THEORY OF THE MOTION OF LARGE VOLATILE PARTICLES IN A DIFFUSING GAS MIXTURE

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Abstract

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THEORY OF THE MOTION OF LARGE VOLATILE PARTICLES IN A DIFFUSING GAS MIXTURE

In the authors' works (^{1}-^{4}), a theory was developed for the motion of large nonvolatile aerosol particles, as well as particles of solutions and volatile substances, in a diffusion field. All the particles indicated were assumed to be so large that the Knudsen number for them satisfies the condition

$$\mathrm{Kn} = \lambda_i / R \ll 1,$$

where λ_i is the mean free path of molecules of the i-th component of a binary gas mixture, and R is the particle radius.

The diffusiophoresis velocity in works (^{1}-^{4}) was calculated by considering the kinetic equations of gas transport through an "aerosol partition." At the same time the symmetry principle of kinetic coefficients (Onsager' s principle) was used. The most general results are those of work (^{4}), where the diffusiophoresis velocity of droplets of solutions with a volatile solvent was obtained.

In the limiting case when the concentration of a nonvolatile substance dissolved in the droplet tends to zero, the following formula was obtained in (^{4}) for the diffusiophoresis velocity of pure volatile droplets relative to the center of inertia of a binary gas mixture:

$$\mathbf{V}_D = -D_{12} \Delta C_1 / H = -D_{12}\,\mathrm{grad}\,C_1, \tag{1}$$

where H is the distance over which the jump in relative concentration ΔC_1 occurs; D_{12} is the coefficient of mutual diffusion of the mixture. Formula (1) was obtained under the condition that $C_1 \ll 1$. However, formula (1) is in contradiction with the result of work (^{5}), in which, for the first time, a method was developed for the direct calculation of the distribution of velocities and pressures around a volatile pure droplet and, on this basis, of the diffusion polarization force acting on the droplet in a diffusing gas mixture. This force, according to (^{5}), causes the particle to move toward the diffusion flux of the vapor, i.e., in the direction opposite to (1). Moreover, in magnitude the velocity obtained in (^{5}) is considerably smaller than that given by formula (1), and is equal (with the opposite sign) to the velocity of the Stefan flow relative to the gas. Therefore the total diffusiophoresis velocity of volatile particles relative to the laboratory coordinate system (connected with the gas), according to (^{5}), turns out to be zero. From formula (1), derived in (^{4}) on the basis of a thermodynamic approach, it follows that a one-component volatile droplet moves relative to the laboratory coordinate system in the direction coinciding with the vapor diffusion flux, with a velocity equal to the sum of the velocities (1) and the velocity of transport of the center of inertia.

The aim of the present work is to carry out a direct calculation of the diffusiophoresis velocity of a droplet of a volatile substance, based on a more correct account of the interaction of the pressure and velocity fields with the diffusion fields around the droplet in the boundary conditions.

Let us consider a droplet of a volatile substance of radius $R \gg \lambda_i$ in a homogeneous field of diffusion of the vapor of this substance in air (or in another gas). It is obvious that the fields of component concentrations arising around the droplet, and the distribution of velocities and pressures, must be found by means of a system

of the equations of convective diffusion and the hydrodynamics of a viscous mixture (^{6}). At small velocities and a small relative concentration of vapor (the first component), this system of equations takes the form:

$$\eta \Delta \mathbf{v} = \operatorname{grad} p; \tag{2}$$

$$\operatorname{div} \mathbf{v} = 0; \tag{3}$$

$$\Delta C_1 = 0, \tag{4}$$

where $\mathbf{v}$ is the total momentum of a unit mass of the mixture; η is the coefficient of viscosity; $C_1 = n_1/n$; n is the total number of molecules per unit volume; n_1 is the number of molecules of the first component per unit volume.

On the surface of the droplet the condition of vapor saturation holds, i.e.

$$n_1(R) = n_1(T), \tag{5}$$

where $n_1(T)$ is the absolute concentration (number of molecules) of the first component corresponding to vapor saturated at temperature T.

At infinity we prescribe an external one-dimensional diffusion flux

$$C_{1\,r\to\infty} = C_{01} + A_1 r\cos\theta, \tag{6}$$

where the constants

$$C_{01} = [C_1]_{\substack{r\to\infty \\ \theta=\pm 90^\circ}}, \qquad A_1 = [\partial C_1/\partial(r\cos\theta)]_{r\to\infty} \tag{7}$$

are regarded as given.

