

Nonequilibrium Thermodynamics of the Sedimentation Potential and Electrophoresis

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(Received May 29, 1952)

The thermodynamics of irreversible processes is developed for a system placed in a centrifugal field and consisting of a number of components, some of which carry electrical charges. It is found that an Onsager reciprocal relation connects the sedimentation potential with a quantity which we call barycentric electrophoresis (i.e., the quotient of the total mass flow and the electrical field at zero centrifugal field). The latter quantity turns out to be ordinary electrophoresis in a colloid (i.e., in a system of one neutral and a number of charged components, one of which consists of colloidal particles) under certain limiting, but frequently realized, circumstances. If conduction relaxation exists, it appears in both connected phenomena described here.

I. INTRODUCTION

THE problem of the connection between sedimentation potential and electrophoresis in arbitrary systems has not heretofore been studied in a systematic manner. It was therefore thought useful to employ the thermodynamical theory of irreversible processes^{1,2} to discuss this problem for a system composed of charged and neutral components. In this paper it is proved (Secs. II-V) that a relationship can be established between the sedimentation potential and a phenomenon which we call barycentric electrophoresis. This latter quantity is defined as the quotient of the total mass flow and electrical field in the absence of a centrifugal (gravitation) field. From the general formulas, the conditions are derived (Sec. 6) under which the relation mentioned above transforms into a connection between sedimentation potential and ordinary electrophoresis (defined as the quotient of a flow of one kind of charged particles and the electrical field at zero centrifugal field). It turns out that these conditions are usually fulfilled when one charged component consists of colloid particles. It is proved that, if relaxation exists, its influence appears in both coupled phenomena.

(It may be noted here that other electrokinetic

effects, *viz.*, electro-osmosis and streaming potentials in diaphragms, have been treated³ by means of the thermodynamics of irreversible processes previously.)

II. THE ENTROPY BALANCE

Let us consider a system composed of n components ($k=1, 2, \dots, n$), of which m carry electrical charges e_k ($k=1, 2, \dots, m$) per unit mass, and of which $n-m$ are neutral ($e_{m+1}=e_{m+2}=\dots=e_n=0$). This system is brought into a centrifugal (gravitation) field \mathbf{g} . The temperature is assumed to be uniform. In this paper we limit ourselves to the study of the behavior of the system in the homogeneous region between the electrodes, and we do not consider the problem of possible electrode reactions here. In the thermodynamics of irreversible processes,^{1,2} "the entropy balance equation," which we shall need further on, is derived from a set of fundamental equations. Those equations have the following forms in our case of a so-called "continuous system," i.e., where the state variables are continuous functions of the space coordinates.

A. Law of Conservation of Mass

For the change of the concentration c_k of component k ,

$$pdc_k/dt = -\text{div } \mathbf{J}_k \quad (k=1, 2, \dots, n). \quad (1)$$

³ P. Mazur and J. Th. G. Overbeek, *Rec. Trav. Chim. Pays-Bas* 70, 83 (1951).

¹ I. Prigogine, *Etude Thermodynamique des Processus Irréversibles* (Thesis, Brussels, 1947), pp. 76, 100.

² S. R. de Groot, *Thermodynamics of Irreversible Processes* (North Holland Publishing Company, Amsterdam, and Interscience Publishers, Inc., New York, 1951), pp. 94, 106.

Here $c_k = \rho_k / \rho$, where ρ_k is the density of k , and ρ is the total density; the flow \mathbf{J}_k of substance k is defined* with respect to the center-of-mass movement \mathbf{v}

$$\mathbf{J}_k = \rho_k(\mathbf{v}_k - \mathbf{v}) \quad (k=1, 2, \dots, n), \quad (2)$$

where \mathbf{v}_k is the velocity of k . The left-hand side of (1) contains the (barycentric) substantial time derivative

$$d/dt = \partial/\partial t + \mathbf{v} \cdot \text{grad}. \quad (3)$$

B. Law of Conservation of Momentum (Force Law)

$$\rho d\mathbf{v}/dt = -\text{grad}P + \sum_{k=1}^n \mathbf{F}_k \rho_k. \quad (4)$$

Here P is the pressure and \mathbf{F}_k is the external force per unit mass on substance k . We have, in our case,

$$\mathbf{F}_k = e_k \mathbf{E} + \mathbf{g} \quad (k=1, 2, \dots, n), \quad (5)$$

where e_k is the charge of k per unit mass, \mathbf{E} the electric field strength, and \mathbf{g} the centrifugal (gravitational) force per unit mass. Coriolis forces do not need to be taken into account when \mathbf{g} is sufficiently uniform, i.e., when the dimensions of the vessel are fairly small compared with its distance from the rotation axis. (Coriolis forces would anyway not contribute to the entropy production, but the Onsager relations might be impaired, and new cross-effects arise.)

