

Gas Mixture Separation in Nanosize Capillaries. Effects of Surface Forces

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Abstract. The flow of a gaseous mixture in ultrafine capillaries whose size is comparable to the range of surface forces is studied with allowance for the effect of surface forces on the gas component transport in the capillaries. The effect of surface forces is shown to be twofold. On the one hand, it is necessary to take into account the Boltzmann distribution of the molecular density in the capillary: it turns out that the contribution of this effect to the transport coefficient values may amount to 20%. On the other hand, an additional kinetic contribution to these coefficients may arise if the temperature in the gas is non-uniform. In this case, the temperature gradient may change the gas component transport coefficients several times, giving rise to a new mechanism of gas component separation that is associated with different potentials of interaction between the gas components and capillary walls. Also, surface forces modify the structure of phenomenological equations for gas component transport that implies entropy production in a non-uniform gas. However, the Onsager symmetry between the cross coefficients is retained.

INTRODUCTION

It is well known [1-3], that there is separation of components of a gas mixture flowing in fine capillaries under the action of pressure and temperature gradients. The separation is due to the difference in masses, cross-sections or accommodation coefficients of the gas mixture components.

In paper [4], it was shown, that in the case of free molecular gas flow in nanosize capillaries under the action of temperature gradient the effects related to the surface forces acting in the vicinity of capillary surface should be taken into consideration. For liquids flowing in ultrafine capillaries these forces determine the velocities of thermal and diffusion osmosis, the mechanocaloric effect and liquid mixture separation [5]. These forces appear naturally in the left-hand side of the Boltzmann kinetic equation for the gas which is non-uniform in temperature. The surface forces significantly affect the flow rate due to the temperature gradient and the termolecular pressure drop (TPD) between the vessels connected with a package of nanosize capillaries under the steady state [2].

The molecules of different kind have different potentials of gas/surface interaction, so the surface forces can affect the separation of components of gas mixture flowing in ultrafine capillary.

In the present communication, the effects of the surface forces on non-isothermal gas mixture flow in nanosize capillaries are considered. The possibility is shown of the gas mixture separation due to the difference in the potentials of molecule/wall interaction for mixture components in the presence of temperature gradient. The explicit expressions for the enrichment coefficient were obtained for both the stationary flow corresponding to the vanishing diffusion fluxes and the given temperature and pressure drops between the capillary ends. The possibility is discussed of the determination of gas/surface interaction parameters by combined measuring the TPD and separation effects.

KINETIC EQUATION

Let us consider the flow of multicomponent gas mixture in the presence of pressure $\partial p / \partial z$, temperature $\partial T / \partial z$ and concentration $\partial y_\alpha / \partial z$ gradients directed along the z axes of a capillary (Greek index denotes the number of gas mixture component). We assume that the gas molecules interact with the surface of capillary wall through potentials $U_\alpha(r)$, where r is the distance from the capillary center. The potentials $U_\alpha(r)$ differ from zero near the surface of moderately thin capillary, i.e. at $r \approx R$, where R is the capillary radius. The state of gas mixture is described by distribution functions $f_\alpha(r, z, \vec{v}_\alpha)$ of mixture molecules over velocities \vec{v}_α .

We assume that, as usual [6, 7], the distribution functions $f_\alpha(r, z, \vec{v}_\alpha)$ can be represented as

$$f_\alpha(r, z, \vec{v}_\alpha) = f_\alpha^{(0)}(1 + \varphi_\alpha), \quad (1)$$

where φ_α are corrections to local Maxwell-Boltzmann distributions $f_\alpha^{(0)}$ having, in our case, the following form:

$$f_\alpha^{(0)} = n_\alpha(z) \left(\frac{m_\alpha}{2\pi kT(z)} \right)^{3/2} \exp \left[-\frac{mv_\alpha^2}{2kT(z)} - \frac{U_\alpha(r)}{kT(z)} \right], \quad (2)$$

Here n_α are the numbers of molecules of components per unit volume, m_α - are their masses, k is the Boltzmann constant.

