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THEORETICAL INVESTIGATION OF VAPOUR TRANSFER THROUGH A CAPILLARY-POROUS BODY

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Abstract—In the first part of the paper an investigation is made of the capillary evaporation under free molecular conditions for a nonisothermal case with assumption made of the evaporation occurring both on a lateral surface and at the bottom. Two modes of reflection from the surface, diffuse and specular, are considered. In both cases approximate expressions are derived for the fluxes of molecules at the capillary exit. In the case of diffuse reflection, the flow of molecules leaving the unit lateral surface and the net surface flow are obtained as well. This expression allowed investigation of the phase transition at the wall depending on the dimensionless length and temperature drop.

In the second part it is shown that the effect of surface diffusion on the capillary conductivity is determined by the dimensionless parameter G_L equal to the squared ratio of the square mean displacement of a molecule over the surface to the capillary length, and preceding the senior derivative in the initial integro-differential equation.

In the third part, based on the approximate theory of the mean free molecular path length, an expression is found for a vapour flow through a high-dispersed porous body when the capillary model is an inexact one.

NOMENCLATURE

$x = \frac{X}{L}$,	dimensionless coordinate;
m,	mass of molecule;
k,	Boltzmann constant;
p_e, n'_e,	pressure and density of saturated vapours, respectively;
α,	evaporation (condensation) coefficient;
Q,	heat necessary for evaporation of one molecule;
L,	length of capillary (thickness of layer);
R,	radius of capillary;
n,	dimensionless surface density of molecules [$n_0 = n(0)$ is a characteristic value which the density is referred to];
D_s,	surface diffusivity;
τ,	time of adsorption;
u, ε,	energy of adsorption and activation per one molecule;
n',	volume density of molecules;
λ,	free molecular path length;
μ,	cosine of angle between velocity vector and normal to area yz;
v,	mean thermal velocity of molecules;
ΔT,	$= T_1 - T_0$.

Subscripts

0,	parameters of the capillary bottom;
1,	exit parameters;
i,	isothermal.

THE STUDY of mass transfer in capillary-porous bodies including phase conversions (liquid evaporation) is not only of physical interest but also of great practical importance for the design of transpiration cooling and duration of drying of moist materials. When studying the mechanism of migration of vaporous moisture in porous bodies the use is usually made of interconnected capillary tubes. A porous body is often considered as an equivalent conic or slit-like capillary. The relations obtained for such a model are extended to real capillary-porous moist bodies in order to explain the mechanism of their drying. In the majority of cases, however, the models are designed at isothermal conditions, while in real porous bodies liquid evaporates in the presence of temperature drop. Temperature drop has an essential effect on the steam pressure near the surface of liquid meniscus. Thus, for example, with temperature fluctuation (20±0·013)°C the relative vapour pressure over the meniscus with a radius of $1{\cdot}47 \times 10^{-2}$ cm changes from 0·9999 to 0·9992 which is equivalent to the decrease in the meniscus radius from $1{\cdot}47 \times 10^{-2}$ to $1{\cdot}47 \times 10^{-4}$ cm, i.e. by the order of two [1]. The model calculations should, therefore, be performed with regard for nonisothermity. Besides, in the majority of cases the moisture transfer in capillaries proceeds according to the relationships of interdiffusion for binary mixture (vapour plus air) with correction for the Stefan flow (diffusional region in mass transfer) or by the Knudsen formula in case of rarefied medium (kinetic region of mass transfer). The second case is very often considered in the works on ice sublimation from a porous body.

More grounded calculations of vapour transfer in capillaries with evaporation are presented, for example in [2], where the account is taken of a thermal slip in the presence of a temperature drop along the capillary wall as well as of diffusional (diffusional drift) and viscous slip. The values of these effects are found to be comparable with the Stefan flow.

The account taken of film motion of liqueous moisture over capillary walls contributes to further improvement of the model mechanism of capillary transfer [3]. Film motion of moisture is caused by the difference of liquid chemical potentials near the capillary wall and in the bulk of liquid. It is the difference of chemical potentials which creates the so-called wedging pressure. The wedging pressure is determined by the pressure difference between the liquid–solid phase on a flat interface between the liquid in a thin layer and the bulk of liquid adjacent to the thin layer. Thus liquid evaporation proceeds not only on the liquid meniscus in a capillary but also from capillary walls covered with a thin liquid layer. Up to now, however, no kinetic consideration has been given to surface evaporation of a thin liquid layer covering the capillary walls.

In the paper an attempt is made to describe in detail the mechanism of vapour transfer with a free-molecular flow in a thin capillary (microcapillary) with account taken of evaporation both from the liquid meniscus and from the lateral side of the capillary in the presence of a temperature gradient along the capillary wall. The analysis of such a mechanism has shown that inside a capillary-porous body partially filled with liquid the evaporation and condensation processes may occur. The dimensionless parameters s and l are the main characteristic values. The first is a product of the dimensionless heat of liquid–vapour phase transition and relative temperature drop along the capillary, and the second is the capillary length to radius ratio (dimensionless length of the capillary).

Rough estimation of s for liquid evaporation into vacuum ($T_0 = 220°$; $T = 10°C$) yields $s \simeq 1{\cdot}3$. Then for $l = s$ and at $l > 1$ (i.e. when the capillary length is greater than the radius), vapour condensation may occur at the capillary meniscus, while near the exit evaporation may proceed. However, if $l < 1$ (the length of the capillary is less than its radius) evaporation takes place at both capillary ends of the same conditions. Thus, the pore structure (l) exerts a considerable effect on the mechanism of vapour migration. The value l is always positive, while s may be negative as well depending on the sign of the temperature gradient ΔT along the capillary ($s \gtrless 0$). If $s < 0$, then with $l = -s$ the mechanism of vapour migration will differ from that at $l = s$. Hence, the direction of the temperature gradient has an effect on evaporation and condensation processes in the capillary. This phenomena is observed only at nonisothermal conditions and may be referred to as the thermal effect of vaporous moisture migration.

