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ON MASS-TRANSFER KINETICS WITH EVAPORATION IN A CAPILLARY

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Abstract—A slow binary gas mixture flow in a capillary with evaporation is studied using the model kinetic equation in the Hamel form. Particularly, in a one-component case the approximate expression is obtained for calculation both of the volumetric flow rate and the velocity profile at $0 \leqslant \alpha \leqslant 5$ ($\alpha \simeq 1/2Kn$). At large α, the asymptotic formula for volumetric vapour flow rate shows that at a certain relationship between α and dimensionless capillary length, the vapour flow rate tends to a constant value corresponding to evaporation from a free surface.

NOMENCLATURE

$f_i, \boldsymbol{\xi}_i, n_i, m_i$, distribution function, molecular velocity, numerical density and mass of the ith species molecule;
n, p, numerical density and pressure of a mixture;
k, Boltzmann constant;
γ_i, $= n_i/n$;
L, capillary length;
l, $= L/r_0$;
$\mathbf{c}_i$, $= \mathbf{v}_i h_i^{1/2}$;
$\mathbf{n}$, unit normal vector to the lateral surface;
ω, refers to the capillary walls;
l, refers to outlet quantities.

AS LUIKOV [1] mentioned many times it is important to study vapour transfer kinetics in an individual capillary for description of transfer processes in capillary-porous bodies. In this case a finite length of the capillary (evaporation recession zone) should be taken into account. In [2] consideration was made of a free molecular flow with regard for evaporation both at the bottom and at the walls of a capillary.

Many works deal with gas flow in an infinite capillary. For example, in [3] the problem is numerically solved over a wide range of the Knudsen numbers, in [4] the asymptotic solution is found for small Kn, similar estimates are given in [5] where the problem is also solved for large Kn. As regards a binary gas mixture flow in a long capillary, works [6–8] should be mentioned.

Consider a slow flow of a binary gas mixture in a cylindrical capillary, r_0 in radius, from one side ($Z = 0$) bounded by a flat bottom, on which component one evaporates. The temperature of the internal capillary surface is assumed constant. The gas molecules are considered to diffusely reflect from the walls, the evaporation (condensation) coefficient being equal to unity.

The gas flow is treated on the basis of the model kinetic equation in the Hamel form [9]:

$$\boldsymbol{\xi}_{iR}\frac{\partial f_i}{\partial \mathbf{R}} + \boldsymbol{\xi}_{iZ}\frac{\partial f_i}{\partial Z} = \sum_{j=1}^{2} A_{ij} n_j (f_{0ij} - f_i), \quad i = 1, 2. \quad (1)$$

Here $R = (X, Y)$, $\boldsymbol{\xi}_{iR} = (\xi_{iX}, \xi_{iY})$, the axis Z coincides with the cylinder axis, $A_{ij} = A_{ji}$ are the quantities characterizing collision cross-sections,

$$f_{0ij} = n_i \left(\frac{h_{ij}}{\pi}\right)^{3/2} \exp\{-h_{ij}(\xi_i - v_{ij})^2\}$$

where

$$h_{ij} = \frac{m_i}{2kT_{ij}}, \quad v_{ij} = \mu_i v_i + \mu_j v_j, \quad \mu_i = \frac{m_i}{m_i + m_j}.$$

Note that for the slow flows considered at $T_i = T_j = T$ to a linear approximation $T_{ij} = T$, i.e. $h_{ij} = h_i = m_i/2kT$.

Introduction of the dimensionless coordinate and velocity

$$z = \frac{Z}{r_0}, \quad \mathbf{r} = \frac{\mathbf{R}}{r_0}, \quad \mathbf{u}_i = \boldsymbol{\xi}_i h_i^{1/2}$$

reduces equation (1) to the form

$$\mathbf{u}_{ir}\frac{\partial f_i}{\partial \mathbf{r}} + u_{iz}\frac{\partial f_i}{\partial z} = r_0 h_i^{1/2} \sum_{j=1}^{2} A_{ij} n_j (f_{0ij} - f_i). \quad (2)$$

Write down the boundary conditions. At the side surface ($r = 1$) for the reflected molecules

$$f_i(\mathbf{n}\cdot\mathbf{u}_{ir} > 0) = n_{i\omega} \exp\{-u_i^2\}\left(\frac{h_i}{\pi}\right)^{3/2}, \quad (3)$$

at the bottom ($z = 0$)

$$f_1(u_z > 0) = n_{1s} \exp\{-u_1^2\}\left(\frac{h_1}{\pi}\right)^{3/2} \quad (4)$$

where n_{1s} is the density of saturated vapour of component one at temperature T. Also prescribe densities n_{il} at $z = l$.