For the stationary gas flow under the low pressure and temperature gradients, the corrections φ_α are found from the solution of linearized kinetic Boltzmann equations which can be represented as

$$v_{\alpha z} \left(\frac{mv_\alpha^2}{2kT} - \frac{5}{2} \right) \tau + v_{\alpha z} k_\alpha + v_{\alpha z} \frac{U_\alpha(r)}{kT} \tau + \vec{v}_{\alpha r} \frac{d\varphi_\alpha}{d\vec{r}} = \sum_\beta I_{\alpha\beta}(\varphi_\alpha, \varphi_\beta), \quad (3)$$

where $I_{\alpha\beta}(\varphi_\alpha, \varphi_\beta)$ are the linearized Boltzmann collision integrals, $\tau = \partial \ln T / \partial z$, $k_\alpha = \partial \ln p_\alpha / \partial z$, p_α is the partial pressure of component α , \vec{r} is two-dimensional vector in the cross-section plane.

Equation (3) differs from the equation considered earlier [6, 7], when describing the gas mixture flow in a capillary under the pressure, temperature and concentration gradients, by the presence of a term related to the potential of surface forces in the left-hand side of this equation.

The results of paper [4] show that the surface force effects are significant only for ultrafine capillaries, which diameter is less than the mean free path of gas molecules under the normal conditions. This enable one to ignore the collision integral in the right-hand side of equation (3) that simplifies significantly the kinetic equation:

$$\vec{v}_{\alpha r} \frac{d\varphi_\alpha}{d\vec{r}} = -v_{\alpha z} \left(\frac{mv_\alpha^2}{2kT} - \frac{5}{2} \right) \tau - v_{\alpha z} k_\alpha - v_{\alpha z} \frac{U_\alpha(r)}{kT} \tau. \quad (4)$$

Integrating equation (4) along the characteristics we obtain [6]:

$$\varphi_\alpha(l) = - \int_{l_B}^l \left[v_{\alpha z} \left(\frac{mv_\alpha^2}{2kT} - \frac{5}{2} \right) \tau + v_{\alpha z} k_\alpha + v_{\alpha z} \frac{U_\alpha(r)}{kT} \tau \right] \frac{dl}{v_{\alpha r}} + \varphi_{\alpha B}, \quad (5)$$

where $\varphi_{\alpha B}$ is the value of φ_α at the capillary walls for molecules of sort α leaving the surface. In the case of complete accommodation that is considered below, we have $\varphi_{\alpha B} = 0$.

The averaged velocities of the mixture components are equal

$$q_\alpha(r) = \left(\frac{m_\alpha}{2\pi kT} \right)^{3/2} \int v_{\alpha z} \varphi_\alpha \exp \left(-\frac{mv_\alpha^2}{kT} \right) d\vec{v}_\alpha = - \left(\frac{2kT}{m_\alpha} \right)^{1/2} \frac{1}{\pi^{3/2}} \int c_{\alpha z}^2 \exp(-c_{\alpha z}^2) dc_{\alpha z} \int \exp(-c_{\alpha r}^2) c_{\alpha r} dc_{\alpha r} d\theta \int_{l_B}^l \left[(c_{\alpha z}^2 + c_{\alpha r}^2 - 5/2) \tau + k_\alpha + \frac{U_\alpha(r)}{kT} \tau \right] \frac{dl}{c_{\alpha r}}, \quad (6)$$

where $\vec{c}_\alpha = (m_\alpha / 2kT)^{1/2} \vec{v}_\alpha$ is dimensionless cross-sectional velocity of component α , $c_{\alpha r}^2 = c_{\alpha x}^2 + c_{\alpha y}^2$.

Integration over c_{α} can be done in a simple way. Integration over θ and l can be transformed into the integration over the channel cross-section Σ in a standard way [6]:

$$q_{\alpha}(r) = -\left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{1}{2\pi} \int \exp(-c_{\alpha}^2) dc_{\alpha} \int_{\Sigma} [(c_{\alpha}^2 - 1)\tau + k_{\alpha} + \frac{U_{\alpha}(\vec{r}')}{kT}\tau] \frac{d\Sigma}{|\vec{r} - \vec{r}'|}. \quad (7)$$

Integrating over c_{α} , we obtain the final result:

$$q_{\alpha}(r) = -\left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{1}{4\pi} \int_{\Sigma} [k_{\alpha} - \frac{1}{2}\tau + \frac{U_{\alpha}(\vec{r}')}{kT}\tau] \frac{d\Sigma}{|\vec{r} - \vec{r}'|}. \quad (8)$$

