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SEDIMENTATION AND DIFFUSION IN A SOLUTION OF TWO ELECTROLYTES, AS DESCRIBED BY IRREVERSIBLE THERMODYNAMICS.

BY

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§ 1. *Introduction*

The weight of the colloidal particles is an important factor in the interpretation of the behaviour of colloidal solutions. Often this weight is derived from measurements of sedimentation and diffusion. In the case of *uncharged* colloidal particles this method is straightforward. In the case of colloidal *electrolytes*, however, the electrical interaction amongst the migrating ions may produce very pronounced non-ideality effects in sedimentation and diffusion. Moreover, it is difficult to avoid the use of unmeasurable quantities, like single ion activities, diffusion potentials etc. in the analysis. These facts have given rise to some doubt [1] about the meaning of the colloid molecular weight that is found from experiments in this case.

This problem will be treated in the present and especially in the following papers.

§ 2. *The system*

In actual systems in which we are interested, the colloidal electrolyte is usually accompanied by one or more low molecular weight electrolytes (buffer solutions, monomeric soap ions, etc.). An analysis will therefore have to cover at least systems with one solvent and two electrolytic solutes.

We shall restrict our discussion to the aqueous solution of *one* electrolyte or to that of *two* electrolytes that have one ion in common. Examples of the latter system are: NaCl+KCl in water or Na-albuminate and NaCl in water. In the present paper we will only derive general equations into which the properties of one particular system have not yet been introduced; later [2] these results will be applied to the special case where one of the electrolytes is a *colloidal* electrolyte.

The common ion will be indicated by 2, the other ions, building with 2 the neutral electrolytes I and II, by 1 and 3. We assume that electro-

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neutrality is obeyed always and everywhere in the solution, so:

$$c_1 e_1 + c_{21} e_2 = 0 \qquad (1)$$
$$c_3 e_3 + c_{23} e_2 = 0$$

where c is the concentration in grams/ml and e the charge per gram of the ions; the charge of c_1 ions 1 is compensated by the charge of c_{21} ions 2 etc.; clearly $c_{21} + c_{23} = c_2$.

§ 3. *Methods of calculation*

In sedimentation and diffusion in the systems chosen in § 2, the differences in mobility of the different ions, and in the forces that are working on them, generate a *sedimentation potential* (field strength E_{sed}) and a *diffusion potential* (field strength E_{diff}).

There are two methods to describe the processes:

a. The first one is the 'kinetic' method. Here the velocity of each kind of ions is considered as the result of the forces on these ions. In our case these forces, per gram of the ions i, are:

A force from the centrifugal field:

$$K_{\text{centr}} = (1 - v_i \varrho)\, \omega^2 x \qquad (2)$$

where v is the partial specific volume, ϱ the density of the solution, and $\omega^2 x$ the centrifugal field strength (ω = angular velocity $= 2\pi\nu$, with ν = number of revolutions per second, and x = distance from the centre of rotation).

A 'force' from the concentration gradient $\mathrm{d}c_i/\mathrm{d}x$:

$$K_{\text{diff}} = -\frac{RT}{M_i} \cdot \frac{1}{c_i} \cdot \frac{\mathrm{d}c_i}{\mathrm{d}x} \qquad (3)$$

where R is the gas constant, T the absolute temperature, and M_i the 'molecular' weight of the ions i.

A force from the electric field:

$$K_{\text{el}} = e_i E. \qquad (4)$$

In dynamic equilibrium the sum of these (primary) forces is compensated by the frictional force K_f; in case of moderate velocities this frictional force is equal to:

$$K_f = -f_i \mathrm{v}_i \qquad (5)$$

where v_i is the velocity of the ions i, and f_i their frictional factor.

Considering the equilibrium between the primary and the frictional forces for a hypothetical (see § 6) process in which the force (2) or (3) is acting separately (: at $E = 0$), the following quantities may be defined: sedimentation constant:

$$s_i(s \text{ at } E = 0\,!) \equiv \frac{\mathrm{v}_i}{\omega^2 x} = \frac{1 - v_i \varrho}{f_i} \qquad (6)$$

diffusion coefficient:

$$D_i(D \text{ at } E=0\,!) \equiv \frac{\mathrm{v}_i c_i}{\frac{\mathrm{d}c_i}{\mathrm{d}x}} = \frac{RT}{M_i f_i}. \tag{7}$$

Furthermore we define:
electrophoretic mobility:

$$u_i \equiv \frac{\mathrm{v}_i}{E} = \frac{e_i}{f_i}. \tag{8}$$

It is generally assumed that the frictional factors in (6), (7) and (8) are the same, but one should bear in mind that this is an assumption. Accepting this assumption, we may express the velocity of the ions in the quantities s_i, u_i and D_i. The result of such a calculation is given in § 4.

We note that in eq. (3) we did not take $-\text{grad}\ \mu_i$, but only the ideal part of $-\text{grad}\ \mu_i$ as the 'force' in diffusion; consequently cross-effects (influences of concentration gradients of other ions) have been omitted. Fortunately, in our systems the electrical interactions due to E_{sed} and E_{diff}, and accounted for in the equations in § 4, largely predominate the omitted interactions. Formally, the interactions not accounted for in this way might be incorporated into the coefficients of friction.