By analogy with the problems on a slow gas flow in an infinite length capillary under a small pressure gradient [10], solution of equation (2) is sought in the form:

$$f_i = f_{il}[1 + K_i(z - l) + u_{iz}\psi_i(\mathbf{r}, \mathbf{u}_{ir})], \quad (5)$$

where K_i is the unknown constant.

From equation (5) it is seen that n_i depends only on z.

Substitution of equation (5) into equation (2), upon linearization, yields ($i = 1, 2, j \neq i$):

$$\psi_i + \frac{\mathbf{u}_{ir}}{\alpha_i}\frac{\partial \psi_i}{\partial \mathbf{r}} = 2[(1-\beta_i\mu_j)c_{iz} + \beta_i(\mu_i\mu_j)^{1/2}c_{jz}] - \frac{K_i}{\alpha_i} \quad (6)$$

where

$$\alpha_i = r_0 h_i^{1/2}(A_{ii}n_{il} + A_{ij}n_{jl}),$$

$\beta_i = A_{ij}n_{jl}/(A_{ii}n_{il} + A_{ij}n_{jl})$ is the fraction of collisions of molecules of the ith component with those of the jth one in the total of collisions of the ith component.

Dimensionless mean mass velocities c_{iz} and c_{jz} due to axial symmetry depend only on r.

Equations (3) and (5) imply that at $r = 1$

$$\psi_i(\mathbf{n} \cdot \mathbf{u}_{ir} > 0) = 0. \quad (7)$$

Write equation (6) in an integral form (integration is made over the characteristics) with regard for condition (7):

$$\psi_i = \alpha_i \int_0^b \frac{1}{u_{ir}} \exp\left\{-\frac{\alpha_i s}{u_{ir}}\right\} \times \left\{2[(1-\beta_i\mu_j)c_i + \beta_i(\mu_i\mu_j)^{1/2}c_j] - \frac{K_i}{\alpha_i}\right\} ds \quad (8)$$

where

$$s = \sqrt{[(x-x')^2 + (y-y')^2]},$$
$$b = -r\cos\theta + \sqrt{(1-r^2\sin^2\theta)}.$$

It should be noted that a similar equation for a plane duct is obtained in [11].

Since according to equation (5)

$$c_{iz} = \frac{1}{\pi^{3/2}} \int u_{iz}^2 \exp\{-u_i^2\}\psi_i \, d\mathbf{u}_i,$$

then multiplication of equation (8) by

$$\frac{u_{iz}^2}{\pi^{3/2}} \exp\{-u_i^2\}$$

and integration with respect to $\mathbf{u}_i$ ($d\mathbf{u}_i = u_{ir}\, du_{iz}\, du_{ir}\, d\theta$) give:

$$c_{iz}(r) = c_i(r) = \frac{\alpha_i}{2\pi} \int_0^{2\pi} \int_0^b I_0(\alpha_i s) \times \left\{2[(1-\beta_i\mu_j)c_i(r') + \beta_i(\mu_i\mu_j)^{1/2}c_j(r')] - \frac{K_i}{\alpha_i}\right\} ds\, d\theta \quad (9)$$

where

$$I_m(s) = \int_0^\infty t^m \exp\left\{-\left(t^2 + \frac{s}{t}\right)\right\} dt.$$

Unlike the quantities presented in the above works K_i are not prescribed but should be found. Two more equations are needed to determine K_i. These are found by equating the flow through an arbitrary capillary cross-section to the flow at the bottom obtained for the first component with regard for equation (4) and for the second one, the former flow is assumed to be zero:

$$\int_0^1 rc_1\, dr = \frac{\frac{n_{1s}}{n_{1l}} - 1 + K_1 l}{2\pi^{1/2}}, \quad (10a)$$

$$\int_0^1 rc_2\, dr = 0. \quad (10b)$$

In expression (5) and when deriving equation (10a) an assumption was made that the distribution function depends on z in the same way up to the bottom. Thus, all following results are valid for $z > z_{i0}$ where $z_{i0} \simeq 1/2\alpha_i$ is the Knudsen layer thickness of the ith component. Consider the case $\alpha_1 = \alpha_2 = \alpha$, i.e. $z_{10} = z_{20} = z_0$. So, the problem has been reduced to solution of equations (9) and (10). Find the expression for the effective diffusion coefficient D. The mean mass velocity of the mixture is defined by:

$$\bar{v} = \frac{m_1 n_1 v_1 + m_2 n_2 v_2}{m_1 n_1 + m_2 n_2}.$$

The diffusion velocity of component one is written according to [12] (with no barodiffusion):

$$V_1 = v_1 - \bar{v} = \frac{n^2}{n_1 \rho} m_2 D \frac{d\gamma_2}{dZ}. \quad (11)$$

