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STATISTICAL-MECHANICAL THEORY OF PASSIVE TRANSPORT THROUGH SEMIPERMEABLE MEMBRANES *

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The first general multicomponent equations for transport through semipermeable membranes are derived from basic statistical-mechanical principles. The procedure follows that used earlier for open membranes, but semipermeability is modelled mathematically by the introduction of external forces on the impermeant species. Gases are treated first in order to clarify the problems involved, but the final results apply to general nonideal solutions of any concentration. The mixed-solvent effect is treated rigorously, and a mixed-solvent osmotic pressure is defined. A useful specific identification of so-called osmotic flow is given, along with a demonstration that such an identification cannot be unique. Results are obtained both for discontinuous membrane models, and for a continuous model.

1. Introduction

In a previous paper [1] we derived equations for transport through open membranes from basic principles of statistical mechanics, starting with the classical-mechanical Liouville equation. Two problems were deliberately bypassed – the detailed structure of the membrane, and the description of semipermeable and sieving or permselective membranes. The purpose of this paper is to extend the results to include semipermeable membranes; that is, to derive the transport equations for the components that can pass through the membrane, taking into account the effects of those components that cannot pass.

Two fundamental conceptual problems arise with semipermeable membranes, both connected with the notion of osmotic pressure. The first problem occurs already with binary solutions, and has to do with the role of the pressure gradient in moving solvent across the membrane, a question that has been recognized for a long time [2–5]. Briefly put, there are two mechanisms for solvent transport, namely diffusion and viscous flow, and the problem is to decide how the addition of an impermeant solute affects each one.

The second problem is more subtle, and arises only when there are three or more components in the solution, of which at least two can pass through the membrane. The problem now occurs in the meaning of osmotic pressure. The osmotic pressure is usually thought of as the pressure that must be applied to a solution to raise the chemical potential of the solvent to equal that of pure solvent on the other side of a semipermeable membrane. This idea is fine for binary solutions, but can be deceiving if the solvent is a mixture of two or more components. Then the application of pressure will change the chemical potentials of the solvent components by different amounts unless they fortuitously have the same partial molar volumes. No osmotic equilibrium can be attained in general by the simple application of pressure – some redistribution of the solvent components must also occur. The equilibrium aspects of this problem were worked out long ago [6], but were apparently forgotten until they arose in connection with the determination of the molecular weights of high polymers using mixed solvents [7]. The transport aspects of the problem, however, have never been treated quantitatively, as far as we are aware. We give in section 4 a generalized definition of osmotic pressure that is suitable for the transport problem.

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In order to clarify the physical difficulties involved, we begin by considering the simple case of a mixture of perfect gases, some of which cannot penetrate a membrane that is idealized as a surface of discontinuity. We have previously used a similar approach to discuss membrane transport phenomena [8–10], through the "dusty-gas" model of gas transport in porous media. The approach is especially useful in problems involving osmotic pressure, as Hobbie [11, 12] has pointed out, because the total pressure is the sum of the partial pressures of the components. This gas model clarifies the first problem mentioned above, but is less clear on the second problem because all perfect gases have equal partial molar volumes. However, enough insight is obtained to guide a general statistical-mechanical derivation. This derivation parallels that for an open membrane [1], but mathematically models the membrane impermeability by external forces on the impermeant components that prevent them from moving. The results are compared with classical notions of osmotic pressure and osmotic flow, and with some previous equations describing transport across semipermeable membranes. The idealization of a discontinuous membrane is then dropped and a continuous membrane model of nonzero thickness is introduced, allowing the results to be extended in principle (by integration) to cases where the differences of concentration, pressures, etc. on the two sides of the membrane are not infinitesimal.