Successive condensation and evaporation in a pore or capillary over liquid menisci were discussed earlier as well but these processes were considered to proceed at isothermal conditions. In the authors' case moisture evaporation and condensation in capillary are determined by the temperature drop along its length and by the geometry of pores and capillaries of the body. This is the principle point in the mechanism of moisture transfer in the capillary under the authors' consideration.

It was found through a number of investigations that surface diffusion of vapour or gas contributes much to the transfer process. Therefore the velocity of vapour migration along the capillary length depends not only on the linear diffusion velocity but also on the time of molecule adsorption on the surface of the capillary wall, i.e. on the velocity of surface diffusion. Such a vapour migration mechanism is discussed in the second part of the paper. The relationships obtained may be used to analyse the mechanism of drying moist materials and transpiration cooling of heat-protecting materials.

To conclude, it is shown how the approximate theory of the mean free path length may be used for investigation of the kinetics of vapour transfer through a highly disperse porous body when the capillary model is inexact.

1. MICROCAPILLARY VAPOUR FLOW INCLUDING PHASE CONVERSIONS

We shall consider a cylindrical capillary with a flat bottom ($X = 0$) from one side, and evaporation (sublimation) proceeding both on the lateral surface and at the bottom. A constant temperature gradient is prescribed along the capillary. The number of molecules evaporating from the unit surface per unit time is

$$j(\alpha, T) = \alpha \frac{p_e(T)}{(2\pi mkT)^{1/2}}.$$

It is assumed that the flow of molecules leaving the unit surface contains α-fraction of evaporating molecules and 1-α-fraction of reflected molecules. In the paper diffuse [4] and specular reflections are considered.

(a) *Diffuse reflection*

With diffuse reflection, for a flow of molecules from the unit lateral surface of a capillary the following equation is obtained [the flow is referred to the value $j(1, T_0) = j_0$]:

$$I(x) = \alpha \frac{p_e(T)}{p_e(T_0)} \left(\frac{T_0}{T}\right)^{1/2} + (1-\alpha)\left[\int_0^1 I(\xi) K_1(|x-\xi|)\,\mathrm{d}\xi + I_0 K(x)\right]. \quad (1)$$

The first summand herein describes evaporating molecules, the second, those getting onto the unit lateral surface in the vicinity of the point x from the remaining lateral surface (integral summand) and from the bottom $[I_0 K(x)]$ and then reflected

$$I_0 = \alpha_0 + 2l(1-\alpha_0)\int_0^1 I(\xi)K(\xi)\,\mathrm{d}\xi, \quad l = \frac{L}{R}.$$

The expressions for the functions $K(x)$ and $K_1(x)$ are given in [5]

$$K(x) = \frac{l^2x^2+2}{2(l^2x^2+4)^{1/2}} - \frac{l}{2}x, \quad K_1(x) = -\frac{\mathrm{d}K(x)}{\mathrm{d}x}.$$

For nonisothermal capillary surface, if the surface temperature varies by the law

$$T(x) = T_0(1+Ax)$$

and $|A| \ll 1$, the pressure p_e may be expressed as follows

$$p_e(x) = B\exp\left\{-\frac{Q}{kT(x)}\right\} = B\exp\left\{-\frac{Q}{kT_0}(1-Ax)\right\}. \quad (2)$$

In a number of works (for example [6]) it is shown that for comparatively short capillaries the functions $K(x)$ and $K_1(x)$ may be substituted by exponents with sufficient degree of accuracy. Thus

$$K(x) = \tfrac{1}{2}\exp\{-lx\}.$$

Using approximate expressions for K and K_1 we substitute (2) into (1). By differentiating (1) twice and combining the relation obtained with the initial one, get the following differential equation

$$\frac{\mathrm{d}^2 I}{\mathrm{d}x^2} - c^2 I = b\exp\{sx\}, \quad (3)$$

where

$$s = \frac{QA}{kT_0}, \quad c^2 = \alpha l^2, \quad b = \alpha(s^2 - l^2).$$

Solution of (3) for $s \neq \pm c$ is of the form

$$I = a_1\exp\{cx\} + a_2\exp\{-cx\} + \frac{b}{s^2-c^2}\exp\{sx\}. \quad (4)$$

The coefficients a_1 and a_2 are sought by substituting (4) into (1) (assuming that $\alpha_0 = \alpha$) and equating the coefficients at $\exp\{lx\}$ and $\exp\{-lx\}$:

$$a_1\frac{\exp\{c\}}{c-l} - a_2\frac{\exp\{-c\}}{c+l} = -\frac{b}{s^2-c^2}\frac{\exp\{s\}}{s-l},$$

$$a_1\left[-\frac{1}{c+l} + \frac{1-\alpha}{c-l}(\exp\{c-l\}-1)\right] + a_2\left[\frac{1}{c-l} - \frac{1-\alpha}{l+c}(\exp\{-(l+c)\}-1)\right] = \frac{b}{(s^2-c^2)(s+l)} - \frac{\alpha}{l} - \frac{b(1-\alpha)}{(s^2-c^2)(s-l)}(\exp\{s-l\}-1).$$

In case of $s = \pm c$ [that for $\alpha = 1$ may be written as $(Q/kT_0)(\Delta T/T_0 l) = \pm 1$], the solution of equation (3) is expressed as follows

$$I = a_1'\exp\{cx\} + a_2'\exp\{-cx\} + \frac{b}{2s}x\exp\{sx\}, \quad (4^1)$$

where a_1' and a_2' as well as a_1 and a_2 in (4) are determined from the system of algebraic equations obtained after substitution of (4^1) into (1).

