

Contribution to the Hydrodynamic-Osmotic Theory of Sedimentation and Diffusion of an Incompressible Two-Component System

OLE LAMM

Divisions of Physical Chemistry, Upsala University (1944), and Royal Institute of Technology, Stockholm 70, Sweden

A theory for the sedimentation diffusion process of a binary system at optional concentration is developed. The procedure and result is analogous to the familiar treatment of the dilute solution in that the diffusion coefficient and the sedimentation coefficients here defined, are expressed in terms of friction and of magnitudes determining the forces. The equations deduced serve the purpose to improve the accuracy of the extrapolation to zero concentration (which is in common use in ultracentrifuge work, e. g. for the determination of sedimentation constants), and to show the nature of the approximations which are introduced when using the "limiting" laws. The result may especially provide a base for experimental work with the ultracentrifuge in non-dilute systems. — The general formulation of the equilibrium condition, being thermodynamical in nature, is familiar to everybody working in this field. However, using the (symmetrical) differential osmotic pressure factor, suggests a formulation of the equilibrium condition which, in certain cases, is of advantage over the traditional formulation using the (unsymmetrical) activity concept.

Since the symmetric hydrodynamic treatment of pure diffusion gave a simple result¹⁻⁷, it was clear that the same must be true for the sedimentation diffusion process, the theory of which is especially of interest in connection with ultracentrifugal measurements. Such a general theory is necessary for the treatment of non dilute systems and for the understanding of the approximations made for instance in the case of dilute solutions. It is also believed to be a point of departure for a refined treatment. The variation of partial volumes in

the cell during the process and the effects of ionic charges have not been considered. The validity of the theory is in general with good approximation unaffected by such effects as dissociation of or association between the components. The inner equilibrium of the solution is supposed to be rapidly adjusted. With the limitations already indicated, we may put the question so: What is revealed by measurements of the sedimentation diffusion process in the general case of a two-component system, for the time dependent as well as in the equilibrium case?

I. Symbols.

M	molecular weight
n	concentration in mole/cm ³
m	» » g/cm ³
N	mole fraction
Y	volume fraction
f	activity coefficient on the mole fraction basis
V	partial specific volume
\bar{v}	» molar »
\bar{v}_{12}	molar volume of a binary mixture
ρ	density of the solution
C	linear velocity
x	force direction
ω	angular velocity
D	diffusion coefficient
s	sedimentation coefficient
φ	frictional coefficient/cm ³
Φ	» » /mole of a component
B_{12}	thermodynamic factor
Q_{12}	differential osmotic factor.

II. Reference equations.

- 1)
$$\rho = \frac{M_1 N_1 + M_2 N_2}{M_1 N_1 V_1 + M_2 N_2 V_2}$$
- 2)
$$\frac{\partial N_1}{\partial x} = \frac{\bar{v}_{12}^2}{\bar{v}_2} \frac{\partial n_1}{\partial x}$$
- 3)
$$\bar{v}_{12} = \frac{1}{n_1 + n_2} = N_1 \bar{v}_1 + N_2 \bar{v}_2$$
- 4)
$$\bar{v}_1 dn_1 + \bar{v}_2 dn_2 = 0$$
- 5)
$$\bar{v}_1 n_1 + \bar{v}_2 n_2 = 1$$
- 6)
$$V_1 m_1 + V_2 m_2 = 1$$

III. *Theory.* We consider a non-compressible two component liquid system of mechanically normal properties. This is exposed to a centrifugal field in a sector shaped cell, as in the ultracentrifuge. The sedimentation diffusion process is convection-free because of the sector shape of the cell and of the control of temperature.