2. Gas mixtures

The transport equations for a mixture of ν perfect gases [1,10] can be rewritten in finite-difference form for an open discontinuous membrane as follows:

$$\sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}}(u_i - u_j) + \frac{u_i}{P_{iK}} = -\Delta \ln p_i + \frac{\Delta\Phi_i}{RT} - \frac{\bar{B}_0}{\eta P_{iK}}(\Delta p - c\Delta\Phi)\,, \qquad (1)$$

where c_j is the molar concentration of component j, $c = \Sigma c_i$ is the total molar concentration, u_i is the transport velocity of component i (flux density divided by concentration), p_i its partial pressure, $\Delta\Phi_i$ is the potential energy difference per mole across the membrane due to external forces on i (Φ_i has the dimensions of external force per mole on i multiplied by membrane thickness), Δp is the total pressure difference across the membrane, and $\Delta\Phi$ is the total potential energy difference across the membrane for all components. The total potential difference per unit volume, $c\Delta\Phi$, is

$$c\Delta\Phi = \sum_{i=1}^{\nu} c_i \Delta\Phi_i\,. \qquad (2)$$

The parameters in eq. (1) are: $\bar{B}_0$, a geometrical constant of the membrane that characterizes its viscous-flow properties; η, the viscosity of the mixture; P_{iK}, the Knudsen permeability coefficient of component i through the membrane, having dimensions of a Knudsen diffusion coefficient divided by membrane thickness; and P_{ij}, the mutual permeability coefficient of species i and j through the membrane, having dimensions of a mutual diffusion coefficient divided by membrane thickness. We have omitted temperature gradient terms from eq. (1) for simplicity of discussion, but they are included for completeness in the next section.

The important thing to notice about eq. (1) is the nature of the terms on the right-hand side, which drive the transport. The terms $\Delta \ln p_i$ and $\Delta\Phi_i$ depend only on component i; only the term $(\Delta p - c\Delta\Phi)$, which drives the viscous flow, refers to the mixture as a whole. Suppose we now add to the mixture some gas k that cannot pass the membrane, keeping the total volume constant. Clearly this added component has no effect on the driving terms $\Delta \ln p_i$ and $\Delta\Phi_i$, nor on the total force term $c\Delta\Phi$ as long as it is given by eq. (2) with the summation running only over the permeant components. The only pressure difference that drives the viscous flow is $\Sigma\Delta p_i$, summed over the permeant components only, but the observed total pressure difference Δp as read on a pressure gauge now includes the contribution Δp_k from the impermeant species k,

$$\Delta p = \sum_{i=1}^{\nu} \Delta p_i + \Delta p_k\,. \qquad (3)$$

Thus the term Δp in eq. (1) must be modified if an impermeant component is added. Other quantities that also might conceivable be modified are η, $\bar{B}_0$, P_{iK}, and cP_{ij}. The quantity $\bar{B}_0$ depends only on the membrane structure; if we assume the added component does not modify this structure, say by jamming up the interstices of the membrane, then $\bar{B}_0$ does not change. Similarly, $P_{i\mathrm{K}}$ depends only on component i and on the membrane structure, and does not change. However, the viscosity η needs modification because only the permeant components flow, but η is ordinarily understood to mean the viscosity of the entire mixture, including impermeant k. Thus η in eq. (1) should be changed to η^0, the viscosity of the mixture before the addition of k. The term cP_{ij} behaves in a somewhat surprising way. The total concentration increases to c from its initial value c^0 because of the added component k, and the permeability coefficient decreases to P_{ij} from its initial value P_{ij}^0 because the added k interferes by collisions with the relative motion of i and j. But in perfect gases the two effects exactly cancel, and

$$c^0 P_{ij}^0 = cP_{ij} , \tag{4}$$

except for a possible small change in the already weak composition dependence of P_{ij}.

The result of the addition of impermeant species k to the mixture of constant volume is therefore to change eq. (1) to

$$\begin{aligned}\sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}} (u_i - u_j) + \frac{u_i}{p_{i\mathrm{K}}} \\ = -\Delta \ln p_i + \frac{\Delta\Phi_i}{RT} - \frac{\bar{B}_0}{\eta^0 P_{i\mathrm{K}}} \left[(\Delta p - \Delta p_k) - \sum_{j=1}^{\nu} c_j \Delta\Phi_j \right].\end{aligned} \tag{5}$$

The result for the addition of k at constant total pressure can be obtained from this expression by expansion of the mixture back to the original total pressure. The form of eq. (5) does not change thereby — all that happens is that the various terms change or not according to their various pressure dependences.

