The Formal Theory of Diffusion, and its Relation to Self-diffusion, Sedimentation Equilibrium, and Viscosity

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Consequences of the generalization of the equation $D = RT/\Phi$ for the problem of self-diffusion in mixtures are discussed. Inequality relations are reported, showing that self-diffusion is slower than the "corrected" regular diffusion at the same composition of the solution.

It is shown that the concept of an over-all mass-flow according to the picture of Hartley and Crank, does not bring about any modification in the generalized theory. It has been tried to apply the simplest possible description compatible with the physical facts.

The use of Fick's (1st) law is discussed. The formulation of the general i-component case of the diffusion theory is discussed. It has been avoided to use Fick's laws, the deduction of which is instead contained in the theory.

The complete support given by the thermodynamic sedimentation-diffusion equilibrium, for the diffusion theory, is emphasized. The interesting connection to the molecular concept and to the osmotic theory is discussed.

Attention is directed towards the limitations, which seem necessarily connected with efforts to find a general relation between the product $D\eta$ and the concentration for a binary mixture, if the magnitudes expressing the friction within each component, contained in the formulae for self-diffusion in a mixture, are taken into account.

1. DIFFUSION AND SELF-DIFFUSION

In a previous paper [1], the self-diffusion of a fluid system was treated using the theory of the diffusion of a three component system. For the two identical (labelled) components, the indices 1 and 2 are used. Seen as a whole (1 + 2), this substance is denoted by the index 0. The self-diffusion proceeds in the presence of a c o n s t a n t concentration of an additional component 3. For the self-diffusion coefficient D_0, the following expression is obtained, which is a mathematically exact consequence of the system of equations (11) —(13) below.

$$D_0 = \frac{RT}{\Phi_{1(2)} + \Phi_{2(1)} + \Phi_{0(3)}} = \frac{RT}{\Phi_{12} + \Phi_{0(3)}} \tag{1}$$

$\Phi_{i(j)}$, the molar friction, is the friction between the components i and j in a volume containing one mole of component i. For the friction/cm^3 we get $\varphi_{ij} = n_i\Phi_{i(j)} = n_j\Phi_{j(i)}$, n being concentration in moles/cm^3. As the two molar frictions are not independent, we denote $\Phi_{1(2)} + \Phi_{2(1)}$ by Φ_{12}, omitting the Σ-sign used in the previous paper.

$\Phi_{0(3)}$ is the friction determining the (differential) diffusion of components 0 and 3 at the same concentrations n_0 and n_3 for which eq. (1) holds, accordingto

$$D_{03} = \frac{RTB_{03}N_3}{\Phi_{0(3)}} \equiv \frac{RTB_{03}}{\Phi_{03}} \equiv \frac{RTB_{03}N_0}{\Phi_{3(0)}} \qquad (2)$$

N is the mole fraction. B_{03} is the symmetrical activity factor $\partial \ln a / \partial \ln N$.

Equation (1) refers to a system 0,3, in which component 0 is made up of two identical components 1 and 2. With the same right we may, instead, divide component 3 in two identical parts, and write the analogous equation for D_3. Indices 4 and 5 being the "labels" put on the two parts into which component 3 is divided, gives for the self-diffusion of component 3

$$D_3 = \frac{RT}{\Phi_{45} + \Phi_{3(0)}} \qquad (3)$$

It seems natural to consider the connection between diffusion in a concentration gradient of the chemically different substances 0 and 3 (sometimes called chemical diffusion) and the two self-diffusion processes, which proceed simultaneously with the former process.

