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BULK AND DIFFUSIONAL TRANSPORT IN THE REGION BETWEEN MOLECULAR AND VISCOUS FLOW*

D. F. DYER and J. E. SUNDERLAND

School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia

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Abstract—Analytical and experimental analyses are presented for bulk and diffusional flow of a binary gas mixture under steady-state conditions. The analyses are valid for the entire region between pure molecular and viscous flow. The analytical analysis is made for flow through a capillary tube subjected to a small pressure gradient. A momentum balance is applied to one component of the gaseous mixture in order to determine an equation for the rate of transport of that component.

Analytical results for the capillary tube are modified for the case of transport through a porous material by considering this material to be a bundle of capillary tubes. Experimental results for the transport of an air–water-vapor mixture through freeze-dried meat are presented; these results compare favorably with the analytical results for the porous material.

NOMENCLATURE

A,	Avogadro's number [molecules/mole];
A_2,	area occupied by component 2 [ft^2];
a,	molar flux factor, $1 + N_2/N_1$, dimensionless;
b_1,	$-N_2aL/c_1$, dimensionless;
b_2,	$b_1c_1\, 8SRT/3\pi aD_{K2}$ [lb$_f$/ft^2];
c_1,	constant given by pD_{12}/RT [mole/ft s];
c_2,	integration constant;
D_{12},	diffusion coefficient for binary mixture [ft^2/s];
D_{K2},	Knudsen's diffusion coefficient, $\frac{2}{3}r\bar{V}_2$ [ft^2/s];
D_t,	average diffusion coefficient, $\dfrac{aRTN_2(x_L - x_0)}{p}\ln\dfrac{1 - y_{2L}}{1 - y_{20}}$ [ft^3/s];
F_2,	external force on component 2 per unit volume [lb$_f$/ft^3];
K,	Boltzmann's constant, R/A [ft lb$_f$/molecule degR];
Kn,	Knudsen's number, characteristic dimension/mean free path, dimensionless;
L,	length of capillary tube [ft];
m_2,	mass of gas component 2 molecule [lb$_m$];
n,	mixture molecular density [molecules/ft^3];
n_1,	molecular density of component 1 [(molecules of component 1)/ft^3];
n_2,	molecular density of component 2 [(molecules of component 2)/ft^3];
N_1,	molar flow rate of component 1 [(moles of component 1)/s ft^2];
N_2,	molar flow rate of component 2 [(moles of component 2)/s ft^2];
p,	total pressure [torr];
Δp,	total pressure drop, $(p_L - p_0)$ [torr];
p_1,	partial pressure component 1 [torr];
p_2,	partial pressure component 2 [torr];
r,	capillary radius [ft];
S,	reflection coefficient, dimensionless;
R,	universal gas constant [ft lb$_f$/mole degR];
T,	temperature [°R];
u,	macroscopic gas mixture velocity [ft/s];
u_1,	macroscopic velocity of component 1 [ft/s];

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u_2,	macroscopic velocity of component 2 [ft/s];
V,	volume occupied by both components [ft^3];
V_2,	volume occupied by component 2 [ft^3];
$\bar{V}_2$,	average molecular velocity of component 2, $(8KT/m_2\pi)^{\frac{1}{2}}$ [ft/s];
x,	axial tube coordinate [ft];
y_1,	concentration of component 1 [moles of component 1/moles of mixture];
y_2,	concentration of component 2 [moles of component 2/moles of mixture];
z,	nondimensional axial distance, x/L, dimensionless.

Subscripts

a,	air;
e,	effective value;
L,	position at tube exit;
w,	water-vapor;
o,	position at tube entrance;
1,	component 1;
2,	component 2.

INTRODUCTION

THERE are many applications requiring the prediction of the combined bulk and diffusional flow rate in the transition regime under the conditions of a non-uniform total pressure gradient. For example, the freeze-drying of food products involves the simultaneous diffusion and bulk movement of a binary mixture of air and water-vapor through a porous material under the influence of a small pressure gradient. The void structure of the porous material is such that the transport occurs in the region between the molecular and viscous condition ($0{\cdot}01 < Kn < 10$). This region will be subsequently referred to as the "transition regime".