The sum of the (pressure-) centrifugal force K'_{12}/cm^3 and the diffusion force K''_{12}/cm^3 on component 1 equals the mutual friction force. The latter is the difference of the component velocities in the direction of the force, $C_1 - C_2$ cm/sec, multiplied by the frictional coefficient φ_{12} of the solution/unit volume*. We obtain

$$K'_{12} + K''_{12} = (C_1 - C_2) \varphi_{12} \quad (1)$$

$$K'_{12} = (1 - V_{10})\omega^2 x \cdot M_1 n_1 \quad (2)$$

$$K''_{12} = -RTB_{12} \frac{\partial \ln N_1}{\partial x} \cdot n_1 \quad (3)$$

B_{12} is the well-known factor $\frac{\partial \ln a_1}{\partial \ln N_1} \equiv 1 + \frac{\partial \ln f_1}{\partial \ln N_1} \equiv 1 + \frac{\partial \ln f_2}{\partial \ln N_2}$. The force/gram is the gradient in "centrifuging potential" (cf. Tiselius⁸) $\frac{\partial \pi}{\partial x} = (1 - V_{10})\omega^2 x$ and $M_1 n_1$ the number of grams/cm³. K''_{12} equals the diffusion force/mole, multiplied by n_1 ** . Further, the linear velocity of the column in bulk in the direction of force will be written

$$x' = C_1 n_1 \bar{v}_1 + C_2 n_2 \bar{v}_2 \quad (4)$$

* The (component) friction for diffusion and for sedimentation are not exactly equal, compare Lamm^{4,p.8} for the special case of associated components.

** A more direct deduction of the total force is arrived at in the following way: The differential of the chemical potential at constant temperature is

$$d\mu = RT \left(\frac{\partial \ln a_1}{\partial x} \right)_P dx + \bar{v}_1 \frac{\partial P}{\partial x} dx ; \left(\bar{v}_1 = \frac{\partial \mu}{\partial P} \right)$$

Presupposing that $d\mu$ causes a force/mole of the magnitude $-\left(\frac{\partial \mu}{\partial x}\right)_T$, we have to add to this the centrifugal force/mole, $M_1 \omega^2 x$, in order to get the total force k_1 /mole of component one. Inserting $\frac{\partial P}{\partial x} = \rho \omega^2 x$ provides

$$k_1 = -\frac{\partial \mu}{\partial x} + M_1 \omega^2 x = -RT \frac{\partial \ln a_1}{\partial x} + M_1 (1 - V_{10}) \omega^2 x$$

Multiplying by n_1 gives the force/cm³, in agreement with equations (2) and (3).

Eliminating C_2 between (1) and (4) we obtain

$$C_1 = (K'_{12} + K''_{12}) \frac{\bar{n}_2 \bar{v}_2}{\varphi_{12}} + x' \quad (5)$$

For parallel flow we have $\frac{\partial n_1}{\partial t} = -\frac{\partial(C_1 n_1)}{\partial x}$, an equation which in the case of cylindrical flow takes the form

$$\frac{\partial n_1}{\partial t} = -\frac{1}{x} \frac{\partial(x C_1 n_1)}{\partial x} \quad (6)$$

Using reference equations 1, 2 and 3, the forces (2) and (3) are transformed to

$$K'_{12} = M_1 M_2 n_1 n_2 (V_2 - V_1) \omega^2 x \quad (7)$$

$$K''_{12} = -RTB_{12} (n_1 + n_2) \frac{\partial N_1}{\partial x} \quad (8')$$

or

$$K''_{12} = -RTB_{12} (n_1 + n_2) \frac{\bar{v}_{12}^2}{\bar{v}_2} \frac{\partial n_1}{\partial x} = -RTB_{12} \frac{1}{(n_1 + n_2) \bar{v}_2} \frac{\partial n_1}{\partial x} \quad (8'')$$

Equation (8') being written also with respect to component 2, by permutation of indices, it is easy to see that the sum of the diffusion forces is zero, using the Gibbs-Duhems relation. Naturally, the same is true of the centrifugal-pressure force according to (7). Specifying the forces in (5) according to (7) and (8''), and introducing C_1 in equation (6) gives

$$\begin{aligned} \frac{\partial n_1}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} [RTB_{12} \frac{n_1 n_2}{\varphi_{12}(n_1 + n_2)} x \frac{\partial n_1}{\partial x} - \\ - \frac{M_1 M_2 n_1^2 n_2^2 (V_2 - V_1) \bar{v}_2}{\varphi_{12}} \omega^2 x - n_1 x x'] \end{aligned} \quad (9)$$