The role of osmotic pressure is quite clear for this simple system. The osmotic pressure difference across the membrane is just the partial pressure difference of the impermeant component, Δp_k [1 i]. This is the only pressure difference that remains after the system comes to equilibrium in the absence of external forces. In this picture the osmotic pressure enters the transport equations only as a sort of correction, because a pressure gauge reads total pressure but the true driving force is the sum of the partial pressures of the permeant components only.

It is now straightforward to attempt a generalization of eq. (5) to arbitrary nonideal solutions. In order that the equation will reduce to the correct equilibrium limit, the partial pressures should be replaced by chemical potentials,

$$\Delta \ln p_i \rightarrow \frac{1}{RT} \Delta\mu_i = \Delta \ln a_i + \frac{\bar{V}_i}{RT} \Delta p , \tag{6}$$

where μ_i is the chemical potential of i, a_i its activity (with mole fraction as reference state to preserve symmetry with respect to components), and Δp is the total hydrostatic pressure difference. Similarly, Δp_k should be replaced by the osmotic pressure difference $\Delta\pi$, which can then be expressed in terms of chemical potential by the Gibbs-Duhem equation,

$$\Delta p_k \rightarrow \Delta\pi = c_k \Delta\mu_k . \tag{7}$$

This expression can also be obtained directly via the same replacement as used in eq. (6). Finally, we replace the Knudsen permeability coefficients $P_{i\mathrm{K}}$ by membrane permeability coefficients $P_{i\mathrm{M}}$ to avoid any connotation of long mean free paths. No other replacements appear to be required, and eq. (5) becomes

$$\begin{aligned}\sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}} (u_i - u_j) + \frac{u_i}{P_{i\mathrm{M}}} = -\frac{1}{RT} (\Delta\mu_i - \Delta\Phi_i) \\ - \frac{\bar{B}_0}{\eta^0 P_{i\mathrm{M}}} - \left[(\Delta p - c_k \Delta\mu_k) - \sum_{j=1}^{\nu} c_j \Delta\Phi_j \right].\end{aligned} \tag{8}$$

Although this generalization seems plausible, it is essentially an empirical guess. We therefore turn to a more fundamental derivation in the next section, based on the principles of statistical mechanics applied to general fluids.

3. Statistical-mechanical derivation

We begin with the transport equations for open membranes, and then mimic impermeability by applying external forces to the impermeant species to hold them stationary. In particular, let there be ν permeant species and τ potentially impermeant species; the transport equations, rewritten in finite-difference form for a discontinuous membrane, are [1]

$$\sum_{j=1}^{\nu+\tau} \frac{c_j}{cP_{ij}} (u_i - u_j) + \frac{u_i}{P_{i\mathrm{M}}} = -\frac{1}{RT} (\Delta_{\mathrm{T}} \mu_i - \Delta\Phi_i) - \frac{\bar{B}_0}{\eta P_{i\mathrm{M}}} \left(\Delta p - \sum_{j=1}^{\nu+\tau} c_j \Delta\Phi \right) - \sum_{j=1}^{\nu+\tau} \frac{c_j}{cP_{ij}} P_{ij}^{\mathrm{T}} \Delta \ln T, \tag{9}$$

for component i, where we have now included the thermal diffusion terms for completeness. In particular, P_{ij}^{T} is a multicomponent thermal permeability coefficient having dimensions of a diffusion coefficient divided by membrane thickness, and $\Delta_{\mathrm{T}}\mu_i$ is the chemical potential difference across the membrane in an isothermal system with the same local state variables and concentration and pressure differences as the real system. The physical interpretation of the various terms in eq. (9) is straightforward. Of the two sets of terms on the left-hand side, the first describes the interdiffusion of component i with all the other components, and the second describes the diffusion of i through the membrane. The three sets of terms on the right-hand side represent the driving forces for the transport. The first set represents diffusion: $\Delta_{\mathrm{T}}\mu_i$ represents both concentration and pressure diffusion, via the two terms in eq. (6), and $\Delta\Phi_i$ represents forced diffusion. The second set represents viscous flow, and the third set represents thermal diffusion.