Integration of equation (11) over the cross-section, linearization and using expression (10a) give:

$$\frac{D}{r_0 h_1^{-1/2}} = \frac{2}{K_2 - K_1}\int_0^1 rc_1\, dr = \frac{\frac{n_{1s}}{n_{1l}} - 1 + K_1 l}{\pi^{1/2}(K_2 - K_1)}.$$

Let us make a study of the extreme cases of small and large α.

Since $s\, ds\, d\theta = dx'\, dy'$,

$$I_0(\alpha s)\, ds\, d\theta = \frac{I_0(\alpha s)}{s} dx'\, dy'.$$

At $r' \to r$, s tends to zero, and at small α, $[I_0(\alpha s)]/s$ tends to infinity. Therefore, $c_i(r')$ may approximately be replaced by $c_i(r)$ at such α in the r.h.s. of equation (9). A similar procedure is performed in [10] when consideration is made of a flow between infinite parallel plates, in this case the kernel of the integral equation has a logarithmic singularity. For c_1 and c_2 the following system of algebraic equations is obtained:

$$d_{i1}c_i + d_{i2}c_j = \frac{K_i}{2\pi} a \quad (12)$$

where

$$a(r) = \int_0^{2\pi}\int_0^b I_0(\alpha s)\, ds\, d\theta = \frac{2}{\alpha}\left[\frac{\pi}{2} - \int_0^\pi I_1(\alpha b)\, d\theta\right],$$

$$d_{i1} = \frac{\alpha}{\pi}(1-\beta_i\mu_j)a - 1,$$

$$d_{i2} = \frac{\alpha\beta_i}{\pi}(\mu_i\mu_j)^{1/2}a.$$

When solving equation (12) c_i is expressed in terms of K_i and K_j; and substitution of the solutions obtained into equations (10) then gives K_i and K_j.

The calculations from equation (12) have shown that at $\alpha \to 0$ the values of vapour flow and diffusion coefficient D tend to those in a free molecular flow.

For $\alpha \to \infty$ the problem is solved as follows. A Taylor series expansion of the function $c_i(r')$ with respect to x' and y', with the first and second derivatives only considered and $x = r$, $y = 0$ assumed for the sake of

calculation convenience gives

$$\left.\frac{\partial c_i}{\partial x'}\right|_{x'=r,y'=0} = \frac{dc_i}{dr}, \quad \left.\frac{\partial c_i}{\partial y'}\right|_{x'=r,y'=0} = 0,$$

$$\left.\frac{\partial^2 c_i}{\partial x'^2}\right|_{x'=r,y'=0} = \frac{d^2 c_i}{dr^2}, \quad \left.\frac{\partial^2 c_i}{\partial y'^2}\right|_{x'=r,y'=0} = \frac{1}{r}\frac{dc_i}{dr},$$

$$\left.\frac{\partial^2 c_i}{\partial x'\partial y'}\right|_{x'=r,y'=0} = 0, \quad x'-x = s\cos\theta, \quad y'-y = s\sin\theta.$$

and

$$c_i(r') = c_i(r) + \frac{dc_i}{dr}\left(s\cos\theta + \frac{1}{2r}s^2\sin^2\theta\right) + \frac{1}{2}\frac{d^2c_i}{dr^2}s^2\cos^2\theta. \quad (13)$$

Substitution of equation (13) into equation (9) and replacement of integration over the capillary cross-sectional area by integration over the circle area with radius B/α where $I_m(B) = 0$ yield equations:

$$-\beta_i\mu_j c_i + \frac{1-\beta_i\mu_j}{2\alpha^2}\frac{1}{r}\frac{d}{dr}\left(r\frac{dc_i}{dr}\right) + \beta_i(\mu_i\mu_j)^{1/2}c_j + \frac{\beta_i(\mu_i\mu_j)^{1/2}}{2\alpha^2}\frac{1}{r}\frac{d}{dr}\left(r\frac{dc_j}{dr}\right) = \frac{K_i}{2\alpha}. \quad (14)$$

