EQUATIONS FOR MEMBRANE TRANSPORT

EXPERIMENTAL AND THEORETICAL

TESTS OF THE FRICTIONAL MODEL

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ABSTRACT   Frictional models for membrane transport are tested experimentally and theoretically for the simple case of a solution consisting of a mixture of two perfect gases and a membrane consisting of a porous graphite septum.   Serious disagreement is found, which is traced to a missing viscous term.   Kinetic theory is then used as a guide in formulating a corrected set of transport equations, and in giving a physical interpretation to the frictional coefficients.   Sieving effects are found to be attributable to entrance effects rather than to true frictional effects within the body of the membrane.   The results are shown to be compatible with nonequilibrium thermodynamics.   Some correlations and predictions are made of the behavior of various transport coefficients for general solutions.

INTRODUCTION

So-called "frictional models" have been widely used for the flux equations describing membrane transport.   As formulated by Spiegler (1) and by Kedem and Katchalsky (2), they have subsequently been applied to a variety of systems (3–9).   The frictional-model equations are equivalent to the Onsager phenomenological equations, in the sense that they have the same mathematical structure and the number of independent parameters to be found experimentally is the same.   However, the virtue of the frictional model is supposed to be that the coefficients in the transport equations can be given a physical interpretation, without the need for a detailed microscopic theory.   Such a physical interpretation gives predictive power to a theory, and makes it susceptible to experimental and theoretical tests other than the mere verification of the Onsager reciprocal relations.

   The purpose of this paper is to subject the frictional-model equations to experimental and theoretical tests by considering the limiting case of an extremely simple type of solution and membrane—a mixture of perfect gases and an inert porous septum.   An extensive series of experiments on a single porous septum is available (10, 11), as is a detailed kinetic theory (12).   Since the frictional model is supposed to

be quite general, any failure in a simple limiting case is apt to be indicative of a basic flaw in the model.

We find that the frictional model predicts a number of results that are in serious disagreement with experiment. Consideration of the nature of the disagreements, and comparison with kinetic theory, reveal that the difficulty is a fundamental one and is related to the omission of a viscous flow term. This term is also omitted from many formulations of the Onsager phenomenological equations on the assumption that mechanical equilibrium prevails; this assumption is invalid if viscous dissipation is occurring. Nevertheless, difficulties from this omission usually do not appear until a physical interpretation of the phenomenological coefficients is attempted.

Once the difficulty of the missing viscous term is recognized, the frictional-model equations are easily modified to include viscous flow, and agreement with experiment is achieved. The physical interpretation of the so-called frictional coefficients can then be further tested by comparison with kinetic theory. An apparent paradox exists between the separative behavior of a membrane in terms of so-called internal friction coefficients, and the operation of such a membrane in a steady state (13, 14). Kinetic theory resolves the apparent inconsistency in the present case by showing that the mechanism for separation is not a frictional effect, but an entrance effect. That is, the separation is caused by differences in the rates at which different species enter a membrane pore, not by differences in their interactions with the pore walls. The latter mechanism can operate to produce effective steady-state sieving only if coupled with another mechanism for removal back out the pore entrance.

FRICTIONAL MODEL

Formulation of Equations

The classical solution to the problem of formulating general transport equations is to assume a general linear relation among fluxes J_i and "forces" X_i,

$$J_i = \sum_j L_{ij} X_j, \tag{1}$$

where the L_{ij} are phenomenological coefficients. Onsager's great contribution was to show that, if the J_i and X_i are chosen properly, then

$$L_{ij} = L_{ji}. \tag{2}$$

The choice of fluxes and forces must be such that they give the entropy production σ in the form

$$T\sigma = \sum_i J_i X_i, \tag{3}$$

and further that the fluxes are chosen as time derivatives of extensive thermodynamic

quantities and the forces as gradients of intensive thermodynamic quantities (15, 16). If a correct choice is made, then there is abundant experimental evidence that the Onsager reciprocal relations of Eq. 2 are valid (15–17).

A difficulty with the Onsager formulation as applied to membrane transport is that it furnishes no mechanistic interpretation of the L_{ij}, and no indication as to the dependence of the L_{ij} on solution or membrane properties. Thus the practical usefulness of the Onsager formulation can often be largely illusory, even though it furnishes a valuable framework for discussion. Not enough is known about the L_{ij} to permit accurate integration of the transport equations, and approximate integration may destroy the reciprocal relations (18). Different forms of the transport Eq. 1 have been sought that yield transport coefficients with a less complicated behavior or a simpler physical interpretation than the L_{ij}. The frictional model attempts to deal with the difficulty by imagining the force X_i to be made up of frictional interactions between the species i and the membrane, and between the species i and the other species j, the interaction being proportional to the difference in velocities of the species. If we define average velocities v_i in terms of the fluxes and concentrations c_i as

$$v_i \equiv J_i/c_i, \tag{4}$$

then the frictional-model transport equations are (1–5)

$$X_i = f_{im}v_i + \sum_j f_{ij}(v_i - v_j), \tag{5}$$

where f_{im} and f_{ij} are so-called frictional coefficients, and the term $f_{im}v_i$ represents the friction with the stationary membrane. It is assumed that the Onsager choice of the X_i is still made, in which case the Onsager reciprocal relations require that

$$c_i f_{ij} = c_j f_{ji}. \tag{6}$$

The transport Eq. 5 makes the desired connection with a mechanistic or molecular interpretation, and has been widely used (1–9).

For mass transport the frictional-model equations have been used with the following choice of X_i:

$$X_i \equiv -\nabla \mu_i, \tag{7}$$

where μ_i is the chemical potential of species i. It is this choice that turns out to be the crucial one in losing the viscous terms.

If the f_{ij} are regarded as phenomenological coefficients in the same sense as the L_{ij}, then Eq. 5 contains no more information than Eq. 1, and any experimental test is at most equivalent to a test of the Onsager reciprocal relations. It is only through the physical interpretation of the f_{ij} that new information and predictive power are introduced, which can be tested experimentally. We therefore turn to the interpreta-

tion of the f_{ij} for the test case of a mixture of perfect gases in an inert porous membrane.

Identification of Frictional Coefficients

For gases the so-called frictional coefficients can be identified by consideration of two limiting cases (6). At very low pressures molecule-molecule collisions are negligible compared with molecule-membrane collisions, and the f_{ij} are therefore negligible compared with the f_{im}. At high pressures molecule-molecule collisions greatly outnumber molecule-membrane collisions, and the f_{im} are negligible compared with the f_{ij}. Moreover, $d\mu_i = RT\, d \ln p_i$ for perfect gases at any pressure, where $p_i = c_i RT$ is the partial pressure of species i. Thus at low pressures the frictional-model equations become identical to the Knudsen diffusion equations,

$$J_i = - (1/f_{im}) \nabla p_i = - (D_{iK}/RT) \nabla p_i, \qquad (8)$$

where the D_{iK} are Knudsen diffusion coefficients. The D_{iK} are known to be independent of pressure and composition, since the species behave independently in the low-pressure Knudsen regime; the f_{im} are thus also independent of pressure and composition.

