THEORY OF THE MOTION OF DROPLETS OF SOLUTIONS IN A DIFFUSING BINARY GAS MIXTURE

PHYSICS

1967

SovietRxiv

Abstract

Full Text

UDC 533.15

PHYSICS

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THEORY OF THE MOTION OF DROPLETS OF SOLUTIONS IN A DIFFUSING BINARY GAS MIXTURE

The theory of diffusiophoresis of large nonvolatile and volatile one-component aerosol particles was constructed by us in papers ($^{1-4}$). Under real conditions, droplets, as a rule, contain dissolved substances, forming dilute solutions. The velocity of such large droplets of solutions (whose Knudsen number $\mathrm{Kn} \ll 1$) is calculated in the present paper.

Analogously to ($^{1-4}$), let us consider two vessels with a binary gas mixture, separated by a partition formed by spherical droplets of a solution of radius $R \gg \lambda_i$ (λ_i is the mean free path of molecules of the i-th component of the mixture), fixed at distances much greater than R. On both sides of the partition there are maintained differences in the component concentrations ΔC_1 and ΔC_2 and a pressure difference Δp. Here $C_1 = n_1/n$ and $C_2 = n_2/n$, where n_1 and n_2 are the numbers of molecules of the mixture components per unit volume, $n = n_1 + n_2$. According to ($^{1-4}$), the general expression for the diffusiophoretic velocity of particles relative to the center of inertia of the mixture is equal to:

$$V_D = -V\big|_{\Delta p=0} = -\frac{n_{01}(\bar{v}_2 - \bar{v}_1)^*\big|_{C_1;C_2}}{\Delta p}\,\Delta_p\mu_1, \tag{1a}$$

where n_{01} is the number of molecules of the first component per unit volume at infinity; $V\big|_{\Delta p=0}$ is the mean velocity of transfer of the center of inertia of the mixture relative to the droplets, taken in the absence of a pressure difference at the ends of the partition; $\Delta_p\mu_1$ is the difference of the chemical potential of the first component at the ends of the partition at $\Delta p = 0$; $(\bar{v}_2 - \bar{v}_1)^*\big|_{C_1;C_2}$ is the total, cross-section-averaged velocity of mutual diffusion of the mixture components in the direction normal to the cross-section of the partition, in the absence of concentration gradients, caused only by the pressure difference. According to ($^{1-4}$)

$$(\bar{v}_2 - \bar{v}_1)^*\big|_{C_1;C_2} = (\bar{v}_2 - \bar{v}_1)\big|_{C_1;C_2} - (\bar{v}_2 - \bar{v}_1)_S\big|_{C_1;C_2} + (\bar{v}_2 - \bar{v}_1)'\big|_{C_1;C_2}, \quad (1b)$$

where

$$(\bar{v}_2 - \bar{v}_1)\big|_{C_1;C_2} = D_{12}\frac{n_0(m_2 - m_1)}{p_0\rho_0}\operatorname{grad} p \quad (2)$$

is the velocity of mutual diffusion in the volume of the gas, undisturbed by aerosol particles; $(\bar{v}_2 - \bar{v}_1)_S\big|_{C_1;C_2}$ is the counterflow caused by local diffusive fluxes; $(\bar{v}_2 - \bar{v}_1)'\big|_{C_1;C_2}$ is the additional flux introduced in order to maintain the conditions

$$C_1 = \text{const}, \qquad C_2 = \text{const}, \quad (3)$$

necessary for the validity of (1a) and (1b). In (2), D_{12} is the mutual-diffusion coefficient; ρ_0 is the density, p_0 the pressure at infinity; m_2 and m_1 are the masses of the component molecules; n_0 is the total number of molecules of the mixture per unit volume at infinity.

To find the second and third fluxes in the right-hand side of (1b), let us calculate the distribution of velocities and pressures around droplets at $\Delta p \neq 0$ and $\Delta C_1 = \Delta C_2 = 0$ by means of the equations

$$\eta\Delta\mathbf{v} = \operatorname{grad} p, \quad (4)$$

$$\operatorname{div}\rho\mathbf{v} = 0; \quad (5)$$

where $\mathbf{v}$ is the total momentum of a unit mass of the mixture; η is the viscosity. Let us choose the origin of coordinates at the center of the drop, and direct the polar axis z along the velocity of the mixture at infinity. The boundary conditions on the vapor-drop surface have the form

$$v_\theta\big|_{r=R} = 0, \quad (6)$$

$$n_{02}v_r\big|_{r=R} - n_0 D_{12}\frac{\partial C_2}{\partial r}\bigg|_{r=R} + \frac{n_0^2 C_{01}C_{02}(m_2 - m_1)}{p_0\rho_0}D_{12}\frac{\partial p}{\partial r}\bigg|_{r=R} = 0, \quad (7)$$

where n_{02} is the number of molecules of the second component per unit volume; C_{01} and C_{02} are the concentrations of the components at infinity.

