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Abstract

Full Text

PHYSICAL CHEMISTRY

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THEORY OF THE FORCE INTERACTION OF RESTING DROPLETS AT ANY DISTANCE AT THE PSYCHROMETRIC TEMPERATURE

In work ⁽¹⁾, the diffusional interaction of droplets was considered in the first approximation, for droplets so far removed from one another that each of them may be regarded as being in the homogeneous diffusion field of the other. The ratio of the partial density of vapor ρ' to the partial density of air ρ'' is a small parameter of this theory,

$$\lambda = \rho' / \rho'' \ll 1. \tag{1}$$

Below are given calculations of the analogous interaction of resting droplets at any* distance under stationary and adiabatic course of the phase transition, taking into account terms of the first and second orders of smallness in λ . Using the similarity of the processes of heat transfer and diffusion, it is not difficult to show that under adiabatic course of the phase transition, i.e., in the absence of sources or sinks of heat in the droplet, the temperature T along the surfaces of the droplets does not change and is equal to the psychrometric temperature. This determines a certain specificity of the interaction and facilitates its consideration.

1. Using (1), let us write the equations and boundary conditions determining the field of velocities and diffusion fluxes during the phase transition on the surfaces of spherical particles (droplets) 1 and 2 of radii R_1 and R_2 , which we shall assume to be isothermal and at rest relative to the vapor-air medium (at ∞); for this purpose we associate spherical coordinate systems with the droplets, with origins at the centers of the droplets:

$$\rho(\mathbf{v}\nabla)\mathbf{v} = -\text{grad } p + \eta\Delta\mathbf{v} + (\zeta + \eta/3)\text{grad div } \mathbf{v}; \tag{2}$$

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

$$\text{div} \left[\rho''\mathbf{v} + D(\rho'' + \rho')\nabla \frac{\rho'}{\rho'' + \rho'} \right] = 0; \tag{4}$$

$$p = RT(\rho''/\mu'' + \rho'/\mu'); \quad (5)$$

$$\mathbf{v}|_{r \rightarrow \infty} = 0; \quad (6)$$

$$\rho'|_{r \rightarrow \infty} = \rho'_\infty = \text{const}; \quad (7)$$

$$\rho'(R_1) = \rho'_s[T(R_1)], \quad \rho'(R_2) = \rho'_s[T(R_2)]; \quad (8)$$

$$\left[\rho'' v_2 + D(\rho'' + \rho') \nabla \frac{\rho'}{\rho'' + \rho'} \right]_{r_1=R_1} = 0, \quad (9)$$

$$\left[\rho'' v_2 + D(\rho'' + \rho') \nabla \frac{\rho'}{\rho'' + \rho'} \right]_{r_2=R_2} = 0;$$

$$v_{\theta_1}(R_1, \theta_1) = 0, \quad v_{\theta_2}(R_2, \theta_2) = 0. \quad (10)$$

* At a very small distance between the surfaces of the droplets, the pressure in the vapor-air gap between them increases greatly ⁽²⁾, as a result of which the shape of the droplets deviates from spherical and the proposed theory becomes inapplicable.

where v is the velocity of the mixture particles, p is the pressure, η and ζ are the coefficients of ordinary and bulk viscosity of air, $\rho = \rho'' + \rho'$, μ' and μ'' are the molecular weights of vapor and air, D is the coefficient of diffusion of vapor in air, and $\rho'_s(T)$ is the density of saturated vapor at temperature T .

The character of the boundary conditions (6)–(10) suggests that there should be a relation between the fields of velocities and partial concentrations:

$$v = -D(1 + \rho'/\rho'') \nabla \frac{\rho'}{\rho'' + \rho'}. \quad (11)$$

Indeed, under this condition (9) and equation (4) are satisfied identically; condition (6) is fulfilled, since (7) holds; condition (10) is fulfilled for isothermal surfaces by virtue of (8) and the smallness of the deviation of ρ'' from a constant value at the surfaces, which follows from a special estimate of the deviation of the pressure from a constant value using (2), (5), (6), and (10). Relation (11) has a simple and important physical meaning: the total flux of air at every point of space (and not only on the boundary surfaces, as already follows from (9) and (10)) is zero; the vapor diffuses through motionless air. It is remarkable that the Stefan laminar flow ($\text{Re} \ll 1$) of a viscous medium turns out to be potential*,

since the right-hand side of (11) is equal to the gradient of the potential φ , equal to:

$$\varphi = -D \ln(1 + \rho' / \rho''). \quad (12)$$

This substantially facilitates the problem of calculating the diffusion forces, since instead of the exceptionally complicated system of equations and boundary conditions (2–10) it is sufficient to consider the equation for φ .