To understand the transition regime, first consider the case where the mean free path of the molecules is much less than the characteristic dimensions of the system such as the tube diameter. If a total pressure gradient exists, both components of the binary mixture are transferred by bulk movement of the gas. If, in addition, a concentration gradient exists the movement of each component is superimposed on the bulk movement. At the opposite extreme, when the mean free path is much greater than the characteristic dimension, there is a negligible interaction between the molecules. Consequently the transport is given by Knudsen's [1] equation for molecular streaming under the influence of either a concentration or total pressure gradient. Between these extremes, when the mean free path and the characteristic dimension are approximately equal, a combination of these transport modes occurs and this phenomenon is termed transition flow.

Evans *et al.* [2] present equations for combined bulk and diffusional transport in the transition regime under the conditions of a non-uniform total pressure distribution. However, the so-called "dusty gas" model was used in which the porous material is idealized as another constituent of immovable large molecules. In addition, the results are valid only for the special case of self-diffusion or counter-diffusion of gases with equal molecular weight. The current paper is concerned with porous materials of a capillaric nature rather than one composed of extremely fine particles for which the dusty gas model is valid. In addition, all flux ratios of the two constituents are considered. A different method (momentum-transfer method) is used in the present case to obtain the governing differential equation.

Harper and Chichester [3] state that experimental thermal conductivity data for gases in the transition regime can be used to predict the product of pressure and diffusion coefficient, pD_{12}. They point out that for the continuous flow regime, simple kinetic theory shows that both the thermal conductivity and pD_{12} are independent of pressure. Furthermore, in the transition regime, due to the analogy between heat and mass transfer, both quantities should decrease in a similar manner with decreasing pressure. However, in the continuous flow regime, Present [1] notes that the simple kinetic theory expression giving thermal conductivity to be independent of pressure gives excellent agreement with experimental data. The corresponding development for pD_{12} shows that it should be independent of pressure but heavily dependent on the concentration of the gaseous components; this expression for pD_{12} cannot be experimentally substantiated. The dichotomy between the simple kinetic theory expression and experimental data results from the basic difference between the nature of the transport of mass and energy. For energy transfer across a given plane, the specific identity of the component molecules (either component 1 or component 2) is not important, whereas for mutual diffusion, the identity of the molecules is quite important. The mass transfer depends in part on whether the molecules collide with like or unlike molecules before crossing the plane. The collision of like molecules prior to crossing the plane does not affect the diffusive transport process, but is greatly affected if unlike molecules collide. Thus since the two mechanisms of transfer are not exactly analogous in the continuous flow regime, it appears unlikely that they would be analogous in the transition regime. It is desirable, therefore, to analytically and experimentally examine the assumption made by Harper and Chichester for combined bulk and diffusion flow of a binary gas mixture. Small total pressure and concentration gradients are assumed to exist simultaneously.

Consequently, the purpose of this paper is to present analytical results to determine the rate of mass transfer under the above conditions. Also, the analytical work is compared with experimental findings and with the results of the theory of Harper and Chichester.

ANALYTICAL INVESTIGATION

Johnson [4] suggests that the steady diffusion equation for continuous transport can be interpreted as an equation of motion of one of the constituent gases. The equation in the form of an equation of motion valid for the one-dimensional transport of a binary gas at uniform total pressure is:

$$F_2 - \mathrm{d}p_2 - \frac{KT}{nD_{12}} n_1 n_2 (u_2 - u_1)\,\mathrm{d}x = 0. \quad (1)$$

The first term in equation (1) is the total external force per unit area on component 2, the second term is the force per unit area on component 2 due to a partial pressure gradient and the third term is the momentum transfer to component 2 due to collisions with component 1.

If a small total pressure gradient exists, the Maxwell–Boltzmann distribution function evaluated at the average pressure is very nearly the same as for the uniform pressure case. Therefore, the last term in equation (1) still adequately describes the momentum exchange between the two constituents. However, the total pressure gradient causes an effective external force on component 2 which is equal to the product of the total pressure gradient and the average area occupied by this component. From Dalton's law, it can be easily shown that the cross-sectional area of component 2 is

$$A_2 = \pi r^2 p_2/p. \quad (2)$$

Since the net force on component 2 due to the total pressure gradient is $A_2\mathrm{d}p$, equation (1) can be written as

$$p_2\mathrm{d}p/p - \mathrm{d}p_2 = \frac{KT}{nD_{12}} n_1 n_2 (u_2 - u_1)\,\mathrm{d}x. \quad (3)$$