C. Law of Conservation of Energy

In the absence of heat flow, this law has the form

$$0 = du/dt + P d\rho^{-1}/dt - \rho^{-1} \sum_{k=1}^n \mathbf{F}_k \cdot \mathbf{J}_k, \quad (6)$$

where u is the (internal) energy per unit mass (specific energy).

D. The Second Law (Gibbs' Relation)

The second law is

$$T ds/dt = du/dt + P d\rho^{-1}/dt - \sum_{k=1}^n \mu_k dc_k/dt, \quad (7)$$

where T is the temperature, s the specific entropy, and μ_k the chemical potential (partial specific Gibbs function) of substance k .

The entropy balance equation follows when c_k from (1) and u from (6) are introduced into (7):

$$\rho ds/dt = -\text{div} \mathbf{J}_s + \sigma. \quad (8)$$

The change of entropy is seen to be the result of an entropy flow

$$\mathbf{J}_s = -\sum_{k=1}^n \mu_k \mathbf{J}_k / T, \quad (9)$$

* Flows and electrical currents will be understood as flow densities and current densities (i.e., they are counted per unit area) throughout this paper.

and an entropy production of source strength σ ,

$$T\sigma = \sum_{k=1}^n \mathbf{J}_k \cdot \mathbf{X}_k, \quad (10)$$

where

$$\mathbf{X}_k = \mathbf{F}_k - \text{grad} \mu_k \quad (k=1, 2, \dots, n). \quad (11)$$

The entropy production σ (10), which is essentially positive, measures the irreversibility of the process. It is the starting point of further considerations.

III. THE ENTROPY PRODUCTION AT MECHANICAL EQUILIBRIUM AND VANISHING VOLUME FLOW

Equation (10) for the entropy source strength σ may be modified for the following two reasons. In the first place, we can assume that the system is in mechanical equilibrium. Then, according to a theorem of Prigogine,^{1,2} Eq. (10) for the entropy production remains invariant when we choose in (2), instead of \mathbf{v} , any arbitrary reference velocity. For our purpose zero is the best choice, or, in other words, we employ absolute flows

$$\mathbf{J}_k^0 = \rho_k \mathbf{v}_k \quad (k=1, 2, \dots, n) \quad (12)$$

in the entropy production σ from

$$T\sigma = \sum_{k=1}^n \mathbf{J}_k^0 \cdot \mathbf{X}_k. \quad (13)$$

(It may be noted, incidentally, that at mechanical equilibrium, i.e., the left-hand side of (4) vanishing, it follows from (4) and (5) that

$$\text{grad}P = \mathbf{g}\rho, \quad (14)$$

because electroneutrality,

$$\sum_{k=1}^m \rho_k e_k = 0, \quad (15)$$

can be assumed.)

In the second place, we can further modify the entropy production σ by introducing the boundary conditions for a liquid contained in a vessel, which may be stated as the vanishing of the total volume flow through a section (cf. appendix)

$$\sum_{k=1}^n v_k \mathbf{J}_k^0 = 0. \quad (16)$$

We shall from now on restrict ourselves to the region in the vessel where concentration gradients are negligible. We have then, because we have also assumed uniform temperature, for (11),

$$\mathbf{X}_k = \mathbf{F}_k - v_k \text{grad}P, \quad (k=1, 2, \dots, n), \quad (17)$$

where v_k is the partial specific volume of k .

With (16) \mathbf{J}_n^0 can be eliminated from (13). This

gives, on introducing (17) and (5),

$$T\sigma = \sum_{k=1}^{n-1} \mathbf{J}_k^0 \cdot \{e_k \mathbf{E} + (1 - v_k/v_n) \mathbf{g}\}, \quad (18)$$

an expression which can be rewritten in the alternative form

$$T\sigma = \mathbf{I} \cdot \mathbf{E} + \mathbf{J} \cdot \mathbf{g}, \quad (19)$$

with the electrical current

$$\mathbf{I} = \sum_{k=1}^m e_k \mathbf{J}_k^0, \quad (20)$$

and the total mass flow

$$\mathbf{J} = \sum_{k=1}^{n-1} (1 - v_k/v_n) \mathbf{J}_k^0 = \rho \mathbf{v}. \quad (21)$$

The last form follows from (16) and the definition of center-of-gravity velocity

$$\mathbf{v} = \left(\sum_{k=1}^n \rho_k \mathbf{v}_k \right) / \rho.$$

The fact that this velocity occurs now in σ is a result of the specializations in this section. This is not in contradiction with the fact that in general \mathbf{v} gives no contribution to σ (see Eq. (10)).