At high pressures the f_{im} are negligible and the frictional-model equations become the same as the Stefan-Maxwell diffusion equations, which are the multicomponent generalization of Fick's law of diffusion (19),

$$- \nabla \ln p_i = \frac{1}{RT} \sum_j f_{ij}(v_i - v_j) = \sum_j \frac{c_j}{cD_{ij}}(v_i - v_j), \qquad (9)$$

where D_{ij} are the binary diffusion coefficients in the membrane. The D_{ij} are known to be inversely proportional to total pressure and to have only a weak dependence on composition (a typical variation of D_{ij} is a few percent over the whole composition range of a trace of i in pure j to a trace of j in pure i). Thus cD_{ij} and hence f_{ij}/c_j can be taken as virtually constant, independent of both pressure and composition. Note that this identification of the f_{ij} is in agreement with the Onsager reciprocal relations through $D_{ij} = D_{ji}$.

The identifications we have found are thus

$$f_{im} = RT/D_{iK}, \qquad (10)$$

$$f_{ij}/c_j = f_{ji}/c_i = RT/cD_{ij}, \qquad (11)$$

in agreement with Spiegler (6). What this achieves is the determination of the pressure and composition dependence of the f_{im} and f_{ij}, from which we can proceed to experimental tests.

COMPARISON WITH EXPERIMENT

Data Available

To test a theory with adjustable parameters we must have more measurements than the minimum necessary to determine the parameters. Gaseous systems are especially advantageous over liquid systems in this regard, since pressure is an easily manipulated variable for gases. The data available are for the interdiffusion of helium and argon in a low-permeability graphite under the influence of a number of imposed pressure gradients, so that diffusion and flow occurred simultaneously (10, 11). The temperature was held constant at 25°C, and a series of measurements was made at each of five average pressures between 1 and 5 atm, with almost pure helium on one side of the membrane and almost pure argon on the other side. The fluxes of both components were measured, their sum giving the total flux. Data are also available for the flow of pure helium and pure argon through the same graphite septum as a function of pressure difference, with the average pressure fixed at various values between 1 and 6 atm.

Working Equations

We wish to limit our considerations to regions linear in Δp, in order to avoid complications over the integration of differential equations. The particular form of the transport equations used is not trivial from this point of view; some forms are linear over larger ranges than others. It is simplest to start with the case of the forced flow of a single gas, for which the flow equation is written in integrated form as

$$J_i = -(K_i/RT)(\Delta p/L), \tag{12}$$

where K_i is the permeability coefficient of pure i, and L is the membrane thickness. The connection of K_i with the frictional coefficient is readily found to be

$$K_i = RT/f_{im}. \tag{13}$$

If a nonuniform binary mixture is involved, so that diffusion as well as forced flow occurs, it is convenient to describe the situation by an expression like Eq. 12 for the total flux J, with an added term for the diffusive contribution to J (11),

$$J = \beta_1 J_1 - (C_2/RT)(\Delta p/L), \tag{14}$$

or by interchange of subscripts,

$$J = \beta_2 J_2 - (C_1/RT)(\Delta p/L), \tag{15}$$

where β_1, β_2, C_1, and C_2 are constants. The term $\beta_1 J_1$ (or $\beta_2 J_2$) represents the contribution of diffusion to total flow. The constant β_1 (or β_2) is determined experimentally by measurement of the fluxes at uniform pressure; writing $J = J_1 + J_2$, we

obtain from Eq. 14

$$\beta_1 = 1 + (J_2/J_1)_{\Delta p \to 0}. \tag{16}$$

A similar expression for β_2 follows from Eq. 15, or from Eq. 16 by interchange of subscripts. The advantage of Eq. 14 or 15 is that $J - \beta_1 J_1$ or $J - \beta_2 J_2$ is linear over a wider range of Δp than either J_1 or J_2, as is illustrated in Fig. 1 for the He + Ar system at an average pressure of 1.49 atm (11). It can be seen that $J - \beta_{Ar} J_{Ar}$ is linear over an extensive range of Δp.

We obtain Eq. 14 or 15 from the frictional model equations by writing

$$d\mu_i = RT d \ln p_i = RT d \ln x_i + RT d \ln p, \tag{17}$$

where x_i is the mole fraction of i, and then eliminating ∇x_1 and ∇x_2 between the two transport equations by use of the identity $dx_1 + dx_2 = 0$. The constants are thereby found in terms of the so-called frictional coefficients to be,

$$\beta_1 = 1 - (f_{1m}/f_{2m}), \tag{18}$$

$$C_1 = RT/f_{1m}, \tag{19}$$

with similar expressions for β_2 and C_2. According to the previous identification of the frictional coefficients, the β's and C's are independent of pressure and composition.

Note that Eqs. 14 and 15 are not independent; one can be obtained from the other through the relation $J = J_1 + J_2$. Moreover, neither equation involves the binary diffusion coefficient D_{12} (or f_{12}). Thus an independent diffusion equation is needed for a complete description of the system. Although such an equation is easily obtained (one of the two frictional-model equations will do, in fact), we shall have no need of it for our experimental tests of the frictional model.

Experimental Tests

The experimental data we shall use are summarized in Fig. 2 as plots of K_{He}, K_{Ar}, C_{He}, and C_{Ar} as functions of mean pressure. Each point was obtained from the least-squared slope of an appropriate plot of flux versus Δp, such as shown in Fig. 1. In the calculations the theoretical values of β were used,

$$\beta_1 = 1 - (m_1/m_2)^{1/2}, \tag{20}$$

where m_1 and m_2 are the molecular masses, since it is known from kinetic theory (12, 20) that $(J_2/J_1)_{\Delta p \to 0} = -(m_1/m_2)^{1/2}$.

We give below five experimental tests of the frictional-model equations. These five are not entirely independent, but to some extent represent different ways of viewing the experimental data.