We can partially integrate in the first and second terms:

$$q_{\alpha}(r) = -\left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{1}{4\pi} \left\{ \left(k_{\alpha} - \frac{1}{2}\tau\right) \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta)} d\vartheta + \tau \int_{\Sigma} \frac{U_{\alpha}(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} \right\}. \quad (9)$$

Calculating the averaged over the cross-section velocities one should keep in mind that there is a non-uniform distribution of concentrations in the presence of gas/surface interaction. This fact results in an additional dependence of velocities of gas mixture component flow under the action of pressure, temperature and concentration gradients. As a result, the averaged over the cross-section velocities have the form:

$$\begin{aligned} \langle q_{\alpha} \rangle = & -\left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{1}{4\pi} \left\{ \frac{(k_{\alpha} - \frac{1}{2}\tau)}{\int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r dr} \int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta)} d\vartheta dr \right. \\ & \left. + \frac{\tau}{\int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r dr} \int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r \int_{\Sigma} \frac{U_{\alpha}(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} dr \right\}. \end{aligned} \quad (10)$$

When the surface forces are not taken into account we obtain the well known result [2, 8]

$$\langle q_{\alpha} \rangle = -\left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{1}{2\pi R^2} \int_0^R r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta)} d\vartheta dr \left(k_{\alpha} - \frac{1}{2}\tau\right) = -\frac{2}{3} R \bar{v}_{at} \left(k_{\alpha} - \frac{1}{2}\tau\right). \quad (11)$$

Here $\bar{v}_{at} = (8kT/\pi m_{\alpha})^{1/2}$ is the mean thermal velocity of molecules of component α .

In what follows we are interesting in the gas flow under the action of temperature gradient. In this case

$$\begin{aligned} \langle q_{\alpha} \rangle = & \left(\frac{2kT}{m_{\alpha}}\right)^{1/2} \frac{\tau}{8\pi} \frac{1}{\int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r dr} \left\{ \int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta)} d\vartheta dr \right. \\ & \left. - 2 \int_0^R \exp(-\frac{U_{\alpha}(r)}{kT}) r \int_{\Sigma} \frac{U_{\alpha}(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} dr \right\}. \end{aligned} \quad (12)$$

One can see from equation (12) that flow velocity of gas mixture components is determined not only by their masses (multiplier $\sim \sqrt{1/m_{\alpha}}$), but also by the potentials of their interaction with capillary surface.

Since each component has its own surface force potential, the surface forces give different contribution to the velocities of the component flow under the action of temperature gradients.

THERMAL DIFFUSION AND THERMOMOLECULAR PRESSURE DROP

Let us calculate the relative velocities of the component flow caused by the temperature gradient and the thermomolecular pressure drop. These effects can be determined using equations (12). We obtain for the difference of the component velocities

$$\begin{aligned}
 < q_\alpha > - < q_\beta > = (2kT)^{1/2} \frac{\tau}{8\pi} \left\{ \frac{1}{\sqrt{m_\alpha}} \frac{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta) d\vartheta} dr}{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r dr} - \right. \\
 & \frac{1}{\sqrt{m_\beta}} \frac{\int_0^R \exp\left(-\frac{U_\beta(r)}{kT}\right) r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta) d\vartheta} dr}{\int_0^R \exp\left(-\frac{U_\beta(r)}{kT}\right) r dr} - \left[\frac{2}{\sqrt{m_\alpha}} \frac{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_\Sigma \frac{U_\alpha(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} dr}{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r dr} - \right. \\
 & \left. \left. \frac{2}{\sqrt{m_\beta}} \frac{\int_0^R \exp\left(-\frac{U_\beta(r)}{kT}\right) r \int_\Sigma \frac{U_\beta(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} dr}{\int_0^R \exp\left(-\frac{U_\beta(r)}{kT}\right) r dr} \right] \right\}. \quad (13)
 \end{aligned}$$

One can see from equation (13), that the difference of the velocities of components flow under the action of temperature gradient is determined by the terms of two kinds. In the first kind terms the surface forces manifest themselves in a thermodynamic manner throw the change of the density of molecules in a capillary. The terms of the second kind are due to the kinetic effect discussed earlier in [4]. Since the surface usually attracts the molecules ($U_\alpha < 0$), the kinetic effect increase the gas transfer throw a capillary.