As the frictions are positive quantities, the equations show that $D_{03}/B_{03}N_3 > D_0$, and $D_{03}/B_{03}N_0 > D_3$. An example of this does the measurement of Wang [2] show, the corrected differential diffusion coefficient of glycine ($N_0 \simeq 1$) being greater than the selfdiffusion coefficient of glycine at the same concentration. —Φ_{45} of equation (3) rapidly approaches zero when $N_0 \to 1$ (if the molecules of component 3 seldom meet, the friction within the component will become very small). Thus in infinitely dilute solution we must have $D_3 = D_{03}$, as also shown by Wang's measurements. The fact that the self-diffusion at finite concentrations is slower than the corresponding, corrected ordinary diffusion, seems most natural to discuss in terms of the additional friction Φ_{45} in the former case, which may reach significant values already at moderate concentrations for a substance of pronounced dipole character like glycine. — Unpublished measurements in this Institute of C. L. Undeman on the self-diffusion of water in electrolytic solutions fulfil the same inequality relation.

Another inequality condition is $D_{03}/B_{03} > D_0D_3/(D_0 + D_3)$. If one of the components (3) is highly viscous and sufficiently concentrated, we expect $D_0 \gg D_3$. In such a case we must have $D_{03}/B_{03} > D_3$, that is the (differential) chemical diffusion, corrected thermodynamically, must be more rapid than the selfdiffusion of the viscous component at the same composition of the mixture.

It is thus seen that a knowledge of the self-diffusions D_0 (eq. 1) and D_3 (eq. 3) does not give the "chemical" coefficient D_{03} (eq. 2). As a matter of fact, the coefficients of self-diffusion are more complicated with respect to friction since they depend upon the friction w i t h i n the component 0 (or

3) as well as the friction b e t w e e n these components. This greater complication in the latter case is (independent of other conventions involved in our formulae) a consequence of the self-diffusion being described as three-component diffusion, whereas the chemical diffusion in question relates to a two-component case.

An equation of the type (1) shows that self-diffusion may be "slow" either owing to a high friction between the identical molecules of component 0 or owing to a high friction between this component and 3, or both.

At the same time, eq. (2) shows that ordinary diffusion of a two-component system may be rapid, even if the corresponding self-diffusion of the components is comparatively slow.

Even if the expressions "slow" and "rapid" of this qualitative description are, from reasons of molecular physics, restricted within certain very narrow limits, our formulae show that the two self-diffusion processes are not so quantitatively related to the ordinary diffusion as one is inclined to believe. Quite apart from the influence of the thermodynamic factor B_{03}, a quantitative description of the latter phenomenon in terms merely of the self-diffusion coefficients cannot be expected to be possible on an e x a c t basis in a formal sence, even though more or less empirical relations might serve practical requirements.

Developing the molecular theory is, of course, very important. The formal theory is based upon the conception that the free energy of the activity gradient is consumed through friction b e t w e e n components but not w i t h i n these. This has to be carefully considered when confronting the formal and the molecular aspects.

Regarding an experimental test of the equations, it has been shown (Ref.[1], eq. (35)), that

$$\frac{1}{D_0} - \frac{n_0 v_0^0}{D_0^0} \simeq \frac{B_{03} N_3}{D_{03}} \tag{4}$$

where v_0^0 and D_0^0 are the molar volume and self-diffusion of the p u r e component 0. The formula supposes that the addition of component 3 does not alter the specific frictional properties of component 0. Experiments are going on to test this connection between the self-diffusion in the mixture (D_0), in the pure component (D_0^0), and the differential diffusion coefficient (D_{03}) for an ideal mixture and, if this is successful, to study the interaction between the components in cases of disagreement.

From reasons of symmetry we would also have

$$\frac{1}{D_0} - \frac{n_3 v_3^0}{D_3^0} \approx \frac{B_{03} N_0}{D_{03}} \tag{5}$$

so that B_{03}/D_{03} may be eliminated using eq. (5) and (4).

2. INTRINSIC DIFFUSION AND VOLUME-COMPENSATING FLOW

In the theory of Hartley and Crank [3] a distinction is made between "pure diffusion" and "real flow" as an expression for the natural tendency to look upon the interdiffusion of two substances as an overlap of two statistical

spreading effects and a necessary volume correcting convection, which must exist also if the mixing proceeds without specific contraction or expansion. The volume transports, resulting from the random motion (and migration) of the components, generally do not balance each other. The result is a volume-correcting flow, which is entangled in and unceasingly accompanies the "intrinsic" diffusion. An analogous picture is known in the kinetic theory of gaseous diffusion.

