THERMODYNAMICS OF ELECTROKINETIC PHENOMENA

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ABSTRACT

The thermodynamics of irreversible processes are applied to electrokinetic experiments. By investigating the correlation between fluctuations in volume and charge in an electroosmosis cell, the Onsager relation for this case is derived. From this and the empirical equation relating flow of liquid and electricity to pressure and potential difference, general relations between electrokinetic effects are derived, showing that for a given system the total electrokinetic behavior is described only by one coefficient. From an application of the same method to the case of suspended particles, relations between electrophoresis and sedimentation are derived.

Attention is drawn to electrokinetic corrections to be applied to the coefficients of permeation or of sedimentation in the form in which they are usually determined.

I. INTRODUCTION

Experiments on electrokinetics usually are interpreted in terms of the ζ-potential. Recently it has become clear that this is an oversimplification. Except when the thickness of the electrical double layer is small compared to the size of particles or pores under investigation, corrections have to be applied to the simple Helmholtz-Smoluchowski equations. Although several attempts have been made, it has not yet been possible to calculate these corrections accurately. A general survey of these attempts has been made by the present author (1), electrophoresis has been investigated by Henry (2), Overbreek (3) and Booth (4), and electroosmosis and streaming potential by Rutgers and DeSmet (5) and by Overbeek and van Est (6).

The question arises as to whether in these more complicated situations some electrokinetic techniques may have advantages over others or whether they all give essentially the same information.

Since all electrokinetic processes are irreversible, this is the type of problem to which the thermodynamics of irreversible processes can be applied. With the aid of this relatively recently developed doctrine, it has been found possible to derive a number of general relations between different electrokinetic processes and to show that for a given system there exists only one electrokinetic coefficient that can be determined by any one of the electrokinetic experiments.

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II. The Method of Fluctuations

This is not the place to treat the fundamentals of the thermodynamics of irreversible processes (7, 8, 9, 10) extensively; however, a brief discussion of the method, as applied to the present case, seems pertinent.

Electrokinetic experiments can be performed on two different types of systems: one, where a liquid moves through a capillary or through the pores of a plug or diaphragm, and the other, where particles (usually solid) move through a liquid that is kept stationary by a surrounding vessel. We shall treat the first system, that is, the one for electroosmosis and streaming potential, completely, and after that the second one, on electrophoresis and sedimentation, only in passing.

The system (see Fig. 1) consists of two reservoirs, I and II, connected by a capillary or diaphragm. The reservoirs are partially filled with an electrolyte solution. The electrical potential and the pressure in the left-hand reservoir are designated E and P, respectively. Potential and pressure in
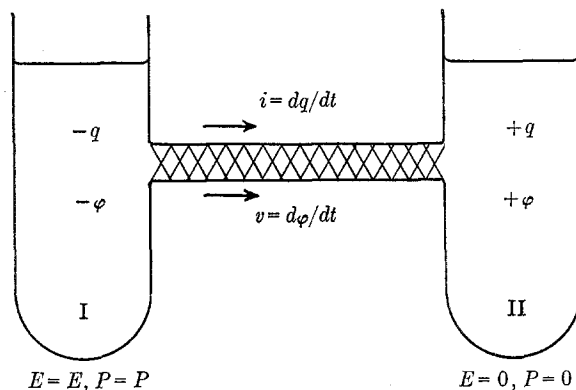

Fig. 1. Cell for electroosmosis and streaming potential.

the right-hand reservoir are assumed to be zero. The right-hand reservoir contains a charge q and a volume of liquid φ in excess of the volume at equilibrium. Charge and excess volume of the left-hand reservoir are $-q$ and $-\varphi$ respectively.

The electric current i through the diaphragm is equal to dq/dt. The hydrodynamic current (volume passing through the diaphragm) is $v = d\varphi/dt$.

If the treatment is limited to the linear region, the most general relations (11) between the "currents" i and v and the "forces" E and P are:

$$i = L_{11}E + L_{12}P$$
$$v = L_{21}E + L_{22}P$$

[1]

where L_{ij} are constants.

Considering now small (thermal) fluctuations q and φ, we may ask for the relation between a fluctuation q at time t and a fluctuation φ at $t + \tau$, τ being a time that is short as compared to the time necessary for the decay of a fluctuation.