Equation (3) is valid for continuous flow when only intermolecular interactions are important. For transitional flow, one must consider molecular encounters with the wall; therefore, equation (3) must be altered to include the resulting momentum exchange with the wall. From kinetic theory, the number of molecules striking the inside of the capillary surface per unit time is $\pi r n_2 \bar{V}_2\ \mathrm{d}x/2$. If diffuse reflections occur, the average velocity change resulting from a molecular collision with the wall is u_2. In general, the average velocity change is $u_2 S$, where S is the reflection coefficient, defined as the number of molecules striking a unit area with completely diffuse momentum exchange divided by total number of molecules striking the unit area.

Therefore, the momentum exchange with the wall for each molecule is $m_2 u_2 S$. Taking this into consideration, equation (3) becomes

$$(p_2/p)\,\mathrm{d}p - \mathrm{d}p_2 = \frac{KT}{nD_{12}} n_1 n_2 (u_2 - u_1)\,\mathrm{d}x + S m_2 u_2 n_2 \bar{V}_2\,\mathrm{d}x/2r. \quad (4)$$

This equation is the final form of the differential equation of motion for one component of a binary gas mixture. It is valid for the case of combined bulk and diffusional flow in the transition regime under the condition of a non-uniform total pressure gradient.

An expression for the average molecular velocity can be determined from kinetic theory if a Maxwellian distribution is assumed. This expression is

$$\bar{V}_2 = (8KT/\pi m_2)^{\frac{1}{2}}. \quad (5)$$

Since

$$p_2 \frac{\mathrm{d}p}{p} - \mathrm{d}p_2 = -p\,\mathrm{d}\,\frac{p_2}{p} = -p\,\mathrm{d}y_2, \quad (6)$$

equation (4) can be combined with equations (5) and (6) to give

$$\frac{-p\,\mathrm{d}y_2}{RT} = N_2\left[\frac{8S}{3\pi D_{K2}} + \left(n_1 - n_2 \frac{N_2}{N_1}\right)\Big/ nD_{12}\right]\mathrm{d}x. \quad (7)$$

From Dalton's law of partial pressures,

$$y_1 + y_2 = 1{\cdot}0, \quad (8)$$

and making use of the definition of a, y_1 and y_2, and substituting equation (8) into equation (7) gives

$$N_2\,\mathrm{d}x = -\frac{pD_{12}\,\mathrm{d}y_2}{RT}\Big/\left[1 - ay_2 + \frac{8SD_{12}}{3\pi D_{K2}}\right]. \quad (9)$$

For the small pressure gradients considered, it is assumed that p can be expanded in a Taylor series neglecting the second-order terms to give

$$p = p_0 + \frac{\mathrm{d}p}{\mathrm{d}x}x. \quad (10)$$

Also, $\mathrm{d}p/\mathrm{d}x$ is approximated by $\Delta p/L$ so that

$$p = p_0 + \frac{\Delta p}{L}x. \quad (11)$$

From kinetic theory,

$$\frac{pD_{12}}{RT} = C_1 \quad (12)$$

where C_1 is a constant. From the definition of z,

$$\mathrm{d}x = L\,\mathrm{d}z. \quad (13)$$

Substituting equations (11)–(13), into equation (9) gives on rearrangement,

$$\frac{\mathrm{d}y_2}{\mathrm{d}z} - \frac{N_2 La}{C_1}y_2 = -\frac{N_2 L}{C_1}\left[1 + \frac{8S}{3\pi D_{K2}}\frac{C_1 RT}{p_0 + \Delta pz}\right]. \quad (14)$$

Substituting the definitions of b_1 and b_2 into equation (14), integrating and applying the boundary conditions $y_2 = y_{20}$ at $z = 0$ and $y_2 = y_{2L}$ at $z = 1$ gives

$$y_{2L} = \frac{1}{a} + \frac{b_2}{\Delta p}\,\frac{\left\{\log(p_0 + \Delta p) + \left[b_1\left(1 + \frac{p_0}{\Delta p}\right)\right] + \frac{1}{(2)2!}\left[b_1\left(1 + \frac{p_0}{\Delta p}\right)\right]^2 + \frac{1}{(3)3!}\left[b_1\left(1 + \frac{p_0}{\Delta p}\right)\right]^3 + \ldots\right\}}{\exp\left[b_1\left(1 + \frac{p_0}{\Delta p}\right)\right]}$$
$$+ \frac{y_{20} - \frac{1}{a} - \frac{b_2}{\Delta p}\exp\left(-\frac{p_0}{\Delta p}b_1\right)\left\{\log p_0 + \frac{b_1}{\Delta p}p_0 + \frac{1}{(2)2!}\left(\frac{b_1}{\Delta p}p_0\right)^2 + \frac{1}{(3)3!}\left(\frac{b_1}{\Delta p}p_0\right)^3 + \ldots\right\}}{\exp(b_1)} \quad (15)$$