For the present we are, in connection with this treatment of the diffusion problem, mainly interested in the exact expressions of the authors mentioned, before they introduce the "viscous resistances" in a way which is of approximate character. In the treatment of the mutual diffusion coefficient D_{03}, Hartley and Crank use Fick's 1st law in accordance with the theory of the present writer, in that it represents the flow relative to a volume-fixed reference frame. In addition to the volume-fixed frame, they use a coordinate moving with the above-mentioned "real flow", so that the transports through a level, fixed in this coordinate, result from "pure diffusion" of the components. These transports are expressed by Fick's law as $-\bar{v}_0\mathscr{D}_0\partial n_0/\partial x$ and $-\bar{v}_3\mathscr{D}_3\partial n_3/\partial x$ for the two components 0 and 3. $\mathscr{D}$ is called the intrinsic diffusion coefficient. We will proceed to show that this picture, however interesting in connection with a physical molecular interpretation, gives the same g e n e r a l result as our treatment, and thus is of no importance for the purpose, set by the present author.

We refer to a previous article [4] p. 1065. The linear velocities C of the components are obtained from the volume transport just mentioned, dividing the latter by the volume fractions $n_0\bar{v}_0$ and $n_3\bar{v}_3$ respectively. Thus

$$C_0 - C_3 = -\mathscr{D}_0\frac{\partial\ln n_0}{\partial x} + \mathscr{D}_3\frac{\partial\ln n_3}{\partial x} \qquad (6)$$

and the condition for stationary movement becomes

$$RTB_{03}n_0\frac{\partial\ln N_0}{\partial x} = \left(\mathscr{D}_0\frac{\partial\ln n_0}{\partial x} - \mathscr{D}_3\frac{\partial\ln n_3}{\partial x}\right)\varphi_{03} \qquad (7)$$

The "real flow" is supposed to proceed practically without friction. Equation (44) of Hartley and Crank reads in symmetrical notation

$$D_{03} = n_0\bar{v}_0\mathscr{D}_0 + n_3\bar{v}_3\mathscr{D}_3 \qquad (8)$$

Applying simple exchange of variables, the last two equations give

$$D_{03} = RTB_{03}\frac{n_0n_3}{\varphi_{03}(n_0+n_3)} \qquad (9)$$

which is identical with equation (2) of the present paper. As the article of Hartley and Crank is easily misunderstood in this respect, it is of interest to state clearly that the special picture of intrinsic diffusion coefficients $\mathscr{D}$ does not introduce anything new regarding the exact generalization of the equation $D = RT/\Phi$ to finite concentrations and non-ideal solutions.

3. THE LAWS OF FICK AND RELATED QUESTIONS

The generalization of Fick's laws to more than two components is obviously of interest, although no special difficulties are met with, as shown by the example for three components [5]. The treatment given by Onsager and Fuoss in a famous paper [6] is concerned with dilute solutions, as stated on p. 2759 of that paper. Onsager, in another paper [7] treats the generalizations of Fick's laws in a way which may be subjected to some detailed remarks. The introductory statement for two components, where "the relative motion of the two components" is described as the flow $J_i = D\nabla n_i$ (i = 1,2), may need a comment. D_{12} being the symmetrical coefficient, we may define unsymmetrical coefficients according to

$$D_{12} \equiv D_1 Y_2 \equiv D_2 Y_1 \tag{10}$$

where $Y = n\bar{v}$ is the volume fraction, and write $J_i = -D_i\nabla n_i$, now describing the relative motion of the components. In order to show that this is true, consider the linear velocities $C_i = -D_i\nabla\ln n_i$. We expect $C_1 = -C_2$, which easily follows from eq. (10) and $\bar{v}_1 dn_1 + \bar{v}_2 dn_2 = 0$. — Using the symmetrical coefficient D_{12}, the equation $J_i = -D_{12}\nabla n_i$ expresses the flow relative to the local frame characterized by $\Sigma \bar{v}_i J_i = 0$, originally proposed in the same paper of Onsager and Fuoss, but not used there consistently owing to the unsymmetrical character of the system, water and dilute electrolyte. Also their expression for t e mobility of a component, although written under the heading of "the general equations for diffusion", is restricted to a dilute solution (cf. Ref.[8]). A more general expression is, in our notation, $1/\Phi_{0(3)}$ of equation (2).