This equation is multiplied by \bar{v}_1 and the corresponding equation for component 2 by \bar{v}_2 and these magnitudes are supposed to be independent of x^* . Addition of left and of right members of the resulting equations gives according to reference equations 4 and 5 $0 = \frac{1}{x} \frac{\partial}{\partial x} (-xx')$. Thus $x' = k/x$, which means a constant flow "in bulk" of the solution in the sectorshaped cell. As a flow of this kind is of no interest in our problem, we may put $k = 0$ and $x' = 0$, this leading to a simplification of equation (9):

* This assumption has to be specially observed in the case of sedimentation of high molecular substances, the concentration of which may become very high at the bottom of the cell.

$$\frac{\partial n_1}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} \left[RTB_{12} \frac{n_1 n_2}{\varphi_{12}(n_1 + n_2)} x \frac{\partial n_1}{\partial x} - \frac{M_1 M_2 n_1^2 n_2^2 (V_2 - V_1) \bar{v}_2}{\varphi_{12} \omega^2 x^2} \right] \quad (10)$$

This is a fundamental equation for the sedimentation diffusion at constant partial volumes. In order to become independent of molecular weights (in the second term on the right), we introduce gram concentrations and partial specific volumes:

$$\frac{\partial m_1}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} \left[RTB_{12} \frac{n_1 n_2}{\varphi_{12}(n_1 + n_2)} x \frac{\partial m_1}{\partial x} - \frac{m_1^2 m_2^2 (V_2 - V_1) V_2}{\varphi_{12} \omega^2 x^2} \right] \quad (11)$$

Measuring the process, we determine coefficients of this equation. It has to be compared with an equation

$$\frac{\partial m_1}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} \left[D_1 x \frac{\partial m_1}{\partial x} - s_1 m_1 \omega^2 x^2 \right] \quad (12)$$

which is analogous to the second diffusion equation of Fick (with variable diffusion coefficient D_1 and sedimentation coefficient s_1), and which easily follows as a generalization of a previously deduced equation⁹ (with constant coefficients). It requires the same restriction as equation (11) regarding absence of total (bulk) velocity. $s_1 \omega^2 x$ is the sedimentation velocity in cm/sec. The comparison gives

$$D_1 \equiv D_2 \equiv D_{12} = RTB_{12} \frac{n_1 n_2}{\varphi_{12}(n_1 + n_2)} \quad (13)$$

which is the generalized Sutherland-Einstein relation, and

$$s_1 = \frac{m_1 m_2^2 (V_2 - V_1) V_2}{\varphi_{12}} \quad (14')$$

and by permutation

$$s_2 = \frac{m_1^2 m_2 (V_1 - V_2) V_1}{\varphi_{12}} \quad (14'')$$

From these equations one obtains

$$s_1 m_1 V_1 + s_2 m_2 V_2 \equiv s_1 n_1 \bar{v}_1 + s_2 n_2 \bar{v}_2 \equiv s_1 Y_1 + s_2 Y_2 = 0 \quad (15)$$

which gives the sedimentation coefficient of one component if that of the other one is known. $Y = mV = n\bar{v}$ is the volume fraction. As s and $\omega^2 x$ represent sedimentation velocities we see from (15) that the condition $\Sigma Cn\bar{v} = 0$ (cf. equation (4)) is valid for sedimentation and for diffusion independently.