(1) Pressure dependence of the permeability coefficients K_{He} and K_{Ar}. The perme-
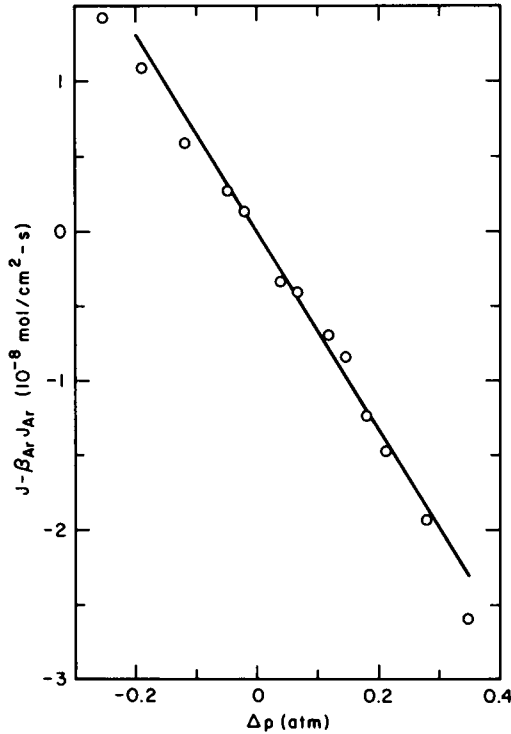
FIGURE 1 Forced flow in a diffusing He + Ar gas mixture in a porous graphite membrane at 1.49 atm and 25°C. The term $\beta_{Ar}J_{Ar}$ is the contribution of diffusion to the total flux J. The slope of the straight line gives the flow parameter C_{He} of Eqs. 14–15. This form of plot gives a linear relation over a wide range of pressure differences.

ability coefficients of pure gases are predicted by Eq. 13 to be independent of pressure. Fig. 2 shows that they depend linearly on pressure.

(2) Pressure dependence of the flow coefficients C_{He} and C_{Ar}. The flow coefficients of a diffusing gas mixture are predicted by Eq. 19 to be independent of pressure, but Fig. 2 shows that they depend linearly on pressure.

(3) Relation between K_i and C_i. From Eqs. 13 and 19 it follows that $K_i = C_i$; this prediction is independent of any statement about the pressure dependence of the co-efficients. Fig. 2 shows that this predicted equality clearly fails, except in the limit of $p \rightarrow 0$.

(4) Flux ratio at uniform pressure. This could also be considered a test of the relation between the β_i and K_i. From Eqs. 13, 16, and 18 we obtain

$$-(J_{He}/J_{Ar})_{\Delta p = 0} = (m_{Ar}/m_{He})^{1/2} = 1 - \beta_{Ar} = f_{Arm}/f_{Hem} = K_{He}/K_{Ar}. \quad (21)$$

That is, the ratio K_{He}/K_{Ar} should equal the square root of the mass ratio, 3.16, but Fig. 2 shows that this is true only in the limit of $p \rightarrow 0$. The ratio decreases with in-
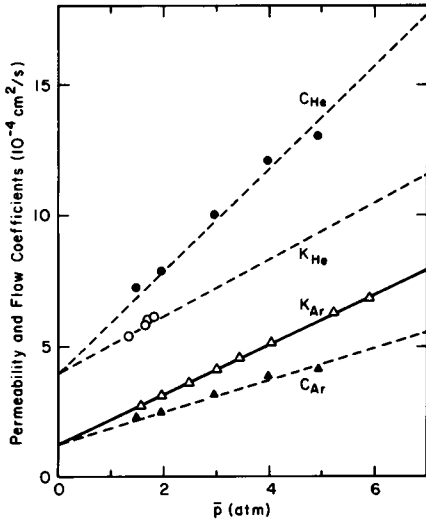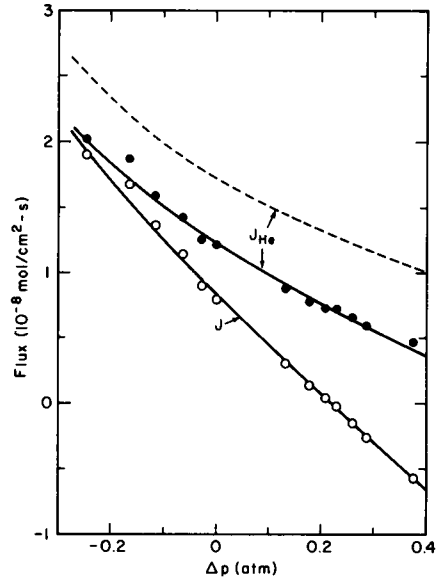
FIGURE 2

FIGURE 3

FIGURE 2   Permeability and flow coefficients as a function of mean pressure for He, Ar, and He + Ar mixtures in a porous graphite membrane at 25°C. Only the solid line for K_{Ar} is drawn to fit the data. The dashed lines are then determined from the K_{Ar} line according to kinetic theory, Eqs. 34–35. The frictional model predicts that all four coefficients are independent of pressure, and that $C_{He} = K_{He}$ and $C_{Ar} = K_{Ar}$.

FIGURE 3   Individual and total fluxes as a function of pressure difference at 1.96 atm for the same system as in Fig. 1. The open circles are the measured total fluxes (proportional to volume flow), and the filled circles are the measured helium fluxes. The solid curve for J is drawn as an empirical representation of the data. The two curves for J_{He} are calculated from the curve for J according to theory—the dashed curve from the frictional model, Eq. 22, and the solid curve from kinetic theory, Eqs. 14 and 35.

creasing pressure, falling to about a value of 2 at 2 atm. However, the frictional model does correctly predict that C_{He}/C_{Ar} is equal to 3.16 at all pressures.

(5) *Prediction of individual fluxes from total flux and permeability coefficients.* This test is another way of examining the prediction that $C_i = K_i$; combination of this equality with Eqs. 14–15 and 18–19 yields

$$J_{He} = (J/\beta_{He}) + (K_{Ar}/\beta_{He}RT)(\Delta p/L),$$

$$= (K_{He}/[K_{He} - K_{Ar}])J + (K_{He}K_{Ar}/[K_{He} - K_{Ar}])(\Delta p/RTL), \quad (22)$$

with a similar expression for J_{Ar}. For a test we choose the measurements at 1.96 atm, which are especially extensive, and compare the measured J_{He} with the result predicted from the observed total J and the values of K_{He} and K_{Ar}. Such a prediction, if accurate, would be extremely useful—it would permit the calculation of an individual diffusive flux from a measurement of volume flow plus independent permeability measurements. The comparison is shown in Fig. 3, and the prediction is seen to fail badly.

Nature of Failure

The failure of the frictional-model equations is easy to diagnose from the behavior of the permeability coefficients shown in Fig. 2. A linear pressure dependence has long been explained on the basis of the viscous flow of a compressible fluid; measurement of the slope of such a plot of K_i vs. $\bar{p}$ is a classic method for the measurement of gas viscosity. In other words, it would appear likely that the failure of the frictional model can be attributed to the lack of any terms describing viscous flow in the equations. Further evidence for this view comes from the identification of the permeability and flow coefficients, K_i and C_i, with f_{im} and hence with the Knudsen diffusion coefficient D_{iK}. This means that the flow mechanism is being attributed solely to the motion of individual molecules (Knudsen diffusion), and not to any viscous mechanism.