2. The equation for φ , obtained from (3) by substituting ρ and v expressed through φ , is conveniently transformed into an equation for the function $\chi = (\varphi - \varphi|_{r \rightarrow \infty}) / D$, which, under condition (1), if only terms of the first and second orders with respect to λ are retained, takes the form

$$\Delta \chi + (1 - \mu'' / \mu') (\Delta \chi)^2 = 0. \quad (13)$$

At infinity χ is equal to zero; on the surfaces of the droplets it takes constant values

$$\chi(R_1, \theta_1) = \tau_1 = \delta \rho'_1 / \rho'' + O(\lambda^2), \quad \chi(R_2, \theta_2) = \tau_2 = \delta \rho'_2 / \rho'' + O(\lambda^2), \quad (14)$$

where

$$\delta \rho'_1 = \rho'(R_1) - \rho'_\infty, \quad \delta \rho'_2 = \rho'(R_2) - \rho'_\infty.$$

Expand χ in a series in powers of λ : $\chi = \chi_1 + \chi_2 + \dots$, where χ_1 will be of order λ , and χ_2 of order λ^2 . To determine χ_1 and χ_2 we obtain the equations

$$\Delta \chi_1 = 0; \quad (15)$$

$$\chi_1(R_1) = \tau_1, \quad \chi_1(R_2) = \tau_2, \quad \chi_1|_{r \rightarrow \infty} = 0; \quad (16)$$

$$\Delta \chi_2 + (1 - \mu'' / \mu') (\nabla \chi_1)^2 = 0; \quad (17)$$

$$\chi_2(R_1) = 0, \quad \chi_2(R_2) = 0, \quad \chi_2|_{r \rightarrow \infty} = 0. \quad (18)$$

* Windless motion gives no solutions of the hydrodynamics of a viscous fluid because, while satisfying the basic equations, it does not satisfy the boundary conditions. The potential character of the Stefan flow is connected with the peculiarity of the boundary conditions at the surfaces of phase transition.

Since χ_1 is a harmonic function, a particular solution of (17) will be $(\mu''/\mu' - 1)\chi_1^2/2$; thus for χ , discarding terms above second order in λ , we obtain

$$\chi = \chi_1 + \psi + (\mu''/\mu' - 1)\chi_1^2/2, \quad (19)$$

where ψ is a harmonic function.

3. The components of the viscous-stress tensor can be expressed directly through χ_1 , taking into account (15), (16), and (19), and expressing p through χ_1 with the aid of (2), which is transformed by interchanging the differential operators and subsequent integration. Then, for the resultant force exerted by drop 1 on drop 2, by means of elementary, though rather cumbersome, transformations that take (19) into account, we obtain

$$\begin{aligned} F &= 2\pi R_2^2 \int_0^\pi (p_{rr} \cos \theta_2 - p_{2\theta} \sin \theta_2) \sin \theta_2 d\theta_2 = \\ &= 4\pi R_2^2 D\eta \{ [1 + (\mu''/\mu' - 1)\chi_1(R_2)] I_1(\chi_1) + I_1(\psi) + \\ &\quad + \frac{1}{2} \left[\left(\frac{4}{3} - \zeta/\eta \right) (\mu''/\mu' - 1) + D/2\nu \right] I_2(\chi_1) \}, \end{aligned} \quad (20)$$

where

$$I_1(\chi_1) = \int_0^\pi \left[\cos \theta_2 \frac{\partial^2 \chi_1}{\partial r_2^2} - \sin \theta_2 \frac{\partial}{\partial r_2} \left(\frac{1}{r_2} \frac{\partial \chi_1}{\partial r_2} \right) \right]_{r_2=R_2} \sin \theta_2 d\theta_2,$$

$$I_2(\chi_1) = \int_0^\pi \left(\frac{\partial \chi_1}{\partial r_2}(R_2) \right)^2 \cos \theta_2 \sin \theta_2 d\theta_2.$$