For the flow of molecules at the capillary exit find

$$N = j_0\pi R^2\left[I_0 K_2(1) + 2l\int_0^1 I(x)K(1-x)\,\mathrm{d}x\right], \quad (5)$$

where

$$\frac{\mathrm{d}K_2(x)}{\mathrm{d}x} = -2lK(x).$$

In a particular case of $\alpha = 1$ and $s \neq c$ for approximate $K(x)$ and $K_2(x)$, obtain from (1) and (5)

$$N = j_0\pi R^2\exp\{-l\}\left[1 + \frac{l}{s+l}(\exp\{s+l\}-1)\right]. \quad (6)$$

It follows from (6) that at $l \gg s$ the flow is expressed by

$$N = j_0\pi R^2\left(1 - \frac{s}{l}\right)\exp\{s\},$$

i.e. N tends to $j_0\pi R^2\exp\{s\}$ being independent of l.

At $\alpha = 1$ and $s = 0$ (isothermal case) the value of flow independent of l is found from (1) and (5)

$$N_i = j_0\pi R^2.$$

The same relationship is arrived at, with exact expressions for the functions $K(x)$ and $K_2(x)$. A similar result is qualitatively explained in [7].

At $\alpha \neq 1$ the expressions for $I(x)$ and N become rather cumbersome. Numerical calculations were performed for ice at $T_0 = 213$°K, with approximate functions $K(x)$, $K_1(x)$ and $K_2(x)$ being used.

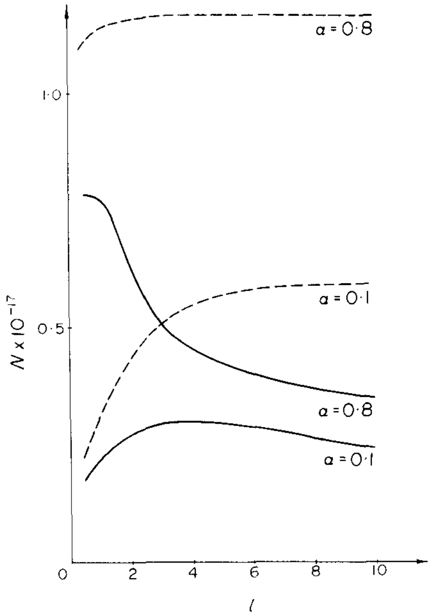

FIG. 1. Flow N at the capillary exit vs l with diffuse reflection ($T_0 = 213°\text{K}$, $l = 10^{-1}$ cm) --- $\Delta T = 0°$; — $\Delta T = -10$.

The calculations showed that for $\alpha \neq 1$ and $\Delta T = 0$ the flow at the capillary exit at small l increases with l, and then practically becomes independent of l (Fig. 1). In case of $\alpha \neq 1$ $\Delta T \neq 0$ the behaviour of the curves characterizing the flow dependence on l was more complicated.

At the lateral surface the net dimensionless flow of molecules is determined by

$$-J(x) = I^-(x) - I(x) = \alpha[I^-(x) - \exp\{sx\}]. \qquad (7)$$

where I^- is a flow of molecules getting onto unit lateral surface. I^- is sought from the equation

$$I^-(x) = \int_0^1 I(\xi) K_1(|x-\xi|)\,d\xi + I_0 K(x). \qquad (8)$$

Upon determining I from (1), we shall calculate I^- from (8) and then the net molecular flow from (7).

Write the flow $J(x)$ for a particular case of $\alpha = 1$ omitting a cumbersome general formula. At $s \neq \pm l$

$$J(x) = \tfrac{1}{2}\exp\{-lx\}\left[\frac{2\beta^2}{\beta^2-1}\exp\{(\beta+1)lx\} - \frac{1}{\beta-1}\exp\{l(2x+\beta-1)\} - \frac{\beta}{\beta+1}\right], \qquad (9)$$

where $\beta = s/l$, and the positive value of J corresponds to evaporation.

It follows from (9) that the behaviour of $J(x)$ is determined by l and β. Thus for $1 < \beta < \exp\{l(\beta-1)\}$ at $x = 0$ $J < 0$, at $x = 1$ $J > 0$. As to the case of $\beta = 0$, i.e. of an isothermal capillary, evaporation occurs along the whole of its length and the flow J attains its maximum value at $x = 1$.

For $s = l$ we have

$$J(x) = \tfrac{1}{2}\exp\{-lx\}[(\tfrac{3}{2} - l(1-x))\exp\{2lx\} - \tfrac{1}{2}], \qquad (10a)$$

where $s = -l$

$$J(x) = \tfrac{1}{2}\exp\{-lx\}[\tfrac{1}{2}(1 + \exp\{2l(x-1)\} - lx]. \qquad (10b)$$

From (10a) it is seen that for $l < 1$ $J(0) > 0$ and $J(1) > 0$, i.e. evaporation takes place at both ends of the capillary and at $l > 1$ $J(0) < 0$, $J(1) > 0$, i.e. with increasing x transition from condensation to evaporation occurs.

Expression (10b) indicates that for all l at $x = 0$ evaporation occurs, for $x = l$ evaporation takes place at $l < 1$ and condensation, at $l > 1$.

When evaporation proceeds only at the bottom with diffuse reflection of molecules from the lateral surface, the flow I may be obtained from (1) assuming $\alpha = 0$.