Finally we remark that the assumption of the equality of the frictional factors in eqs. (6)–(8) is equivalent to the assumption that:

$$\frac{1-v_i\varrho}{s_i} = \frac{RT}{M_i D_i} = \frac{e_i}{u_i}, \tag{9}$$

b. The second method is that of irreversible thermodynamics. A detailed discussion of this method follows after § 4.

We prefer this method above the kinetic one, because no assumptions have to be made about frictional factors or separate ion activities, while nevertheless mutual influences can be accounted for completely.

§ 4. *Results of the kinetic treatment*

In the usual experimental set-up no net transport of charge through the solutions is possible, i.e. the electric current density I_{el} is zero:

$$I_{\text{el}} = \sum_i c_i e_i \mathrm{v}_i = 0. \tag{10}$$

This implies that the result of every sedimentation or diffusion process is a displacement of the neutral electrolytes I and II, with a velocity $\mathrm{v}_{\text{I}} = \mathrm{v}_1$ and $\mathrm{v}_{\text{II}} = \mathrm{v}_3$. For this reason we define the following mass flows:

$$\begin{aligned} J_{\text{I}} &\equiv c_{\text{I}}\mathrm{v}_1 \\ J_{\text{II}} &\equiv c_{\text{II}}\mathrm{v}_3. \end{aligned} \tag{11}$$

For each ion constituent in a mixture of electrolytes in a centrifugal field $K_{\text{centr}} + K_{\text{el}} + K_f$ is put equal to zero. Eq. (10) is used to eliminate E. This method has been worked out previously by TISELIUS [3], SVEDBERG and PEDERSEN [4] [5].

In case of our system of § 2, the mass flows (11) are then given by:

$$(12)\quad \begin{cases} J_{\mathrm{I,sed}} = c_{\mathrm{I}}\,\omega^2 x\left[s_1-\tau_1(s_1-s_2)-\dfrac{c_{23}}{c_{21}}\,\tau_1(s_3-s_2)\right] \\ J_{\mathrm{II,sed}} = c_{\mathrm{II}}\,\omega^2 x\left[s_3-\tau_3(s_3-s_2)-\dfrac{c_{21}}{c_{23}}\,\tau_3(s_1-s_2)\right] \end{cases}$$

where τ are transport numbers defined by

$$\tau_i \equiv \frac{c_i\,e_i\,u_i}{\sum c_i\,e_i\,u_i}.$$

As the mobilities u_i are considered with respect to the vessel and not with respect to the solvent, these transport numbers are not exactly equal to Hittorf transport numbers.

These equations will be discussed in § 7*b*.

In a similar way the behaviour of a mixture of two electrolytes in a solution with concentration gradients has been studied by NERNST [6] and, later, a.o. by HARTLEY and ROBINSON [7]. The mass flows in diffusion can be shown to be equal to:

$$(13)\quad \begin{cases} J_{\mathrm{I,diff}} = -\left[D_1-\tau_1(D_1-D_2)\right]\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}-\left[-\dfrac{c_{23}/c_{\mathrm{II}}}{c_{21}/c_{\mathrm{I}}}\,\tau_1(D_3-D_2)\right]\dfrac{\mathrm{d}c_{\mathrm{II}}}{\mathrm{d}x} \\ J_{\mathrm{II,diff}} = -\left[D_3-\tau_3(D_3-D_2)\right]\dfrac{\mathrm{d}c_{\mathrm{II}}}{\mathrm{d}x}-\left[-\dfrac{c_{21}/c_{\mathrm{I}}}{c_{23}/c_{\mathrm{II}}}\,\tau_3(D_1-D_2)\right]\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}. \end{cases}$$

We shall come back to these equations in § 7*c*.

§ 5. *General remarks on the treatment by irreversible thermodynamics*

In irreversible thermodynamics [8] [9] [10] attention is directed towards the entropy production that results from irreversible processes. This entropy production per second per unit volume will be indicated by σ. It can be expressed as the sum of products of two terms. For isothermal processes this expression is:

$$(14)\quad T\sigma = \sum_{j=1}^{n} J_j\,X_j.$$

There is some freedom in choosing J_j and X_j; often they are easily visualized as macroscopic 'fluxes' and 'forces'.

If we describe a system by a certain set of state parameters (e.g. temperature and chemical potentials), the deviation of these parameters from their equilibrium values may be seen as the 'forces' which cause the irreversible processes, in the form of 'fluxes' (e.g. heat flow and mass flow).

In general every flux will be a function of all forces and they are linear functions for small deviations from equilibrium:

$$(15)\quad J_j = \sum_{l=1}^{n} L_{jl}\,X_l \qquad (j=1,\,\dots\,n).$$

The eqs. (15) are called the phenomenological equations. Using the argument of microscopic reversibility in time, it has been shown [11] that the following relations (Onsager relations) exist between the coefficients L_{jl}:

$$L_{lj} = L_{jl}. \tag{16}$$

For every problem first an equation (14) must be derived. This is done by writing down the total rate of change of entropy of the system. If we are dealing with continuous systems, where the state parameters vary continuously in space, we consider the entropy change in an infinitesimal volume element.