We now suppose that external forces are applied to species $\nu+1, ..., \nu+\tau$ to keep them motionless. To help keep matters straight, we will now use the dummy index k for these impermeant species and keep the indices i, j for the permeant species. Two obvious changes now occur in eq. (9) — all the τ values of the u_k become zero, and the viscosity η is replaced by η^0, the viscosity of the mixture of permeant species only. Because all $u_k = 0$, we switch τ terms from the first set of terms on the left-hand side of eq. (9) to the second, which becomes

$$\left(\sum_{k=\nu+1}^{\nu+\tau} \frac{c_k}{cP_{ik}} + \frac{1}{P_{i\mathrm{M}}} \right) u_i \approx \frac{u_i}{P_{i\mathrm{M}}}. \tag{10}$$

The meaning of this is that the molecules of species i must find their way through the now stationary molecules of the species k, just as they must find their way through the stationary particles of the membrane. (The term $P_{i\mathrm{M}}$ in fact arose in this way in the original derivation.) However, the impediment offered by the impermeant species k must be very small compared to that offered by the membrane, unless the concentration of species k is very high and the membrane is very open (an unlikely situation for a semipermeable membrane). Hence it should be a good approximation to neglect the terms involving P_{ik}, as indicated by the right-hand side of eq. (10) above.

The thermal diffusion terms P_{ik}^{T} should also be negligible to a good approximation. Indeed, the corresponding membrane terms $P_{i\mathrm{M}}^{\mathrm{T}}$ were dropped in the original derivation of eq. (9) on the basis that they give rise to thermal transpiration in rarefied gases, a phenomenon that is already very small for gases at ordinary densities and is therefore probably negligible for liquids. The P_{ik}^{T} terms should be even smaller than $P_{i\mathrm{M}}^{\mathrm{T}}$.

Eq. (9) thus assumes the form

$$\sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}} (u_i - u_j) + \frac{u_i}{P_{i\mathrm{M}}} = -\frac{1}{RT} (\Delta_{\mathrm{T}} \mu_i - \Delta\Phi_i) - \frac{\bar{B}_0}{\eta^0 P_{i\mathrm{M}}} \left(\Delta p - \sum_{j=1}^{\nu} c_j \Delta\Phi_j - \sum_{k=\nu+1}^{\nu+\tau} c_k \Delta\Phi_k \right) - \sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}} P_{ij}^{\mathrm{T}} \Delta \ln T, \tag{11}$$

where we have explicitly separated the $\Delta\Phi_k$ in the viscous-flow terms. These $\Delta\Phi_k$ are the only overt indication in eq. (11) that we are dealing with a semipermeable membrane, and they are responsible for major osmotic flow effects. To evaluate the $\Delta\Phi_k$ in terms of measurable quantities, we write eq. (11) for one of the impermeant species k, solve for $\Delta\Phi_k$, and substitute back. Since the impermeant species undergo no viscous flow, or any other motion for that matter, we drop the viscous-flow terms from eq. (11) and obtain

$$\sum_{j=1}^{\nu} \frac{c_j}{cP_{kj}} (-u_j) = -\frac{1}{RT} (\Delta_{\mathrm{T}} \mu_k - \Delta\Phi_k) - \sum_{j=1}^{\nu} \frac{c_j}{cP_{kj}} P_{kj}^{\mathrm{T}} \Delta \ln T, \tag{12}$$

from which

$$\sum_{k=\nu+1}^{\nu+\tau} c_k \Delta\Phi_k = \sum_{k=\nu+1}^{\nu+\tau} c_k (\Delta_{\mathrm{T}} \mu_k - \delta_k), \tag{13}$$

where

$$\delta_k = RT\sum_{j=1}^{\nu}\frac{c_j}{cP_{kj}}(u_j - P^{\mathrm{T}}_{kj}\Delta\ln T)\,. \tag{14}$$

Substituting back into eq. (11) we obtain our final result,

$$\sum_{j=1}^{\nu}\frac{c_j}{cP_{ij}}(u_i - u_j) + \frac{u_i}{P_{i\mathrm{M}}} = -\frac{1}{RT}(\Delta_{\mathrm{T}}\mu_i - \Delta\Phi_i)$$
$$-\frac{\bar{B}_0}{\eta^0 P_{i\mathrm{M}}}\left[\Delta p - \sum_{k=\nu+1}^{\nu+\tau} c_k(\Delta_{\mathrm{T}}\mu_k - \delta_k) - \sum_{j=1}^{\nu} c_j\Delta\Phi_j\right]$$
$$-\sum_{j=1}^{\nu}\frac{c_j}{cP_{ij}}P^{\mathrm{T}}_{ij}\Delta\ln T\,. \tag{15}$$

Except for the terms in δ_k and the additional thermal diffusion terms, this result is the same as eq. (8), which has guessed by analogy with gas mixtures.

