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Abstract

Full Text

Physical Chemistry

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APPLICATION OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES TO THE THEORY OF ELECTROOSMOSIS, ELECTROPHORESIS, CAPILLARY OSMOSIS, AND DIFFUSIOPHORESIS IN ELECTROLYTES

In works (1−3) the theory of the streaming potential and the Dorn effect was generalized by taking diffusion effects into account. To clarify the role of diffusion in electroosmosis it is expedient to apply the thermodynamics of irreversible processes, which makes it possible, from formulas for the streaming potential and the Dorn effect, to obtain formulas for the reciprocal effects—electroosmosis and electrophoresis.

1. To derive equations expressing fluxes through linear combinations of thermodynamic forces, we shall use the expression derived in (4), specially for considering electrokinetic phenomena, for the rate of entropy production Td_{iS}/dt under isothermal flow of an electrolyte through a porous diaphragm of thickness l from reservoir I to reservoir II at given differences of electric potential $\Delta\varphi$, pressure Δp, and chemical potentials $\Delta\mu_k$ ($k = 1, 2$ corresponds to cations and anions, $k = 3$ to the solvent):

$$Td_{iS}/dt = -\sum_{k=1}^{3} \Delta(\mu_k + e_k\varphi)I_k, \tag{1}$$

where Δ denotes the difference of the corresponding quantities in the reservoirs; e_k is the charge per unit mass of component k; I_k is the mass flux of component k; T is the absolute temperature. We generalize the consideration of electrokinetic phenomena on the basis of the thermodynamics of irreversible processes in (4,5) by taking diffusion effects into account. For this purpose we shall assume that differences of weight concentrations Δc_k are also maintained between the reservoirs. Therefore $\Delta\mu_k = (\partial\mu_k/\partial p)\Delta p + (\partial\mu_k/\partial c_k)_p\Delta c_k = v_k\Delta p + \Delta_p\mu_k$, where $\Delta_p\mu_k = \sum(\partial\mu_k/\partial c_k)_p\Delta c_k$; v_k is the partial specific volume. Substituting these values of $\Delta\mu_k$ into (1) and taking into account that $J = -\sum I_k v_k$ is the volume velocity, and $I = -\sum e_k I_k$ is the electric current, we obtain

$$T d_{iS}/dt = J\Delta p + I\Delta\varphi + \sum I_k \Delta_p \mu_k. \tag{2}$$

Using the Gibbs–Duhem theorem, according to which $\sum c_k \Delta\mu_k = 0$, it is easy to show that

$$\sum I_k \Delta_p \mu_k = \sum I_k^* \Delta_p \mu_k, \tag{3}$$

where $I_k^* = I_k - c_k V$ is the flux of matter after subtracting its transport as a whole, and V is the mean barycentric velocity.

On the basis of the expression for the rate of entropy production obtained by substituting (3) into (2), we obtain the following equations:

$$I_1^* = L_{11}\Delta_p\mu_1 + L_{12}\Delta_p\mu_2 + L_{13}\Delta_p\mu_3 + L_{14}\Delta\varphi + L_{15}\Delta p, \tag{4}$$

$$I_2^* = L_{21}\Delta_p\mu_1 + L_{22}\Delta_p\mu_2 + L_{23}\Delta_p\mu_3 + L_{24}\Delta\varphi + L_{25}\Delta p, \tag{5}$$

$$I_3^* = L_{31}\Delta_p\mu_1 + L_{32}\Delta_p\mu_2 + L_{33}\Delta_p\mu_3 + L_{34}\Delta\varphi + L_{35}\Delta p, \tag{6}$$

$$I = L_{41}\Delta_p\mu_1 + L_{42}\Delta M_p\mu_2 + L_{43}\Delta_p\mu_3 + L_{44}\Delta\varphi + L_{45}\Delta p, \tag{7}$$

$$J = L_{51}\Delta_p\mu_1 + L_{52}\Delta M_p\mu_2 + L_{53}\Delta M_p\mu_3 + L_{54}\Delta\varphi + L_{55}\Delta p. \tag{8}$$

and the Onsager relations, of which we shall need only the following:

$$L_{51} = L_{15}, \quad L_{52} = L_{25}, \quad L_{53} = L_{35}, \quad L_{54} = L_{45}. \tag{9}$$