This entropy change is not necessarily positive; e.g. in the 'higher concentration part' in a diffusion cell it is negative. The irreversible part, σ, of the entropy change however (the sum of the total entropy change and the divergence of the entropy flow through the volume element) is always positive. E.g. in a constant concentration gradient of a single substance just as much material leaves the volume element as has entered into it; leaving it, however, it has a higher entropy (per unit of mass) than when it came in; the total entropy of the volume element remaining constant, σ is positive.

Sedimentation as well as diffusion are typical irreversible processes. In both cases the system is moving to a more probable state. If there is no external field, as in diffusion, this means to a homogeneous concentration distribution; if there is an external field, as in sedimentation, this means: to a state of lower free energy.

For diffusion the nature of the entropy production in a volume element was discussed above. In sedimentation there is also an entropy production. Considering a volume element in the 'constant concentration region' in the sedimentation cell and working isothermally, there is no entropy change; the entropy production is equivalent to the frictional work done by the field on the volume element, and is delivered to the surroundings as heat. No essentials have to be added to this discussion for the combined processes of sedimentation and diffusion.

When dealing with electrically charged particles, an external electric field may also contribute to the entropy production, just as a centrifugal field. A short discussion of the nature of the electric field in sedimentation is given in the next section, a more comprehensive treatment is postponed to § 8.

§ 6. *The entropy production and the phenomenological equations*

An expression has been derived by Hooyman et al. [12] for the entropy production σ in a system of n components (which may have an electrical charge) where a centrifugal field ($\omega^2 x$), an electric field strength (E) and gradients of the chemical potential ($(\operatorname{grad} \mu_k)_{P,T}$) are present ($P$ is the pressure). Temperature gradients are excluded and the condition (17) of electroneutrality has already been introduced:

$$\sum_{k=1}^{n} c_k e_k = 0. \tag{17}$$

This expression is:

$$(18)\qquad T\sigma = \sum_{k=1}^{n} J_k{}^a\{(1-\varrho v_k)\,\omega^2 x + e_k E - (\operatorname{grad}\mu_k)_{P,T}\}.$$

The superscript a in the mass flows $J_k{}^a \equiv c_k \mathbf{v}_k{}^a$ means that the velocities may be chosen relative to an arbitrary reference velocity; this is permitted [13] [14] when the time derivative of the weight-mean velocity (centre of mass velocity) of the components in a volume element is zero, a condition which may be assumed to be satisfied in our case.

Eq. (18) was already applied [14] by HOOYMAN to a multicomponent system of uncharged particles; we will apply it to our system chosen before, where charged particles are present. An equation analogous to (18) for the case that there are charged particles, but no concentration gradients, was derived by DE GROOT, MAZUR and OVERBEEK [15].

We choose as reference velocity the mean volume velocity $\mathbf{v}^0$, defined by:

$$(19)\qquad \mathbf{v}^0 \equiv \sum_k c_k v_k \mathbf{v}_k = \sum_k v_k J_k$$

where $\mathbf{v}_k$ is the velocity relative to the wall of the vessel. So:

$$(20)\qquad J_k{}^0 = c_k(\mathbf{v}_k - \mathbf{v}^0)$$

$\mathbf{v}^0$ is zero if [15] v_k does not depend on pressure and concentrations. We suppose this condition to be satisfied, so:

$$(21)\qquad \mathbf{v}^0 = 0.$$

By using (19), (20) and (21) we may eliminate the mass flow $J^0{}_{\text{solvent}}$ from (18). The resulting equation is again of the type (14).

From here we will restrict our discussion to the simple system chosen before. Because the solution may be considered as being built up from three electroneutral components 0 (solvent), I and II, and an electric current may be present, but zero volume flow imposes one restriction, there are three pairs of forces and fluxes. We choose as fluxes of matter:

$$(22)\qquad \begin{cases} J_{\text{I}} = c_{\text{I}}\mathbf{v}_1 \\ J_{\text{II}} = c_{\text{II}}\mathbf{v}_3 \end{cases}$$

where, in view of (20) and (21), the superscript 0 has been omitted. The electric current (23) is chosen as the third flux:

$$(23)\qquad I_{\text{el}} = \sum_{i=1}^{3} J_i{}^0 e_i = \sum_{i=1}^{3} J_i e_i.$$

Then, by using the following relations:

$$c_1 v_1 + c_{21} v_2 = c_{\text{I}} v_{\text{I}};\quad c_3 v_3 + c_{23} v_2 = c_{\text{II}} v_{\text{II}};$$

$$c_1 \mu_1 + c_{21}\mu_2 = c_{\text{I}}\mu_{\text{I}};\quad c_3\mu_3 + c_{23}\mu_2 = c_{\text{II}}\mu_{\text{II}};$$

$$c_{\text{I}} v_{\text{I}} + c_{\text{II}} v_{\text{II}} + c_0 v_0 = 1$$

the entropy production may be written as (writing grad μ for grad $\mu_{P,T}$):