(b) *Elucidate the effect of specular reflection of molecules on the net flow at the capillary exit*

The number of molecules that evaporated from the side surface and left the capillary after multiple specular reflections, is written as follows [8]

$$N_w = 2\pi R^2 l \int_0^1 j(\alpha, T) S_1(1-x)\,dx, \qquad (11)$$

where

$$S_1(x) = K(x) + \sum_{n=1}^{\infty} (1-\alpha)^n \left[K\left(\frac{x}{n+1}\right) - K\left(\frac{x}{n}\right)\right].$$

For the number of molecules evaporated from the bottom, then multiply reflected from the walls and left the capillary obtain (by assuming $\alpha_0 = \alpha$)

$$N_b = \pi R^2 j(\alpha, T_0) S_2(1), \qquad (12)$$

where

$$S_2(x) = K_2(x) + \sum_{n=1}^{\infty} (1-\alpha)^n \left[K_2\left(\frac{x}{n+1}\right) - K_2\left(\frac{x}{n}\right)\right].$$

Besides, the account should be taken of the molecules which left the capillary after they had evaporated from the lateral surface, got to the bottom and reflected specularly from it. They are allowed for approximately through substitution by the diffusely reflected molecules

$$N'_w = 2\pi R^2 l S_2(1)(1-\alpha)\int_0^1 j(\alpha, T)S_1(x)\,\mathrm{d}x. \quad (13)$$

The flow at the capillary exit is determined by summation of (11)–(13).

It follows from the calculation results for diffuse and specular reflections that at small l the values of exit flows are similar. In case of specular reflection with increasing l the rate of flow increase is higher than with diffuse reflection.

The case of the bottom evaporation with specular reflection from the bottom and diffuse reflection from the side surface is considered in the second part of the manuscript.

2. SURFACE DIFFUSION EFFECT ON FREE-MOLECULAR VAPOUR FLOW THROUGH A CAPILLARY

Experimental investigation of gas flows in capillaries at free-molecular regime revealed the difference between the conductivity measured and that calculated by the Knudsen formula. One of the reasons of this difference is surface diffusion [9]. The latter is explained by the fact that at low density the molecules adsorbed on the surface may be considered as two-dimensional gas and thus in the presence of the density gradient a two-dimensional diffusion flow takes place which is described by

$$J_s = -D_s\frac{\mathrm{d}n}{\mathrm{d}X}.$$

Some works are known with account taken of the surface diffusion effect. Thus, in [10] the problem is considered on the Knudsen flow in a long tube with surface diffusion flow, wherein the effect of surface diffusion due to linear dependence of the surface density on the coordinate shows itself through contribution of this flow to the Knudsen flow.

In other works an integro-differential equation is solved for the surface density of molecules which in a limited case of no surface diffusion transits into the integral Klausing equation. In [11], particularly, the solution of this equation is built by the iteration method for the case of a short capillary ($l = L/R \ll 1$) and in [5, 12] a similar problem is solved numerically for any l. In these studies, however, no investigation is made of the effect of different terms in the integro-differential equation on the capillary conductivity.

This part of the manuscript deals with an approximate analytical investigation of a free-molecular vapour flow with regard for surface diffusion in a cylindrical capillary bounded by a flat surface of evaporating liquid from one side ($X = 0$) and connected with the tank filled with the vapours of this liquid, from the other ($X = L$). The surface of liquid is characterized by the specular reflection coefficient σ.

An integro-differential equation for the surface density of molecules is of the form

$$\frac{1}{L^2}\frac{\mathrm{d}}{\mathrm{d}x}\left[D_s(x)\frac{\mathrm{d}n}{\mathrm{d}x}\right] = \frac{n(x)}{\tau(x)} - \int_0^1 \frac{n(\xi)}{\tau(\xi)} [K_1(|x-\xi|)+\sigma K_1(x+\xi)]\,\mathrm{d}\xi - \frac{N_0}{n_0}K(x) - \frac{N_1}{n_0}[K(1-x)+\sigma K(1+x)]. \quad (14)$$

Here N_0 and N_1 are flows of molecules diffused from the unit surface of the bottom and of those from the tank passed through a unit area of the open end, respectively.

In equation (14) the term in the left-hand side is specified by the surface diffusion of molecules. The integral term in the right-hand side corresponds to the flow of molecules falling per unit surface of the capillary side from the remaining surface as a result of desorption by the cosine law (the first summand) and of specular reflection from the bottom (the second summand).

The first term out of the integral sign describes a flow of molecules diffusing from the bottom and falling per unit surface of a capillary, the second and third terms are flows of molecules entering the capillary through the open end and falling onto the wall directly and after specular reflection from the bottom.

We shall formulate the boundary conditions for integro-differential equation (14). It should be noted that surface diffusion takes place not only in a capillary but on an internal surface of the tank as well. In this case it is considered that at a distance of the order of $X = 1/\sqrt{E_1}$ adsorption equilibrium is achieved on the tank surface, i.e. the density of molecules (dimentional) is determined by

$$n_e = N_1\tau_1.$$

Then for the open end of the capillary, with account taken of the conjugation conditions (equality of densities and fluxes) on the capillary–tank interface, the following condition of the third kind may be written

$$\frac{\mathrm{d}n}{\mathrm{d}x} = L\sqrt{E_1}(n_e - n), \quad (15)$$

where

$$E_1 = \frac{1}{\tau_1(1)D_s(1)}.$$

For correct formulation of the boundary condition at $x = 0$ the values characterizing the kinetics of two-dimensional evaporation should be prescribed [13]. Since there are no such data available in the literature, the use is made of the following condition

$$n(0) = 1. \quad (16)$$

The flows N_0 and N_1 have been determined by the formulae

$$N_0 = (1-\sigma)\frac{p_e}{(2\pi mkT_0)^{1/2}}, \quad N_1 = \frac{p_1}{(2\pi mkT_1)^{1/2}}.$$