Electroosmosis is determined by the volume velocity V_E of motion of the liquid under the action of a potential difference in the absence of pressure and concentration differences; accordingly, in equation (8) we set $\Delta_p\mu_k$ and Δp equal to zero, so that V_E can be expressed in terms of L_{54}, or, according to (9), in terms of L_{45}. We obtain

$$V_E = L_{45}\Delta\varphi. \tag{10}$$

Capillary osmosis (^{6,7}) is determined by the volume velocity produced by gradients of the ion concentrations (and, consequently, by the accompanying gradient of the solvent concentration), at $\Delta p = 0$ and $\Delta\varphi = 0$, so that the velocity V_D can be expressed in terms of L_{51}, L_{52}, and L_{53}, or, according to (9), in terms of L_{15}, L_{25}, L_{35}:

$$V_D = L_{15}\Delta_p\mu_1 + L_{25}\Delta_p\mu_2 + L_{35}\Delta_p\mu_3. \tag{11}$$

To calculate the coefficients L_{k5} ($k = 1, 2, 3, 4$), consider equations (4), (5), (6), and (7) at a given Δp and at $\Delta\varphi = 0$:

$$L_{k5} = \left[I_k^* - L_{k1}\Delta_p\mu_1 - L_{k2}\Delta_p\mu_2 - L_{k3}\Delta_p\mu_3\right]/\Delta p. \tag{12}$$

Following (^{7}), let us call the mass fluxes I_k^*, under the conditions

$$\Delta\varphi = 0, \tag{13}$$

$$\Delta c_k = 0 \tag{14}$$

being satisfied, the masses of transfer $I_k^*|_{c,\varphi}$. Then from formula (12) it follows that

$$L_{k5} = (\Delta p)^{-1} I_k^*|_{c,\varphi}. \tag{15}$$

2. When a liquid moves inside a diaphragm, concentration gradients ∇c_k arise (^{1}), even if initially $\Delta c_k = 0$. Entrainment of the diffuse part of the adsorption layer by the motion of the liquid gives rise to excess fluxes $I_{k\xi}$; for a diaphragm consisting of cylindrical capillaries of the same radius and length l, they are equal to

$$I_{k,\xi} = c_k\xi_k\Delta p/\eta l, \tag{16}$$

where

$$\xi_k = \gamma_k^{-1}\int_0^\infty \left[\gamma_k(h) - \gamma_{k\infty}\right] h\,dh$$

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 the concentrations at distance h and beyond the layer, referred to unit volume; η is the viscosity. These excess fluxes originate at the entrance to the capillaries owing to absorption of matter from the bulk, and then the same amount of matter is released at the exit from the capillaries. In order that these effects should not disturb, acting continuously, conditions (13) and (14), it is necessary to introduce sources and sinks of mass on both sides of the diaphragm, which by definition are equal to the masses of transfer, with power equal to

$$I_k^*|_{c,\varphi} = c_k\xi_k\Delta p/\eta l. \tag{17}$$

Substituting these values into formulas (15), we obtain

$$L_{k5} = c_k \xi_k / \eta l. \tag{18}$$

Substituting these values for L_{k5} into formula (11) and using the Gibbs-Duhem theorem and the electroneutrality condition of the solution $z^+c^+ - z^-c^- = 0$, which makes it possible to express the concentrations of anions and cations $c^\pm$ through one and the same function $c = c^\pm / z^\mp$ and the valences $z^\pm$ ($c^\pm = z^\mp c$), we obtain

$$V_D = \left[z^-(\xi^+ - \xi_3) + z^+(\xi^- - \xi_3) \right] c \nabla \mu(c). \tag{19}$$