An interesting puzzle now arises. If the frictional model fails so badly for gases, how was Spiegler (6) able to successfully describe many features of the diffusion of gases across porous media? Investigation shows that Spiegler treated only the cases of isobaric ($\Delta p = 0$) and equal countercurrent ($J = 0$) diffusion. These are just the two cases, and the only two, for which the influence of the viscous flow drops out at all pressures (21). Thus the apparent puzzle is really indirect evidence that neglect of viscous flow is the source of the trouble.

The lack of a viscous flow term in the frictional-model equations is a fundamental omission, caused by the basic assumption of mechanical equilibrium of the fluid in the membrane (Manning[9] has also pointed out the need for viscous terms). Fortunately this assumption is not crucial, and viscous flow has been incorporated into irreversible thermodynamics by Bearman and Kirkwood (22–24). We could use their results as a basis for modifying the frictional model, but we prefer to proceed by way of kinetic theory in order to gain physical insight. The methods are consistent, and the same final equations are obtained whichever route is followed.

KINETIC THEORY

The kinetic-theory equations that describe the experiments discussed in the preceding section are well known (12), and confirm the diagnosis of a missing viscous flow term. We wish to do more than confirm this omission, however—we wish to cast the general multicomponent kinetic theory results into a form which admits of a direct phenomenological generalization, as a basis for modifying the frictional model. We first give the equations as obtained from the most general kinetic theory procedure presently available; this is sometimes referred to as the "dusty-gas" model, in which the porous membrane is treated mathematically as one component of the gas mixture, consisting of giant molecules held stationary in space (12). We then show how the same equations can be obtained more simply but less rigorously on the basis of momentum-transfer arguments (25). The phenomenological generalization follows directly by plausibility arguments.

Dusty-Gas Model

The diffusion equations for a multicomponent mixture are simplest when written, not as a flux of one component proportional to gradients involving all components (Onsager form), but as gradients involving one component proportional to fluxes of all components (Stefan-Maxwell form). If we define an average diffusion velocity for component i as

$$v_{iD} \equiv J_{iD}/c_i, \tag{23}$$

where J_{iD} is that portion of the flux due to diffusion alone, then the diffusion equations for an isothermal mixture of ν components are (19)

$$-d_i = \sum_{j=1}^{\nu} \frac{c_i c_j}{c^2 D_{ij}} (v_{iD} - v_{jD}), \tag{24}$$

a total of ν equations, of which only $\nu - 1$ are independent. The gradient factor d_i contains three terms corresponding to concentration diffusion, pressure diffusion, and forced diffusion, respectively, as follows (in one dimension):

$$d_i = \frac{d}{dz}\left(\frac{c_i}{c}\right) + \frac{c_i}{c}\left(\frac{\overline{M} - M_i}{\overline{M}}\right)\frac{d\ln p}{dz} - \frac{1}{p}\frac{c_i}{c}\left(cF_i - \frac{M_i}{\overline{M}}\sum_{k=1}^{\nu} c_k F_k\right), \tag{25}$$

where M_i is the molecular weight of component i, $\overline{M}$ is the mean molecular weight of the mixture, and F_i is the external force on the ith component.

We now take one component as stationary, uniformly distributed, and having a very high molecular weight; this comprises the porous membrane, and is denoted by the subscript d for "dust." Then c, p, D_{ij}, and $\overline{M}$ of Eqs. 24 and 25 include the dust as one component, and are given a prime unless the dust is explicitly removed from the counting. However, kinetic theory shows that to an excellent approximation,

$$c' D'_{ij} = c D_{ij}. \tag{26}$$

An external force is needed to keep the dust stationary in the presence of pressure gradients in the gas mixture; a simple force-balance argument shows that (12)

$$c_d F_d = dp/dz, \tag{27}$$

where p is the actual gas pressure. Insertion of these conditions into Eqs. 24 and 25 leads to considerable cancellation, and the result is

$$-\frac{d\ln p_i}{dz} = \frac{v_{iD}}{D_{iK}} + \sum_{j} \frac{c_j}{c D_{ij}} (v_{iD} - v_{jD}), \tag{28}$$

where the Knudsen diffusion coefficient D_{iK} is

$$D_{iK} \equiv cD_{id}/c_d. \tag{29}$$

In Eq. 28 we have assumed that no external forces act on the gas molecules; this would not be true for ions, but the forced diffusion terms are easily added if needed. The sums now include only the gas components, not the dust.

The average total velocity is obtained by adding the average viscous flow velocity to the average diffusion velocity,

$$v_i = v_{iD} + v_{\text{visc}}, \tag{30}$$

or in terms of fluxes,

$$J_i = J_{iD} + x_i J_{\text{visc}}. \tag{31}$$

This additivity follows directly from the kinetic theory in that there are no viscous flow terms in the diffusion equations, and no diffusion terms in the viscous flow equations; the two are entirely independent in the sense that there are no direct coupling terms in these equations.[1] The viscous flow velocity is computed by a force-balance argument such as is used for the derivation of Poiseuille's law, and is

$$v_{\text{visc}} = -(B_o/\eta)(dp/dz), \tag{32}$$

where B_o is a geometric constant characteristic of the membrane. Combining these results with Eq. 28 and substituting for the chemical potential from Eq. 17, we obtain

$$-\frac{1}{RT}\frac{d\mu_i}{dz} = \frac{1}{D_{iK}}\left(v_i + \frac{B_o}{\eta}\frac{dp}{dz}\right) + \sum_j \frac{c_j}{cD_{ij}}(v_i - v_j), \tag{33}$$

which is the desired result.