It should be noted that at equal masses of the molecules of different components in the presence of surface forces the difference of the component flow velocities can differ from zero if the potentials of the component/surface interaction are different. This shows that the surface forces change the behavior of the mixture not only in quantitative, but in qualitative manner. The quantity of the thermal diffusion, as estimates analogous to that done in [4] show can be increased several hundred of percents.

Assuming $k_\alpha = \partial \ln p / \partial z$ from equation (11) we find for the thermomolecular pressure drop (we ignore the secondary effects)

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2} \right)^{\beta_T/2}, \quad (14)$$

where p_1 and p_2 are the pressures established in connected vessels maintained at temperatures T_1 and T_2 and

$$\beta_T = 1 - 2 \sum_\alpha \frac{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_\Sigma \frac{U_\alpha(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r} - \vec{r}'|} dr}{\int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta) d\vartheta} dr}. \quad (15)$$

Hence, surface forces can substantially affect the value of thermomolecular pressure drop in gases.

ESTIMATES

Let us estimate the contribution of the surface forces to the effects discussed. We assume that the surface van der Waals' forces of attraction fall in accordance with the power law with an increase in the distance $x = R - r$ from the surface of channel walls and take advantage of the following expression [7]

$$U_\alpha(x) = -\frac{\hbar\omega_0\alpha_\alpha\alpha_s N_s}{x^3}, \quad (16)$$

where \hbar is Planck's constant, ω_0 is characteristic frequency of electron transitions ($\hbar\omega_0$ is approximately equal to ionization potential), α_α, α_s are the polarizabilities of molecules of kind α and the matter of channel walls, respectively, N_s is the number of atoms per unit volume.

Assuming that x is equal to 0.5 nm, the capillary radius is 10 nm and taking the corresponding values of the polarizability for argon and glass, we find the following value for the additional-to-unity coefficient of equation (16) at room temperature:

$$\begin{aligned} & 2\sum_\alpha \int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_\Sigma \frac{U_\alpha(\vec{r}')}{kT} \frac{d\Sigma}{|\vec{r}-\vec{r}'|} dr / \\ & \sum_\alpha \int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_0^{2\pi} \int_0^\pi \sqrt{(R^2 - r^2 \sin^2 \vartheta) d\vartheta dr} \approx \frac{4x}{R} \frac{\hbar\omega_0\alpha_\alpha\alpha_s N_s}{x^3 kT} \approx 0.3. \end{aligned} \quad (17)$$

Even having in mind some indefiniteness of parameter x , one can easily see that accounting for the surface forces results in a noticeable increase in the gas transfer through the capillary under the temperature gradient. As the temperature decrease, the effect of surface forces rises. Note also that relation (17) gives the lower estimate of correction. The same value can be considered as the estimates of the other effects discussed.

A more exact estimate of these contributions can be made using a potential free of a singularity at $x = 0$. Let the potential be

$$U_\alpha(r)/kT = -\frac{a_\alpha}{4[(R-r)^2 + \Delta_\alpha]^{3/2}} \frac{T_0}{T}, \quad (18)$$

where T_0 is room temperature, the distance is measured in nanometers, parameter a_α is normalized so that it equals unity for argon/glass system, and Δ_α provide the finiteness of potential at $r = R$. Figures 1 and 2 plot the mean flow velocities of the components in the presence of temperature and pressure gradients in capillary against parameter a_α . The velocities are normalized by those obtained in the absence of surface forces. It is seen that surface forces affect the gas flow in nanodimensional channels, this influence increasing with decreasing radius. Also, surface forces have a noticeable effect when Δ_α is small, i.e. when the effective value of a_α is large.

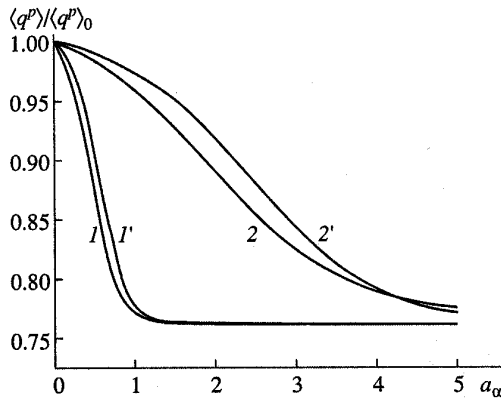


FIGURE 1. Relative velocity of the pressure-gradient related component flow vs. parameter a_α for a capillary of radius $R = (1, 2)$ 10 and $(1', 2')$ 20 nm. $\Delta_\alpha = (1, 1')$ 0.1 and $(2, 2')$ 0.3.