The series contained in the braces converges for all values of $b_1(p_0/\Delta p)$ and $b_1(p_0 + \Delta p)/\Delta p$. It is convenient to define an average diffusion coefficient D_t for the transition regime by means of the following equation:

$$N_2 = \frac{pD_t}{RTLa} \ln \frac{1 - y_{2L}}{1 - y_{20}} \qquad (16)$$

Equations (15) and (16) can be solved by the following trial and error procedure. First, assume a value of D_t and then calculate the corresponding value of N_2 from equation (16). Next use this value of N_2 to calculate y_{2L} from equation (15) and then compare the magnitude of the calculated value of y_{2L} with the known value from the boundary condition at the tube exit. This procedure can be repeated until the correct value of D_t is obtained.

APPLICATION TO FLOW IN POROUS MEDIA

The usual porous material contains numerous small voids which form complex flow paths for vapor transport. These flow paths are nonuniform in cross-section and are not straight. The method used for analysing this case is to assume the voids form circular and straight capillaries. However, for actual substances, the analytical equations resulting from these assumptions should be altered to include the effects of devious flow paths and blockages caused by the structure of the porous sample. Parameters which account for these irregularities are called "effective parameters".

The analytical results presented in this paper can be used for actual porous media in obtaining the magnitude of the effective diffusion coefficient if the values of D_{12} and D_{K2} used in the definitions of b_1 and b_2 are the effective values for the porous sample. Effective values are defined so that the vapor flux can be written in terms of the total sample area and its actual thickness. Due to the complexities of the structure of porous materials, the effective values of D_{12} and D_{K2} are not predicted analytically; but, instead, are measured experimentally. In order to reduce the amount of experimental data required, Scott and Dullien [5] suggest that

$$(D_{12})_e/(D_{K2})_e = D_{12}/D_{K2}. \qquad (17)$$

Thus by obtaining the value of $(D_{12})_e$ by a single experiment, the value of $(D_{K2})_e$ can be calculated by substituting the experimental value of $(D_{12})_e$ and the known values of D_{12} and D_{K2} into equation (17). To calculate a theoretical value for $(D_t)_e$ for the porous sample, the values of $(D_{12})_e$ and $(D_{K2})_e$ are used to obtain b_1 and b_2 from their definitions, and then equations (15) and (16) are solved by the iteration previously described.

EXPERIMENTAL INVESTIGATION

The experimental equipment used is shown schematically in Fig. 1. The absolute pressure on the lower side of the porous sample was measured by means of a Wallace and Tiernan* pressure gage. The pressure drop across the sample was determined with a Dwyer† differential pressure gage. The temperatures above and below the porous material were determined with copper–constantan thermocouples. The species concentrations above and below the material were determined with Hygrodynamics‡ electric hygrometer sensing elements. These elements were calibrated by means of the procedure described in reference [6]. The weight was measured with a Mettler§ balance.

Tests were conducted on several samples of porous freeze-dried beef steak using an air–water-vapor mixture. The procedure involved placing several small cubes of ice in an insulated cup located in the inner cylinder (see Fig. 1). The porous sample was then sealed as shown over the open end of the inner cylinder and the vacuum chamber was closed. Valve 1 (solenoid operated) was opened so that during pump down no pressure gradient existed between the inner cylinder and the vacuum chamber. Valve 2 was

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* Wallace and Tiernan, Inc., Bellville, N.J.

† F. W. Dwyer Mfg. Co., Michigan City, Indiana.

‡ Hygrodynamics, Inc., Silver Spring, Maryland.

§ Mettler Instrument Corp., Highstown, New Jersey.

