PHYSICAL CHEMISTRY

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Abstract

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APPLICATION OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES TO THE THEORY OF CAPILLARY OSMOSIS AND DIFFUSIOPHORESIS

In paper ([1]), a number of effects, caused by diffusion in molecular non-ionized adsorption layers and similar to electrokinetic phenomena caused by diffusion in ionic layers, were theoretically predicted and experimentally established. Thus, when a solution flows through a porous partition, a concentration difference arises (an analogue of the streaming potential). By the method of an auxiliary molecular field ([1]), the inverse effect was predicted: the appearance of a flow of solution (called capillary osmosis) under the influence of a difference in the chemical potential of its components along a capillary (diaphragm), which was also confirmed experimentally.

1. To describe this complex of phenomena, we shall apply the thermodynamics of irreversible processes, considering two reservoirs separated by a porous partition of thickness l and homogeneous both in temperature T and in composition. For this purpose we shall use the well-known expression ([2]) for the rate of entropy production Td_iS/dt in the isothermal flow of an electrolyte solution from reservoir I to reservoir II through a porous diaphragm at a prescribed pressure difference Δp and concentration differences Δc_k ($k = 1$–solute, $k = 2$–solvent), and consequently also chemical-potential differences $\Delta\mu_k$, in the reservoirs:

$$Td_iS/dt = -\sum I_k \Delta\mu_k, \tag{1}$$

where I_k is the mass flux of component k through the diaphragm; $\Delta\mu_k = (\partial\mu_k/\partial p)\Delta p + \Delta_p\mu_k = v_k\Delta p + \Delta_p\mu_k$, $\Delta_p\mu_k = (\partial\mu_k/\partial c_k)_p\Delta c_k$; v_k is the partial specific volume. Taking into account that $J = -\sum I_k v_k$ expresses the volumetric velocity, we transform (1) to the form

$$Td_iS/dt = J\Delta p + \sum I_k \Delta_p\mu_k. \tag{2}$$

Using the Gibbs–Duhem theorem, according to which

$$\sum c_k \Delta_p \mu_k = 0, \tag{3}$$

it is not difficult to show that

$$\sum I_k \Delta_p \mu_k = \sum I_k^* \Delta_p \mu_k, \tag{4}$$

where $I_k^* = I_k - c_k V$ characterizes the flux of a substance after subtracting its transport as a whole, V is the mean barycentric velocity of the flow. On the basis of the expression for entropy production obtained by substituting (4) into (2), we obtain:

$$I_1^* = L_{11}\Delta_p \mu_1 + L_{12}\Delta_p \mu_2 + L_{13}\Delta p, \tag{5}$$

$$I_2^* = L_{21}\Delta_p \mu_1 + L_{22}\Delta_p \mu_2 + L_{23}\Delta p, \tag{6}$$

$$V = L_{31}\Delta_p \mu_1 + L_{32}\Delta_p \mu_2 + L_{33}\Delta p \tag{7}$$

and the Onsager relations

$$L_{12} = L_{21}, \qquad L_{13} = L_{31}, \qquad L_{23} = L_{33}. \tag{8}$$

Capillary osmosis can be characterized by the flow rate of the liquid caused by the chemical-potential gradient at $\Delta p = 0$, so that J

can be expressed from (7) through the coefficients L_{31} and L_{32}, or, if the Onsager relations (8) are used, through L_{13} and L_{23}. We obtain

$$V = L_{13}\Delta_p \mu_1 + L_{23}\Delta_p \mu_2. \tag{9}$$

The values of the coefficients L_{13} and L_{23} in (5) and (6) can be found by calculating mass transports under the conditions

$$\Delta_p \mu_k = 0, \tag{10}$$

of which, according to the Gibbs-Duhem theorem, only one is independent. These quantities $I_{1|c}^*$, $I_{2|c}^*$, by analogy with heat transport ([2]), will be called transport masses. From (5) and (6) it follows that

$$L_{k3} = I_{k|c}^* (\Delta p)^{-1}, \tag{11}$$

so that

$$V = \left[I^*_{1|c}\Delta_p\mu_1 + I^*_{2|c}\Delta_p\mu_2\right](\Delta p)^{-1}. \tag{12}$$