For the velocity components the boundary conditions will be

$$v_\theta = 0; \tag{8}$$

$$n_{0,2} v_r\big|_{r=R} - n_0 D_{12}\frac{\partial C_2}{\partial r}\bigg|_{r=R} + \frac{n_0^2 C_{01} C_{02}(m_2 - m_1)}{p_0\rho_0} D_{12}\frac{\partial p}{\partial r}\bigg|_{r=R} = 0, \tag{9}$$

where (8) is the condition of adhesion of the molecules on the surface of the volatile particle, and (9) is the condition that the total flux of air through any element of the droplet surface be equal to zero.

Since at any point outside the droplet the identity

$$C_1 + C_2 = 1, \tag{10}$$

holds, in (9) one may introduce $-\partial C_1/\partial r$ instead of $\partial C_2/\partial r$, and (9) takes the form:

$$n_{0,2} v_r\big|_{r=R} + n_0 D_{12}\frac{\partial C_1}{\partial r}\bigg|_{r=R} + \frac{n_0^2 C_{01} C_{02}(m_2 - m_1)}{p_0\rho_0} D_{12}\frac{\partial p}{\partial r}\bigg|_{r=R} = 0. \tag{11}$$

In relations (9) and (11) the following notation has been introduced: n_{02} is the number of air molecules per unit volume at infinity; n_0 is the total number of molecules per unit volume at infinity; $C_{01} = n_{01}/n_0$, $C_{02} = n_{02}/n_0$; n_{01} is the number of molecules of the first component (vapor) per unit volume at infinity; D_{12} is the coefficient of mutual diffusion; p_0 is the pressure of the mixture; ρ_0 is the mass density of the mixture at infinity; m_2 and m_1 are, respectively, the masses of air and water-vapor molecules.

It should be noted that boundary condition (11) differs substantially from the corresponding boundary condition in ([5]). Indeed, in (11) a third term with $\partial p/\partial r$ has been introduced, taking into account the phenomenon of barodiffusion of air. This leads to the inclusion of an essential correlation between the pressure field (and also the velocity field) and the concentration field. These fields are, as it were, coupled with one another precisely through condition (11).

If $|\mathbf{u}|$ is the absolute value of the velocity of the vapor-air mixture at infinity relative to the droplet, then, proceeding from equations (2), (3), and (4) and the boundary conditions (5)–(9) and (11), in the form (^{6,7}):

$$v_r = (A_2/r^3 + \beta/r + |\mathbf{u}|)\cos\theta + A_3/r^2, \tag{12}$$

$$v_\theta = (A_2/2r^3 - \beta/2r - |\mathbf{u}|)\sin\theta, \tag{13}$$

$$p = p_0 + \beta\eta\cos\theta/r^2, \tag{14}$$

$$C_1(r,\theta) = C_{01} + A_1 r\cos\theta + \beta\cos\theta/r^2. \tag{15}$$

For the correct use of condition (5), a relation between the relative and absolute density of the particles is necessary. For small concentration gradients and, correspondingly, small pressure gradients, the following relations will be valid:

$$n_1(r,\theta) = n_{01} + n_1'(r,\theta), \tag{16}$$

$$n(r,\theta) = n_0 + n'(r,\theta), \tag{17}$$

where $n_1(r,\theta)$ and $n(r,\theta)$ are, respectively, the number of molecules of the first component and the total number of molecules of the mixture per unit volume; $n_1'(r,\theta)$ and $n'(r,\theta)$ are the deviations of these quantities caused by the presence of an external concentration gradient and of the pressure gradient arising around the droplet. In this case

$$n_1'/n_{01} \ll 1, \qquad n'/n_0 \ll 1. \tag{18}$$

Keeping in $C_1 = n_1/n$ the terms linear in the concentration perturbations, we obtain