From Eq. 33 we can readily obtain the forms for the permeability and flow coefficients, and show that they agree with experiment (12). After a little algebra we find the permeability coefficient of a single gas i to be

$$K_i = D_{iK} + (B_o/\eta_i)p, \tag{34}$$

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[1] Of course this does not mean that viscous flow and diffusion do not interact in a very real sense, but only through boundary conditions and the behavior of the transport coefficients, not through direct coupling terms in the equations (12). For instance, the viscosity of a mixture depends on its composition, which in turn depends on the diffusion occurring. Thus, viscous flow is influenced by diffusion. Conversely, the pressure distribution may be largely determined by the viscous flow, which thereby influences the diffusion through the pressure dependence of the diffusion coefficients.

and the flow coefficients C_1 and C_2 of a binary mixture to be (with $i = 1$ or 2),

$$C_i = D_{iK}[1 + (B_o/\eta_{\text{mix}})(p/\bar{D}_K)],$$ (35)

where η_{mix} is the viscosity of the mixture, and

$$1/\bar{D}_K \equiv (x_1/D_{1K}) + (x_2/D_{2K}).$$ (36)

The constant β_1 for a binary mixture is

$$\beta_1 = 1 - (D_{2K}/D_{1K}) = 1 - (m_1/m_2)^{1/2},$$ (37)

with a similar expression for β_2. These equations show that K_i and C_i are linear in pressure, and that $K_i = C_i$ only at $p \to 0$, in accord with the data shown in Fig. 2. The data displayed in Fig. 2 can be summarized by eight empirical numbers—four intercepts and four slopes—but Eqs. 34–37 contain only two independent parameters, B_o and one of the Knudsen diffusion coefficients. If these two are known, the other six can be predicted from knowledge of viscosities and molecular masses. Thus a good test of Eqs. 34–37 is to fit one line to the data to determine the two parameters, and from this fit predict the other three lines and see how well they agree with the experiments. Accordingly, we fitted the K_{Ar} data by least squares, obtaining $D_{\text{Ar}K} = 1.24 \times 10^{-4}$ cm^2/s from the intercept, and $B_o = 2.13 \times 10^{-14}$ cm^2 from the slope, with η_{Ar} taken as 226 μP at 25°C. Since Eq. 37 states that the D_{iK} vary as $m_i^{-1/2}$, we predict that $D_{\text{He}K} = 3.93 \times 10^{-4}$ cm^2/s. This value, together with $\eta_{\text{He}} = 198 \mu P$, determines the line for K_{He}. Experimental measurements of the viscosities of He + Ar mixtures show that η_{mix} depends only weakly on composition over a large range; the linear average over the composition range yields a value of 228 μP. This value, together with the value of $\bar{D}_K$ calculated from Eq. 36, determines the lines for C_{He} and C_{Ar}. As can be seen in Fig. 2, the agreement between kinetic theory and experiment is quite good.

Kinetic theory also makes an accurate prediction for the flux data shown in Fig. 3. The curve for J_{He} is calculated according to Eqs. 14 and 35 from the curve drawn for total J, using the value of C_{Ar} predicted as in Fig. 2 and the theoretical value of β_{He} according to Eq. 37.

Momentum-Transfer Model

The basic idea goes back to Maxwell (26) and to Stefan (27). It was re-invented during World War II in connection with isotope separation (28). The extension to multicomponent mixtures and to Knudsen diffusion is straightforward (25, 29), but does not seem to be widely known. Since pressure is due to the transfer of momentum by collisions according to the kinetic theory of gases, it is argued that the gradient of partial pressure of one species is due to the momentum transferred to that species by collisions with the other species and with the wall. Thus the gradient is built up by additivity of momentum transfers. The contribution of the wall collisions is easily

written down as

$$-(1/RT)(dp_i/dz)_K = J_{iD}/D_{iK} = c_i v_{iD}/D_{iK}, \quad (38)$$

which is essentially just the definition of the Knudsen diffusion coefficient, D_{iK}. The contribution of the molecular collisions can be found from a detailed molecular argument (30), which we do not reproduce here, but can be easily guessed by rewriting the diffusion equations for a binary mixture in terms of the partial pressure gradient. For pure diffusion at zero pressure gradient, these equations are

$$J_{1D} = -D_{12}(dc_1/dz) + x_1 J_D, \quad (39\,A)$$

$$J_{2D} = -D_{12}(dc_2/dz) + x_2 J_D, \quad (39\,B)$$

which are essentially just the definition of D_{12}. Combining these two and eliminating the total diffusive flux J_D, we find

$$-(1/RT)(dp_1/dz)_D = (x_2 J_{1D} - x_1 J_{2D})/D_{12} = (c_1 c_2/D_{12})(v_{1D} - v_{2D}). \quad (40)$$

The extension to multicomponent mixtures is then plausible: for each new species there is a new momentum-transfer term on the right,

$$-(1/RT)(dp_1/dz)_D = (c_1 c_2/D_{12})(v_{1D} - v_{2D}) + (c_1 c_3/D_{13})(v_{1D} - v_{3D}) + \ldots, \quad (41)$$

with similar equations for each of the other species. Combining Eqs. 38 and 41 we can write the total momentum transfer for species i as

$$-(1/RT)(dp_i/dz) = c_i v_{iD}/D_{iK} + \sum_j (c_i c_j/cD_{ij})(v_{iD} - v_{jD}). \quad (42)$$

This is the same as Eq. 28 obtained by the dusty-gas model, on substitution of $c_i = p_i/RT$. An additional set of terms for the action of external forces could also be added in an obvious way, but we shall not bother with this extension.

The independence of diffusive and viscous flows is actually more general than kinetic theory, and is valid for any isotropic system. It depends only on the fact that all the equations are linear in fluxes and gradients, and that quantities of different tensorial character do not couple in the linear regime (Curie's theorem) (31). Thus the inclusion of viscous flow in the momentum-transfer model proceeds exactly as in the dusty-gas model, and we end up again with Eq. 33, the desired result.

Phenomenological Generalization

We first remove the specifically gas-like portions of Eq. 33 by defining pressure-independent parameters,

$$\xi_{im} \equiv RT/D_{iK}, \quad (43)$$

$$\zeta_{ij} \equiv RT/cD_{ij} = \zeta_{ji}. \quad (44)$$

For gases, ξ_{im} represents the interaction between species i and the membrane, independent of the other species in the mixture, and ζ_{ij} represents the interaction between species i and j, almost but not quite independent of the other species (32, 33). Then the transport equations become

$$-\nabla\mu_i = \xi_{im}[v_i + (B_o/\eta)\nabla p] + \sum_j c_j \zeta_{ij}(v_i - v_j), \qquad (45)$$

which are exactly the same as the frictional-model equations, except for the viscous term. The relation of the coefficients is $\xi_{im} = f_{im}$, and $\zeta_{ij} = f_{ij}/c_j = f_{ji}/c_i$. Eq. 45 is thus expected to be generally applicable to all fluids, including dense gases and liquid solutions, without restriction as to density or ideality.