2. In order to obtain a formula for capillary osmosis and diffusiophoresis, let us calculate the transport mass when a solution flows through a diaphragm composed of randomly arranged spheres of radius a, with the distance between neighboring spheres much smaller. Entrainment of the diffusion part of the adsorption layer by the motion of the liquid leads ([1]) to the appearance, in the vicinity of each sphere, of fields of excess concentrations δc_k, which, for a small Péclet criterion $\mathrm{Pe} = au/D_k$ (u is the flow velocity, D_k are the diffusion coefficients), are similar to the electric field of a dipole. In a spherical coordinate system with the pole at the center of the sphere and the θ-axis in the direction of the liquid flow, we have

$$\delta c_k(r,\theta) = d_k \cos\theta / r^2, \tag{13}$$

where the analogue of the dipole moment d_k is equal to

$$d_k = \frac{3}{2}\, uac_k\xi_k/D_k, \tag{14}$$

where $\xi_k = \int_0^\infty (\gamma_k(h) - \gamma_{k\infty})\, h\, dh$ are characteristics of the diffuseness of the adsorption layer; h is the distance from the slip plane; $\gamma_k(h)$ and $\gamma_{k\infty}$ are concentrations at distance h and beyond the adsorption layer, referred to unit volume.

When the distance between the spheres is large, the diffusion fields of each of them do not overlap, so that in summing them the superposition principle is applicable, as in averaging local electric fields in a dielectric polarized by a uniform electric field. For concentration differences during the flow of a solution through such a diaphragm we obtain

$$\Delta c_k = 4\pi n d_k l, \tag{15}$$

where n is the number of spheres per unit volume.

The appearance of concentration differences between the boundaries of the partition will disturb the homogeneity in composition of each reservoir, or condition (10). To eliminate both disturbances, one must introduce mass sources at the entrance to the diaphragm and mass sinks of equal strength at its exit. If the strengths of these sources are equal to $(D_k/l)4\pi n d_k l$, conditions (10) will be satisfied, since, by Fick' s law, Δc_k will appear, compensating the differences (15). For each sphere the flux of substance through any secant plane due to entrainment of the adsorption layers by the motion of the liquid is equal in magnitude

and opposite in direction to the total diffusion flux around it through the same plane. This follows from the stationarity of the state considered. The result is preserved after summing the fields of all particles. Therefore, after the introduction of mass sinks and sources and thereby upon fulfillment of conditions (10), the mass fluxes will be equal to $D_k \Delta c_k / l$. Thus, the desired transport masses are equal to the strengths of the introduced sources

$$I^*_{k|c} = D_k \Delta c_k / l. \tag{16}$$

Substituting these values into formula (12) and using formulas (14), (15) and the Gibbs–Duhem theorem, we obtain

$$V = 6\pi u a n c_1 (\xi_1 - \xi_2) \Delta \mu_1 / \Delta p. \tag{17}$$

Taking into account the relation between the pressure drop Δp and the resulting velocity, which follows from Stokes' law,

$$\Delta p = 6\pi \eta a u n l, \tag{18}$$

from (17) we obtain the following formula for the velocity of capillary osmosis:

$$V = c_1 (\xi_1 - \xi_2) \eta^{-1} \operatorname{grad}_p \mu_1. \tag{19}$$

If now, conversely, the liquid is immobile, then, for a given $\operatorname{grad}_p \mu_1$, the spheres will move with a velocity determined by formula (19), but in the opposite direction. The motion of particles in solutions under the action of a concentration gradient, called diffusiophoresis, was first predicted theoretically and established experimentally in ([1]). Using the formula given in that work for the concentration differences arising inside a diaphragm composed of capillaries of equal length and radius, caused by absorption of the substance at the entrance to the capillary and its release at the exit,

$$\Delta c_k = \xi_k c_k \Delta p / \eta l, \tag{20}$$

one can, in the same way as was done for the diaphragm of spheres, obtain for capillary osmosis in a diaphragm of cylindrical capillaries a formula which proves to coincide with formula (19).

3. A. N. Frumkin ([4]) and V. G. Levich ([5]) indicated a new type of diffusiophoresis for small Péclet numbers. If, in a solution containing drops of another liquid, a concentration gradient of a surface-active substance is imposed, then along the surface of a drop the adsorption, and consequently also the surface tension, must vary, which will cause circulation of the liquid inside the drop and its motion relative to the medium at the

expense of "reactive" forces. Since the velocity of this motion can be calculated directly on the basis of hydrodynamics or by the method described above, based on the thermodynamics of irreversible processes, comparison of the results makes it possible to check the correctness of the latter.