As already discussed by Hartley and Crank [3], not all experimental methods give the symmetrical coefficient D (D_{03} of equations (2) and (9)). The latter is, however, most commonly measured (especially when the theory of the experimental method is based upon the Fick-Wiener expression $\partial n/\partial t = \partial (D\partial n/\partial x)/\partial x$), and should naturally be accepted as a standard value for tabulation purposes. Similar considerations hold also for m o b i l i t y as calculated from diffusion data.

In order to arrive at a simple formulation of the diffusion theory for the case of i components arbitrarily mixed with one another, let K_i be the force, originating from the chemical potential field, which acts on the amount of component i which is contained in one cm³ of the solution at a certain level of the diffusion coordinate x. The movements resulting from these forces are the linear component velocities C_i cm/sec. The movements are stationary owing to the high mutual frictional resistances, denoted by $\varphi_{ij} = \varphi_{ji}$. The latter are, as the forces, expressed per cm³ of the mixture. We obtain for the forces *

$$K_i = -n_i \frac{\partial \mu_i}{\partial x}; \quad \Sigma K_i = 0 \tag{11}$$

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* If electrolytes are concerned (Onsager and Fuoss p. 2691), the chemical potential μ includes the electrochemical potential, and the electrical potential comes in as a new variable, whereas the (analytical) electroneutrality condition gives an additional relation.

The latter equation is equivalent to the well-known Gibbs-Duhem's relation. The condition for stationary movement provides

$$K_i = \sum_j (C_i - C_j) \varphi_{ij} \tag{12}$$

A conventional reference frame for the velocities is defined by

$$\Sigma C_i n_i \bar{v}_i = x' = 0 \tag{13}$$

At constant partial volumes, x' is constant and, for convenience, put equal to zero. This case is believed to be of quite dominating interest from the point of view of principles, so that we do not here give the integral equation which is necessary in order to settle the value of x' in terms of a bulk volume change *. Eliminating K_i, we have altogether the i independent equations which are necessary to determine the velocities C_i or the flows $C_i n_i$. Each of the resulting expressions for the flows represents a generalized Fick's first law. The corresponding "second law" (Fick-Wiener) is obtained by inserting the value of C_i into the equation for parallel flow

$$\frac{\partial n_i}{\partial t} = - \frac{\partial}{\partial x} (C_i n_i) \tag{14}$$

t being the diffusion time. — In this presentation, the mathematical solution contains concentrations, chemical potentials (or activities), frictions/cm³, x and t. The introduction of "diffusion coefficients" is a matter of convention, and seems to be practical only in the two-component case. This is evident for t h r e e   c o m p o n e n t s [5], which is described by the frictions φ_{12}, φ_{23}, φ_{31}, and two independent thermodynamic factors. To describe a system of more than two components in terms of diffusion coefficients as proposed by Onsager [6] is certainly an unnecessary complication. A detailed discussion of Onsager's equations is outside the scope and competence of this article. However, in view of earlier calculations [9], it is concluded that a mixture of i d e n t i c a l components may always be characterized by a diffusion coefficient, which for the special case of   t h r e e   components can be written

$$D_{123} = RT n_1 n_2 v / \varphi_{12} \equiv RT n_2 n_3 v / \varphi_{23} \equiv RT n_3 n_1 v / \varphi_{31} = \text{const.} \tag{15}$$

or in molar frictions

$$D_{123} = RT(n_1 + n_2)v / \Phi_{12} \equiv \text{etc.}; \quad \Phi_{12} = \Phi_{1(2)} + \Phi_{2(1)} \tag{16}$$

v is the molar volume of the substance.