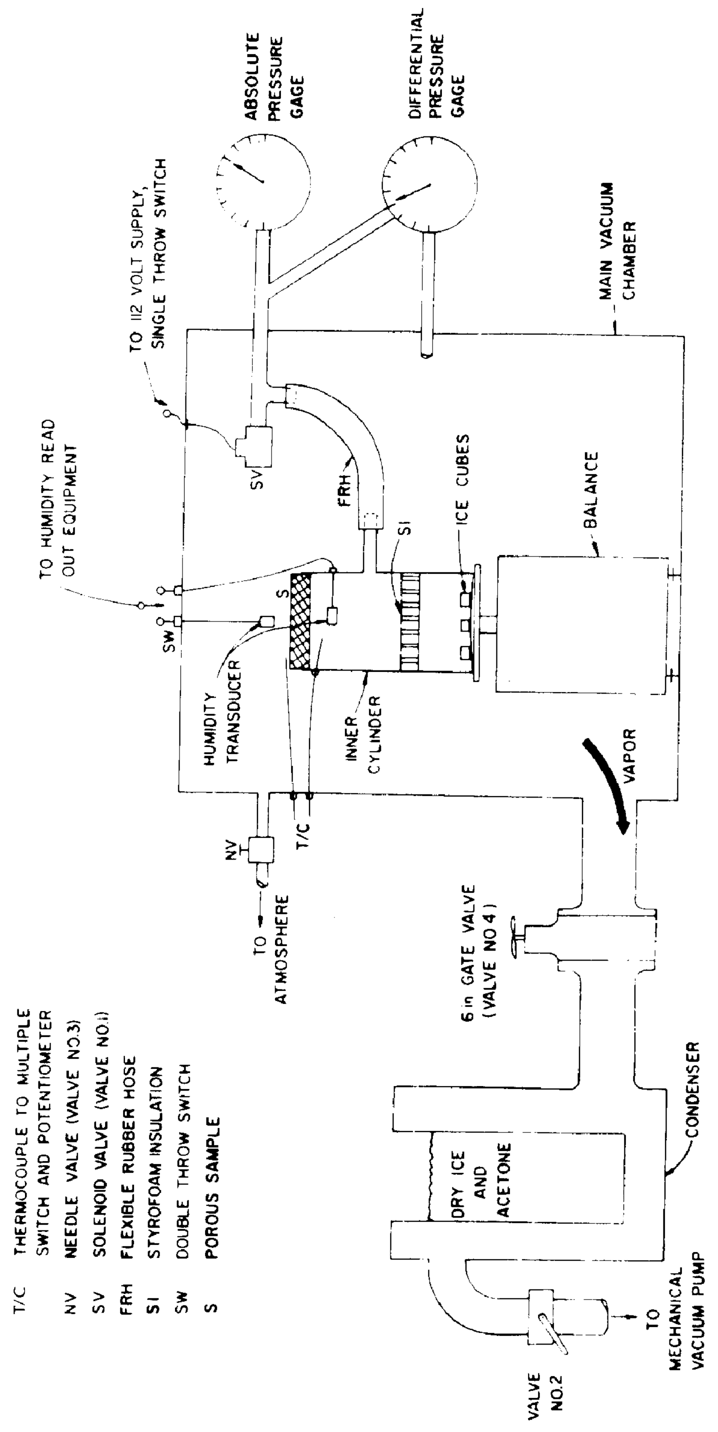

FIG. 1. Experimental apparatus.

opened and the chamber pumped until the desired pressure was obtained and then this valve was closed. Valve 3 was opened and closed for admitting air as required to obtain the desired concentrations. Valve 1 was then closed so that the water-vapor would flow through the porous sample and eventually to the condenser. Dry ice and acetone were used as the condenser coolant. Valve 4 was then adjusted to give the desired back pressure.

In order to determine when equilibrium conditions existed, the pressure, concentration, and temperatures above and below the sample were measured. If these measured quantities remained unchanged for a period of 2 h, it was assumed that equilibrium conditions held and the pressure, temperature, and water-vapor concentration above and below the sample were recorded. The weight was measured with a Mettler balance and was recorded. This procedure was repeated at 30 min intervals over a 2 h period. If conditions remained constant, the measurements were considered valid. The mass-flow rate was calculated from the weight loss; from this known rate, the thickness of the sample, and the pressure, temperature, and concentration data, the effective average diffusion coefficient was calculated from equation (16).