We surmise that the terms in δ_k will be negligible in most cases of interest, but we are not certain that they will be negligible under all circumstances, and so have kept them to play safe. Their physical significance is that they represent the interference of the stationary impermeant components with the viscous flow of the permeant components, which is our main reason for expecting them to be small. For simplicity of discussion, we shall henceforth ignore the δ_k.

Transport equations for discontinuous membranes are necessarily written in finite-difference rather than differential form. Since the equations we have so far used represent linear relations between fluxes and driving forces, the finite difference must generally be small in order for linear relations to be accurate. In particular, for an open membrane the $\Delta_{\mathrm{T}}\mu_i$, $\Delta\Phi_i$, Δp, and $\Delta\ln T$ should all be small. But for a semipermeable membrane only the difference $(\Delta p - \Sigma c_k\Delta_{\mathrm{T}}\mu_k)$ for the impermeant species must be small to maintain linearity, and neither Δp nor $\Delta_{\mathrm{T}}\mu_k$ must necessarily be individually small. However, our derivation starting from the equations for an open membrane has forced $\Delta_{\mathrm{T}}\mu_k$ to be small, since the c_k in the summation becomes ambiguous unless Δc_k is also small. This limitation will be removed when we consider a continuous membrane model in section 6.

4. Generalized definition of osmotic pressure

We now wish to check how the foregoing analysis has dealt with the "mixed solvent" problem mentioned in the Introduction. Suppose we let a multicomponent system come to equilibrium across a semipermeable membrane. The temperature will then be constant, and for simplicity let there be no external forces on the permeant components. Then in eq. (15) all the terms vanish except Δp and $\Delta\mu_k$. The $\Delta\mu_k$ stay essentially at their initially fixed values, and Δp adjusts so that at equilibrium the fluxes vanish and

$$\Delta p_{\mathrm{eq}} = \sum_k c_k\Delta\mu_k\,. \tag{16}$$

The same relation can be obtained directly from the Gibbs-Duhem relation,

$$\sum_{i=1}^{\nu} c_i\Delta\mu_i + \sum_{k=\nu+1}^{\nu+\tau} c_k\Delta\mu_k = \Delta p\,, \tag{17}$$

since $\Delta\mu_i = 0$ for all ν of the permeant species at equilibrium. We now ask whether an equilibrium osmotic pressure difference across the membrane, $\Delta\pi$, can be defined that is equal to Δp_{eq}. The answer is unambiguously *yes* if there is only one permeant species (solvent), but the matter is less simple if there are two or more permeant species (mixed solvents). In particular, it is important to specify very carefully what is meant by osmotic pressure.

To fix ideas, we consider a three-component system consisting of permeant species 1 and 2 (solvents) and an impermeant species s (solute). The generalization to an arbitrary number of components is obvious once the fundamental difficulties are resolved. The situation at equilibrium is illustrated schematically in fig. 1, which serves to define possible generalized osmotic pressures.

Consider first the equilibrium between the solutions in the two main compartments of fig. 1, across the membrane of interest. By definition we would have $\Delta p_{\mathrm{eq}} \equiv p'' - p'$, and the chemical potentials are equal, $\mu_1' = \mu_1''$, $\mu_2' = \mu_2''$. Assuming for simplicity that partial molar volumes are independent of pressure, we can write