As a result of the insensitivity of all equations of motion to a change in the sign of the time, a completely equivalent system is obtained by changing the sign but not the value of all velocities of ions, molecules, electrons, etc. Consequently, the average relationship between $q(t)$ and $\varphi(t + \tau)$ must be the same as that between $q(t)$ and $\varphi(t - \tau)$. Thus,

$$\overline{q(t)\varphi(t + \tau)} = \overline{q(t)\varphi(t - \tau)} \qquad [2]$$

or, shifting all the times at the right-hand side by τ, we get

$$\overline{q(t)\varphi(t + \tau)} = \overline{q(t + \tau)\varphi(t)} \qquad [3$$

in which the bar denotes that the average has to be taken over the time, t. Subtracting the average value of $q(t)\,\varphi(t)$ from both sides, we get

$$\overline{q(t)[\varphi(t + \tau) - \varphi(t)]} = \overline{\varphi(t)[\varphi(t + \tau) - q(t)]}. \qquad [4]$$

If we assume that on the average fluctuations die out in agreement with the macroscopic laws as given in Eq. [1], Eq. [4] can be replaced by

$$\overline{q(t)\left(\frac{d\varphi}{dt}\right)}\tau = \overline{\varphi(t)\left(\frac{dq}{dt}\right)}\tau \qquad [5]$$

or

$$\overline{qv} = \overline{\varphi i}. \qquad [6]$$

If we substitute v and i from Eq. [1], this becomes

$$L_{21}\,\overline{qE} + L_{22}\,\overline{qP} = L_{11}\,\overline{\varphi E} + L_{12}\,\overline{\varphi P}. \qquad [7]$$

Now the fluctuations in charge and pressure (at the same moment) or in volume and electric potential are independent of each other. Consequently,

$$\overline{qP} = \overline{\varphi E} = 0. \qquad [8]$$

But there is an obvious correlation between the fluctuation in charge and potential or between volume and pressure. Considering[1] the combinations charge and potential or volume and pressure as degrees of freedom of the system, the average potential energy in such a degree of freedom, according to the law of equipartition, is equal to $\frac{1}{2}\,kT$, and thus,

$$\overline{qE} = \overline{\varphi P} = -kT. \qquad [9]$$

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[1] It is realized that this is not a completely rigorous proof, but it comes as close to it as is possible without actually performing the necessary calculations of statistical mechanics. See, e.g., De Groot (9) p. 13 ff.

From [7], [8], and [9] *Onsager's* relation

$$L_{12} = L_{21}$$

immediately follows.

III. Conclusions from Combination of the Phenomenological Equations with the Onsager Relation

With the system as described, four different experiments in electrokinetics can be performed (plus an infinite number of combinations), namely, rate of electroosmosis at zero pressure, electroosmotic pressure at zero rate of flow, streaming potential (at zero current), and streaming current (at zero potential difference). These phenomena can be expressed as functions of current, potential difference, flow of liquid, or pressure difference, leading to eight electrokinetic coefficients. Because of the existence of the Onsager relation these coefficients are pairwise equal.

The coefficient for streaming potential is found by putting $i = 0$ in Eq. [1], and thus

$$(E/P)_{i=0} = -L_{12}/L_{11} , \qquad [10]$$

$$(E/v)_{i=0} = \frac{-L_{12}}{L_{11} L_{22} - L_{12} L_{21}} . \qquad [11]$$

For the rate of electroosmosis when $P = 0$,

$$(v/i)_{P=0} = L_{21}/L_{11}, \qquad [12]$$

$$(v/E)_{P=0} = L_{21}. \qquad [13]$$

Similarly it is found that for the streaming current when $E = 0$,

$$(i/P)_{E=0} = L_{12}, \qquad [14]$$

$$(i/v)_{E=0} = L_{12}/L_{22}, \qquad [15]$$

and for the electroosmotic pressure when $v = 0$,

$$(P/E)_{v=0} = -L_{21}/L_{22} , \qquad [16]$$

$$(P/i)_{v=0} = \frac{-L_{21}}{L_{11} L_{22} - L_{12} L_{21}} . \qquad [17]$$

It appears that the absolute values of these coefficients are pairwise equal; e.g.,

$$(E/P)_{i=0} = -(v/i)_{P=0}, \qquad [18]$$

$$(i/P)_{E=0} = (v/E)_{P=0}. \qquad [19]$$

But regardless of what experiment is done or what combination is chosen, the system is described completely by the three constants L_{11}, L_{22}, and $L_{12} =$

L_{21}. Of these constants, L_{11} represents the electric conductance, L_{22} the hydrodynamic conductance, and the cross coefficient $L_{12} = L_{21}$ the electrokinetic effect.

Incidentally, the coefficient L_{12}, when interpreted in the usual way in terms of the ζ-potential, is given by

$$L_{12} = \epsilon\zeta A/4\pi\eta,$$

where ϵ represents the dielectric constant, ζ the ζ-potential, η the viscosity, and A the effective cross section through the diaphragm.

Consequently there is no reason to do more than one electrokinetic experiment with a given system, and the choice is determined by convenience or by reasons of accuracy rather than by principle. At high conductivity of the liquid (L_{11} large), for instance, the streaming potential will be extremely low and difficult to determine, whereas the streaming current will have a normal value; thus, although both experiments lead to the same quantity L_{12}, the second may be preferred.

Incidentally, it is easy to see that it makes a difference whether electrical conuctance is measured at zero flow or at zero pressure difference, for

$$\left(\frac{i}{E}\right)_{P=0} = L_{11},\qquad\qquad [20]$$

but

$$\left(\frac{i}{E}\right)_{v=0} = L_{11} - \frac{L_{12}\,L_{21}}{L_{22}}.\qquad\qquad [21]$$

The correction may be considerable when the pores are narrow and the major transport of electricity takes place in the form of electroosmosis, included in L_{11} but eliminated in $(i/E)_{v=0}$.