For this purpose let us consider a diaphragm consisting of randomly arranged drops of radius a, assuming that they are fixed and are not carried along by the motion of the liquid. The method of fixation must not distort the velocity field inside and outside the drop; it must remain the same as in the case of a free drop.* Therefore the resistance exerted by each drop to the motion of the liquid at Pe $\ll 1$ can be expressed by means of the formula of A. N. Frumkin and V. G. Levich ([6]), § 74), if one assumes that the distance between the drops is much greater than their radius:

$$F = 6\pi\eta a u(2\eta + 3\eta' + 3\gamma)/3(\eta + \eta' + \gamma),$$

where η is the viscosity of the substance of the particle; γ is the retardation coefficient; $\gamma = 3(\Gamma_1/D)\partial\sigma/\partial c_1$; Γ_1 and c_1 are the adsorption and concentration of the dissolved substance; σ is the surface tension of the drop. Then the pressure drop for a diaphragm thickness l is equal to

$$\Delta p = nl6\pi\eta a u(2\eta + 3\eta' + 3\gamma)/3(\eta + \eta' + \gamma). \tag{21}$$

The entrainment of the adsorption layer as a whole by the motion of the drop leads ([7]) to the appearance around it of a local concentration field, similar to the field of a solid sphere (13); the magnitude of the analogue of the dipole moment d_k in the present case is equal to

$$d_k = a^2\Gamma_k V_0/D_k, \tag{22}$$

where $V_0 = u\eta/2(\eta + \eta' + \gamma)$ is the value of the velocity at the equator of the drop.

* One may, for example, assume that each drop is fixed on a vertical thin thread passing through the center of the drop and intersecting it at those points of the surface where the velocity becomes zero. The fact that the technical realization of such a diaphragm is difficult is of no importance. What is important is that its existence does not contradict thermodynamics.

In view of the complete similarity of the local concentration fields of droplets and solid spherical particles and of the convective transport of adsorbed substance along their surfaces, one can repeat the arguments and calculations of the preceding item and conclude that the transport masses are determined by equation (16), while the concentration difference in the present case is expressed

by formula (15), with the velocity V being determined by formula (12). Substituting into these formulas d_k according to (22) and Δp according to (21), and neglecting Γ_2, we obtain

$$V = \frac{a\Gamma_1}{2\eta + 3\eta' + 3\gamma} \operatorname{grad} \mu_1 = \frac{a|\partial\sigma/\partial c_1|}{2\eta + 3\eta' + (\Gamma_1/D)|\partial\sigma/\partial c_1|} \operatorname{grad} c_1. \tag{23}$$

For the purpose of an independent check of the correctness of the method presented, let us calculate the velocity on the basis of hydrodynamics, or, what is the same, on the basis of the analogy of this phenomenon with the motion of a mercury drop in an external electric field E due to the electrocapillary change of surface tension along its surface, which, according to the theory of A. N. Frumkin and V. G. Levich ([8]), is expressed by the formula

$$\Delta\sigma(\theta) = [{}^3/_2\, \varepsilon E a - V_0 \varepsilon^2/\chi] \cos\theta, \tag{24}$$

where ε is the charge density on the surface of the drop, and χ is the specific electrical conductivity.

For small Pe numbers, the concentration distribution in the vicinity of the drop, for a value of $\operatorname{grad} c_1$ prescribed at infinity, must satisfy the Laplace equation

$$\Delta c_1 = 0 \tag{25}$$

and simple boundary conditions which, in a spherical coordinate system with the pole at the center of the particle and the θ-axis oriented parallel to $\operatorname{grad} c_1$, are written as follows:

$$c_1|_{r\to\infty} = c_{01} + |\operatorname{grad} c_1|\, r\cos\theta; \qquad \frac{\partial c_1}{\partial r}(a,\theta) = \frac{2V_0\Gamma_1}{aD_1}\cos\theta, \tag{26}$$

where $c_{01} = c_1(r, \pi/2)$.

The concentration distribution satisfying (25) and (26) is determined without difficulty, and for $\Delta\sigma$, with a linear dependence of adsorption on concentration, we obtain a formula analogous to (24):

$$\Delta\sigma(\theta) = \frac{\partial\sigma}{\partial c_1}(c_1(a,\theta) - c_{01}) = \frac{\partial\sigma}{\partial c_1}\left[{}^3/_2 |\operatorname{grad} c_1| a - V_0\Gamma_1/D_1\right]. \tag{27}$$

In view of the complete similarity of formulas (24) and (27), the velocity of motion in the case of interest to us can be expressed by means of the formula for the velocity of motion of a mercury drop due to the electrocapillary effect ([6]), §99

$$V = \frac{\varepsilon E a}{2\eta + 3\eta' + \varepsilon^2/\chi}. \tag{28}$$

If, according to (24) and (27), we make in it the substitution $a\varepsilon E \rightarrow \frac{\partial \sigma}{\partial c_1} a \operatorname{grad} c_1$, $\varepsilon^2/\chi \rightarrow (\Gamma_1/D_1)\partial\sigma/\partial c_1$, then we finally obtain a formula coinciding with that obtained above on the basis of the thermodynamics of irreversible processes (23).

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