$$(24)\quad \left\{\begin{aligned} T\sigma = I_{\mathrm{el}}&\left[E+\frac{1}{e_2}\left(1-\frac{v_2}{v_0}\right)\omega^2 x-\frac{1}{e_2}\operatorname{grad}\mu_2+\frac{1}{e_2}\cdot\frac{v_2}{v_0}\operatorname{grad}\mu_0\right]\\ &+J_{\mathrm{I}}\left[\left(1-\frac{v_{\mathrm{I}}}{v_0}\right)\omega^2 x-\frac{1}{c_0 v_0}\{(1-c_{\mathrm{II}}v_{\mathrm{II}})\operatorname{grad}\mu_{\mathrm{I}}+c_{\mathrm{II}}v_{\mathrm{I}}\operatorname{grad}\mu_{\mathrm{II}}\}\right]\\ &+J_{\mathrm{II}}\left[\left(1-\frac{v_{\mathrm{II}}}{v_0}\right)\omega^2 x-\frac{1}{c_0 v_0}\{(1-c_{\mathrm{I}}v_{\mathrm{I}})\operatorname{grad}\mu_{\mathrm{II}}+c_{\mathrm{I}}v_{\mathrm{II}}\operatorname{grad}\mu_{\mathrm{I}}\}\right]\end{aligned}\right.$$

or

$$(25)\qquad T\sigma = I_{\mathrm{el}}\varphi+J_{\mathrm{I}}\chi+J_{\mathrm{II}}\psi.$$

As a result of choosing simple fluxes, we have run into rather complicated expressions (φ, χ and ψ) for the forces. Other choices would have been possible, but with no essential gain in simplicity.

The phenomenological equations, to be chosen from (25) are:

$$(26)\qquad \left\{\begin{aligned} I_{\mathrm{el}} &= A_{11}\varphi+A_{12}\chi+A_{13}\psi\\ J_{\mathrm{I}} &= A_{21}\varphi+A_{22}\chi+A_{23}\psi\\ J_{\mathrm{II}} &= A_{31}\varphi+A_{32}\chi+A_{33}\psi\end{aligned}\right.$$

in which, according to eq. (16)

$$(27)\qquad A_{21}=A_{12};\ A_{31}=A_{13};\ A_{32}=A_{23}.$$

All quantities at the right hand side of eq. (25) are measurable. For the fluxes this is self-evident; the forces χ and ψ contain only measurable properties of electroneutral substances, as may be seen by inspection of eq. (24). The force φ, however, contains the unmeasurable quantities v_2 and μ_2 of the ions 2, and E itself is measurable only in the absence of concentration gradients and centrifugal field. Nevertheless φ itself can be measured. From eq. (26) we have:

$$(28)\qquad \varphi = \frac{I_{\mathrm{el}}-A_{12}\chi-A_{13}\psi}{A_{11}}$$

or, using eq. (27):

$$(29)\qquad \varphi = \frac{I_{\mathrm{el}}-A_{21}\chi-A_{31}\psi}{A_{11}}.$$

In eq. (29) all quantities at the right hand side can be measured; for I_{el}, χ and ψ this was mentioned above, and according to eqs. (30), (31) and (32) A_{11}, A_{21} and A_{31} are also accessible quantities.

As mentioned above E is only measurable at $\omega^2 x=0$ and in the absence of concentration gradients. In that case E is the only contribution to φ. This allows us to find simple meanings for the coefficients A_{11}, A_{21} and A_{31}, viz.:

$$A_{11} = \left(\frac{I_{\mathrm{el}}}{E}\right)_{\substack{\omega^2 x=0\\ \mathrm{grad}\, c_{\mathrm{I}}=0\\ \mathrm{grad}\, c_{\mathrm{II}}=0}} = \varkappa_{\mathrm{spec}} \text{ (specific conductivity)} \tag{30}$$

$$A_{21} = \left(\frac{J_{\mathrm{I}}}{E}\right)_{\substack{\omega^2 x=0\\ \mathrm{grad}\, c_{\mathrm{I}}=0\\ \mathrm{grad}\, c_{\mathrm{II}}=0}} = c_{\mathrm{I}}\, u_1 \tag{31}$$

$$A_{31} = \left(\frac{J_{\mathrm{II}}}{E}\right)_{\substack{\omega^2 x=0\\ \mathrm{grad}\, c_{\mathrm{I}}=0\\ \mathrm{grad}\, c_{\mathrm{II}}=0}} = c_{\mathrm{II}}\, u_3. \tag{32}$$

No simple meaning can be attached to the coefficients A_{22}, $A_{23}=A_{32}$ and A_{33}. They can be determined by measuring J_{I} and J_{II} in experiments in which χ and ψ are varied independently. This cannot be done in sedimentation experiments at constant concentration, because then χ and ψ are strictly proportional to each other. In diffusion experiments, however, $\mathrm{grad}\, \mu_{\mathrm{I}}$ and $\mathrm{grad}\, \mu_{\mathrm{II}}$ can be varied independently and thus A_{22}, $A_{23}=A_{32}$ and A_{33} can be determined.

Finally we want to mention that the application of irreversible thermodynamics to sedimentation and diffusion has also been discussed by HAASE [16], MILLER [17] and SCHÖNERT [18].

§ 7. *Application of the general equations to special cases*

In the present section we shall analyze a number of special cases without, however, introducing the particular components into the irreversible equations; this will be done in a succeeding paper.

a. Sedimentation and diffusion in a solution of *one* electrolyte.