Multiplying equations (14) by $\mu_i^{1/2}/\beta_i$, respectively, summing them up, using relation

$$\frac{\beta_i}{\beta_j} = \frac{n_{jl}}{n_{il}}\left(\frac{\mu_i}{\mu_j}\right)^{1/2}$$

and passing to dimensional velocities, we have:

$$m_1^{1/2}n_{1l}v_1 + m_2^{1/2}n_{2l}v_2 = \frac{(2kT)^{1/2}\alpha}{4}(n_{1l}K_1 + n_{2l}K_2)(r^2-1) + C. \quad (15)$$

Multiplying equation (15) by $m_1^{1/2}/\rho_l$ and using relation similar to equation (11) yield

$$\bar{v} = \frac{\alpha}{4n_l[m_2^{1/2}+\gamma_1(m_1^{1/2}-m_2^{1/2})]}\left(\frac{2}{kT}\right)^{1/2}(r^2-1)\frac{dP}{dz} + \frac{Dn_l(m_1^{1/2}m_2 - m_2^{1/2}m_1)}{r_0\rho_l[m_2^{1/2}+\gamma_1(m_1^{1/2}-m_2^{1/2})]}\frac{d\gamma_1}{dz} + v_\omega.$$

Here the first summand is the Poiseuille flow; v_ω is the viscous slip, and the summand involving $d\gamma_1/dz$ describes diffusional slip, it is the same as the appropriate term of work [13].

The solution procedure of the problem for intermediate values of α is given below. Pass to a more simple one-component case when evaporation occurs at the bottom. Then, instead of equation (9) we have:

$$w(r) = \frac{\alpha}{\pi}\int_0^{2\pi}\int_0^b\left[w(r') + \frac{1}{\alpha}\right]I_0(\alpha s)\,ds\,d\theta \quad (16)$$

where

$$w = -\frac{2c}{K}.$$

Note that for small α use of the above method gives:

$$w_0 = \frac{1}{\frac{\pi}{a(r)} - \alpha}, \quad (17)$$

for $\alpha \to \infty$

$$w = \frac{\alpha}{2}(1-r^2) + w_\omega. \quad (18)$$

Here w_ω is the slip velocity. According to [4]

$$w_\omega = 1{\cdot}016 + \frac{0{\cdot}548}{\alpha}.$$

For intermediate α, the approximate analytical solution for $w_1(r)$ may be found as follows. Substitution of $w(r')$ in the form (13) into equation (16) and replacement of dw/dr, d^2w/dr^2 by their values at large α taken from equation (18) yield:

$$w_1(r) = w_0(r) - \alpha^2\frac{a_1(r) + 0{\cdot}5a_2(r)}{\pi - \alpha a(r)} \quad (19)$$

where

$$a_1(r) = \int_0^{2\pi}\int_0^b s\cos\theta I_0(\alpha s)\,ds\,d\theta = -\frac{2}{\alpha}\int_0^\pi\cos\theta\left[bI_1(\alpha b) + \frac{1}{\alpha}I_2(\alpha b)\right]d\theta,$$

$$a_2(r) = \int_0^{2\pi}\int_0^b s^2 I_0(\alpha s)\,ds\,d\theta = 2\int_0^\pi\left[-\frac{1}{\alpha}I_1(\alpha b)b^2 - \frac{2}{\alpha^2}I_2(\alpha b)b - \frac{2}{\alpha^3}I_3(\alpha b) + \frac{1}{\alpha^3}\right]d\theta.$$

The dimensionless volume flow rate per unit area based on $-K/2$ is equal to:

$$N^* = -\frac{2}{K}N = 2\int_0^1 rw(r)\,dr. \quad (20)$$

According to calculations up to α of order 1, the values of $w_0(r)$ and $w_1(r)$ (and consequently of N^*) coincide practically. Differences between $w_0(r)$ and $w_1(r)$ increase with α.

The integrals in the functions $a(r)$, $a_1(r)$ and $a_2(r)$ are calculated numerically. In this case the values of $I_m(t)$ at $t \leqslant 1$ are approximated by series [14], and at $t > 1$, by the sum of two exponents (section $t = 1 \div 10$ is divided into two).

The values of N^* from equations (17) and (19) are compared with the numerical results of work [3] (Table 1). There is a good agreement between the values of N^* determined from w_0 (or w_1) and those from [3] at $\alpha \leqslant 1$. For larger α, flows N^* evaluated from w_1 also

Table 1. Values of volume flow rate N^* as function of α

α	0·1	0·2	0·3	0·4	1	2	3	4	5
N^* by(19)	1·404	1·383	1·379	1·383	1·482	1·726	1·997	2·274	2·554
N^* from [3]	1·404	1·382	1·377	1·380	1·459	1·661	1·885	2·119	2·358
N^* by (17)	1·404	1·383	1·379	1·385	1·501	1·865	2·424	3·240	4·411

agree satisfactorily with the values of [3]; moreover, the distribution $w_1(r)$ at $\alpha = 5$ agrees well with the velocity distribution of [4]. All this allows formula (19) to be used for calculation of the velocity profile and flow.