(a) *Isothermal case*

Assuming $\tau = \text{const}$, $D_s = \text{const}$ and substituting $K(x)$ by the exponent, from (14) we get

$$G_L \frac{d^2n}{dx^2} = n(x) - \frac{l}{2}\int_0^1 n(\xi)[\exp\{-l|x-\xi|\} + \sigma\exp\{-l(x+\xi)\}]\,d\xi - \frac{N_0\tau}{2n_0}\exp\{-lx\} - \frac{N_1\tau}{2n_0}[\exp\{-l(1-x)\} + \sigma\exp\{-l(1+x)\}], \quad (17)$$

where

$$G_L = \frac{1}{EL^2}.$$

It follows from (17) that the larger the dimensionless parameter G_L, the greater contribution of the surface diffusion into n distribution over the capillary surface. In particular, at $G_L \gg 1$ the density n is found by solution of the equation

$$\frac{d^2n}{dx^2} = 0$$

with boundary conditions (15) and (16), i.e. it varies linearly

$$n = 1 + Bx, \qquad B = \frac{L\sqrt{E}(n_e - 1)}{1 + L\sqrt{E}}.$$

On the other hand, in case of $G_L \ll 1$ equation (17) possesses a minor parameter at a major derivative. Therefore, at any infinitesimal values of G_L at the capillary ends the regions (boundary layers) exist where a differential term in equation (17) should be regarded for, i.e. the minor parameter method being used, the disturbed solution will not be equally applicable for the whole range of x variation. This non-uniformity is known [14] to be displayed when the perturbation parameter is a ratio of two lengths. In the present problem $G_L^{1/2}$ is a ratio of the mean square displacement of a particle over the surface $1/\sqrt{E}$ to the capillary length L.

To solve equation (17) it is differentiated twice over x. Combination of the expression obtained with initial equation (17) yields

$$\frac{d^4n}{dx^4} - c_1^2\frac{d^2n}{dx^2} = 0, \qquad c_1^2 = l^2 + G_L^{-1}. \quad (18)$$

Solution of equation (18) is written as follows

$$n = a_1\exp\{-c_1x\} + a_2\exp\{-c_1(1-x)\} + a_3x + a_4. \quad (19)$$

By substituting (19) into (18) and equating the coefficients at $\exp\{-lx\}$ and $\exp\{lx\}$, we obtain two equations for a_1, a_2, a_3 and a_4 determination. Two other equations are sought from boundary conditions (15) and (16). Hence, to calculate four unknown coefficients a system of four linear equations should be solved

$$a_1l\left[\frac{1}{l-c_1} + \frac{\sigma}{l+c_1}(\exp\{-(c_1+l)\}-1)\right] + a_2l\left[\left(\frac{1}{l+c_1} + \frac{\sigma}{c_1-l}\right)\exp\{-c\} - \frac{\sigma}{c_1-l}\exp\{-l\}\right] + \frac{a_3}{l}[-1-\sigma+\sigma\exp\{-l\}(l+1)] + a_4(1-\sigma+\sigma\exp\{-l\}) = \frac{\tau}{n_0}(N_0+\sigma N_1\exp\{-l\}),$$

$$\frac{la_1}{l+c_1}\exp\{-c_1\} + \frac{la_2}{l-c_1} + a_3\frac{l+1}{l} + a_4 = \frac{N_1\tau}{n_0},$$

$$a_1\exp\{-c_1\}(1-c_1G_L^{1/2}) + a_2(1+c_1G_L^{1/2}) + a_3(1+G_L^{1/2}) + a_4 = n_e,$$

$$a_1 + a_2\exp\{-c_1\} + a_4 = 1. \quad (20)$$

To investigate the solution obtained, numerical calculations have been performed. Of particular interest is the case of $G_L \ll 1$ (note that for $G_L = 0$ solution of equation (17) is a linear function). As it could be expected, for such values of G_L the existence of boundary layers is distinctly seen at the capillary ends and in the middle the curve $n(x)$ transits into a linear function (Fig. 2) whose slope coincides with that of a straight line being a solution of equation (14) at $G_L = 0$. The explanation is that in this range the right-hand side of equation (17) makes a major contribution into its solution. This peculiarity of the dependence of n on x at $G_L \ll 1$ is seen in the figure where the results of

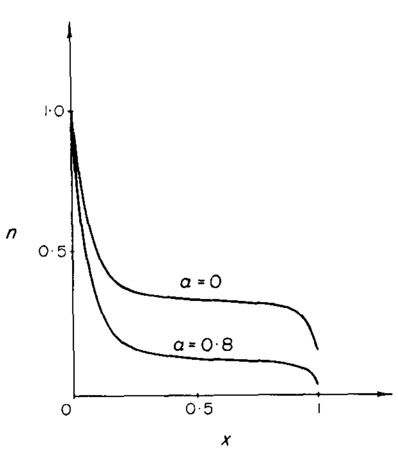

FIG. 2. Surface density of molecules vs longitudinal coordinate.

numerical calculations are presented for water with the following parameters: $G_L = 4 \times 10^{-3}$; $l = 0{\cdot}1$; $\sigma = 0$ and $0{\cdot}8$; $T = 300°\mathrm{K}$; $p_e = 3430\,\mathrm{N/m^2}$; $p_1 = 490\,\mathrm{N/m^2}$.

As to the flows in case of G_L being of the order of unity, the curve $n(x)$ cannot be divided into three zones.

The net flow of molecules at the capillary exit is equal to the sum of surface diffusion flow $N_s(1) = 2\pi R J_s(1)$ and flow of molecules $N(1)$ emitting through the open end of the capillary. It should be kept in mind that at $G_R \gg 1$, $N_S \gg N$ and at $G_R \ll 1$ $N_s \ll N$ (since $G_R = 1/ER^2$ characterizes the ratio of conductivities due to surface and Knudsen diffusion).

The expression for N is of the form

$$N = \pi R^2\{N_0 K_2(1) - N_1[1-\sigma K_2(2)]\} + \frac{2\pi R^2 n_0 l}{\tau}\int_0^1 n(x)[K(1-x)+\sigma K(1+x)]\,\mathrm{d}x. \quad (21)$$

Here the first term describes a flow of molecules that diffused from the bottom and covered the distance L without collisions. The second term is a flow of molecules entering the capillary through the open end. The third term stands for a flow of molecules which reached the bottom without collisions, reflected specularly from it and then emitted through the open end. The integral term characterizes the flow of molecules desorbed by the internal surface of the capillary and left it without collision against the wall and after specular reflection from the bottom.