Since $I = \mathrm{F}\,(z^+I^+ - z^-I^-)$, where F is the Faraday number, L_{45} is expressed in terms of L_{15} and L_{25}:

$$L_{45} = \mathrm{F}\,(z^+L_{15} - z^-L_{25}) = (\mathrm{F}/\eta)(z^+c^+\xi^+ - z^-c^-\xi^-) = \mathrm{F}cz^+z^-(\xi^+ - \xi^-)/\eta, \tag{20}$$

and taking into account the relation of ξ^+ and ξ^- to the ζ-potential (2)

$$Fcz^+z^-(\xi^- - \xi^+) = \varepsilon\zeta/4\pi, \tag{21}$$

after substituting L_{45} into equation (10), we obtain for electroosmosis the well-known Smoluchowski formula

$$V_E = (\varepsilon\zeta/4\pi\eta)\nabla\varphi. \tag{22}$$

3. The theory of diffusiophoresis and electrophoresis can be constructed analogously, if one first calculates the velocities of capillary osmosis and electroosmosis in a diaphragm consisting of randomly arranged spheres of radius a, the distances between which considerably exceed the latter, and changes the signs in front of the formulas.* Thus, the velocities of diffusiophoresis and electrophoresis can be calculated from formulas differing from formulas (10) and (11) only in sign; moreover, the problem of calculating the coefficients L_{k5}, according to (15), reduces to calculating the masses of transfer. These latter are easily calculated if one uses the results of the diffusion-electric theory of the Dorn effect (7) at small values of the diffusion Péclet number, according to which the entrainment of the diffuse part of the adsorption layer of a solid sphere by the motion of the liquid leads to the formation of a local electric field $\varphi(r, \theta)$ and a concentration field $c(r, \theta)$, whose structure is similar to that of the electric field of a dipole. In a spherical coordinate system, with the pole at the center of the sphere and the θ-axis oriented in the direction of the flow, these fields have the form

$$c(r,\theta) = d_c \cos\theta / r^2, \qquad \varphi(r,\theta) = d_\varphi \cos\theta / r^2, \tag{23}$$

where, for the analogues of the dipole moments d_c and d_φ, the formulas obtained were

$$d_c = \frac{3ua\,(D^- z^- \xi^+ + D^+ z^+ \xi^-)\,c}{2D^+ D^- (z^+ + z^-)}, \qquad d_\varphi = \frac{3uaRT\,(D^- \xi^+ - D^+ \xi^-)}{2FD^+ D^- (z^+ + z^-)}, \tag{24}$$

where u is the velocity of motion of the sphere, R is the universal gas constant, and $D^\pm$ are the diffusion coefficients of the ions. Summation of the local concentration fields and, correspondingly, of the local electric fields leads to the appearance of concentration differences Δc_k and electric potential differences $\Delta\varphi$, which can be expressed through dipole moments on the basis of the well-known formula of the theory of dielectrics

$$\Delta c^\pm = 4\pi n z^\mp d_c, \qquad \Delta\varphi = 4\pi n d_\varphi, \tag{25}$$

where n is the number of spheres per unit volume.

Because these differences of concentration and potential arise between the boundaries of the partition, the homogeneity of each reservoir with respect to composition or conditions (13) and (14) is violated. To prevent this, mass sources of components 1 and 2 must be introduced at the entrance to the diaphragm, and mass sinks of equal power at the exit. If the powers of the sources are $(\mp x^\pm \Delta\varphi - D^\pm \Delta c^\pm)/l$, where $x^\pm = (F/RT) D^\pm z^\pm z^\mp c$ are partial electrical conductivities, then concentration and potential differences will appear that compensate the above-mentioned (25). 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 also retained after summation of the fields of all particles. Therefore, after introduction of sinks and sources and thereby upon fulfillment of conditions (12) and (14), the mass fluxes will be equal to $(\mp x^\pm \Delta\varphi - D^\pm \Delta c^\pm)/l$. Thus, the masses of transfer are equal to the powers of the introduced sources and, taking equations (25) into account, may be represented in the form:

$$\begin{aligned} I^+_{c,\varphi} &= (4\pi n/l)(-x^+ d_\varphi - D^+ z^- d_c), \\ I^-_{c,\varphi} &= (4\pi n/l)(x^- d_\varphi - D^- z^+ d_c). \end{aligned} \tag{26}$$

* This method has fully justified itself in the theory of diffusiophoresis and capillary osmosis in nonelectrolytes (7).

