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Abstract

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THEORY OF DIFFUSIOPHORESIS OF LARGE NONVOLATILE AEROSOL PARTICLES

In works by one of us ([1,2]), a theory of diffusiophoresis of small aerosol particles was developed ($\mathrm{Kn} = \lambda_i/R \gg 1$), where R is the particle radius, λ_i is the mean free path of molecules of the i-th component of a binary mixture. Brock ([3]) attempted to calculate the diffusiophoretic velocity of large particles ($\mathrm{Kn} \ll 1$). Taking into account the effect of "diffusiophoretic slip," he erroneously assumed that the distribution of velocities of gas molecules striking the surface of an aerosol particle differs insignificantly from the bulk one.

In the present work the diffusiophoretic velocity of large particles is found from the kinetic equations of gas transfer through an "aerosol partition"separating two vessels. The same method was applied in the theory of thermophoresis of large aerosol particles ([4–5]), as well as of diffusiophoresis of particles in solutions ([6]). The temperature is everywhere equal to T. Differences in the concentrations of the first and second gases, ΔC_1 and ΔC_2, and a pressure difference Δp are maintained between the vessels. Here $C_1 = n_1/n$, $C_2 = n_2/n$, where n_1 and n_2 are the numbers of molecules of the mixture components per unit volume, $n = n_1 + n_2$.

The rate of entropy production $\Delta\dot{S}$ for this case has the form ([7–8])

$$\Delta\dot{S} = -I_1\frac{\Delta\mu_1}{T} - I_2\frac{\Delta\mu_2}{T}, \tag{1}$$

where $I_1 = n_1\bar{v}_1$ and $I_2 = n_2\bar{v}_2$ are the volume flows of the gases through the partition; $\bar{v}_1$ and $\bar{v}_2$ are the mean linear components of the molecular velocities in the direction of the normal to the partition; $\Delta\mu_1$ and $\Delta\mu_2$ are differences of chemical potentials.

The barycentric volume flow velocity may be represented in the form

$$V = -I_1(\partial\mu_1/\partial p)_{C_1;C_2} - I_2(\partial\mu_2/\partial p)_{C_1;C_2}, \tag{2}$$

where $(\partial\mu_{1,2}/\partial p)_{C_1;C_2}$ are partial specific volumes, and (1) takes the form

$$\Delta\dot{S}_1 = V\Delta p - I_1\Delta_p\mu_1 - I_2\Delta_p\mu_2, \tag{3}$$

where

$$\Delta_p\mu_{1,2} = (\partial\mu_{1,2}/\partial p)_p\Delta C_1 + (\partial\mu_{1,2}/\partial p)_p\Delta C_2. \tag{4}$$

Introduce the quantity

$$I_k^* = I_k - n_{kV}, \tag{5}$$

(where $k = 1, 2$), which determines the volume flow of the given component after subtracting the transfer of it with the mean linear barycentric flow velocity. With the aid of the Gibbs-Duhem theorem it is easy to obtain

$$I_1\Delta_p\mu_1 + I_2\Delta_p\mu_2 = I_1^*\Delta_p\mu_1 + I_2^*\Delta_p\mu_2. \tag{6}$$

Substituting (6) into (3), we obtain:

$$\Delta\dot{S} = V\Delta p - I_1^*\Delta_p\mu_1 - I_2^*\Delta_p\mu_2, \tag{7}$$

where

$$I_1^* = -L_{11}\Delta_p\mu_1 - L_{12}\Delta_p\mu_2 + L_{13}\Delta p; \tag{8}$$

$$I_2^* = -L_{21}\Delta_p\mu_1 - L_{22}\Delta_p\mu_2 + L_{23}\Delta p; \tag{9}$$

$$V = -L_{31}\Delta_p\mu_1 - L_{32}\Delta_p\mu_2 + L_{33}\Delta p. \tag{10}$$

According to (8), (9) and Onsager' s principle,

$$L_{31} = L_{13} = \frac{I_1^*|_{C_1;C_2}}{\Delta p}; \qquad L_{23} = L_{32} = \frac{I_2^*|_{C_1;C_2}}{\Delta p}. \tag{11}$$

From (10) and (11) we obtain the velocity of diffusional osmosis:

$$V|_{\Delta p=0} = -\left(\frac{I_1^*|_{C_1;C_2}}{\Delta p}\Delta_p\mu_1 + \frac{I_2^*|_{C_1;C_2}}{\Delta p}\Delta_p\mu_2\right), \tag{12}$$

or, with the aid of (6):

$$V|_{\Delta p=0} = -\left(\frac{I_1|_{C_1;C_2}}{\Delta p}\Delta_p\mu_1 + \frac{I_2|_{C_1;C_2}}{\Delta p}\Delta_p\mu_2\right). \tag{13}$$

Writing the Gibbs-Duhem relation in the form

$$n_1\Delta_p\mu_1 + n_2\Delta_p\mu_2 = 0, \tag{14}$$

one can obtain from (13) and (14)

$$V\big|_{\Delta p=0} = \frac{n_1(\overline{v}_2 - \overline{v}_1)\big|_{C_1;C_2}}{\Delta p}\,\Delta_p\mu_1. \tag{15}$$

Let us consider (15) for a partition made of spheres of radius $R \gg \lambda_i$, fixed at random at distances much greater than the radius.