The comparison of the approximate analytical solution of equation (14) and its numerical solution for the exact function $K(x)$ has shown that there is but slight difference between the values of $n(x)$ corresponding to exact and approximate expressions for $K(x)$, this difference increasing with decrease of G_L and increase of l. As for the appropriated values of N, they differ from one another in a greater degree than those of $n(x)$ do.

In (21), in order to decrease the calculation errors, an exact solution for the function $K(x)$ should be used rather than an approximate one. For $G_R \ll 1$, however, integration of the terms with a_1 and a_2 yields a small contribution into the value of N. To simplify integration, therefore, in (21) an approximate exponential expression for $K(x)$ may be particularly used (in the summands including a_1 and a_2).

With no surface diffusion, we have for N relationship (21) wherein $n(x)$ is the solution to integral equation (17) at $G_L = 0$ with an exponential kernel, i.e. it is a linear function. This allows easy calculation of the integral term in (21) with exact kernel $K(x)$. In case of $L > R$ and $N_1 = 0$, particularly, obtained within R^2/L^2

$$N = \frac{7}{3}\frac{R}{L}\frac{N_0}{1-\sigma+2\dfrac{R}{L}}\left(1-\frac{6\sigma}{7}\frac{R}{L}\right).$$

This expression is a generalization of the known Knudsen formula [15] for the case of evaporation from a finite length capillary. To compare, it should be noted that the exact Knudsen formula ($L/R \gg 1$, $\sigma = 0$) includes coefficient 8/3, and when the exponential kernel is used in (21), coefficient 2.

(b) *Nonisothermal case*

The values τ and D_s are related with the surface temperature as follows [9]

$$\tau = \tau_0 \exp\left\{\frac{u}{kT(x)}\right\}, \quad D_s = D_{s0}\exp\left\{-\frac{\varepsilon}{kT(x)}\right\}.$$

Assume that $T = T_0(1+Ax)$ and $A \ll 1$. Then linearization and substitution of the variable

$$n_1(x) = n(x)\exp\left\{-\frac{u}{kT(x)}\right\}$$

reduce equation for n_1 to the form similar to that in case of an isothermal capillary except for the fact that in the left-hand side a term containing the first variable $\mathrm{d}n_1/\mathrm{d}x$ appears. Herein, the ratio of the coefficients of the first and second derivatives

$$\gamma = \frac{\Delta T}{T_0}\frac{\varepsilon-2u}{kT_0}.$$

Since from an approximate analysis [9] follows that $\frac{1}{2} \leqslant \varepsilon/u \leqslant \frac{2}{3}$, and $u/kT_0 \gg 1$, the order of the magnitude of γ is equal to $\Delta T/T_0 \times u/kT_0$. If $\gamma \simeq 1$, then at $G_L(0) \ll 1$, i.e. in case of short boundary layers the term containing the second derivative is much greater than the summand with the first derivative. Hence, the solution of the equation for n_1 can be presented in the form

$$n_1(x) \simeq \frac{n_i(x)\tau_0}{\tau_i}$$

i.e.

$$n(x) \simeq n_1(x)\exp\left\{\frac{u}{kT(x)}\right\} = \frac{n_i(x)\tau(x)}{\tau_i} \quad (22)$$

everywhere but in the nearest vicinity of the open end (where the temperature T_1 effect appears due to the boundary condition at the exit (15)).

The flow N at the capillary exit is expressed by the formula differing from (21) only by $1/\tau(x)$ included in the subintegral expression. Because of relationship (22), nonisothermity has almost no effect on the integral for $|A| \ll 1$. The first summand in (21) depends only on T_0. Two other ones containing the flow N_1 depend on $T_1^{-1/2}$ but since $T_1 = T_0(1+A)$ and $|A| \ll 1$ this dependence is not significant. At low temperature drop the flow N, therefore, is independent of the non-isothermity, while the surface densities $n(x)$ for $A = 0$ and $A \neq 0$ are essentially different. Hence, in a non-isothermal case the net molecular flow $N+N_s$ differs from the appropriate flow in an isothermal capillary $\{\text{since } N_s = -[2\pi D_s(1)n_0/l][\mathrm{d}n/\mathrm{d}x](1)\}$.

The numerical solution to equation (14) for the case of ice evaporation showed the validity of the above considerations and expression (22), in particular. As to the cases of $G_L(0) \approx 1$, i.e. the absence of boundary layers, and of $|A| \approx 1$, i.e. high temperature drops, equation (14) was solved numerically to determine $n(x)$ and N.

3. THE KINETICS OF VAPOUR TRANSFER THROUGH A POROUS BODY

We shall consider a plane-parallel layer of a high-dispersed porous body limited with evaporating liquid from below and with its vapours from above. The system is under isothermal conditions.

The transient vapour flow regime that is often encountered in technological processes is the most complicated to be theoretically described. Consider the vapour flow through a dry layer of a porous body by representing the porous body–gas system as binary mixture. The molecules of one of the components are fixed, their sizes and mass greatly exceed the sizes and mass of the second component (real gas) [16–18].

The account is taken of, that the possibility of covering the distance X by a molecule without collision is $\exp\{-(X/\lambda)\}$ [19]. Below it is assumed that the free molecular path length is constant. In the model under consideration λ is of the form [19, 20]

$$\frac{1}{\lambda} = \frac{1}{\lambda_{11}} + \frac{1}{\lambda_{12}},$$

where λ_{11} is free path length of real molecules relative to the molecules themselves; λ_{12} is free path length of real molecules relative to fixed molecules. When determining λ_{12} the account should be taken of the proper volume of fixed molecules and the possibility of their mutual overlapping.