In this case eq. (24) reduces to:

$$\left\{\begin{aligned} T\sigma = I_{\mathrm{el}}\left[E + \frac{1}{e_2}\left(1-\frac{v_2}{v_0}\right)\omega^2 x - \frac{1}{e_2}\,\mathrm{grad}\,\mu_2 + \frac{1}{e_2}\cdot\frac{v_2}{v_0}\,\mathrm{grad}\,\mu_0\right] + {}\\ + J_{\mathrm{I}}\left[\left(1-\frac{v_{\mathrm{I}}}{v_0}\right)\omega^2 x - \frac{1}{c_0 v_0}\,\mathrm{grad}\,\mu_{\mathrm{I}}\right]\end{aligned}\right. \tag{33}$$

or:

$$T\sigma = I_{\mathrm{el}}\,\varphi' + J_{\mathrm{I}}\,\chi' \tag{34}$$

from which:

$$\left\{\begin{aligned} I_{\mathrm{el}} &= R_{11}\,\varphi' + R_{12}\,\chi'\\ J_{\mathrm{I}} &= R_{21}\,\varphi' + R_{22}\,\chi'. \end{aligned}\right. \tag{35}$$

We consider the sedimentation ($\omega^2 x \neq 0$, $\mathrm{grad}\,\mu_{\mathrm{I}}=0$) and the diffusion ($\omega^2 x=0$, $\mathrm{grad}\,\mu_{\mathrm{I}}\neq 0$) separately, both at the experimental condition

$I_{\mathrm{el}}=0$. Then we find:

$$(36)\quad \begin{cases} s_{\mathrm{I,exp}} \equiv \dfrac{1}{c_{\mathrm{I}}\omega^2 x}\{J_{\mathrm{I}}\}_{\substack{I_{\mathrm{el}}=0\\ \mathrm{grad}\,\mu_{\mathrm{I}}=0}} = \\ \qquad = \left\{-R_{21}\cdot\dfrac{R_{12}}{R_{11}}+R_{22}\right\}\left(1-\dfrac{v_{\mathrm{I}}}{v_0}\right)\dfrac{1}{c_{\mathrm{I}}} \equiv P\left(1-\dfrac{v_{\mathrm{I}}}{v_0}\right)\dfrac{1}{c_{\mathrm{I}}} \end{cases}$$

$$(37)\quad \begin{cases} D_{\mathrm{I,exp}} \equiv -\dfrac{1}{\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}}\{J_{\mathrm{I}}\}_{\substack{I_{\mathrm{el}}=0\\ \omega^2 x=0}} = \\ \qquad = \left\{-R_{21}\cdot\dfrac{R_{12}}{R_{11}}+R_{22}\right\}\dfrac{\mathrm{grad}\,\mu_{\mathrm{I}}}{c_0 v_0\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}} \equiv P\dfrac{\mathrm{grad}\,\mu_{\mathrm{I}}}{c_0 v_0\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}}. \end{cases}$$

From (36) and (37) we see that the concentration dependence, as far as the factor P is concerned, is exactly the same for sedimentation and diffusion. For non-electrolytes this conclusion could already be derived from HOOYMAN's results [12].

The diffusion in a mixture of electrolytes was treated by ONSAGER and FUOSS [19]. Their basic equation for the diffusion of one electrolyte was:

$$D_{\mathrm{I,\,exp}} = \Omega\,\frac{\mathrm{grad}\,\mu_{\mathrm{I}}}{\dfrac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x}}$$

in which Ω is a mobility factor calculated in the theory. It is equivalent to our factor P/c_0v_0 and this means that Onsager and Fuoss' calculation can also be used for sedimentation.

From (36) and (37) the wellknown equation (38) for M_{I} can easily be derived. In the derivation use is made of the expressions

$$c_0v_0(1-v_{\mathrm{I}}/v_0)=1-v_{\mathrm{I}}\varrho \text{ and } \mathrm{grad}\,\mu_{\mathrm{I}}=(iRT/M_{\mathrm{I}})\,\mathrm{grad}\ln f_{\mathrm{I}}c_{\mathrm{I}}.$$

$$(38)\qquad M_{\mathrm{I}}=\frac{i\,RT\,s_{\mathrm{I,\,exp}}\,(1+\mathrm{dln}\,f_{\mathrm{I}}/\mathrm{dln}\,c_{\mathrm{I}})}{D_{\mathrm{I,\,exp}}\,(1-v_{\mathrm{I}}\varrho)}$$

b. Sedimentation in a solution of two electrolytes.