RESULTS

The experimental results for $(D_t)_e$ from measurements made on several samples of beef are given in Table 1. In addition, the values of $(D_t)_e$ calculated by using the theory presented in this paper are given for each of the conditions used in the experimental work. In applying the theory, a value for $(D_{12})_e$ of $\frac{1}{3}$ the value for free diffusion in air at atmospheric pressure as suggested by Harper and Chichester [3] was used. Completely diffuse momentum transfer was assumed giving $S = 1$. Although S has not been measured for the present case, data presented by Carman [7] for similar cases indicate that this assumption is relatively accurate. It is seen that close agreement exists between these theoretical and experimental values of $(D_t)_e$ appearing in Table 1. Since different samples were used, the property variation of the samples can account for most of the deviation between theory and experiment.

The final information presented in Table 1 is the value of $(D_t)_e$ predicted by the theory given in reference [3]. A much wider discrepancy exists between this theory and the experimental data than exists for the analytical work given above. This lack of correlation probably lies in the assumption of reference [3] that the transfer modes of heat conduction and diffusion are analogous. As discussed in the introduction of this paper, these modes are not analogous; as a consequence, a large variation from experiment is to be expected.

Table 1. Effective average diffusion coefficient for freeze-dried beef

Average pressure $(p_0 + p_L)/2$ (torr)	y_{wo}	y_{wL}	$(D_t)_e$ obtained experimentally (ft^2/s)	$(D_t)_e$ obtained by theory of this paper (ft^2/s)	$(D_t)_e$ calculated by theory of reference [3] (ft^2/s)
1·44	0·805	0·585	0·015	0·017	0·031
1·58	0·77	0·565	0·019	0·018	0·028
1·64	0·856	0·57	0·012	0·015	0·028
2·25	0·813	0·52	0·010	0·010	0·021
2·28	0·683	0·55	0·017	0·015	0·020

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Résumé—Une analyse théorique et une étude expérimentale sont exposées pour les écoulements en bloc et de diffusion d'un mélange gazeux binaire en régime permanent. Ces études sont valables dans toute la gamme entre l'écoulement moléculaire et l'écoulement visqueux. La théorie de l'écoulement à travers un capillaire sous l'effet d'un faible gradient de pression a été effectuée. On établit le bilan de la quantité de mouvement d'un constituant du mélange gazeux afin d'obtenir une équation pour la vitesse de transport de ce constituant.

Les résultats théoriques pour le capillaire sont modifiés dans le cas de transport à travers un matériau poreux en le considérant comme un faisceau de capillaires. Les résultats expérimentaux pour le transport d'air humide à travers de la viande lyophilisée sont présentés; ces résultats sont en bon accord avec les résultats théoriques pour le matériau poreux.

Zusammenfassung—Analytische und experimentelle Analysen wurden für die Gesamtströmung und die Diffusionsströmung eines binären Gasgemisches im stationären Zustand angegeben. Die analytische Untersuchung wurde an der Strömung durch ein Kapillarrohr bei kleinem Druckgradienten gemacht. Für eine Komponente des Gasgemisches ist eine Impulsbilanz durchgeführt um eine Gleichung für die Transportgeschwindigkeit dieser Komponente zu erhalten.

Die analytischen Ergebnisse für das Kapillarrohr sind im Falle des Transports durch poröses Material derart modifiziert, dass dieses Material als ein Bündel von Kapillarrohren angesehen wird. Versuchsergebnisse für den Transport eines Luft–Wasserdampfgemisches durch gefriergetrocknetes Fleisch sind angegeben; diese Ergebnisse stimmen gut mit den analytischen für poröses Material überein.

Аннотация—Выполнен теоретический и экспериментальный анализ диффузионного течения смеси бинарного газа при стационарном режиме. Анализ справедлив для всей области между чисто молекулярным и вязким течениями. Проведен теоретический анализ течения в капиллярной трубке, подвергаемой действию небольшого градиента давления. При помощи метода баланса количества движения получено уравнение переноса отдельного компонента газовой смеси.

Теоретические результаты, полученные на капиллярной трубке, использованы для расчёта переноса через пористый материал, который рассматривался как пучок апиллярных трубок. Приведены экспериментальные данные по переносу смеси воздух–вода-пар в мясе, подвергаемом сушке замораживанием. Эти результаты довольно хорошо согласуются с теоретическими данными дл пористого материала.