IV. THE PHENOMENOLOGICAL LAWS

The expressions for the entropy production (18) and (19) have the form of a sum of products of so-called "fluxes" and "forces." In the thermodynamics of irreversible processes, linear relationships are assumed between these fluxes and forces, which are called phenomenological laws. From (18) we obtain

$$\mathbf{J}_k^0 = \sum_{j=1}^{n-1} a_{kj} \{e_j \mathbf{E} + (1 - v_j/v_n) \mathbf{g}\} \quad (k=1, 2, \dots, n-1) \quad (22)$$

with, between the phenomenological coefficients, the Onsager relations⁴

$$a_{kj} = a_{jk}, \quad (k, j=1, 2, \dots, n-1), \quad (23)$$

which follows from the time reversal invariance of the equations of motion of individual constituent particles ("microscopic reversibility"). With the fluxes and forces of (19), the phenomenological laws are

$$\mathbf{I} = b_{11} \mathbf{E} + b_{12} \mathbf{g}, \quad (24)$$

$$\mathbf{J} = b_{21} \mathbf{E} + b_{22} \mathbf{g}, \quad (25)$$

with the Onsager relation

$$b_{12} = b_{21}. \quad (26)$$

⁴L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931); H. B. G. Casimir, Revs. Modern Phys. 17, 343 (1945), or, Phillips Research Rept. 1, 185 (1945).

The following relations exist between the phenomenological coefficients:

$$b_{11} = \sum_{k,j=1}^m a_{kj} e_k e_j, \quad (27)$$

$$b_{12} = \sum_{j=1}^{n-1} (1 - v_j/v_n) \sum_{k=1}^m a_{kj} e_k, \quad (28)$$

$$b_{22} = \sum_{k,j=1}^{n-1} (1 - v_k/v_n)(1 - v_j/v_n) a_{kj}. \quad (29)$$

The Onsager relations have been used in these expressions. Since σ is positive definite, we have inequalities

$$\left. \begin{aligned} a_{kk} &\geq 0, & |a_{kj}| &= |a_{jk}| \leq (a_{kk} a_{jj})^{\frac{1}{2}}, \\ b_{11} &\geq 0, & b_{22} &\geq 0, & |b_{12}| &= |b_{21}| \leq (b_{11} b_{22})^{\frac{1}{2}}, \end{aligned} \right\} \quad (k, j=1, 2, \dots, n-1), \quad (30)$$

etc., between the phenomenological coefficients.

V. THE PHYSICAL MEANING OF THE PHENOMENOLOGICAL COEFFICIENTS AND OF THE ONSAGER RELATIONS

We shall now consider the physical meaning of the coefficients in (24) and (25), and of the relation (26).

The diagonal coefficients b_{11} and b_{22} are the specific electric conductivity and the sedimentation rate in a short-circuited vessel, because from (24) and (25) it follows that

$$(\mathbf{I}/\mathbf{E})_{\sigma=0} = b_{11}, \quad (31)$$

$$(\mathbf{J}/\mathbf{g})_{E=0} = b_{22}. \quad (32)$$

The cross-coefficient b_{12} is connected with the sedimentation phenomena, *viz.*, the sedimentation potential and current. For both effects two definitions can be given. The sedimentation potential is defined as the electrical field per unit centrifugal force (or sometimes per unit total mass flow) in the stationary state of zero electrical current. From (24) and (25) the effect follows immediately:

$$(\mathbf{E}/\mathbf{g})_{I=0} = -b_{12}/b_{11}, \quad (33)$$

$$(\mathbf{E}/\mathbf{J})_{I=0} = -b_{12}/(b_{11}b_{22} - b_{12}b_{21}). \quad (34)$$

