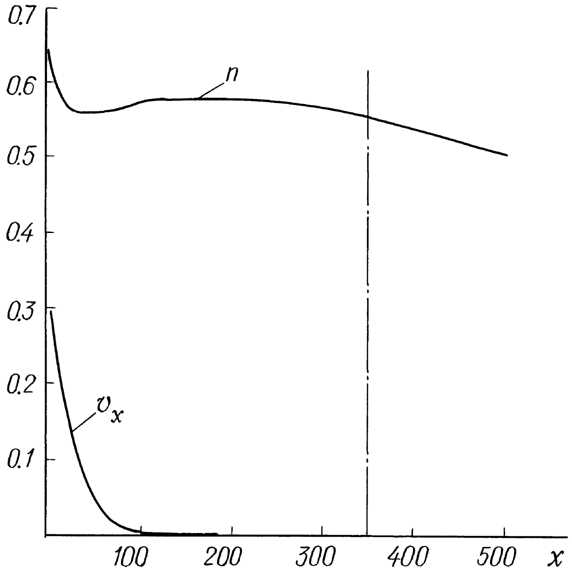

Fig. 4. Distributions of the density and numerical velocity of the gas mixture in Case A.

The use of the method of direct statistical simulation made it possible to obtain the profiles of the resultant flows I_1 (Fig. 2) and I_2 (Fig. 3) in the condensation (trapping) zone. Attention should be paid to the fact that in a stationary regime the dependence $I_2(x)$ is not a monotonic function. The thing is that the process of trapping of a non-condensing gas in a sufficiently dense gas medium ($Kn \approx 10^{-2}$) is determined not only by the intensity of condensation of Component 1 (i.e., by the value of I_1), but also by the 'transportation' of Component 2 to the condensation surface, i.e., by mass transfer in the porous layer. In our problem, at small values of x the value of I_1 is large, but the values of n_2 are very small. Therefore, the intensity of trapping near the evaporation surface is small. Further, with an increase in x the value of flow $I_2(x)$ increases, passes through the maximum and then begins to decrease because the quantity I_1 near the boundary of the condensation zone is very small, although the values of n_2 are large.

Case B. The distributions of the basic macroscopic parameters in the porous layer are presented in Fig. 5. In this case the gas medium is more rarefied, the diffusion resistance is smaller and the escape of the mixture of gases from the porous layer is more intense than in Case A. The condensation zone is about $155\lambda_g$. Note that the density of molecular flow of Component 1 in the condensation zone exceeds the flow density of condensing molecules ($n_1 v_{1x} > I_1$) by a much greater value than in Case A, i.e., a substantial portion of the molecules of the condensing gas passes through the porous layer without condensation.

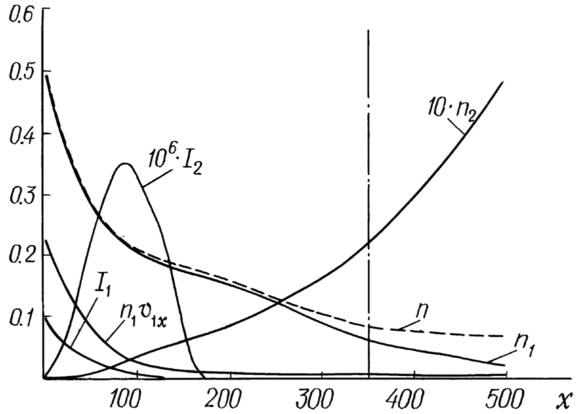

Fig. 5. Distributions of macroscopic quantities in Case B.

Now, let us compare the efficiencies of the absorption of non-condensing gas molecules by the porous layer and the plane surface. We will present the values of some quantities which are necessary for numerical estimations:

$$n_{1e}\sqrt{\frac{2kT_0}{m_1}} = 5.9 \cdot 10^{24}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1},$$

$$S = 4.3 \cdot 10^{-2}/\lambda_g = 3 \cdot 10^3\ \mathrm{m}^{-1}$$

$$j_2 = n_s\sqrt{\frac{kT_\varepsilon}{2\pi m_2}}\exp(-Q_2/kT) = 4.3 \cdot 10^{26}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}.$$

Case A. Since the dimension of the condensation (trapping) zone along the z-axis is approximately $100\lambda_g$, the volume of the portion of the porous body, in which the trapping of the molecules of Component 2 occurs, is equal to $100 \times 500 \times 100\lambda_g$. Then the number of the molecules absorbed per 1 s is equal to

$$I_{2\mathrm{por}} = n_{1e}\sqrt{\frac{2kT_0}{m_1}}\int_0^{100\lambda_g} I_2(x)\,\mathrm{d}x \cdot 500\lambda_g \cdot 100\lambda_g$$

$$\times\frac{4.3 \cdot 10^{-2}}{\lambda_g} \approx 8.8 \cdot 10^{15}\ \mathrm{s}^{-1}.$$