For the hydrodynamic resistance a similar conclusion can be drawn; this resistance is smaller when short-circuited electrodes connect the two reservoirs than when no electric current is allowed to flow in an outside circuit.

$$\left(\frac{v}{P}\right)_{E=0} = L_{22};\qquad\qquad [22]$$

$$\left(\frac{v}{P}\right)_{i=0} = L_{22} - \frac{L_{12}L_{21}}{L_{11}}.\qquad\qquad [23]$$

There need be no fear that the correction terms may become larger than the main term because if $L_{12}L_{21} > L_{11}L_{22}$, a combination of values of P and E could be found which would make the energy dissipation $iE + Pv$ negative, and this would be in disagreement with the second law of thermodynamics.

IV. SUSPENDED PARTICLES

In the case of suspended particles the "currents" and "forces" that are most easy to handle are the electric current density, i, and the electric field strength, E, on the one hand, and the velocity, v, of the center of

gravity of the system (with respect to the vessel in which it is contained) and the centrifugal or gravitational acceleration, g, multiplied by the density, d, on the other hand.

The phenomenological or empirical equations are now:

$$i = L_{11}E + L_{12}dg;$$
$$v = L_{21}E + L_{22}dg. \qquad [24]$$

It can again be proved[2] that

$$L_{12} = L_{21} \qquad [25]$$

In order to apply these equations successfully, the velocity of the center of gravity, which is not measured directly, has to be converted into other quantities. For colloidal systems the velocity of the particles, neglecting the motions of all other ions, is a suitable choice. In systems containing only electrolytes the motion of all charged particles expressed by the transport numbers, and the volume changes near the electrodes have to be introduced.

In the colloid case, designating the velocity of the particles U, we find with good approximation.

$$vd = U\,C_p(1 - V_p d_{\text{sol}}) \qquad [26]$$

where C_p is the concentration of particles in grams per milliliter; V_p, the specific volume of the particles; and d_{sol}, the density of the particle-free solution.

If we combine Eq. [26] with [24] and use the Onsager relation [25], the following relations between electrophoresis and sedimentation (or centrifugation) potential or current are easily derived:

$$\left(\frac{U}{E}\right)_{g=0} = \left[\frac{i}{C_p(1 - V_p d_{\text{sol}})g}\right]_{E=0} \qquad [27]$$

electrophoretic velocity   sedimentation current

$$\left(\frac{U}{i}\right)_{g=0} = \left[\frac{-E}{C_p(1 - V_p d_{\text{scl}})g}\right]_{i=0} \qquad [28]$$

electrophoretic velocity   sedimentation potential

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[2] It will be clear that a judicious choice of currents and forces is necessary to obtain the relationship again in this simple form. The criterion for the choice is that the sum of the products of currents and forces have to be equal to the absolute temperature times the entropy production. In this case

$$T\frac{dS}{dt} = iE + vdg.$$

See Onsager (7), Casimir (8), De Groot (9), and Prigogine (10); and for this particular case, De Groot, Mazur, and Overbeek (12).

These relations show that the measurement of sedimentation potential or current gives the same information as that of electrophoretic velocity and that the choice between the methods should be governed by convenience and not by principle. The derivation given shows that the validity of the relations [27] and [28] is independent of the possibility to express the electrokinetic coefficients by an explicit formula, as for instance $(U/E)_{g=0} = \epsilon\zeta/4\pi\eta$.

Again, as in the case of the liquid moving through a plug, we may remark here that the sedimentation constant U/g will depend on whether the cell contains two short-circuited electrodes or not.
In fact,

$$\left(\frac{U}{g}\right)_{i=0} = \frac{d^2}{C_p(1 - V_p\, d_{\text{sol}})}\left(L_{22} - \frac{L_{12}\,L_{21}}{L_{11}}\right);\qquad [29]$$

$$\left(\frac{U}{g}\right)_{E=0} = \frac{d^2}{C_p(1 - V_p\, d_{\text{sol}})}\,L_{22}\qquad [30]$$

In the usual sedimentation or centrifugal experiments the first rather than the second coefficient is determined, and it is easily seen that the correction term becomes small when (1) the experiment is carried out near the isoelectric point (L_{12} is small), (2) at low colloid concentration ($L_{12} :: C_p$), or (3) at high conductivity (L_{11} is large).

In a consideration of solutions of electrolytes not containing colloid particles, Eq. [26], which only takes account of the motion of one kind of particles, is not valid any more. The velocity of the center of gravity has now to be connected with the mobilities of all species present. Moreover, the volume changes at the electrodes give rise to displacements comparable to those caused by the sedimentation. If all this is taken into account, a relation between the sedimentation potential and the transport numbers can be derived, which was already known from Des Coudres' (13) work and which has been used again recently by MacInnes and Ray (14).

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