The sedimentation current is the electrical current per unit centrifugal force (or per unit total mass flow) in the absence of an electrical field (i.e., in a short-circuited vessel). In formulas

$$(\mathbf{I}/\mathbf{g})_{E=0} = b_{12}, \quad (35)$$

$$(\mathbf{I}/\mathbf{J})_{E=0} = b_{12}/b_{22}. \quad (36)$$

The other cross-coefficient, b_{21} , is connected with the electrophoretic phenomena. We define the barycentric electrophoresis coefficient as the mass flow per unit electrical current (or per unit electrical field) in the

absence of centrifugal forces. This gives from (24) and (25)

$$(\mathbf{J}/\mathbf{I})_{g=0} = b_{21}/b_{11}, \quad (37)$$

$$(\mathbf{J}/\mathbf{E})_{g=0} = b_{21}. \quad (38)$$

The other electrophoretic phenomenon has no conventional name. It is the gravitational field per unit electrical field (or per unit electrical current) in the stationary state of zero mass flow. Its magnitude is

$$(\mathbf{g}/\mathbf{E})_{J=0} = -b_{21}/b_{22}, \quad (39)$$

$$(\mathbf{g}/\mathbf{I})_{J=0} = -b_{21}/(b_{11}b_{22} - b_{12}b_{21}). \quad (40)$$

It is clear that the Onsager relation (26) connects a sedimentation with an electrophoretic phenomenon. We have, for instance, from (33), (37), and (26),

$$(\mathbf{E}/\mathbf{g})_{I=0} = -(\mathbf{J}/\mathbf{I})_{g=0}, \quad (41)$$

the connection between sedimentation potential and barycentric electrophoresis. Similar Onsager connections exist between (34) and (40), between (35) and (38), and between (36) and (39). In practice, usually the sedimentation potential (33) and the barycentric electrophoresis coefficient (38) are measured. When the Onsager relation (26) is employed one finds the following connection between these two effects and the electrical conductivity coefficient (31):

$$(\mathbf{J}/\mathbf{E})_{g=0} = -(\mathbf{I}/\mathbf{E})_{g=0}(\mathbf{E}/\mathbf{g})_{I=0}. \quad (42)$$

Besides the ordinary electrical and material conductivities (31) and (32), one could measure these conductivities in the stationary states of zero mass flow and zero electrical current. The electrical conductivity in the stationary state of zero mass flow follows from (24) and (25)

$$(\mathbf{I}/\mathbf{E})_{J=0} = b_{11} - (b_{12}b_{21}/b_{22}). \quad (43)$$

The sedimentation rate in the stationary state of zero electrical current is

$$(\mathbf{J}/\mathbf{g})_{I=0} = b_{22} - (b_{12}b_{21}/b_{11}). \quad (44)$$

In practice, not all the coefficients defined in this section are measured. The usual ones are the ordinary electrical conductivity (31), the sedimentation potential (33), the sedimentation current (35), the electrophoresis usually in the form of (38) but less frequently also as (37), and finally the sedimentation rate at zero electrical current (44), because the condition of zero electrical field would rather complicate the sedimentation experiment.

From (31) and (33) or from (38) the coefficient b_{12} ($=b_{21}$) can be calculated. The coefficient b_{22} should be determined from (44) in combination with (31) and (38) or directly from (32) if the experiment with zero electrical field can be done.

VI. THE CASE OF A COLLOID

We can apply the general formalism of the preceding sections to special cases. Let us consider a mixture of four components ($n=4$), of which three ($m=3$) carry electrical charges. We shall assume that the particles of the first charged component (the colloid) are very much larger than those of the other three. The second and third components are ions of opposite charge. The fourth component is a neutral solvent.

All relations derived in the previous section apply to this system. We shall prove, however, that in some limiting cases these formulas may be reduced to a new form. For the system considered here, Eqs. (27)–(29) can be written in the following way, if (12) and (22) are taken into account:

$$b_{11} = \sum_{j=1}^3 e_j \rho_j (\mathbf{v}_j/\mathbf{E})_{g=0}, \quad (45)$$

$$b_{12} = \sum_{j=1}^3 (1 - v_j/v_4) \rho_j (\mathbf{v}_j/\mathbf{E})_{g=0}, \quad (46)$$

$$b_{22} = \sum_{j=1}^3 (1 - v_j/v_4) \rho_j (\mathbf{v}_j/\mathbf{g})_{E=0}. \quad (47)$$

As a rule $(1 - v_j/v_4)$ is of the order 1, and $(\mathbf{v}_1/\mathbf{E})_{g=0}$ is not very much smaller than $(\mathbf{v}_2/\mathbf{E})_{g=0}$ and $(\mathbf{v}_3/\mathbf{E})_{g=0}$. Consequently the second and third terms on the right-hand side of (46) may be neglected provided that

$$\rho_1 \gg \rho_2 \quad \text{and} \quad \rho_1 \gg \rho_3, \quad (48)$$

conditions which are frequently fulfilled in colloidal systems. If these conditions are satisfied, the second and the third term of (47) may be neglected *a fortiori*. This is not possible with (45), where the terms contain factors e_j (the specific charges), which, on account of the condition of electroneutrality (15), compensate the effect of conditions (48).