Onsager Relations

To show that our phenomenological generalization of kinetic theory is consistent with irreversible thermodynamics, we need only prove that Eq. 45 obeys the Onsager relations. The proof will also suggest a way to modify the frictional model to include viscous flow terms. If we define

$$J_i = c_i v_i, \qquad (46\,\text{A})$$

$$X_i = -\nabla\mu_i - \xi_{im}(B_o/\eta)\nabla p, \qquad (46\,\text{B})$$

then Eq. 45 is readily arranged into the form

$$X_i = \sum_j F_{ij} J_j, \qquad (47)$$

or in matrix notation

$$\mathbf{X} = \mathbf{FJ}, \qquad (48)$$

where

$$F_{ij}(i \neq j) = -\zeta_{ij}, \qquad (49\,\text{A})$$

$$F_{ii} = c_i^{-1}(\xi_{im} + \sum_{k \neq i} c_k \zeta_{ik}). \qquad (49\,\text{B})$$

The matrix $\mathbf{F}$ is symmetric because $\zeta_{ij} = \zeta_{ji}$. Formally solving Eq. 48, we write

$$\mathbf{J} = \mathbf{LX}, \quad \text{where} \quad \mathbf{L} = \mathbf{F}^{-1}. \qquad (50)$$

Since $\mathbf{F}$ is symmetric, so is $\mathbf{L}$, and Eq. 45 obeys the Onsager relations.

Permeability and Tracer Diffusion

In gases it is easy to separate the contributions of diffusion and viscous flow by measuring the pressure dependence of the permeability coefficient of a single gas, as

shown by Fig. 2 and Eq. 34. This technique is not available for liquids, and the problem is usually studied by comparing the solvent permeability coefficient as measured with a pressure gradient (hydraulic conductivity) to the solvent "self-diffusion" coefficient as measured with isotopic tracers (34). It is therefore interesting to make a similar comparison for gases. The tracer diffusion coefficient D_1^* is found to be (12)

$$1/D_1^* = (1/D_{1K}^*) + (1/D_{11}^*), \qquad (51)$$

where D_{1K}^* is the Knudsen diffusion coefficient of the tracer, and D_{11}^* is the ordinary diffusion coefficient of the tracer in the normal solvent. From this we see that $D_1^* \leq D_{1K}^*$, and from Eq. 34 we see that $K_1 \geq D_{1K}$. Thus $K_1 \geq D_1^*$, as expected, and the sign of equality holds only if everything is in the Knudsen regime.

MODIFICATION OF FRICTIONAL MODEL

Revised Derivation

With the acuity of hindsight, one can now see how the frictional-model arguments might have been modified to include the viscous term. The most fundamental way would be to choose the forces X_i to include a viscous force as well as the gradient of chemical potential—in particular, the choice shown in Eq. 46B leads exactly to our generalized kinetic-theory result of Eq. 45. This choice of the X_i is equivalent to the modification found by Bearman and Kirkwood (22–24) for the introduction of viscous flow into irreversible thermodynamics. Thus all three approaches—irreversible thermodynamics, frictional model, and kinetic theory—become completely consistent with each other and with experiment.

Another way to introduce viscous flow into the frictional-model equations is to add a term to include the interaction between species i and the viscous flow of all the other species, so that the equations become

$$- \nabla \mu_i = f_{im} (v_i - v_{visc}) + \sum_j f_{ij}(v_i - v_j). \qquad (52)$$

Taking v_{visc} from the analogue of Poiseuille's law,

$$v_{visc} = -(B_o/\eta) \nabla p,$$

we obtain the equivalent of Eq. 45, the generalized kinetic-theory result.

Yet another way to revise the derivation of the frictional-model equations is suggested by the momentum-transfer model of kinetic theory discussed in the previous section. From this model it is clear that the transport equations can be constructed by combining momentum transfers or chemical potential gradients like resistors in series, where voltage drops are additive, and then combining the resultant diffusive flux with the viscous flux like resistors in parallel where currents are additive. A mnemonic diagram for generating Eq. 45 from such considerations is shown in Fig. 4

$J_i(\text{total})$

Diffusive
Branch
$J_{iD} = c_i v_{iD}$

Viscous - Flow
Branch
$J_{i\,visc} = c_i v_{visc}$

membrane
interaction
$(\nabla \mu_i)_m = -\xi_{im} v_{iD}$

$v_{visc} =$
$= -(B_0/\eta) \nabla p$

species
interaction
$(\nabla \mu_i)_D =$
$= -\sum_j \zeta_{ij} c_j (v_{iD} - v_{jD})$
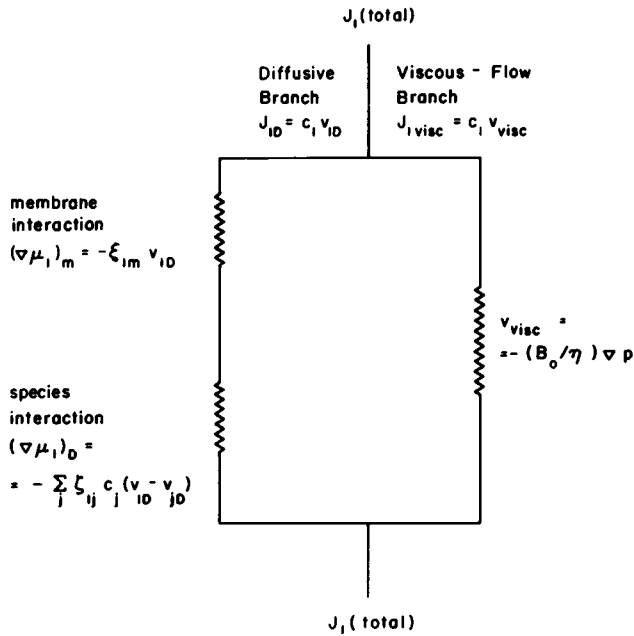
$J_i(\text{total})$

FIGURE 4 Series-parallel electrical diagram as a mnemonic device for writing down the transport equations for coupled flow and diffusion in membranes. Diffusive fluxes combine by addition of chemical potential gradients (analogue of voltage drops), and the net diffusive flux then combines additively with the viscous flux (analogue of currents).

(25). The procedure is to first obtain the diffusive branch by adding up the contributions to the chemical potential gradient, including the interaction with the membrane and with the other series in the mixture, and if necessary including the contribution of external forces. Then the viscous flux is included by replacing each diffusive velocity v_{iD} by $(v_i - v_{visc})$, and substituting for v_{visc} in terms of the viscosity and pressure gradient. Here only the membrane interaction term is affected, since the species interaction terms involve the difference $(v_{iD} - v_{jD})$, which is equal to $(v_i - v_j)$. This series-parallel analogy gives a simple recipe for writing down Eq. 45, but it is best regarded as a mnemonic device only, and not as a basis for giving physical interpretation to the transport coefficients.

Physical Interpretation of Coefficients

We can use the present results to gain some further insight into the physical meaning of the frictional-model coefficients. Anderson and Quinn (35) compared the frictional model with a hydrodynamic model, using Poiseuille's equation to identify the frictional coefficients, and concluded that the two models did not agree. We can now see that any comparison involving viscosity in the interpretation of the frictional coefficients is of necessity doomed to failure; viscosity enters the frictional-model equations as an entirely separate term, completely independent of any of the original terms in the equations.