$$C_1 = n_{01}/n_0 + \left(n_1'/n_0 - n_{01}n'/n_0^2\right). \tag{19}$$

Proceeding from the definition of n' and relation (14), we obtain

$$n' = p'/kT = \beta\eta\cos\theta/kTr^2. \tag{20}$$

On the basis of (15)–(17), (19), and (20), we seek n_1' in the form

$$n_1' = a\cos\theta/r^2 + \gamma_1 r\cos\theta + \gamma_2 R/r. \tag{21}$$

Then, with the aid of boundary condition (5), we obtain

$$n_1'(R) = n_1(T) - n_{01}. \tag{22}$$

With the aid of the boundary conditions (6), (8), (9), (11)–(15), taking into account relations (19)–(22), one can obtain the constants $\gamma_2, \gamma_1, a, A_2$. If relation (11) is regarded as the projection onto the direction of the radius vector $\mathbf{r}$, then from it we obtain

$$\vec{\beta} = -\frac{3\,(-A_1 n_0 D_{12} + n_{02}\mathbf{u})}{\dfrac{2\eta n_0 C_{01} D_{12}}{p_0 R^3}\left[1 - \dfrac{n_0 C_{02}(m_2 - m_1)}{\rho_0}\right] + \dfrac{2n_{02}}{R}}. \tag{23}$$

The volatile particle moves under the action of the force of diffusion polarization and the force of viscous resistance. If the particle moves uniformly, then the sum of these forces is equal to zero. This resultant force can be calculated from relation (6, 7)

$$F = \int_0^\pi \left(-p\big|_{r=R}\cos\theta + \sigma_{rr}\big|_{r=R}\cos\theta - \sigma_{r\theta}\big|_{r=R}\sin\theta\right) 2\pi R^2 \sin\theta\, d\theta, \tag{24}$$

where σ_{rr} and $\sigma_{r\theta}$ are components of the stress tensor. As a result of integrating (24), we obtain

$$F = -\frac{6\pi\eta\,[A_1 n_0 D_{12} - n_{02}\mathbf{u}]}{\dfrac{\eta n_0 C_{01} D_{12}}{p_0 R^3}\left[1 - \dfrac{n_0 C_{02}(m_2 - m_1)}{\rho_0}\right] + \dfrac{n_{02}}{R}}. \tag{25}$$

Equating F to zero, we obtain

$$\mathbf{u} = \frac{n_0}{n_{02}} D_{12} A = \frac{n_0}{n_{02}} D_{12} \frac{\partial C_1}{\partial(r\cos\theta)}. \tag{26}$$

Further, recalling that $-\mathbf{u}$ is the velocity of diffusiophoresis, and that $\partial C_1/\partial(r\cos\theta) = \Delta C_1/H$ is the gradient of the mean concentration, we obtain, for the case $n_{02} \gg n_{01}$ and $n_0 \simeq n_{02}$,

$$\mathbf{V}_D = -D_{12}\Delta C_1/H. \tag{27}$$

Thus, the diffusiophoresis velocity obtained by direct calculation of the force acting on a one-component volatile droplet coincides

both in magnitude and in direction with the velocity obtained by us in (4) and expressed by formula (1).

Let us consider the practically encountered case of a vapor–gas mixture placed in a vessel, one wall of which serves as a source of vapor, while the opposite wall, parallel to it, is its absorber; the ordered component of the velocity of the gas molecules, normal to these walls, is equal to zero. In this case, as shown in ([2,3]), at a low vapor concentration ($n_1 \ll n$) the velocity of the center of inertia $\mathbf{V}_{\text{c.i.}}$ relative to the walls (or to the gas at rest) is equal to:

$$\mathbf{V}_{\text{c.i.}} \approx -D_{12}\frac{m_1}{m_2}\frac{\Delta C_1}{H}. \tag{28}$$

The diffusiophoretic velocity relative to the given laboratory coordinate system (i.e., relative to the gas) in this case is equal to the sum of (27) and (28):

$$\mathbf{V}_D^{(\ell)} = -D_{12}\left(1+\frac{m_1}{m_2}\right)\frac{\Delta C_1}{H}. \tag{29}$$

From comparison of formula (29) with the velocity of diffusiophoresis of non-volatile particles in the laboratory coordinate system, obtained by us in ([2,3]),

$$\mathbf{V}_D^{(n)} = -D_{12}\frac{n_0 m_2}{\rho}\frac{\Delta C_1}{H} \approx -D_{12}\frac{\Delta C_1}{H} \tag{30}$$

it is seen that (29) is somewhat larger than (30).

It should be noted that the velocity (29) will be many times greater than the velocity of a nonvolatile particle (30) if $m_1 \gg m_2$, for example, in the case of vapors of cetyl alcohol in an atmosphere of air or hydrogen.

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