The velocity of mutual diffusion $(\overline{v}_2 - \overline{v}_1)$ is obtained from the diffusion equation with allowance for barodiffusion ([9,11,12]):

$$(\overline{v}_2 - \overline{v}_1) = \frac{n^2}{n_1 n_2} D_{12}\left\{\overline{\operatorname{grad} C_1} + \frac{n_1 n_2(m_2 - m_1)}{\rho p}\,\overline{(\operatorname{grad}\ln p)}\right\}. \tag{16}$$

For $\overline{\operatorname{grad} C_1} = 0$, (16) takes the form

$$(\overline{v}_2 - \overline{v}_1)\big|_{C_1;C_2} = D_{12}\frac{n(m_2 - m_1)}{n\rho}\,\overline{\operatorname{grad} p}. \tag{17a}$$

In equations (16) and (17) ρ is the mean density of the mixture; m_2 and m_1 are the molecular masses; D_{12} is the coefficient of mutual diffusion. The flux (17a) cannot be directly substituted into (15), owing to the presence of local diffusion fluxes penetrating the considered section of the partition in the direction opposite to the flux (17a), and amounting to 2/3 of it, as is shown by a calculation analogous to that carried out in the theory of thermophoresis ([4,5]).

Therefore, instead of (17a) we have:

$$(\overline{v}_2 - \overline{v}_1)\big|_{C_1;C_2} = \frac{1}{3}D_{12}\frac{n(m_2 - m_1)}{\rho p}\,\overline{\operatorname{grad} p}. \tag{17b}$$

However, (17b) is not equal to the true velocity of mutual diffusion of the mixture under the condition

$$C_1 = \text{const}, \qquad C_2 = \text{const} \tag{18}$$

because of the perturbing influence of the gas concentration fields around each sphere, which violate conditions (18). Analogously ([4,5]), it was necessary to take into account the thermal polarization of each sphere and of the partition as a whole.

To determine the concentration field around a sphere at small velocities, we integrate the equation ([13,14])

$$\Delta C_1' = 0 \tag{19}$$

with the boundary conditions

$$C_1'(r) \to 0 \quad \text{as } r \to \infty, \tag{20}$$

$$-nD_{12}\frac{\partial C_1'}{\partial r}\bigg|_{r=R} + \frac{n^2 C_1 C_2 (m_2 - m_1)}{\rho p} D_{12}\overline{\operatorname{grad}_r p}\bigg|_{r=R} = 0. \tag{21}$$

Equation (19) is obtained if one takes the divergence of the diffusion flux of the first component I_1^* and takes into account the smallness of $\Delta p/p$ and the equality $\operatorname{div}\operatorname{grad} p = 0$, which follows from the Navier-Stokes equations ([19])

$$\eta \Delta \mathbf{v} = \operatorname{grad} p, \qquad \operatorname{div} \mathbf{v} = 0. \tag{22}$$

In (21) the term with the surface divergence of the flux (mass transfer) of component I in the Knudsen layer, caused by the tangential shear stress, has been omitted. This has been done by analogy with (15), where it was shown that, in calculating thermophoresis, heat transfer in the Knudsen layer may be neglected. In what follows, the theory will be refined by taking transfer in the Knudsen layer into account.

To determine $\overline{\operatorname{grad}_r p}\big|_{r=R}$ in condition (21), it is necessary to integrate equations (22) with the boundary conditions:

$$\mathbf{v} = \mathbf{u} \quad \text{as } r \to \infty; \qquad v_r = 0 \quad \text{at } r = R;$$

$$v_\theta = C_m \lambda \left[r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial \theta} \right]_{r=R}. \tag{23}$$

In the boundary condition (23), v_θ and v_r are the polar and radial components of the velocity, equal to the momentum per unit mass of the gas mixture, and r and θ are polar coordinates with the axis OZ, parallel to the flow velocity $\mathbf{u}$ far from the sphere; C_m, according to (16), for diffuse reflection of molecules is

equal to 1.09; λ is their mean free path. An analysis of the boundary conditions (23) is given in ([17,18]). The solution of equations (22) gives

$$\operatorname{grad} p = A\eta[3(\mathbf{ur})\mathbf{r}/r^5 - \mathbf{u}/r^3], \tag{24}$$

where η is the viscosity and

$$A = {}^3\!/_4 R(1 + 2C_m\lambda/R)/(1 + 3C_m\lambda/R). \tag{25}$$

The solution of equation (19) with the boundary conditions (20) and (21), taking (24) into account, has the form:

$$C_1'(r) = 2nC_1C_2(m_2 - m_1)A\eta|\mathbf{u}|\cos\theta/\rho p r^2. \tag{26}$$