Here grad c_{I} and grad c_{II} are zero. Considering again the situation where $I_{\mathrm{el}}=0$, the following expressions can easily be derived from (24), (25) and (26):

$$(39)\quad \begin{cases} \{J_{\mathrm{I}}\}_{\substack{I_{\mathrm{el}}=0\\ \mathrm{grad}\,c_{\mathrm{I}}=0\\ \mathrm{grad}\,c_{\mathrm{II}}=0}} \equiv J_{\mathrm{I,sed}} = \left[N_{\mathrm{I-I}}\left(1-\dfrac{v_{\mathrm{I}}}{v_0}\right)+N_{\mathrm{I-II}}\left(1-\dfrac{v_{\mathrm{II}}}{v_0}\right)\right]\omega^2 x \\ \qquad\qquad J_{\mathrm{II,sed}} = \left[N_{\mathrm{II-I}}\left(1-\dfrac{v_{\mathrm{I}}}{v_0}\right)+N_{\mathrm{II-II}}\left(1-\dfrac{v_{\mathrm{II}}}{v_0}\right)\right]\omega^2 x \end{cases}$$

in which:

$$(40)\qquad \left\{\begin{aligned} N_{\text{I-I}} &\equiv -A_{21}\cdot\frac{A_{12}}{A_{11}}+A_{22}\\ N_{\text{I-II}} &\equiv -A_{21}\cdot\frac{A_{13}}{A_{11}}+A_{23}\\ N_{\text{II-I}} &\equiv -A_{31}\cdot\frac{A_{12}}{A_{11}}+A_{32}\\ N_{\text{II-II}} &\equiv -A_{31}\cdot\frac{A_{13}}{A_{11}}+A_{33} \end{aligned}\right.$$

where, from (27):

$$(41)\qquad N_{\text{II-I}} = N_{\text{I-II}}.$$

For a further evaluation of (39), expressions for the A's must be introduced. From (24)–(26) we have:

$$(42)\qquad \left\{\begin{aligned} &A_{11}\cdot\frac{1}{e_2}\left(1-\frac{v_2}{v_0}\right)+A_{12}\left(1-\frac{v_{\text{I}}}{v_0}\right)+A_{13}\left(1-\frac{v_{\text{II}}}{v_0}\right)=\left\{\frac{I_{\text{el}}}{\omega^2 x}\right\}_{\substack{E=0\\ \operatorname{grad} c_{\text{I}}=0\\ \operatorname{grad} c_{\text{II}}=0}}=\\ &\qquad = c_1 e_1 s_1 + c_2 e_2 s_2 + c_3 e_3 s_3 \end{aligned}\right.$$

$$(43)\qquad \left\{\begin{aligned} &A_{21}\cdot\frac{1}{e_2}\left(1-\frac{v_2}{v_0}\right)+A_{22}\left(1-\frac{v_{\text{I}}}{v_0}\right)+A_{23}\left(1-\frac{v_{\text{II}}}{v_0}\right)=\left\{\frac{J_{\text{I}}}{\omega^2 x}\right\}_{\substack{E=0\\ \operatorname{grad} c_{\text{I}}=0\\ \operatorname{grad} c_{\text{II}}=0}}=\\ &\qquad = c_{\text{I}} s_1 \end{aligned}\right.$$

$$(44)\qquad \left\{\begin{aligned} &A_{31}\cdot\frac{1}{e_2}\left(1-\frac{v_2}{v_0}\right)+A_{32}\left(1-\frac{v_{\text{I}}}{v_0}\right)+A_{33}\left(1-\frac{v_{\text{II}}}{v_0}\right)=\left\{\frac{J_{\text{II}}}{\omega^2 x}\right\}_{\substack{E=0\\ \operatorname{grad} c_{\text{I}}=0\\ \operatorname{grad} c_{\text{II}}=0}}=\\ &\qquad = c_{\text{II}} s_3. \end{aligned}\right.$$

Introducing (42), (43) and (44) and (30), (31) and (32) in (39) and (40) we find:

$$(45)\qquad \left\{\begin{aligned} J_{\text{I, sed}} &= c_{\text{I}}\,\omega^2 x\left[s_1-\tau_1(s_1-s_2)-\frac{c_{23}}{c_{21}}\,\tau_1(s_3-s_2)\right]\\ J_{\text{II, sed}} &= c_{\text{II}}\,\omega^2 x\left[s_3-\tau_3(s_3-s_2)-\frac{c_{21}}{c_{23}}\,\tau_3(s_1-s_2)\right] \end{aligned}\right.$$

where again electric transport numbers, defined before, are used.

The equations (45) are the same as the 'Tiselius-equations' (12). They are formally correct, but have the disadvantage that they contain the unmeasurable quantities s_i; these entered into the present treatment from the expressions (42)–(44) for the A's in terms of these unmeasurable s_i's.

The statement made at the end of section 6, that sedimentation measurements alone are not sufficient to determine the whole set of A's is easily verified here. Measurement of $J_{\mathrm{I,sed}}$ and $J_{\mathrm{II,sed}}$ gives only two relations between 3 N's or with the aid of eq. (30), (31), (32) and (40) five relations between 6 A's. The introduction of the s_i's does not change this situation.