As in a previous work ⁷ we introduce a factor Q_{12} based upon the osmotic pressures p_1 and p_2

$$-Q_{12} = n_2 \frac{\partial p_1}{\partial n_2} \equiv n_1 \frac{\partial p_2}{\partial n_1} \quad (16)$$

Unlike B_{12} this is independent of a choice of molecular weights. These magnitudes are related to one another by the equation

$$Q_{12} = \frac{RTB_{12}}{(n_1 + n_2)\bar{v}_1\bar{v}_2} \equiv \frac{RT}{M_1V_1} \frac{\partial \ln a_1}{\partial \ln m_1} \quad (17)$$

Introducing Q_{12} in the expression (13) provides

$$D_{12} = \frac{Q_{12}m_1m_2V_1V_2}{\varphi_{12}} \equiv \frac{Q_{12}Y_1Y_2}{\varphi_{12}} \quad (18)$$

Eliminating the friction using equation (14'') gives

$$Q_{12} = \frac{D_{12}m_1V_1 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)}{s_2} \quad (19)$$

Equations (19) and (17) show the possibility of measuring activity, from the sedimentation and diffusion processes, by integration.

We will now proceed to discuss the determination of molecular weights by the sedimentation diffusion process. For this purpose φ_{12} is eliminated between (13) and (14'')

$$m_1M_2 + m_2M_1 = \frac{RTB_{12}s_2}{D_{12}(V_1 - V_2)Y_1} \quad (20)$$

If, now, component 2 is dilute and macromolecular, $m_1M_2 \gg m_2M_1$ is an extremely advantageous approximation, so we may in this case write

$$M_2 = \frac{RTB_{12}s_2}{D_{12}(1 - V_2/V_1)Y_1^2} \quad (21)$$

Further $(1 - V_2/V_1)Y_1 \equiv 1 - V_2 \rho$. Formula (21) represents a generalization of Svedberg's equation $M_2 = RTs/D(1 - V \rho)$ to finite concentration and non-ideal solution. As has been discussed at some length in an earlier paper ⁷ B_{12}

is not defined unless the molecular weights of the components are known or values of these have been assumed. B_{12} being a correction factor in (21), the practical use of this factor for molecular weight determinations should be of the character of a successive approximation. The molecular theory is then introduced in other ways, *e.g.* by using the vapour pressure of the solvent as an activity measure.

Equation (20) may be transformed into the symmetrical formula

$$m_1 M_2 + m_2 M_1 = \frac{RTB_{12} [(-s_1) + s_2]}{D_{12}(V_1 - V_2)} \quad (22)$$

This corresponds to writing (19)

$$Q_{12}[(-s_1) + s_2] = D_{12} \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \quad (23)$$

The equations (19), (20), (22) and (23) are of identical meaning. (19) and (23) are independent of molecular weights. Thus, the other two do not express anything regarding the molecular weights either, if not through the introduction of the molecular theory by special assumptions.

Analogous to (21) we obtain from (22):

$$M_2 = \frac{RTB_{12} [(-s_1) + s_2]}{D_{12}(1 - V_2/V_1)Y_1} \quad (24)$$

For the ideal solution activity and mole fraction are, by definition, identical so we obtain $B_{12} = 1$ and

$$M_2 = \frac{RT[(-s_1) + s_2]}{D_{12}(1 - V_2 \varrho)} \quad (25)$$

From this is seen that Svedberg's molecular weight expression, which is the fundamental limiting law for a dilute solution, may be regarded to hold for finite concentrations if the relative sedimentation of the components is introduced.

IV. *Solvation.* The definition of components is always arbitrary in the sense that these may be A, B or A(B)_n, B etc. In the latter case, AB_n may express the solvation of the substance A. In our equations, magnitudes such as the sedimentation coefficients and the partial volumes and others depend on how the components are defined. When applying Stokes' law or any other hydrodynamic friction formula, it may be advantageous to define a component in the way indicated, and to use the relative sedimentation velocity sw^2x between the components AB_n and B, where $s = (-s_1) + s_2 = s_2/Y_1 =$

— s_1/Y_2 . Such a procedure bears a close connection to a theory of Enoksson¹³ on the influence of solvent movement on the sedimentation. Enoksson's equation (4) is, from the practical point of view, identical with our expression $s_1 = -sY_2$, if AB_n represents the solvated, macromolecular particle A and $s_1\omega^2x$ is the directly observed sedimentation velocity of this relative to the cell.