Since for the solvent there is only a diffusion flux, I_3^* can be calculated in exactly the same way as in [7]:

$$I_3^*\big|_c = 4\pi n D_3 d_3/l. \tag{27}$$

Taking into account that the resistance of a unit sphere to the flow of a liquid is expressed by Stokes' formula, we may write

$$\Delta p = nl6\pi\eta a u. \tag{28}$$

Substituting the transport masses, expressed according to (26), into the formulas for the kinetic coefficients L_{15} and L_{25}, we then compose the expression for L_{45}, according to (20):

$$L_{45} = (4\pi n F/\Delta p)\left[(z^+x^+ + z^-x^-)d_\varphi - (D^+ - D^-)z^+z^-d_c\right]. \tag{29}$$

Substituting into this formula the values of d_c and d_φ according to formulas (24), and Δp according to (28), we may then, substituting the expression obtained for L_{45} into formula (10) and changing the sign in it, obtain the electrophoresis velocity, which turns out to coincide with formula (22) with the opposite sign. Substituting the transport masses, expressed according to (26), into the formulas for the kinetic coefficients L_{15} and L_{25}, and taking into account formulas (28) for Δp and (27) for L_{35}, we express the right-hand side of formula (11) for capillary osmosis or, respectively, allowing for the change of sign, for diffusiophoresis [8] as follows:

$$V_D = \{(2/3\eta)[(x^+ - x^-)d_\varphi - (D^+z^- + D^-z^+)d_c] - (z^+ + z^-)\xi_3\}\, c\nabla\mu. \tag{30}$$

If in this formula one substitutes d_c and d_φ according to formulas (24), then for the diffusiophoresis velocity of a spherical particle in an electrolyte one obtains a formula coinciding with formula (19) for the capillary-osmosis velocity.

4. Although we start from the formula for the Dorn effect, which takes diffusion effects into account, for the electrophoresis velocity the Smoluchowski formula has been obtained. As is known, it is obtained when electrophoresis is considered in the zero approximation, i.e., when the deformation of the spherically symmetric double ionic layer of the particle by the external field is ignored. In reality, the asymmetric perturbed distribution of ions of the double layer, arising upon deformation by the external field and by the motion of the particle, produces an electric field which, at not small values of the ζ-potential, is comparable in magnitude with the external field; as a result, the Smoluchowski formula proves to be incorrect (relaxation effect) [9].

However, if the theory of the Dorn effect is generalized by taking relaxation into account, then, on the basis of the general interrelation established in the present work between the Dorn effect and electrophoresis, the theory of electrophoresis can immediately be refined with allowance for relaxation.

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CITED LITERATURE

1. B. V. Deryagin, *Koll. zhurn.*, **22**, 148 (1960).
2. B. V. Deryagin, S. S. Dukhin, DAN, **129**, 1328 (1959).
3. B. V. Derjaguin, S. S. Dukhin, *Vorträge in Originalfassung des III Intern. Kongr. grenzflächenaktive Stoffe*, 12–17 X 1960 in Köln am Rhein.
4. C. P. de Groot, *Thermodynamics of Irreversible Processes*, 1956, § 68.
5. P. Mazur, J. Th. G. Overbeek, *Rec. trav. chim. Pays-Bas*, **70**, 83 (1951); S. R. de Groot, P. Mazur, J. Th. G. Overbeek, *J. Chem. Phys.*, **20**, 1825 (1952).
6. B. V. Deryagin, G. Sidorenko, E. Zubashchenko, E. Kiseleva, *Koll. zhurn.*, **9**, 335 (1947).
7. S. S. Dukhin, B. V. Deryagin, DAN, **159**, 177 (1964).
8. B. V. Deryagin, S. S. Dukhin, A. A. Korotkova, *Koll. zhurn.*, **23**, 53 (1961).
9. J. Th. G. Overbeek, *Kolloid-Beihefte*, **54**, 287 (1943); F. Booth, *Proc. Roy. Soc. A*, **203**, 514 (1950).

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