4. As is known (d' Alembert' s paradox), a body moving in an ideal incompressible fluid experiences no resistance. Although the potential Stefan flow has a laminar viscous character, it is likewise possible to show for it that the resultant force acting on a drop* in a viscous medium is equal to zero if the velocity potential is a harmonic function, while the inertial term, which in this case is of the second order of smallness, may be neglected. Since under these restrictions the resultant force contains only the terms with $I_1(\chi_1)$ and $I_1(\psi)$, the statement formulated above follows from the equality of $I_1(\psi)$ to zero, where φ is an arbitrary harmonic function. Taking the second approximation into account,

$$F = \kappa 2\pi R_2^2 \int_0^\pi \left(\frac{\partial \chi_1}{\partial r_2} \Big|_{r_2=R_2} \right)^2 / 2 \cos \theta_2 \sin \theta_2 d\theta_2, \quad (21)$$

where

$$\kappa = 2D\eta \left[\left(\frac{4}{3} - \zeta/\eta \right) (\mu''/\mu' - 1) + \frac{D}{2\nu} \right],$$

is naturally called the constant of diffusion interaction. Thus, in the first approximation and for $\text{Re} \ll 1$, the interaction of drops at all distances is equal to zero. This conclusion, obtained on the basis of a general consideration of the question, agrees perfectly with the result of a direct calculation of the interaction of drops at large distances in the first approximation, which proved to be equal to zero.

* Not only spherical, but of arbitrary shape and size.

5. From formula (21) there follows a remarkable analogy between diffusion and electrostatic interaction, since the resultant electric force acting on a conducting sphere is expressed in terms of the electric-field potential V in exactly the same way as in terms of χ_1 ; in this case the dielectric constant ε may be put in correspondence with the constant of diffusion interaction. The value of the established analogy increases considerably in view of the fact that χ_1 and V both satisfy Laplace's equation and assume constant values on the boundary surfaces. This makes it possible* to express the force of diffusion interaction of droplets directly by means of the formula for the electrostatic interaction of conducting spheres, by replacing ε by \varkappa and the values of V on the surfaces of the spheres by the values of χ_1 on the surfaces of the droplets,

$$F = \frac{\varkappa}{2\varepsilon(\rho'')^2} \left[\frac{\partial c_{11}}{\partial h} (\delta\rho'_1)^2 + 2 \frac{\partial c_{12}}{\partial h} \delta\rho'_1 \delta\rho'_2 + \frac{\partial c_{22}}{\partial h} (\delta\rho'_2)^2 \right],$$

where h is the distance between the centers of the droplets, and C_{11} , C_{12} , C_{22} are the capacitance coefficients computed for the case of interaction of spheres in (3), where after substitution of (14) terms of third and higher orders of smallness have been omitted.

Let us give the expression for the interaction of droplets at large distances, obtained directly from Coulomb's law:

$$F = 4\pi\varkappa \left(\frac{\delta\rho'_1}{\rho''} \right) \left(\frac{\delta\rho'_2}{\rho''} \right) \frac{R_1 R_2}{h^2}.$$

Although the absolute magnitude of the diffusion force is not large when the relative magnitude of the vapor-concentration difference is small, its slow decrease, inversely proportional to the square of the distance, is significant. The sign of the diffusion force is determined by the coincidence or difference of the directions of phase transition on the surfaces of the droplets, and also by the sign of \varkappa , i.e., by the qualitative composition of the vapor-gas mixture. In the interaction of water droplets in air, $\mu'' > \mu'$, $\zeta/\eta < \frac{4}{3}$, so that \varkappa is positive. In this case the droplets repel one another during simultaneous evaporation or condensation and attract one another if the directions of phase transition on the droplet surfaces do not coincide.

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* If the influence of diffusion on the heat-transfer process is taken into account, the similarity of the temperature and vapor-concentration fields is violated, as a result of which a change in temperature is found along the surface of the droplets. This displacement of the droplet temperatures, violating their isothermality, leads to a certain deviation of the Stefan flow from potentiality. In view of the smallness of this effect, the correction to the results of Sec. 5 caused by it apparently should not be significant. A rigorous consideration of this question presents great mathematical difficulties. It should be noted that the deviation of the droplet temperature field from isothermality is an effect of second order of smallness and cannot affect the results set forth in Secs. 1-4, which are based on consideration of the Stefan flow in the first approximation.

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

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