Consider the interface between evaporating liquid and porous body. The evaporating liquid occupies the portion Π of the whole surface area. The part of the surface $1-\Pi$ is occupied with solid particles of the porous body and reflects diffusely all the molecules that fell on it.

The total flow of molecules passing through the dry layer of porous body in the direction of the axis X consists of the difference between the number of molecules flying upwards and those flying downwards. At steady state this flow does not depend on the coordinate and, with the above in view, is of the form

$$N = \left\{\frac{2\Pi\alpha p_e}{(2\pi mkT)^{1/2}} + 4(1-\alpha\Pi)\left[L\int_0^1 \frac{n'(\xi)v}{4\lambda} E_2\left(\xi\frac{L}{\lambda}\right)\mathrm{d}\xi + \frac{p(1)}{(2\pi mkT)^{1/2}}\cdot E_3\left(\frac{L}{\lambda}\right)\right]\right\} E_3\left(x\frac{L}{\lambda}\right) + L\int_0^x \frac{n'(\xi)v}{2\lambda} E_2\left(\frac{L}{\lambda}(x-\xi)\right)\mathrm{d}\xi - L\int_x^1 \frac{n'(\xi)v}{2\lambda} E_2\left(\frac{L}{\lambda}(\xi-x)\right)\mathrm{d}\xi - \frac{2p(1)}{(2\pi mkT)^{1/2}} \times E_3\left(\frac{L(1-x)}{\lambda}\right), \quad (23)$$

where

$$E_n(x) = \int_0^1 \mu^{n-2}\exp\left\{-\frac{x}{\mu}\right\}\mathrm{d}\mu.$$

In equation (23) the first four terms present the number of molecules passing upwards through the plane yz being at a distance of X from the liquid surface. They include evaporated molecules, those scattered in the layer between the evaporating surface and the plane yz, the molecules which scattered in the layer with the thickness L, fell onto the boundary surface and diffusely reflected from it, and the molecules from the volume over the porous body diffusely reflected from the boundary surface. Two last terms are the molecules from the gas medium over the porous body and those collided in the porous body of thickness L–X.

Equation (24) when being in a general form fails to be solved. Therefore, the functions E_2 and E_3 are substituted by exponential functions similarly to [21].

By differentiating twice equation (23) and combining the expression obtained with the initial one, we arrive at a differential equation for the molecular density. From the equation derived and (23) obtain the expression for a flow of molecules

$$N = \frac{4\lambda\Pi\alpha}{(2\pi mkT)^{1/2}}\frac{p_e - p(1)}{4\lambda + 3L\alpha\Pi}. \quad (24)$$

At $\lambda/L \to \infty$ find from (24) an expression for evaporation from free surface

$$N_0 = \alpha\Pi\frac{p_e - p}{(2\pi mkT)^{1/2}}.$$

At $\lambda/L \to 0$ we get an ordinary expression for a diffusion flow if in the given diffusional approximation, it is assumed that $n_e \approx n(0)$:

$$N = -\frac{1}{3}v\lambda\frac{n'(1) - n'(0)}{L}.$$

In a transient case, a flow of particles depends on the coordinate and time. Consider the case when $\alpha\Pi = 1$. Under zeroth initial conditions with the use of the Laplace transformation and the assumptions made when solving equation (23), it is easy to show that the equation for a flow of molecules in dimensionless coordinates ($t_1 = t/t^*$, t^* is characteristic time of the problem) is of the form

$$-\frac{4}{9}\left(\frac{\lambda}{L}\right)^2\frac{\partial^2 N}{\partial x^2}+\left(\frac{\lambda}{ct^*}\right)^2\frac{\partial^2 N}{\partial t_1^2}+N+2\frac{\lambda}{ct^*}\frac{\partial N}{\partial t_1}=-\frac{1}{3}v\frac{\lambda}{L}\frac{\partial n'}{\partial x}. \quad (25)$$

Since λ/L and λ/ct^* are usually small, we retain in the equation the terms of the first order of smallness. Then equation (25) takes the form

$$N=-2\frac{\lambda}{ct^*}\frac{\partial N}{\partial t^*}-\frac{1}{3}v\frac{\lambda}{L}\frac{\partial n'}{\partial x^*}$$

where the first term from the right accounts for the finite velocity of mass propagation c [1].