One additional assumption allows us to determine all N's and A's. As such we may choose the model assumption (9), putting $\varrho \approx 1/v_0$, which is a good approximation for dilute solutions

$$s_i e_i = u_i(1 - v_i/v_0). \tag{9}$$

With this assumption, and combining the v_i's into v_{I} and v_{II}, the eqs. (45) are converted into a more practical form in which the coefficients N are now written in terms of accessible quantities.

$$\left\{\begin{aligned} J_{\mathrm{I,sed}} &= \left[\left\{c_{\mathrm{I}}^2 \frac{u_1}{c_1 e_1}(1-\tau_1)\right\}\left(1-\frac{v_{\mathrm{I}}}{v_0}\right) - \left\{c_{\mathrm{I}} c_{\mathrm{II}} \frac{u_1}{c_3 e_3}\tau_3\right\}\left(1-\frac{v_{\mathrm{II}}}{v_0}\right)\right]\omega^2 x \\ J_{\mathrm{II,sed}} &= \left[-\left\{c_{\mathrm{I}} c_{\mathrm{II}} \frac{u_3}{c_1 e_1}\tau_1\right\}\left(1-\frac{v_{\mathrm{I}}}{v_0}\right) + \left\{c_{\mathrm{II}}^2 \frac{u_3}{c_3 e_3}(1-\tau_3)\right\}\left(1-\frac{v_{\mathrm{II}}}{v_0}\right)\right]\omega^2 x. \end{aligned}\right. \tag{46}$$

It should be realized, however, that by introducing eq. (9), it is postulated that the interaction terms, except those described by the sedimentation potential, are identical for electrophoresis and for sedimentation, and that in many actual cases this postulate will be incorrect.

c. Diffusion in a solution of two electrolytes.

Here $\omega^2 x = 0$. Again we study only the situation where $I_{\mathrm{el}} = 0$. The form of the resulting equations will come out to be completely the same as that of the equations derived by Hooyman [20] for uncharged particles.

For reasons of convenience we will restrict ourselves, without loosing essentials, to the case of dilute solutions where we have:

$$c_0 v_0 \approx 1$$

$$1 - c_{\mathrm{II}} v_{\mathrm{II}} \approx 1 \approx 1 - c_{\mathrm{I}} v_{\mathrm{I}}$$

$$c_{\mathrm{II}} v_{\mathrm{I}} \approx 0 \approx c_{\mathrm{I}} v_{\mathrm{II}}.$$

Then we find from eqs. (24)–(26) and (40):

$$\left\{\begin{aligned} \{J_{\mathrm{I}}\}_{\substack{\omega^2 x = 0 \\ I_{\mathrm{el}}=0}} &\equiv J_{\mathrm{I,diff}} = -N_{\mathrm{I-I}} \operatorname{grad} \mu_{\mathrm{I}} - N_{\mathrm{I-II}} \operatorname{grad} \mu_{\mathrm{II}} \\ \{J_{\mathrm{II}}\}_{\substack{\omega^2 x = 0 \\ I_{\mathrm{el}}=0}} &\equiv J_{\mathrm{II,diff}} = -N_{\mathrm{II-I}} \operatorname{grad} \mu_{\mathrm{I}} - N_{\mathrm{II-II}} \operatorname{grad} \mu_{\mathrm{II}}. \end{aligned}\right. \tag{47}$$

Usually diffusion is described in terms of concentration gradients viz.:

$$\left\{\begin{aligned} J_{\mathrm{I,diff}} &= -D_{\mathrm{I-I}} \frac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x} - D_{\mathrm{I-II}} \frac{\mathrm{d}c_{\mathrm{II}}}{\mathrm{d}x} \\ J_{\mathrm{II,diff}} &= -D_{\mathrm{II-I}} \frac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}x} - D_{\mathrm{II-II}} \frac{\mathrm{d}c_{\mathrm{II}}}{\mathrm{d}x}. \end{aligned}\right. \tag{48}$$

By introducing:

$$(49)\quad \begin{aligned} \operatorname{grad}\mu_{\mathrm{I}} &= \frac{\partial\mu_{\mathrm{I}}}{\partial c_{\mathrm{I}}}\frac{dc_{\mathrm{I}}}{dx} + \frac{\partial\mu_{\mathrm{I}}}{\partial c_{\mathrm{II}}}\frac{dc_{\mathrm{II}}}{dx} \\ \operatorname{grad}\mu_{\mathrm{II}} &= \frac{\partial\mu_{\mathrm{II}}}{\partial c_{\mathrm{I}}}\frac{dc_{\mathrm{I}}}{dx} + \frac{\partial\mu_{\mathrm{II}}}{\partial c_{\mathrm{II}}}\frac{dc_{\mathrm{II}}}{dx} \end{aligned}$$

or inversely by expressing dc/dx as a function of the grad μ's, the N's can be expressed in terms of D's and $\partial\mu/\partial c$'s. The reciprocity relation (41) gives a relation between the four diffusion coefficients (in general $D_{\mathrm{I-II}} \neq D_{\mathrm{II-I}}$). Recently the experimental verification of the Onsager relations, among them of the relation (41) from diffusion measurements, has been reviewed by MILLER [21].

Two remarks can be made:

1. In principle the four diffusion coefficients in eq. (48) may be derived from experiments; important work in this field has been done by GOSTING c.s. [22] [23]. From the D's and $\partial\mu/\partial c$'s which have to be determined separately, the three N's can be calculated and from them the complete set of A's (eq. (26)) is accessible.

Once the N's are known from diffusion experiments, the sedimentation behaviour (eq. (39)) may be predicted. As indicated before, however, the reverse procedure, prediction of diffusion from sedimentation, is not possible.