$$\Delta\mu_i = \bar{V}_i\Delta p + RT\Delta\ln a_i\,, \tag{18}$$

where $i = 1, 2$. Using the relation $\mu_i' = \mu_1''$, we obtain

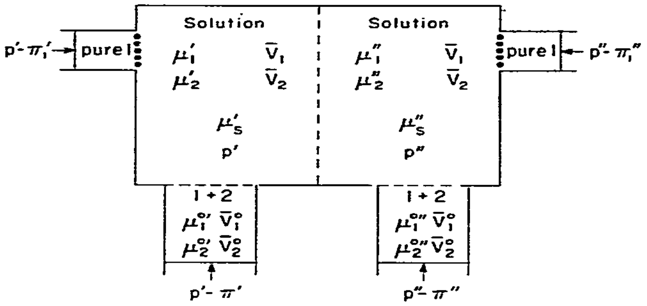

Fig. 1. Schematic diagram for discussion of osmotic pressure in mixed solvents. The membranes indicated by dashes pass both 1 and 2 but not s, whereas the dotted membranes pass only 1. For simplicity the partial molar volumes are assumed to be nearly constant.

$$\bar{V}_i(p''-p') + RT\ln(a_i''/a_i') = 0 \,. \tag{19}$$

Writing this result for each component, we obtain a relation for the relative concentrations of 1 and 2 in the two solutions,

$$\begin{aligned}\Delta p_{\text{eq}} &\equiv p''-p' = (RT/\bar{V}_1)\ln(a_1'/a_1'') \\ &= (RT/\bar{V}_2)\ln(a_2'/a_2'') \,,\end{aligned} \tag{20}$$

in agreement with Wall [7].

A simple relation between Δp_{eq} and an osmotic pressure can be obtained if we consider the equilibrium between solution and pure component 1 (or 2) across a special membrane permeable *only* to 1 (or 2), as indicated by the upper auxiliary compartments in fig. 1. This special hypothetical membrane is indicated by dots to distinguish it from the membrane of interest, which is indicated by dashes. At equilibrium the chemical potentials in these auxiliary compartments are equal to those in the main compartments,

$$\mu_1'\,(\text{pure }1) = \mu_1' = \mu_1'' = \mu_1''\,(\text{pure }1) \,, \tag{21}$$

with similar relations for component 2. From the outer equality, μ_1' (pure 1) = μ_1'' (pure 1), we obtain an expression like eq. (19), but now a_1' (pure 1) is necessarily equal to a_1'' (pure 1) by virtue of the definition of activity. Thus we find

$$\Delta p_{\text{eq}} \equiv p''-p' = \pi_1''-\pi_1' = \pi_2''-\pi_2' \,, \tag{22}$$

where the definition of the π's is clear from fig. 1. Thus Δp_{eq} is equal to an osmotic pressure difference, but not one defined across the membrane of interest. The multicomponent generalization of this result is $\Delta p_{\text{eq}} = \Delta\pi_i$, where $\Delta\pi_i$ is measured across a special membrane permeable only to species *i*. For use in transport equations, we will define the mixed solvent osmotic pressure to be this $\Delta\pi_i$.

Another plausible definition of osmotic pressure that leads to $\Delta\pi \neq \Delta p_{\text{eq}}$ is indicated by the lower auxiliary compartments in fig. 1. According to this part of the diagram, we would define the osmotic pressure of a solution of (1 + 2 + s) as the equilibrium pressure difference between it and a solution of (1 + 2) a across a membrane permeable to 1 and 2 and impermeable to s (that is, across the membrane of interest). The relative concentrations of 1 and 2 in the solution and in the mixed solvent will in general be different unless the partial molar volumes are fortuitously equal, as indicated in the Introduction. At equilibrium we have

$$\mu_i^{0\prime} = \mu_i' = \mu_i'' = \mu_i^{0\prime\prime} \,. \tag{23}$$

From the outer equality, $\mu_i^{0\prime} = \mu_i^{0\prime\prime}$, we obtain via eq. (18) the result,

$$(p''-\pi'')-(p'-\pi') = \Delta p_{\text{eq}} - \Delta\pi = (RT/\bar{V}_i^0)\ln(a_i^{0\prime}/a_i^{0\prime\prime}), \tag{24}$$

where $\Delta\pi \equiv \pi''-\pi'$. Thus Δp_{eq} is *not* equal to $\Delta\pi$ unless $a_i^{0\prime} = a_i^{0\prime\prime}$, which will not in general be true unless all the partial molar volumes are equal. The multicomponent generalization of eq. (24) is straightforward: the general definition of Δp_{eq} is given by eq. (16), the summation running over all impermeant components and the relation to $\Delta\pi$ is still given by eq. (24), where the subscript *i* refers to any permeant component.