Condition (6) is the condition of adhesion of molecules to the surface of the volatile drop. Diffusional slip of the mixture along the surface contributes about 10% to the total rate of diffusiophoresis, as shown in (^{4}), and we do not take it into account. Condition (7) expresses the absence of a total flux of the second component through the surface of the drop. The first term in (7) is the flux caused by the radial mass-average transport velocity of the mixture, the second is the diffusion flux caused by the presence of a concentration gradient, and the third is the radial barodiffusion flux, calculated on the basis of the kinetic theory of gases (^{5}, ^{7}). From the obvious condition $C_1 + C_2 = 1$ at any point of the volume of the mixture, we obtain

$$\partial C_1/\partial r = -\partial C_2/\partial r. \tag{8}$$

From (7) and (8) we have:

$$n_{02} v_r\big|_{r=R} + n_0 D_{12} \frac{\partial C_1}{\partial r}\bigg|_{r=R} + \frac{n_0^2 C_{01} C_{02} (m_2 - m_1)}{p_0 \rho_0} D_{12} \frac{\partial p}{\partial r}\bigg|_{r=R} = 0. \tag{9}$$

At infinity the gas velocity is $\mathbf{u}$, and the pressure is p_0. The concentration field of the dissolved substance in the drop C (for $r < R$) and outside the drop C_1 (for $r > R$) at small velocities is determined from the equations of stationary diffusion

$$\nabla^2 C = 0, \qquad \nabla^2 C_1 = 0. \tag{10}$$

On the surface of the drop, according to Raoult' s law, we have

$$n_1(R) = n_1(T)[1 - C(R, \theta)], \tag{11}$$

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

The radial flux of the first component is continuous at the surface of the drop:

$$-n_0 D_{12} \frac{\partial C_1}{\partial r}\bigg|_{r=R} + \frac{n_{01} n_{02} (m_1 - m_2)}{p_0 \rho_0} D_{12} \operatorname{grad}_r p\big|_{r=R} =$$

$$= n_{1i} v'_r\big|_{r=R} - n_{iD} \frac{\partial C_{1i}}{\partial r}\bigg|_{r=R}, \tag{12}$$

where C_{1i} and n_{1i} are the relative and absolute concentrations of the first component (volatile) inside the drop; n_i is the total number of molecules per unit volume of the drop; D is the diffusion coefficient of the dissolved substance; v'_r is the mass-average radial velocity of the liquid inside the drop.

Since $C + C_{1i} = 1$ for $r \leq R$, then

$$\partial C_{1i}/\partial r = -\partial C/\partial r. \tag{13}$$

The condition that the radial flux of the nonvolatile substance dissolved in the drop through its surface be equal to zero has the form

$$(n_c v_r' - n_{iD} \partial C/\partial r)_{r=R} = 0, \tag{14}$$

where n_c is the number of molecules of the dissolved substance per unit volume of the drop. Note that $C|_{r=0} = C_0$. Further, to within terms proportional to the small perturbation of the concentrations inside the drop, we have $C_0 \approx n_c/n_i$. By

by definition

$$C_1 = n_1/n = [n_{01} + n_1'(r,\theta)]/[n_0 + n'(r,\theta)], \tag{15}$$

where $n_1'(r,\theta)$ and $n'(r,\theta)$ are deviations from the values of the absolute concentrations at infinity, caused by the presence of local diffusion fields around the droplets. In view of the smallness of the perturbations, $n_1'(r,\theta) \ll n_0$ and $n'(r,\theta) \ll n_0$. From (15), accurate to terms of first order of smallness, we have:

$$C_1 = n_{01}/n_0 + n_1'/n_0 - (n_{01}/n_0)(n'/n_0). \tag{16}$$

For what follows we need the following solutions of equations (4), (5), and (10), taking into account the boundary conditions (6), (7), (11)–(14) and relation (16):

$$p = p_0 + \frac{\beta\eta}{r^2}\cos\theta, \qquad C_1 = \frac{n_1(T)}{n_0}(1 - C_0) + \frac{B_1 \cos\theta}{r^2}, \tag{17}$$

where

$$B_1 = -\frac{n_1(T)}{n_0}\left[B_2 R^3 + \frac{\beta\eta(1 - C_0)}{p_0}\right]; \tag{18}$$

$$B_2 = \frac{2C_0 \eta D_{12}[n_0^2 C_{01} C_{02}(m_2 - m_1) - n_1(T)\rho_0(1 - C_0)]}{p_0 \rho_0 R^3 [2n_1(T) D_{12} C_0 + n_{1i} D]}\beta; \tag{19}$$

$$\beta = -\frac{3}{2}|u|\left[\frac{R}{\gamma_2 + D_{12}(n_1(T)/n_{02})R\gamma_1 + D_{12} n_1(T)\eta(1 - C_0)/n_{02} p_0 R^2}\right]; \tag{20}$$

$$\gamma_1 = \frac{2C_0\eta D_{12}[n_0^2 C_{01}C_{02}(m_2-m_1) - n_1(T)\rho_0(1-C_0)]}{p_0\rho_0 R^3[2n_1(T)D_{12}C_0 + n_{1i}D]}; \tag{21}$$

$$\gamma_2 = \left[1 - \frac{n_0^2 C_{01}C_{02}(m_2-m_1)D_{12}\eta}{p_0\rho_0 n_{02}R^2}\right]. \tag{22}$$