— There is in Enoksson's work evidence for the view that, for certain protein solutions, s is independent of concentration (in the measured region). This would mean that the solution is both thermodynamically and hydrodynamically ideal, indicating a fixed degree of solvation.

V. *Sedimentation equilibrium*. Returning to equation (11), the sedimentation equilibrium is characterized by $\frac{\partial m_1}{\partial t} = 0$ and the condition $\frac{\partial m_1}{\partial x} = 0$ for $x = 0$ (the axis of rotation). This gives, using equation (17), the equilibrium condition

$$Q_{12} \frac{\partial \ln m_1}{\partial x} = \left(\frac{1}{V_1} - \frac{1}{V_2} \right) Y_2 \omega^2 x \quad (26)$$

This is suited for the determination of Q_{12} , which is needed in connection with diffusion work on binary mixtures, compare equation (18). The equation is applicable without the use of molecular weights.

On the other side, we may ask if the present treatment gives something new regarding the determination of molecular weights. Equations (26) and (17) give, after permutation of indices

$$M_2 = \frac{RT \frac{\partial \ln a_2}{\partial x}}{(1 - V_2/V_1) (1 - m_2 V_2) \omega^2 x} \quad (27)$$

This is a thermodynamic relation, the literature concerning which has been especially completely given by Drucker¹⁵ *cf.* Tiselius⁸ and Pedersen¹⁴. According to (12) we may also use the equilibrium condition

$$D_{12} \frac{\partial \ln m_2}{\partial x} = s_2 \omega^2 x \quad (28)$$

and combine this with the approximate equation (21) in order to get

$$M_2 = \frac{RTB_{12} \frac{\partial \ln m_2}{\partial x}}{(1 - V_2/V_1) (1 - m_2 V_2)^2 \omega^2 x}; 1 - m_2 V_2 \equiv Y_1 \quad (29)$$

This expression is easy to obtain also from equation (27), putting $a_2 = N_2 f_2$ and using $m_1 M_2 \gg m_2 M_1$ (after derivation), just as we proceeded in deducing

equation (21). — It is seen that we again are met with a factor Y_1 which the older treatments of dilute solutions ($B_{12} = 1$) have not observed. Although it is here arrived at in a rather trivial way, the method of correct approximation is not quite simple, as is seen from an earlier, unsuccessful attempt ⁶.

The sedimentation diffusion equilibrium is most conveniently measured by the refractive index \bar{n} of the mixture. Let \bar{n}_1^0 and \bar{n}_2^0 be the refractive indices of the pure components, then the following expressions, based on the Dale-Gladstone formula, may prove to be sufficiently good approximations

$$\begin{aligned}\bar{n} &= \bar{n}_1^0 m_1 V_1^0 + \bar{n}_2^0 m_2 V_2^0 * \\ \frac{\partial \bar{n}}{\partial x} &= \bar{n}_1^0 V_1^0 \frac{\partial m_1}{\partial x} + \bar{n}_2^0 V_2^0 \frac{\partial m_2}{\partial x}\end{aligned}\quad (30)$$

Index ⁰ denotes the pure component. Taking the concentration derivatives from equation (26) and its analogue after permutation, we obtain the approximate formula

$$Q_{12} \frac{\partial \bar{n}}{\partial x} = (\bar{n}_1^0 - \bar{n}_2^0) \left(\frac{1}{V_1} - \frac{1}{V_2} \right) m_1 m_2 V_1^0 V_2^0 \omega^2 x \quad (31)$$