Finally, we should mention that Δp_{eq} is *not* equal to the pressure difference that will just stop volume flow when the system is not at equilibrium, as might perhaps be expected, except for a binary system [7]. (See eq. (31) of section 5 following.)

In summary, osmotic pressure can be an ambiguous term for multicomponent solutions unless the properties of the membrane involved are carefully specified. Fortunately, the definition of the pressure-difference correction in the transport equations is unambiguous, even though its relation to a plausible conventional osmotic pressure difference is not always simple.

5. Identification of osmotic flow

We turn now to the other problem mentioned in the Introduction, namely the difference between diffusive flow and osmotic flow, or the role of the pressure gradient in moving solvent across a semipermeable membrane. The idea that such a distinction can even be made seems to be based on simple arguments somewhat like the following. Consider pure solvent on both sides of a membrane with no pressure difference and no external forces, and add solute to one side only, keeping the pressure difference zero. The added solute reduces the chemical potential of the solvent, so that solvent begins to diffuse through the membrane into the solution. This is all that happens if the membrane is permeable to the solute as well as to the solvent, except that a counterdiffusion of solute will also occur. If, however, the membrane is impermeable to the solute, the transport of the solvent is usually much faster, and one speaks of an additional "osmotic flow" of the solvent, driven by the osmotic pressure difference.

Although some objections can be raised about the foregoing picture, it is interesting that our present equations do give a definite interpretation to the distinction between diffusive and osmotic flow. To show this generally, we rewrite eq. (15) in somewhat simplified form,

$$\sum_{j=1}^{\nu}\frac{c_j}{cP_{ij}}(u_i-u_j)+\frac{u_i}{P_{i\mathrm{M}}}=-\frac{1}{RT}(\Delta_{\mathrm{T}}\mu_i-\Delta\Phi_i)$$
$$-\frac{\bar{B}_0}{\eta^0 P_{i\mathrm{M}}}(\Delta p-\Delta p_{\mathrm{eq}}-c\Delta\Phi)$$
$$-\sum_{j=1}^{\nu}\frac{c_j}{cP_{ij}}P_{ij}^{\mathrm{T}}\,\Delta\ln T\,, \tag{25}$$

where

$$\Delta p_{\mathrm{eq}}\equiv\sum_{k=\nu+1}^{\nu+\tau}c_k\,\Delta_{\mathrm{T}}\mu_k\,, \tag{26}$$

$$c\Delta\Phi\equiv\sum_{j=1}^{\nu}c_j\Delta\Phi_j\,. \tag{27}$$

The only difference between eq. (25) and the corresponding equation for an open membrane [1] is the term Δp_{eq}, which is equal to the conventional osmotic pressure for a binary mixture. Clearly this term contributes only to the viscous component of the flow, since it occurs associated with the factor $\bar{B}_0/\eta^0$. Moreover, if the total (external) pressure difference Δp is zero, then the pressure difference Δp_{eq} must lie within the membrane. Thus eq. (25) implies that "osmotic flow" is a viscous flow driven by an internal pressure gradient, in agreement with many current ideas [3–5].

To make the identification of osmotic flow more specific, consider the simple case of pure solvent (subscript w) on the left of a membrane and a solution (solvent w and solute s) on the right, assumed ideal ($a_i=x_i$) and with uniform temperature and no external forces. From eq. (25) the flux of solvent is

$$J_{\mathrm{w}}=c_{\mathrm{w}}u_{\mathrm{w}}\approx-cP_{\mathrm{wM}}\Delta x_{\mathrm{w}}-(c_{\mathrm{w}}\bar{V}_{\mathrm{w}}P_{\mathrm{wM}}/RT)\Delta p$$
$$-(c_{\mathrm{w}}\bar{B}_0/\eta_{\mathrm{w}})\Delta p+(c_{\mathrm{w}}\bar{B}_0/\eta_{\mathrm{w}})\Delta p_{\mathrm{eq}}\,. \tag{28}$$