Regarding the several component diffusion it is desirable to take standpoint here to the f o r m a l side of the approach made by Onsager, Ref. [7], p. 242, from which we quote

$$J_i = \sum_{k=1}^{s} D_{ik} \text{ grad } n_k \tag{17}$$

and

$$- \text{grad} \mu_i = \sum_{k=1}^{s} R_{ik} J_k \tag{18}$$

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* This procedure is essentially different for liquids (constant pressure) and for gases (constant volume).

The work of Onsager and Fuoss contains the analogous equation

$$J_i = - \sum_{k=1}^{s} \Omega_{ik} \text{ grad } \mu_k \qquad (19)$$

The equations (17) and (19) express the flows J as linear functions of the gradients of concentration n or of the chemical potentials μ. Ω, R, and D are coefficients, of which Ω/n has the d i m e n s i o n of mobility, Rn of molar friction, and D of diffusion coefficient. In the last equation i is the number of s o l u t e s p e c i e s, but in equations (17) and (18) i is the total number of components as in our equations (11)—(14) above. The analogy between (17) and (19) (to be observed also between (18) and (12)), suggests however to look also upon equation (19) as a general expression for i components, although the coefficients Ω are undertermined without an additional condition for the flows. We will discuss the symmetry relation $R_{ik} = R_{ki}$. Calculations were made with i = 3, but there is no reason to question a general validity of the conclusions. The calculations, using equations (11) and (12) without assuming $\varphi_{ij} = \varphi_{ji}$, have shown that $R_{ik} = R_{ki}$ is equivalent to the assumption $\varphi_{ij} = \varphi_{ji}$. *
The latter condition is, however, self-evident from physical reasons. — Further the calculations show that the flows J are obtained from (12) in the indefinite form 0/0, when considering that the sum of the forces/cm³ is zero, (11), and that $\varphi_{ij} = \varphi_{ji}$. — The coefficients D_{ik} are easy to calculate and to express in terms of φ, concentrations, and thermodynamic factors. D_{ik} proves to be of no special simplicity. — Finally it is seen that the condition (11) regarding the sum of the forces/cm³ makes it possible to express the flows, equation (19), by equations in which one of the forces has been eliminated. From symmetry reasons the choice $\Omega_{ii} = 0$ is obvious.

The equations (11)—(14) are simple to use and to survey, and seem to contain what can be expected of a generalization of the formal theory of ordinary diffusion, from the classical two component and dilute case, to a general (mechanically normal) fluid mixture. The supposed difficulty [7] of obtaining a general scheme of description, which covers also the simple 2-component case, appears irrelevant. It seems desirable to follow up the statistical-thermodynamic treatment made by Onsager, upon this simpler formal basis.

4. DIFFUSION THEORY AND SEDIMENTATION EQUILIBRIUM

The diffusion equation (9) may be written

$$D_{12} = \frac{RTB_{12}}{\left(\dfrac{1}{n_1} + \dfrac{1}{n_2}\right) \varphi_{12}} = \frac{L_{12}}{\varphi_{12}} \qquad (20)$$

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* The equations are reproduced here for the sake of clearness

$$- \text{ grad } \mu_1 = \frac{\varphi_{12} + \varphi_{13}}{n_1^2} J_1 - \frac{\varphi_{12}}{n_1 n_2} J_2 - \frac{\varphi_{13}}{n_1 n_3} J_3$$

$$- \text{ grad } \mu_2 = - \frac{\varphi_{21}}{n_1 n_2} J_1 + \frac{\varphi_{21} + \varphi_{23}}{n_2^2} J_2 - \frac{\varphi_{23}}{n_2 n_3} J_3$$

$$- \text{ grad } \mu_3 = - \frac{\varphi_{31}}{n_1 n_3} J_1 - \frac{\varphi_{32}}{n_2 n_3} J_2 + \frac{\varphi_{31} + \varphi_{32}}{n_3^2} J_3$$

$$n_1 \text{ grad } \mu_1 + n_2 \text{ grad } \mu_2 + n_3 \text{ grad } \mu_3 = 0$$