demonstrating the determination of Q_{12} by the ultracentrifuge. As the relative change in concentration will be small over the centrifuge cell (for low molecular solutions), this equation means that $\partial \bar{n} / \partial x$ is approximately proportional to x . Such a sedimentation equilibrium is well measurable already in moderate fields, at least in non-dilute solutions and if the components are not unfavourably chosen. This is fortunate, as the methods of determining the activity or osmotic properties of ordinary mixtures are quite limited. In addition to equation (17) we quote the following formulation of Q_{12}

$$Q_{12} = RT \left(\frac{N_1}{v_2} + \frac{N_2}{v_1} \right) \frac{\partial \ln a_1}{\partial \ln N_1} \quad (32)$$

which suggests how activity may be determined from equilibrium measurements by integration of the functions $Q_{12}(N_1)$ or $Q_{12}(m_1)$. Concerning the question of activity measurements by the ultracentrifuge, compare the articles by K. O. Pedersen ¹⁴ and C. Drucker ¹⁵. The present theory has, on principles, nothing to add to their thermodynamic treatment of the sedimentation equilibrium.

VI. *Isotopically labelled components.* Although a selfsedimentation analogous to selfdiffusion does not exist, it may be appropriate to give here the

* This formula gives good result also for a non ideal mixture such as ethanol — water.

equations, valid for the process at optional concentrations if the only difference between the components are their molecular weights. For this purpose, the formulas are expressed in molar quantities, as the molar volumes are identical, $\bar{v}_1 = \bar{v}_2 = v$. The friction per cm^3 φ_{12} is replaced by the "characteristic friction sum" $\Sigma\Phi_{12}$ according to the relation $\Sigma\Phi_{12} = \varphi_{12} \left(\frac{1}{n_1} + \frac{1}{n_2} \right)$, the reason being that this sum is independent of the concentration in the case of selfdiffusion, according to (compare ref. 7 and 16)

$$D_{12} = \frac{RTB_{12}}{\Sigma\Phi_{12}} \quad (B_{12} = 1 \text{ for selfdiffusion}) \quad (33)$$

From equation (14') is obtained

$$s_1 = \frac{(M_1 - M_2)Y_2}{\Sigma\Phi_{12}} = \text{const. } Y_2 \quad (34)$$

From this is seen that, unlike the diffusion coefficient, the sedimentation coefficient is fundamentally concentration dependent.

For the sedimentation equilibrium the same assumptions give, as is seen from equations (26) and (32) ($Q_{12} = RT/v$)

$$RT \frac{\partial \ln Y_1}{\partial x} = (M_1 - M_2)Y_2\omega^2x ; Y_1 + Y_2 = 1 \quad (35)$$

which is directly integrable.

The fundamental equation (11) for the sedimentation diffusion process cannot be integrated in the general case, as B_{12} and φ_{12} are unknown functions according to (13) and (14'). In the special case under consideration, the equation should be integrable, as we may write

$$\frac{\partial n_1}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} \left[D_{12}x \frac{\partial n_1}{\partial x} - K'_0 n_1 (1 - n_1 v)x^2 \right] \\ K'_0 = (M_1 - M_2)\omega^2 / \Sigma\Phi_{12} \quad (36)$$

where all the parameters (D_{12} , K'_0 and v) are constants. (When permutating indices $1 \rightarrow 2$, consider $K' \rightarrow -K'$, $D_{12} \rightarrow D_{21}$ and $n_1 + n_2 = 1/v$).

For the corresponding process in a parallel-sided cell in a homogeneous gravitational field g one obtains

$$\frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x} \left[D_{12} \frac{\partial n_1}{\partial x} - K''_0 n_1 (1 - n_1 v) \right] \\ K''_0 = (M_1 - M_2)g / \Sigma\Phi_{12} \quad (37)$$

The boundary condition at the top and the bottom of the cell, expressing their impermeability, coincides with the equilibrium condition as given by equation (35) for the centrifugal field, and for the gravitational field as well ($\omega^2x = g$). This means that at the boundaries the concentration gradients have values which make the diffusion force equal and opposite to the centrifugal — pressure force. Compare the paper of Archibald ²².