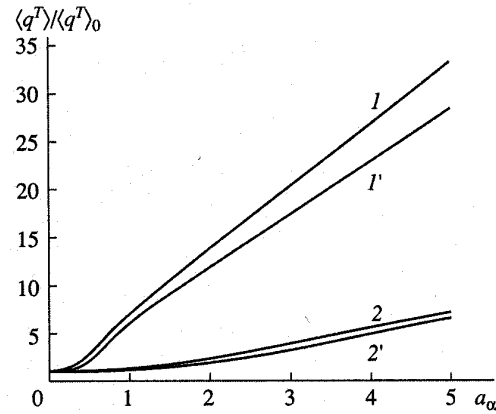


FIGURE 2. Relative velocity of the temperature-gradient related component flow vs. parameter a_α for a capillary of radius $R = (1, 2)$ 10 and $(1', 2')$ 20 nm. $\Delta_\alpha = (1, 1')$ 0.1 and $(2, 2')$ 0.3.

NON-EQUILIBRIUM THERMODYNAMICS OF GAS FLOW

It is interesting to note that the presence of surface forces slightly modifies the expression for the entropy production in the non-uniform gas mixture flowing through the capillary under the pressure, temperature and concentration gradients. Taking into account the contribution from intermolecular collisions and collisions of molecules with the surface of channel walls to the entropy production after transformations similar to those used in [2, 8], we arrive at the following expression for the entropy production

$$\Delta S = -\langle q_m \rangle \frac{\nabla p}{T} + [\langle J'_q \rangle + \langle J_1 U_1 \rangle + \langle J_2 U_2 \rangle] \frac{\nabla T}{T^2} - \frac{p}{T} (\langle q_1 \rangle - \langle q_2 \rangle) \nabla y_1, \quad (19)$$

where $\langle q_m \rangle$ is molar-averaged velocity of components, $\langle J'_q \rangle = \langle J_q \rangle - \frac{5}{2} \sum_{\alpha=1}^2 p_\alpha \langle q_\alpha \rangle$ is the reduced heat flux, J_1, J_2 are the particle number flux densities.

Phenomenological equations of non-equilibrium thermodynamics acquire now the following form

$$\begin{aligned} \langle q_m \rangle &= \lambda_{11} \frac{\nabla p}{T} + \lambda_{12} \frac{\nabla T}{T^2} + \lambda_{13} \frac{p}{T} \nabla y_1 \\ \langle J'_q \rangle + \langle J_1 U_1 \rangle + \langle J_2 U_2 \rangle &= \lambda_{21} \frac{\nabla p}{T} + \lambda_{22} \frac{\nabla T}{T^2} + \lambda_{23} \frac{p}{T} \nabla y_1 \\ \langle q_1 \rangle - \langle q_2 \rangle &= \lambda_{31} \frac{\nabla p}{T} + \lambda_{32} \frac{\nabla T}{T^2} + \lambda_{33} \frac{p}{T} \nabla y_1, \end{aligned} \quad (20)$$

where kinetic coefficients λ_{ij} should satisfy Onsager symmetry relation $\lambda_{ij} = \lambda_{ji}$. This symmetry relation can be easily proved within the framework of kinetic theory, for example, as was done in [9]. We do not perform these calculations in this work in order to avoid complicated mathematical manipulations, but consider the applicability of this relation at a qualitative level.

The presence of surface forces leads to appearance of additional summands in the expression for the matter flow caused by temperature gradient, i. e. in the kinetic coefficients λ_{12} and λ_{32} . These summands are proportional to the gas/surface potentials. During the flow of gas mixture under the pressure and concentration gradients, such summands are absent in the kinetic equation. However, the second equation of system (20) contains in its left-hand side the summands proportional to the gas/surface potentials. These additional terms provide the dependence of coefficients λ_{21} and λ_{23} on gas/surface potentials. Thereby, the identical structure of the λ_{12} and λ_{32} , and λ_{21} and λ_{23} coefficients and Onsager symmetry is evident.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Researches, project no. № 06-01-00374.

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