More interest attaches to the interpretation connected with the separation mechanism for sieving or hyperfiltration membranes, in view of the apparent paradox between a frictional mechanism and steady-state operation. It is convenient to present the discussion in terms of the reflection coefficient, σ, for a two-component system. The definition of σ follows by arranging Eq. 45 for ideal solutions into the form (4)

$$J = -L_p(\nabla p - \sigma RT\nabla c_1). \tag{53}$$

If we take Eq. 53 as defining σ, then σ represents the fraction of the theoretical osmotic pressure realized with a "leaky" membrane,

$$\sigma \equiv (\Delta p/RT\Delta c_1)_{J=0}. \tag{54}$$

In terms of the so-called frictional coefficients, the expression for σ turns out to be

$$\sigma = \frac{f_{1m} - f_{2m}}{x_1 f_{2m} + x_2 f_{1m} + c\zeta_{12} + (cB_o/\eta)[x_1 f_{1m}(f_{2m} + c\zeta_{12}) + x_2 f_{2m}(f_{1m} + c\zeta_{12})]}, \tag{55}$$

in which we have included the originally omitted viscous term and have used ζ_{12} in preference to f_{12} and f_{21}. An analogous expression for L_p can be obtained, but is not needed here. The important feature of Eq. 55 is its numerator, which shows that the factor causing sieving (i.e. causing σ to be different from zero) is the difference in the two membrane frictional coefficients, $(f_{1m} - f_{2m})$. This strongly suggests that sieving is due to differences in the frictional interactions of solute and solvent within the membrane. Aside from its inconsistency with steady-state operation (13, 14), we wish to show that such an interpretation is incorrect, according to kinetic theory, for the simple case of perfect gases.

We first show that the experimental system discussed in the previous section exhibits sieving, in the sense that σ is nonzero. From the combined flow and diffusion experiments it is straightforward to pick out the pressure difference for which $J = 0$, and calculate σ according to the definition of Eq. 54, in the form

$$\sigma = (\Delta p/\bar{p}\,\Delta x_{Ar})_{J=0}, \tag{56}$$

where we have arbitrarily chosen argon as the solute and helium as the solvent. The experimental points are shown in Fig. 5 for the five experimental pressures. Also shown is the theoretical curve calculated according to Eq. 55, using the numerical values of B_o, η, and the D_{iK} (or f_{im}) already quoted. The value of D_{12} (or ζ_{12}) was obtained from independent experiments at uniform pressure with the same porous graphite membrane (10); the value was $D_{12} = 1.06 \times 10^{-4}$ cm^2/s at a nominal pressure of 1 atm. The agreement is excellent. It is worth noting that at $p = 0$, the limiting value of σ is slightly *greater* than unity. It would seem from Fig. 5 that the graphite
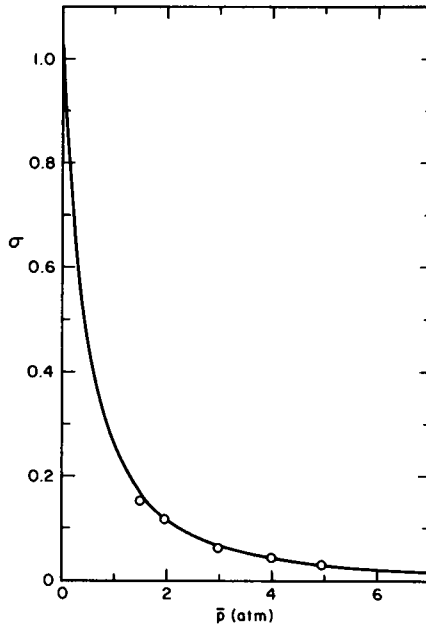
FIGURE 5 Reflection coefficient σ as a function of mean pressure for the same He + Ar "solution" and membrane as in Figs. 1–3. The "sieving" effect shown is actually a kinetic entrance effect, not a frictional effect within the body of the membrane as suggested by the frictional model. The curve is from kinetic theory, Eq. 55.

membrane exhibits a substantial osmotic effect with an Ar + He solution; the pressure differences in the experiments amounted to about 0.2 atm (11, 12).

To trace the molecular interpretation of the apparent sieving behavior of the porous graphite membrane shown in Fig. 5, we note that in the kinetic-theory results nonzero σ corresponds to $\xi_{Arm} \neq \xi_{Hem}$, which in turn corresponds to $D_{ArK} \neq D_{HeK}$. We therefore only need to understand why Knudsen diffusion coefficients differ, and this is a simple problem because collisions between molecules do not enter into consideration. The derivation of a detailed expression for D_{iK} is a classical problem in kinetic theory (30, 36), and shows that this mechanism for separation is not a true frictional effect, but an *entrance* effect. For instance, for free-molecule diffusion through a long capillary tube with diffusely reflecting internal walls, the Knudsen diffusion coefficient is

$$D_{iK} = \tfrac{1}{3}\bar{u}_i d, \tag{57}$$

where d is the tube diameter and $\bar{u}_i = (8kT/\pi m_i)^{1/2}$ is the mean molecular speed of species i. The separation thus depends on $\bar{u}_i$ and thereby on $m_i^{-1/2}$. But $\bar{u}_i$ enters the derivation through the counting of the number of species i molecules that *enter* the tube per unit time, not from any consideration of how long they take to get through the

tube once they have entered. That is, more fast molecules enter the tube per unit time than slow molecules, so that a relative enrichment occurs immediately on entrance; how long it then takes to get through the tube is irrelevant as far as separation is concerned. Considerations of different tube geometries or gas-surface interactions change only the numerical and geometrical factors in Eq. 57, and do not affect the $\bar{u}_i$. Most of the complications in the calculation of D_{iK} are of a geometric nature, and involve the computation of the probability that a molecule will find its way back out the entrance after it has entered (30, 36). This probability is usually the same for different species, in which case separation is entirely an entrance effect. Some separative behavior can in principle be caused by preferential back-reflection out the entrance for different species, but this is rare (and destroys the $m_i^{-1/2}$ behavior of the D_{iK}). The behavior shown in Fig. 5 is entirely an entrance effect, as shown by the $m_i^{-1/2}$ dependence of the D_{iK} demonstrated in Fig. 2.

This interpretation of the ξ_{im} and hence of the so-called frictional coefficients f_{im} in terms of entrance effects rather than frictional effects within the body of the membrane completely avoids the conflict with steady-state operation. This conflict arises because internal friction causes accumulation of material within the membrane, and a steady state cannot be reached unless a removal mechanism for accumulated material coexists with the rejection mechanism. Any physical interpretation of frictional-model coefficients must take this fact into account.