It is of interest to discuss our problems in the cases in which a complete description is obtainable by mathematical analysis of the differential equations (36) and (37). This must be reserved for later publication.

The properties of the differential equation for the sedimentation diffusion process in the case of a dilute solution were investigated by Faxén ¹⁰, Oka ^{17,18} and Archibald ¹⁹⁻²².

VII. *Conclusions.* The general signification of measuring the three processes of diffusion, sedimentation velocity, and sedimentation equilibrium may be expressed in terms of the differential osmotic pressure factor Q_{12} and the friction coefficient/cm³ φ_{12} of the two-component system according to the following scheme:

1. Diffusion measurement gives Q_{12}/φ_{12} , equation (18).
2. Sedimentation velocity measurement gives φ_{12} , equation (14) *.
3. Sedimentation equilibrium method gives Q_{12} , equation (26) (compare (31)).

The theory of these processes does not contain molecular weights of the components in such a form that these can be experimentally determined unless approximations are introduced. Equation (27) may, at first sight, seem to contradict this. The activity is, however, not defined unless the molecular weight is known or, at least, an agreement has been made regarding this.

Reviewing the molecular weight relations which are used in ultracentrifugal work, from the point of view of clarifying the approximations introduced, shows that a factor of the magnitude of the volume fraction of the solvent may be considered in order to increase the accuracy of the relations in question at finite concentrations.

The symmetrical treatment of the two components and the resulting formulae makes it natural to speak of sedimentation coefficients in analogy with the diffusion coefficient. The former are concentration dependent also if the components differ only by (ideal) isotopic labelling. A simple formula (15) connects the sedimentation coefficients of "solvent" and "solute".

The special case of components, only differing in their molecular weights, was treated because it represents a rare instance in which the sedimentation

* Combining 1. and 2. measures Q_{12} according to equation (19).

diffusion process of a non-dilute system can be described by equations with constant coefficients, with the result that these are completely integrable.

REFERENCES

1. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **17 A** (1943) No. 9.
2. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **18 A** (1944) No. 2.
3. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **18 A** (1944) No. 9.
4. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **18 A** (1944) No. 10.
5. Lamm, O. *Arkiv Kemi, Mineral. Geol.* **18 B** (1944) No. 5.
6. Lamm, O. *The Svedberg 1884-1944*, Almqvist & Wiksell, Uppsala 1944, p. 182.
7. Lamm, O. *J. Phys. & Colloid Chem.* **51** (1947) 1063.
8. Tiselius, A. *Z. physik. Chem.* **124** (1926) 449.
9. Lamm, O. *Arkiv Mat. Astron. Fysik* **21 B** (1929) No. 2.
10. Faxén, O. H. *Arkiv Mat. Astron. Fysik* **21 B** (1929) No. 1.
11. Svedberg, T., and Pedersen, K. O. *The Ultracentrifuge*, Oxford 1940.
12. Bjerrum, N. *Z. physik Chem.* **104** (1923) 406.
13. Enoksson, B. *Nature* **161** (1948) 934.
14. Pedersen, K. O. *Z. physik Chem.* **170** (1934) 41.
15. Drucker, C. *Z. physik Chem. A* **180** (1937) 359, 378.
16. Lamm, O. *Acta Chem. Scand.* **6** (1952) 1331.
17. Oka, S. *Proc. Phys.-Math. Soc. Japan* [3] **18** (1936) 519.
18. Oka, S. *Proc. Phys.-Math. Soc. Japan* [3] **19** (1937) 1094.
19. Archibald, W. J. *Ann. N. Y. Acad. Sci.* **43** (1942) 211.
20. Archibald, W. J. *Phys. Rev.* **53** (1938) 746.
21. Archibald, W. J. *J. Applied Phys.* **18** (1947) 362.
22. Archibald, W. J. *J. Phys. & Colloid Chem.* **51** (1947) 1204.

Received May 12, 1952.