2. The cross diffusional coefficients $D_{\mathrm{I-II}}$ and $D_{\mathrm{II-I}}$ in eq. (48) describe the mutual interaction of the two diffusing species. For ideal non-electrolyte solutions their value is zero. In ideal electrolyte solutions, however, they contain important electrical interactions, as described formally by the coefficients

$$D_{\mathrm{I-II}} = -\frac{c_{23}/c_{\mathrm{II}}}{c_{21}/c_{\mathrm{I}}}\tau_1(D_3-D_2) \text{ and } D_{\mathrm{II-I}} = -\frac{c_{21}/c_{\mathrm{I}}}{c_{23}/c_{\mathrm{II}}}\tau_3(D_1-D_2)$$

in the simple kinetic eqs. (13). It may be interesting to check whether these equations, though not containing non-ideality effects, are consistent at least with the Onsager relation (41). This is indeed found to be the case if ideal relations between concentrations and chemical potentials are assumed and eq. (9) is used for the interconversion of transport numbers (containing u_i) and individual diffusion constants (D_i).

d. Sedimentation equilibrium in a solution of two electrolytes.

In the sedimentation equilibrium the gradient in chemical potential of each electroneutral component is compensated by its gradient in potential energy. Therefore:

$$(50)\quad \begin{cases} \operatorname{grad}\mu_{\mathrm{I}} = (1-v_{\mathrm{I}}\varrho)\,\omega^2 x \\ \operatorname{grad}\mu_{\mathrm{II}} = (1-v_{\mathrm{II}}\varrho)\,\omega^2 x. \end{cases}$$

These equations follow immediately from equilibrium thermodynamics.

They can also be derived from the irreversible equations, by putting all fluxes in the phenomenological equations (26) equal to zero, while applying:

$$c_I + c_{II} + c_0 = \varrho \text{ and } c_I v_I + c_{II} v_{II} + c_0 v_0 = 1.$$

In sedimentation equilibrium the equations (50) are valid everywhere in the cell. At every moment during sedimentation, however, they may be applied to the meniscus and the bottom of the cell, where automatically all the fluxes are zero, a statement due to Archibald [24].

§ 8. *Field strength and electromotive force in sedimentation cells*

It may be worth while to pay attention to the distinction that can be made between the field strength E and the electromotive force per unit length F.

In a solution without concentration gradients the field strength E can be derived from the first of the eq. (26).

$$(51)\quad E = \frac{I_{el} - c_I u_1 (1 - v_I/v_0)\,\omega^2 x - c_{II} u_3 (1 - v_{II}/v_0)\,\omega^2 x}{\varkappa_{spec}} - \frac{1}{e_2}\left(1 - \frac{v_2}{v_0}\right)\omega^2 x.$$

The electromotive force per unit length between electrodes that are reversible to the ion 2 is given by eq. (52). See Koenig and Grinnell [25], Miller [17] or MacInnes [26]

$$(52)\quad F = \frac{I_{el} - c_I u_1^* (1 - v_I \varrho)\,\omega^2 x - c_{II} u_3^* (1 - v_{II} \varrho)\,\omega^2 x}{\varkappa_{spec}} - \frac{1}{e_2}(1 - v_{2\,elec}\,\varrho)\,\omega^2 x.$$

The main difference between the two expressions is given by the replacement of v_2, the specific volume of the ions 2 by $v_{2\,elec}$, their specific volume in the electrode. Other differences (which disappear for dilute solutions) are the replacement of $1/v_0$ in (51) by ϱ in (52) and the difference between the mobilities u_i (with respect to the cell) and u_i^* (with respect to the solvent).

If the cell is allowed to come to sedimentation equilibrium, E and F are given by

$$(53)\qquad E_{equil} = -\frac{1}{e_2}(1 - v_2 \varrho)\,\omega^2 x + \frac{1}{e_2}\,\text{grad}\,\mu_2$$

$$(54)\qquad F_{equil} = -\frac{1}{e_2}(1 - v_{2\,elec}\,\varrho)\,\omega^2 x.$$

The first equation is easily derived from the postulate of constancy of the chemical potential (including pressure and electric contribution) for the ion 2. The second one states that the only source of work is displacement of the species 2 from one electrode to the other.

Sedimentation E.M.F.'s of the type (52) (at $I_{el} = 0$) have been measured by MacInnes c.s. [26], Elton c.s. [27] and by Rutgers and Jacobs c.s. [28]. By some authors [27] [28], using colloidal solutions, the measured values have been interpreted as if they were the unmeasurable E's in the solution. Fortunately, if one of the ions is very large, its contribution to the sedimentation potential or E.M.F. may be overwhelming so that the difference between E and F may be neglected in those cases.

Further, it appears from eqs. (53) and (54) that at sedimentation equilibrium in general both the sedimentation E.M.F. and the sedimentation field strength differ from zero. The statement [29] that at equilibrium the shift of the positive ions relative to the negative ones is zero does not seem to be correct.

Summary

Some aspects of the sedimentation and diffusion in a solution of one electrolyte and in a solution of two electrolytes that have one common ion are investigated.

General equations for the mass-flows in sedimentation and diffusion are derived by using thermodynamics of irreversible processes. These equations are compared with those derived earlier from a kinetic description.

Special attention is paid to the measurability of the phenomenological coefficients in the irreversible equations and to the meaning of the sedimentation potential.

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