By analogy with electrostatics, one may assert that the concentration field (26) is produced by a dipole with moment

$$\mathbf{K}_0 = 2nC_1C_2(m_2 - m_1)A\eta|\mathbf{u}|/\rho p. \tag{27}$$

When the distance between spheres is large, the concentration fields of the individual spheres are summed, and the partition acquires, as a polarized dielectric, a moment of concentration polarization $\mathbf{K} = N\mathbf{K}_0$ (where N is the number of spheres per unit volume), forming a concentration drop

$$\Delta C_1' = -4\pi KH. \tag{28}$$

Analogously to (28), $\Delta C_2'$ is calculated. The occurrence of the concentration drops $\Delta C_1'$ and $\Delta C_2'$ at the partition will violate condition (18); to eliminate this it is necessary to introduce compensating mass sources and sinks at the surfaces of the partition. In this case the velocity of mutual diffusion due to these sources is calculated from (16) for $\operatorname{grad}\ln p = 0$, if $\Delta C_1'/H$ is substituted instead of $\overline{\operatorname{grad} C_1}$, and, with the aid of (27), (28), and (16), we obtain

$$(\overline{v_2 - v_1})'|_{C_1;C_2} = D_{12}\frac{n(m_2 - m_1)}{\rho p}\frac{\Delta p}{H}. \tag{29}$$

In deriving (29) we used the relation obtained in ([5])

$$\Delta p/NH = F = 8\pi\eta|\mathbf{u}|A.$$

We obtain the true diffusion velocity by summing (17b) and (29):

$$(v_2 - v_1)^*|_{C_1;C_2} = \frac{4}{3} D_{12} \frac{n(m_2 - m_1)}{\rho p} \frac{\Delta p}{H}. \tag{30}$$

The velocity of gas transfer relative to the spheres from (30) and (15) is equal to

$$V_{\text{pollen}} = \frac{4}{3} D_{12} \frac{n_1 n(m_2 - m_1)}{\rho p} \frac{\Delta_p \mu_1}{H}. \tag{31}$$

The mean gradient of the chemical potential is

$$\Delta_p \mu_1 / H = \overline{\operatorname{grad}_p \mu_1} = kT \, \overline{\operatorname{grad} C_1 / C_1}. \tag{32}$$

Substituting (32) into (31) and using the relation $p = nkT$, we obtain:

$$V_{\text{pollen}} = \frac{4}{3} D_{12} \frac{n(m_2 - m_1)}{\rho} \overline{\operatorname{grad} C_1}. \tag{33}$$

The "barycentric" velocity of diffusiophoresis of the spheres is obtained by changing the sign to the opposite:

$$V_D = -V_{\text{pollen}} = -\frac{4}{3} \frac{D_{12} n(m_2 - m_1)}{\rho} \overline{\operatorname{grad} C_1}. \tag{34}$$

Let us now consider diffusiophoresis in a vapor-gas mixture in a vessel, one wall of which is a vapor source (1), and the opposite one is an absorber. Relative to the walls of the chamber $\overline{v_2} = 0$, and the center of inertia of the mixture, as is easy to show, moves with velocity ([10])

$$V_{\text{c.i.}} = -D_{12} \frac{n m_1}{\rho} \overline{\operatorname{grad} C_1}. \tag{35}$$

Summing (34) and (35), we obtain the diffusiophoretic velocity of aerosol particles relative to the gas:

$$V_D = -D_{12} \frac{n(4m_2 - m_1)}{3\rho} \operatorname{grad} \overline{C}_1. \tag{36}$$

From (36), for the diffusiophoretic force on a particle we obtain

$$F_D = 6\pi\eta R V_D. \tag{37}$$

Formula (37) can be compared with the results of measurements by P. S. Prokhorov and L. F. Leonov [(20)] of the repulsive force between a silvered glass

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

sphere and an evaporating water droplet, plotted in Fig. 1 along the ordinate axis as a function of the distance between them. Curve 1 corresponds to an air humidity of 0%, curve 2 to 40%. We see that the theory

Fig. 1

Fig. 2

is in satisfactory agreement with experiment. Formula (36) was compared with measurements of the diffusiophoretic velocity [22] from the deflection of a thin aerosol jet, by a method previously successfully applied to measure the thermophoretic velocity [21].

In the measurements an aerosol of vaseline oil was used; the experimental values for vaseline oil with a mean particle radius of about $0.25 \cdot 10^{-4}$ cm are plotted in Fig. 2 as a function of $1/p^2$. Straight line 1 is constructed from formula (36), straight line 2 from the formula derived earlier by B. V. Deryagin and S. P. Bakanov [1,2], for the opposite limiting case

$$\mathrm{Kn} \equiv \lambda/R \gg 1.$$

For $\mathrm{Kn} < 0.5$ formula (36) is well applicable; the formula for small particles is obeyed for $\mathrm{Kn} > 0.7$. Thus, the transition region between the regimes of "small" and "large" particles proves to be very narrow.

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Note: Figure translations are in progress. See original paper for figures.