For a plane surface, the flow density of deposited molecules I_2 should be calculated from equation (10) and the result obtained should be multiplied by the value of the area $500 \times 100\lambda_g$. Here to estimate the value of the dimensional one-sided flow density of incident molecules the following expression in used:

$$I_{2a} = 0.085 n_{1e}\sqrt{\frac{2kT_0}{m_1}}$$

where the coefficient 0.085 represents an approximate value of the dimensionless one-sided flow density of Component 2 (its dimensional quantity is determined as $\frac{1}{4} n_{2\infty}\sqrt{(8kT_0/\pi m_2)} = \frac{1}{4} \cdot 0.5 n_{1e}\sqrt{(8kT_0/\pi m_2)}$. To estimate the quantity I_1 in (10), its calculated value at small values of x was used: $I_1 \approx 0.1 n_{1e}\sqrt{(2kT_0/m_1)}$. As a result we have $I_{2\text{pl}} = 7.4 \cdot 10^{15}\ \text{s}^{-1}$. Thus, although $I_{2\text{por}}$ and $I_{2\text{pl}}$ are the quantities of the same order of magnitude, in the given case the porous layer absorbs by about 16% more molecules of a non-condensing admixture than a plane surface.

However, it is necessary to emphasize the following. For the porous layer in the given problem geometry we considered the worst (in the sense of absorption efficiency) variant of steady regime, when the 'transportation' of the molecules of Component 2 to the zone of intense condensation is inhibited. As a matter of fact, in a non-steady regime at initial times the density n_2 near the surface $x = 0$ is close to $0.5n_{1e}$ and the intensity of absorption of the non-condensing gas molecules is much higher than in the steady-state regime. Thus, it should be expected that in the case when the density of admixture molecules n_2 is comparable with the density n_{1e}, the number of non-condensing gas molecules absorbed by the porous layer can considerably exceed the number of the molecules absorbed by the plane surface.

Case B. From estimates similar to those given above it follows that in the present case a porous layer in a stationary regime absorbs the molecules of a non-condensing gas much worse (by more than an order of magnitude) than the plane surface. In the first place this is connected with the fact that in Case B there is a significant drop of the density n in the porous layer and the flow density of the first component n_1v_{1x} exceeds I_1 (Fig. 5), i.e., a considerable portion of the molecules of Component 1 passes through the thin porous layer without condensation. As a result, the intensity of condensation and consequently, of trapping is much smaller than in Case A.

5. Conclusions

(1) Based on the method of direct statistical simulation, a physical–mathematical model has been developed for gas mixture mass transfer in a highly porous body under the conditions of condensation of one of the components and trapping of a non-condensable admixture.

(2) The profiles of the macroscopic quantities in the porous body have been obtained. It is shown that, generally speaking, in a stationary regime the profile of the resultant flow $I_2^{(x)}$ of the 'trapped' component is not a monotonic function in the condensation (trapping) zone. The thing is that the process of trapping of a non-condensing gas is determined not only by the intensity of condensation of Component 1 (i.e., by the value of I_1), but also by the 'transportation' of Component 2 to the condensation surface, i.e., by mass transfer in the porous layer.

(3) It follows from comparison of the efficiencies of the admixture absorption in the porous layer and on the plane surface that in the case when the admixture density n_2 is comparable with n_{1e}, the number of the molecules of the non-condensing gas absorbed by the porous layer can considerably exceed the number of the molecules absorbed by the plane surface. In the case of $n_1 \ll n_{1e}$ the trapping efficiency substantially decreases as the density of molecular flow of Component 1 in the condensation zone exceeds the resultant flow density $I_1(n_1v_{1x} > I_1)$ by a much greater value than in a previous case, i.e., a substantial portion of the molecules of the condensing gas passes through the thin porous layer without condensation.

(4) The efficiency of absorption of a non-condensing gas by a porous layer can be increased by changing the characteristics of this layer (by increasing the specific surface S), as well as by changing the process of mass transfer in it (in particular, by arranging the inflow of both components into the porous layer from the side of the evaporation surface). With an increase of $\Delta T = T_0 - T_\varepsilon$, not only I_1 increases, but also the width of the condensation (trapping) zone.

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