DISCUSSION

We believe that Eq. 45 supplies a set of generally valid transport equations for any type of solution in any open membrane. Whether it is regarded as obtained by a generalization of kinetic-theory equations or by a modification of the frictional-model equations is a matter of taste, since the result is the same. Advantages of this formulation over the Onsager formulation lie in the behavior of the coefficients and in their possible physical interpretation. Regarding behavior, for gases the coefficients ξ_{im} (or f_{im}) depend only on species i and the membrane and not on any other species, and the coefficients ζ_{ij} depend only on species i and j to an excellent approximation. This simple behavior may not hold for condensed phases, but hopefully the dependence of the ξ_{im} and ζ_{ij} on the other species in the solution will be weaker than that of the Onsager coefficients L_{ij}. Certainly this is true for gases, where the multicomponent diffusion coefficients corresponding to the L_{ij} depend on the composition of the whole mixture in a very complicated way (19, 37, 38).

Regarding physical interpretation of the coefficients, the comparison with kinetic theory suggests that any steady-state separation occurring through an open membrane is likely to be an entrance effect rather than an internal friction effect. The entrance effect can be either a kinetic one as in Knudsen flow, or a steric one if the molecular diameter is comparable to the membrane pore diameter (39, 40). An important implication of this conclusion is that any explanation of a steady-state separative effect in membranes as other than an entrance effect must probably involve some heteroporos-

ity or mosaic structure of the membrane, so that part of the membrane is permeable and part is impermeable to some of the species.

Some further physical interpretation of transport coefficients can be obtained from Eq. 45, leading to predictive power such as was shown in Fig. 2 for gases, although there is less scope for liquids than for gases because total pressure is not a practical variable for liquids. We consider a binary solution, and convert Eq. 45 into two independent working equations of particularly convenient form. Making no assumptions about ideality of solutions, we use the Gibbs-Duhem relation for the chemical potential gradients,

$$\sum_i c_i \nabla \mu_i = \nabla p \quad (\text{constant } T), \tag{58}$$

and algebraically eliminate the term involving ζ_{12} in Eq. 45 to obtain the first working equation,

$$J = \beta_1 J_1 - (C_2/RT)\nabla p, \tag{59}$$

where

$$\beta_1 = 1 - (\xi_{1m}/\xi_{2m}), \tag{60}$$

$$C_2 = \frac{RT}{\xi_{2m}} \left[1 + \frac{B_o}{\eta_{\text{mix}}} \left(\frac{x_1 \xi_{1m} + x_2 \xi_{2m}}{x_1 \overline{V}_1 + x_2 \overline{V}_2} \right) \right] \tag{61}$$

We have used the relation $c = (x_1 \overline{V}_1 + x_2 \overline{V}_2)^{-1}$, where $\overline{V}_1$ and $\overline{V}_2$ are partial molar volumes. This equation is of course analogous to Eqs. 14–15 that we used for gases. A similar equation can be written in terms of species 2 by interchange of the subscripts 1 and 2, but the two equations are not independent. An independent diffusion equation can be obtained from Eq. 45 by substituting $J_2 = J - J_1$ and writing the chemical potential gradient as

$$\nabla \mu_1 = RT \nabla \ln a_1 + \overline{V}_1 \nabla p, \tag{62}$$

where a_1 is the (dimensionless) activity. The result can be arranged into the physically appealing form,

$$\begin{aligned} J_1 = &-D_{1\text{eff}}[(d \ln a_1)/(d \ln c_1)] \nabla c_1 - D_{1\text{eff}}(c_1 \overline{V}_1/RT) \nabla p + x_1 \delta_1 J \\ &- [x_1(1 - \delta_1)(B_o/\eta_{\text{mix}})/(x_1 \overline{V}_1 + x_2 \overline{V}_2)]\nabla p, \end{aligned} \tag{63}$$

where

$$D_{1\text{eff}} \equiv RT(\xi_{1m} + c\zeta_{12})^{-1}, \tag{64}$$

$$\delta_1 \equiv c\zeta_{12}(\xi_{1m} + c\zeta_{12})^{-1} = \zeta_{12}(D_{1\text{eff}}/RT)(x_1 \overline{V}_1 + x_2 \overline{V}_2)^{-1}. \tag{65}$$

A similar equation holds for species 2, but is not an independent equation. Each of the four terms on the right-hand side of Eq. 63 can be given a physical interpretation, with a simple analogue in perfect gas mixtures. The first term is an ordinary diffusion term, but with an effective diffusion coefficient $D_{1\,eff}$ whose value reflects the relative importance of molecule-membrane interactions and molecule-molecule interactions. If molecule-membrane interactions dominate, then $D_{1\,eff}$ equals RT/ξ_{1m}, corresponding to the Knudsen regime in gases. If molecule-molecule interactions dominate, then $D_{1\,eff}$ equals $RT/c\zeta_{12}$ and is proportional to the ordinary diffusion coefficient D_{12}, the constant of proportionality depending only on membrane geometry; this limit corresponds to the continuum regime in gases. The second term is a pressure diffusion term; in perfect gases the first two terms merge together because of the equation of state, $p_i = c_i RT$. The third term is a net drift term, and the quantity δ_1 varies between 0 and 1 as molecule-membrane or molecule-molecule interactions dominate. In perfect gases, net drift does not contribute in the Knudsen regime ($\delta_1 = 0$), but contributes fully in the continuum regime ($\delta_1 = 1$). The fourth term has the nature of a correction term; in gases it makes only a small contribution unless the pressure gradient is large. Moreover, it becomes negligible in the molecule-molecule regime ($\delta_1 \rightarrow 1$), and is probably also negligible in the molecule-membrane regime because if $\xi_{1m} \gg c\zeta_{12}$, the factor $(x_1\overline{V}_1 + x_2\overline{V}_2) = c^{-1}$ in the denominator of the last term is probably large.

Eqs. 59 and 63 are thus recommended as the working transport equations for a binary mixture. They are especially suitable for integration and interpretation, as judged by their success for perfect gases (12). Moreover, they allow some transferral of knowledge from solution to solution using the same membrane. In particular, if solution diffusion coefficients in free solution are known, then only one ζ_{ij} must be measured experimentally since

$$\zeta_{12}/\zeta_{34} = (D_{34}/D_{12})([x_1\overline{V}_1 + x_2\overline{V}_2]/[x_3\overline{V}_3 + x_4\overline{V}_4]). \tag{66}$$

Thorough testing of this and other consequences of Eq. 45 awaits a comprehensive set of measurements on a single membrane with well-characterized solutions.

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