Whereas B_{12}, n_1, and n_2 contain the molecular weights, this is not the case with L_{12}. The sedimentation diffusion equilibrium of a two-component incompressible solution has been shown to be given by (*cf.* Ref.[10])

$$L_{12}\frac{\partial \ln m_2}{\partial x} = (V_1 - V_2)V_1 m_1^2 m_2 \omega^2 x \qquad (21)$$

where $\omega^2 x$ is the centrifugal acceleration and m the concentration in g / cm³. As expected, this thermodynamical expression does not contain molecular weights. The analogy between equations (20) and (21) is believed to be an additional support for the appropriateness of the conventions underlying the diffusion theory, eq. (21) being thermodynamically exact. The factor L_{12} has no obvious physical meaning, but it is closely connected to the general differential osmotic pressure factor Q

$$-Q_{12} \equiv n_1 \frac{\partial P_2}{\partial n_1} \equiv n_2 \frac{\partial P_1}{\partial n_2} \qquad (22)$$

by the relation

$$L_{12} = Q_{12}V_1V_2 m_1 m_2 \qquad (23)$$

where V is the partial specific volume.

The theory of sedimentation velocity falls naturally into the same scheme.

As is well known, molecular weight does not enter thermodynamical formulae and cannot be determined without an equation of state. The simplest assumption regarding the equation of state is in this connection to assume $B_{12} = 1$ (ideal solution). This means, according to equations (20) and (21), that the following functions of the molecular weights *

$$\frac{1}{n_1} + \frac{1}{n_2} \equiv \frac{M_1}{m_1} + \frac{M_2}{m_2} \qquad (24)$$

is directly measured by the sedimentation equilibrium of an ideal mixture, (that is, without integration). The occurance of the function (24) in a thermodynamical equilibrium equation is of special interest, as it also plays an important rôle in the diffusion theory of two components. Thus, for instance, $1/n_1 + 1/n_2$ is the volume in which, in the case of self-diffusion, the friction between the components is independent of the labelling concentrations. This is true also in the presence of an additional, chemically different component. This is the case treated in section 1 of this paper, but is seen only in the fuller treatment [1].

If the solution is r e g u l a r (van Laar, Hildebrand), a more complicated function of the molecular weights is directly measured by the sedimentation equilibrium.

In the sedimentation equilibrium the self-diffusion proceeds without an equilization of concentrations. To study this theoretically, one way is to deduce the sedimentation diffusion equation for a three-component mixture, which ought not give rise to any considerable difficulties.

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* The molecular weights of this expression do not necessarily coincide with "kinetic" molecular weights (*cf.* Ref.[1]).

5. NOTE ON DIFFUSION AND VISCOSITY

The problem of diffusion in relation to viscosity η for ordinary liquid systems was treated by H. Eyring *et al.* in fundamental papers, and summarized by Kincaid, Eyring and Stearn [11]. One interesting point is the difficult question of how much simpler the product $D\eta$ might be than each of these magnitudes taken separately. For two-component systems, the results of Eyring *et al.* propose that, for normal liquids, $D\eta/B$ approximates to a linear function of the mole fraction of the mixture. Thus Onsager [7] writes this result in the form

$$D\eta/B = \beta_{21}N_1 + \beta_{12}N_2 \qquad (25)$$

Cases of non-ideal mixtures are well known to fall outside the range of validity of this formula. Later, Hartley and Crank [3] arrived at a similar expression.

A theory of $D\eta$ implies, as $D = RTB / \Phi$ (equation (2)), that we expect to be able to express the viscosity of a mixture as a function of the friction between the components; $\eta = f(\Phi)$. From the standpoint of the present paper, it would seem that this is too much to expect from the relation b e t w e e n the components and that too little consideration has been taken of the friction between equal parts within the mixture. A relation $\eta_{03} = f(\Phi_{03}, \Phi_{12}, \Phi_{45})$ would appear to be an increasingly necessary extension, the further the actual conditions of the mixture are from the hydrodynamic picture in the sense of Stokes' law.

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