It therefore follows that the expressions (46) and (47), or the equivalent (28) and (29), can be simplified, with the aid of conditions (48), to

$$b_{12} = (1 - v_1/v_4) \sum_{k=1}^3 a_{1k} e_k, \quad (49)$$

$$b_{22} = (1 - v_1/v_4) \sum_{k=1}^3 (1 - v_k/v_4) a_{1k}. \quad (50)$$

From (22) and (25), one obtains, employing these relations and only the a_{kj} occurring in them, the following formula for our limiting case:

$$\mathbf{J} = (1 - v_1/v_4) \mathbf{J}_1^0, \quad (51)$$

which connects the total mass flow \mathbf{J} with the flow \mathbf{J}_1^0 of the colloid particles alone. This is a very important special case for colloidal systems, and we shall give a

few results which can be derived from the general formalism of the preceding section, employing the approximation (51).

Equation (42), for instance, becomes then,

$$(\mathbf{J}_1^0/\mathbf{E})_{g=0} = -(\mathbf{I}/\mathbf{E})_{g=0} \{ \mathbf{E}/g(1-v_1/v_4) \}_{r=0}. \quad (52)$$

At the left-hand side we have now the ordinary electrophoresis coefficient, instead of the barycentric electrophoresis coefficient. At the right-hand side the sedimentation potential is now expressed with respect to a modified centrifugal field instead of the centrifugal field g .

Similar formulas for colloidal systems could be derived from the other results of Sec. 5, employing the approximation (51). The first members of (32) and (44), for instance, take, on employing (51), the form

$$\{ \mathbf{J}_1^0/g(1-v_1/v_4) \}_{r=0} \quad (53)$$

of the quotient of the flow of colloid particles and the reduced centrifugal field.

An important conclusion can be drawn from the formula (49), because it shows the influence of conduction relaxation on sedimentation and electrophoresis phenomena. If relaxation exists, it manifests itself in the coefficients a_{12} , a_{13} and in contributions to the coefficients a_{11} , a_{22} , a_{33} , and a_{23} . All relations such as (52), which connect a sedimentation phenomenon (depending on b_{12}) with an electrophoresis phenomenon (depending on b_{21}) are ultimately Onsager relations (26). The value of the coefficients b_{12} and b_{21} is given by (49). We can draw the conclusion that relaxation phenomena contribute always to both the sedimentation and the electrophoresis phenomena in exactly the same way.

Furthermore, even when the approximation (49) is not valid, this conclusion holds. To show this, we may remark that, in the first place, our conclusion is correct for barycentric instead of ordinary electrophoresis, as can be seen, for instance, from the Onsager relation (42) (of which (52) was the approximation considered

above). In the second place it is clear that if, in the general case, ordinary electrophoresis is affected by relaxation phenomena, this will also be the case for barycentric electrophoresis, and consequently (e.g., (42)) for sedimentation phenomena. Thus, if relaxation exists, its influence should be taken into account in the interpretation of sedimentation experiments.

VII. APPENDIX

The condition (16) of zero total volume flow can be connected with other physical characteristics of the system in the following way.

For the densities and the partial specific volumes, one has the identity

$$\sum_k \rho_k v_k = \rho v = 1. \quad (54)$$

From this follows

$$\sum_k v_k \partial \rho_k / \partial t + \sum_k \rho_k \partial v_k / \partial t = 0. \quad (55)$$

From this relation and the conservation of mass

$$\partial \rho_k / \partial t = -\operatorname{div} \mathbf{J}_k^0 \equiv -\operatorname{div} \rho_k \mathbf{v}_k \quad (56)$$

the following expression is obtained:

$$\operatorname{div} \sum_k v_k \mathbf{J}_k^0 = \sum_k \rho_k (\partial v_k / \partial t + \mathbf{v}_k \cdot \operatorname{grad} v_k). \quad (57)$$

At the right-hand side between the parentheses one recognizes a substantial derivative of the partial specific volume v_k with respect to the velocity \mathbf{v}_k . It vanishes if we assume that v_k does not appreciably depend on pressure and concentrations. Then the divergence of (16) turns out to be zero, and therefore also (16) itself.

One of us (P.M.) wishes to acknowledge the financial assistance received from the Centre de Chimie physique moléculaire Belge, which enabled him to pursue this research.