Based on equations (10a) and (20) we have:

$$K = \frac{1 - \dfrac{n_s}{n_l}}{l + \dfrac{\pi^{1/2} N^*}{2}},$$

$$N = \frac{\dfrac{n_s}{n_l} - 1}{\dfrac{2l}{N^*} + \pi^{1/2}}. \tag{21}$$

At large α from equation (21), use of the relation $N^* = \frac{1}{4}\alpha + W_\omega$ obtained from equations (18) gives:

$$N = \frac{\dfrac{n_s}{n_l} - 1}{\dfrac{8l}{\alpha + 4w_\omega} + \pi^{1/2}}. \tag{22}$$

Thus, equation (22) implies that at $l \ll \pi^{1/2}\alpha/8$ the Hertz–Knudsen formula may be used for evaporation from a free surface with regard for a mass velocity in the distribution function of molecules impinging on the bottom [15], i.e. unlike the case of an infinite tube [3] at $\alpha \to \infty$ flow N tends to a constant value.

It should be noted that the parameters n_l, l and α may not be chosen independently: α should vary with n_l or r_0. That α be changed with r_0 and n_s/n_l being constant, it is necessary to change n_s, i.e. the temperature of the system (n_s and T are related by the equation for a saturated vapour density). Thus dimensional velocities and flows may be passed over to by using different factors depending on temperature, i.e. on α. However, since the expression for saturated vapour density involves an exponential dependence on T, this difference is not large, e.g. for ice change in α from 0·1 to 5 gives rise to 1·17-fold increase in temperature.

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SUR LA CINETIQUE DU TRANSFERT DE MASSE AVEC EVAPORATION DANS UN CAPILLAIRE

Résumé—Un écoulement lent d'un mélange binaire gazeux dans un capillaire avec évaporation est étudié en utilisant un modèle d'équation cinétique sous la forme de Hamel. En particulier, dans le cas d'un seul composant, une expression approchée est obtenue pour le calcul du débit volumique et du profil de vitesse pour $0 \leqslant \alpha \leqslant 5$ ($\alpha = 1/2\,Kn$). Aux grandes valeurs de α, la formule asymptotique donnant le débit volumique de la vapeur montre que, lorsqu'une certaine relation entre α et la longueur réduite du capillaire est vérifiée, le débit de vapeur tend vers une valeur constante qui correspond à l'évaporation sur une surface libre.

KINETIK DES STOFFAUSTAUSCHS BEI VERDAMPFUNG IN EINER KAPILLARE

Zusammenfassung—Unter Verwendung der kinetischen Modellgleichung in der Form von Hamel wird die langsame Kapillarströmung einer verdampfenden binären Gasmischung untersucht.

Im Bereich $0 \leqslant \alpha \leqslant 5$ ($\alpha \approx 1/2\,Kn$) wird zur Berechnung aus der volumetrischen Strömungsgeschwindigkeit und aus dem Geschwindigkeitsprofil ein angenäherter Ausdruck erhalten, der besonders im Fall einer Komponente Gültigkeit hat.

Bei großen Werten von α zeigt die asymptotische Gleichung für die volumetrische Dampfgeschwindigkeit, daß bei einem besonderen Verhältnis zwischen α und der dimensionslosen Länge der Kapillare die Dampfgeschwindigkeit einen konstanten Wert erreicht, entsprechend der Verdampfung an einer freien Oberfläche.

О КИНЕТИКЕ МАССОПЕРЕНОСА ПРИ ИСПАРЕНИИ В КАПИЛЛЯРЕ

Аннотация — На основе модельного кинетического уравнения в форме Гамеля исследуется медленное течение бинарной смеси газов в капилляре при наличии испарения в нем. В частности, в однокомпонентном случае получено приближенное выражение для расчета как объемного расхода, так и профиля скорости при $0 \leqslant \alpha \leqslant 5$ ($\alpha \simeq 1/Kn$). В случае больших значений α из найденной асимптотической формулы для объемного расхода пара следует, что при определенном соотношении между α и безразмерной длиной капилляра расход стремится к постоянному значению, соответствующему испарению с открытой поверхности.