REFERENCES

1. A. V. Luikov, *Heat and Mass Transfer*. Handbook, Energiya, Moscow (1972).
2. V. V. Levdansky and N. V. Pavlyukevich, On convective diffusion with macrocapillary evaporation, *Inzh.-Fiz.Zh.* **20**, 1093–1095 (1971).
3. B. V. Deryagin, S. V. Nerpin and N. V. Churaev, To the theory of liquid evaporation from capillaries, *Kolloid. Zh.* **26**, 301–307 (1964).
4. M. N. Kogan and N. K. Makashev, Knudsen layer contribution into the theory of heterogeneous reactions and the flows with surface reactions, *Mech. Zh. Gaza* **6**, 3–12 (1971).
5. W. L. Winterbottom, Vapor–solid interactions and the effusion oven, *J. Chem. Phys.* **47**, 3546–3556 (1967).
6. A. I. Ivanovsky, Some interaction problems between measuring cavity and a rarefied gas flow, *Trudy Tzentr. Aerolog. Observ.* **56**, 49–96 (1964).
7. R. F. Strickland-Constable, *Kinetics and Mechanism of Crystallization*. Academic Press, New York (1968).
8. R. Berman and F. E. Simon *et al.*, The thermal conductivity of diamond at low temperatures, *Proc. R. Soc.* **220**, 171–183 (1953).
9. J. H. de Boer, *The Dynamic Character of Adsorption*. Clarendon Press, Oxford (1953).
10. G. W. Sears, A note on the flow of gases through very fine tubes, *J. Chem. Phys.* **22**, 1252–1253 (1954).
11. W. L. Winterbottom and J. P. Hirth, Diffusional contribution to the total flow from a Knudsen cell, *J. Chem. Phys.* **37**, 784–793 (1962).
12. T. R. Bates and A. T. Forester, Coupled molecular flow and surface diffusion. Application to Cesium transport, *J. Appl. Phys.* **38**, 1956–1968 (1967).
13. A. S. Akhmatov, *Molecular Physics of Boundary Friction*. Fizmatgiz, Moscow (1963).
14. M. Van Dyke, *Perturbation Methods in Fluid Mechanics*. Academic Press, New York (1964).
15. M. Devienne, *Frottement et Echanges Thermiques dans les Gas Rarefiês*. Gauthier–Villars, Paris (1958).
16. D. K. Maxwell, Some notes to the gas kinetic theory, in *The Founders of the Kinetic Theory of Materials*. Collected Papers. ONTI, pp. 185–215 (1937).
17. B. V. Deryagin and E. P. Bakanov, Gas flow theory in a porous body near Knudsen region, *Zh.Tekh.Fiz.* **27**, 2056–2070 (1957).
18. E. A. Mason, A. P. Malinauskas and R. B. Evans, Flow and diffusion of gases in porous media, *J. Chem. Phys.* **46**, 3199–3216 (1967).
19. R. D. Present, *Kinetic Theory of Gases*. McGraw-Hill, New York (1958).
20. R. Clausius, Kinetic theory of gases, in *The Founders of the Kinetic Theory of Materials*. Collected Papers. ONTI, pp. 39–163 (1937).
21. E. M. Sparrow and R. D. Cess, *Radiation Heat Transfer*. Wardsworth, Belmont (1966).

ETUDE EXPERIMENTALE DU TRANSFERT DE VAPEUR A TRAVERS UN CORPS POREUX

Résumé—Dans la première partie de l'article on étudie l'évaporation capillaire dans des conditions de régime moléculaire libre pour un cas non isotherme, en supposant que l'évaporation se fait à la fois sur la surface latérale et sur le fond. On considère deux modes de réflexion sur la surface, soit diffus soit spéculaire. Dans les deux cas on obtient des expressions approchées des flux de molécules à la sortie du milieu capillaire. Dans le cas de la réflexion diffuse, on obtient à la fois le flux de molécules quittant l'unité de surface et le flux net surfacique. On étudie la transition de phase à la paroi en fonction d'une longueur adimensionnelle et de la chute de pression.

Dans la seconde partie, on montre que l'effet de la diffusion en surface, sur la conductivité capillaire est déterminé par le paramètre adimensionnel G_L égal au rapport de la racine carrée de la moyenne quadratique du déplacement d'une molécule en surface, à la longueur capillaire. On traite l'équation intégro-différentielle initiale.

Dans la troisième partie basée sur la théorie approchée du libre parcours moyen, on trouve une expression pour un écoulement de vapeur à travers un corps poreux fortement dispersé quand le modèle capillaire n'est plus exact.

THEORETISCHE UNTERSUCHUNG DER DAMPFÜBERTRAGUNG DURCH EINEN KAPILLAR-PORÖSEN KÖRPER

Zusammenfassung – Im ersten Teil der Arbeit wird eine Untersuchung der kapillaren Verdampfung unter der Bedingung freier Molekularbewegung für einen nicht isothermen Fall behandelt, wobei vorausgesetzt ist, daß die Verdampfung an der Seitenwand und am Boden stattfindet. Zwei Arten der Reflexionen von der Oberfläche, diffus und spiegelnd, werden betrachtet. Für beide Fälle werden Näherungsbeziehungen für den Molekularstrom am Kapillarende abgeleitet. Im Fall der diffusen Reflexion stimmen der Molekularstrom an den Seitenflächen und der reine Oberflächenstrom überein. Dieser Ausdruck erlaubt Untersuchungen des Phasenüberganges an der Wand, der von der dimensionslosen Länge und der Temperaturdifferenz abhängt.

Im zweiten Teil wird gezeigt, daß die Wirkung der Oberflächendiffusion auf die kapillare Leitfähigkeit durch den dimensionslosen Parameter G_L bestimmt wird, der gleich dem Quadrat des Verhältnisses von mittlerer quadratischer Verschiebung eines Moleküls über die Oberfläche zur Kapillarlänge ist; dies ergänzt die frühere Ableitung der integralen Differentialgleichung in ihrer Ausgangsform. Im dritten Teil wird, wenn das Kapillarmodell zu ungenau ist, mit der Näherungstheorie einer mittleren freien, molekularen Weglänge eine Beziehung für einen Dampfstrom durch einen hoch dispersen, porösen Körper angegeben.

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ПРОЦЕССА ПЕРЕНОСА ПАРА ЧЕРЕЗ КАПИЛЛЯРНО-ПОРИСТОЕ ТЕЛО

Аннотация — В первой части исследовано испарение из капилляра в условиях свободномолекулярного режима для неизотермического случая в предположении, что испарение происходит как на боковой поверхности, так и на дне. Рассмотрены две схемы отражения от поверхности — диффузная и зеркальная. В обоих случаях получены приближенные выражения для потоков молекул на выходе из капилляра, а при диффузном отражении найдены также поток молекул, вылетающих с единицы боковой поверхности, и результирующий поток на поверхности. Последнее выражение позволило исследовать характер фазового перехода на стенке в зависимости от безразмерных длины и температурного перепада.

Во второй части работы показано, что влияние поверхностной диффузии на проводимость капилляра определяется безразмерным параметром G_L, равным квадрату отношения среднеквадратичного смещения молекулы по поверхности к длине капилляра и стоящим перед старшей производной в исходном интегро-дифференциальном уравнении.

В третьей части работы на основе приближенной теории средней длины свободногопробега найдено выражение для потока пара через высокодисперсное пористое тело, когда капиллярная модель является неточной.