The concentration field (17) around each droplet is produced by a dipole with moment $|\mathbf{k}_0| = B_1$, by analogy with (1-4). Since the distances between the spheres are large in comparison with their sizes, a unit volume of the partition acquires (analogously to a polarized dielectric) a moment of concentration polarization

$$|\mathbf{k}| = N|\mathbf{k}_0| = NB_1, \tag{23}$$

where N is the number of spheres per unit volume.

At the ends of a partition of length H there arises a concentration difference $\Delta C_1 = -4\pi|\mathbf{k}|H$, which determines the gradient of the concentration averaged over the cross section of the partition in the direction perpendicular to the partition in the volume of the gas:

$$\Delta C_1/H = \mathrm{grad}\,\overline{C}_1 = -4\pi|\mathbf{k}|. \tag{24}$$

To eliminate the resulting violations of condition (3), we introduce sources and sinks of mass at the ends, neutralizing ΔC_1 and ΔC_2. The rate of mutual diffusion due to the additional sources is determined from the general diffusion equation for a binary gas mixture, taking into account (23) and (24), and is equal to

$$(\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1)'\,\Big|_{C_1;C_2} = 4\pi\,\frac{n_0^2}{n_{01}n_{02}}\,D_{12}B_1N. \tag{25}$$

Let us calculate the flux that is the second term on the right-hand side of relation (3). The radial, local, barodiffusion, isoconcentration flux at the surface of the sphere is equal to (1-4)

$$n_{01}(\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1)_{r=R}\,\Big|_{C_1;C_2} = \frac{n_{01}n_{02}(m_2-m_1)}{p_0\rho_0}\,D_{12}\,\mathrm{grad}_r\,p\,\Big|_{r=R}. \tag{26}$$

Using (26), taking (17) into account, one can calculate (as in papers (1-4)) the total flux averaged over the cross section of the partition, caused by the presence of local diffusion fluxes that begin and end at the surface of the drops and pass through the cross section of the partition in the direction opposite to flux (2):

$$n_{01}(\bar{\mathbf{v}}_2 - \bar{\mathbf{v}}_1)_S\big|_{C_1;\,C_2} = {}^2/_3\,\frac{n_{01}n_0(m_2 - m_1)}{p_0\rho_0}\,D_{12}\frac{\Delta p}{H}. \tag{27}$$

In papers (2–4) we showed that the average pressure gradient over the cross section of the partition, $\overline{\operatorname{grad} p}$, entering into (2), and the gradient of the mean pressure, $\operatorname{grad}\bar{p}$, equal to $\Delta p/H$, are related by

$$\overline{\operatorname{grad} p} = {}^2/_3 \Delta P/H. \tag{28}$$

Consequently, $(\bar{\mathbf{v}}_2 - \bar{\mathbf{v}}_1)^*\big|_{C_1;\,C_2}$, from relation (16), taking into account (2), (27), (28), (25), and (18), is found to be

$$(\bar{\mathbf{v}}_2 - \bar{\mathbf{v}}_1)^*\big|_{C_1;\,C_2} = -\frac{4\pi n_1(T)n_0}{n_{01}n_{02}}\,D_{12}\left[\gamma_1 R^3 + \frac{\eta(1 - C_0)}{p_0}\right]\beta N. \tag{29}$$

After substituting (29) into (1a), taking into account relation (6, 8)

$$F = -4\pi\beta\eta = \Delta p/NH \tag{30}$$

and the obvious expression $\Delta_p\mu_1 = kT\Delta C_1/C_\alpha$, we have

$$V_D = -D_{12}\frac{n_1(T)n_0}{n_{02}n_{01}\eta}\left[p_0\gamma_1 R^3 + \eta(1 - C_0)\right]\frac{\Delta C_1}{H}. \tag{31}$$

For one-component drops $C_0 = 0$. Then $\gamma_1 = 0$, and, for $n_{01} \ll n_{02}$, we obtain

$$V_D^{(\text{vol})} = -D_{12}\Delta C_1/H, \tag{32}$$

which coincides with the velocity obtained by us by direct calculation of the forces acting on a volatile one-component drop in a diffusion field (9).

For nonvolatile particles the diffusion coefficient inside the particle is $D = 0$, and formula (31) takes the form

$$V_D^{(\text{nonvol})} = -\frac{n_0(m_2 - m_1)}{\rho_0}\,D_{12}\frac{\Delta C_1}{H}, \tag{33}$$

which coincides with the velocity calculated by us by the same method, but for the case of impermeable solid aerosol particles (2, 3).

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Received
3 XII 1966

CITED LITERATURE

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