The four terms on the right-hand side represent concentration diffusion, pressure diffusion, viscous flow, and osmotic flow, respectively. Just as in the case of gases, Δp_{eq} in both eqs. (25) and (28) appears in the role of a correction to Δp; that is, the difference $(\Delta p-\Delta p_{\mathrm{eq}})$ is the pressure that is effective in driving viscous flow. If we assume that the external pressure difference Δp is zero and that, for simplicity, the solution is dilute, then in the first term we have $c\Delta x_{\mathrm{w}}=c(-\Delta x_{\mathrm{s}})=-\Delta c_{\mathrm{s}}$, the second and third terms vanish, and in the fourth term we have $\Delta p_{\mathrm{eq}}=c_{\mathrm{s}}\Delta\mu_{\mathrm{s}}=RT\Delta c_{\mathrm{s}}$, so that eq. (28) reduces to

$$J_{\mathrm{w}}=P_{\mathrm{wM}}\,\Delta c_{\mathrm{s}}+(c\bar{B}_0RT/\eta_{\mathrm{w}})\,\Delta c_{\mathrm{s}}\,. \tag{29}$$

Here the first term on the right represents diffusive flow and the second represents osmotic flow. If the membrane is open rather than semipermeable, we instead obtain

$$J_{\mathrm{w}}=P_{\mathrm{wM}}\,[1+(P_{\mathrm{sM}}/P_{\mathrm{sw}})]^{-1}\,\Delta c_{\mathrm{s}}\,, \tag{30}$$

which represents only diffusive flow. The diffusion terms in eqs. (29) and (30) differ because there is a counterdiffusion of solute in the latter case. (Further differences appear if the solution is not ideal and dilute, caused for example by volume changes on mixing and by the contribution of solute flux to net volume flow, but these are not essential for the present purpose of identifying osmotic flow.) This simple case illustrates how osmotic flow is neatly separated from diffusive flow by the present equations.

A possibly more familiar equation involving osmotic flow in a dilute two-component system is [3–5]

$$J_{\mathrm{V}} = -L_{\mathrm{p}}(\Delta p - \Delta\pi) , \tag{31}$$

where $J_{\mathrm{V}} = c_{\mathrm{w}}u_{\mathrm{w}}\bar{V}_{\mathrm{w}} + c_{\mathrm{s}}u_{\mathrm{s}}\bar{V}_{\mathrm{s}}$ is the so-called volume flux, L_{p} is the hydraulic coefficient, and $\Delta\pi$ is the osmotic pressure difference. (We have included a minus sign in eq. (31) for consistency with the other sign conventions used in this paper.) For a binary system we have $\Delta p_{\mathrm{eq}} = \Delta\pi$, and eq. (31) follows immediately from eq. (25), with L_{p} identified as

$$L_{\mathrm{p}} = P_{\mathrm{wM}}/cRT + \bar{B}_0/\eta_{\mathrm{w}} . \tag{32}$$

The diffusive and viscous contributions appear separately in L_{p} and can be identified as such if desired. Eq. (29) of the previous paragraph is equivalent to $J_{\mathrm{V}} = L_{\mathrm{p}}\Delta\pi$.

Two objections may be raised at this point, one somewhat technical and the other more fundamental. The first objection is that osmotic flow rapidly creates a layer of nearly pure solvent on the solution side of the membrane, thereby reducing Δp_{eq} across the membrane and nearly stopping the osmotic flow until the layer is substantially dissipated by diffusion. Thus in real cases the overall transport may be diffusion controlled, and osmotic flow as such may play only a minor role. This problem can be avoided by limiting observations to an initial period before the solvent layer builds up appreciably, or by dissipating the layer through stirring or rapid by-flow past the membrane surface. A good account from an experimental point of view has been given by Heyer, Cass, and Mauro [13].

The second objection can be aptly summarized by a quotation from Onsager [14]: "Viscous flow is a relative motion of adjacent portions of a liquid. Diffusion is a relative motion of its different constituents. Strictly speaking, the two are inseparable; for the 'hydrodynamic' velocity in a diffusing mixture is merely an average determined by some arbitrary convention." In other words, the distinction we have drawn between diffusive and osmotic flow is arbitrary. This objection is fundamentally correct, and the most we would care to claim for our identification of osmotic flow is that it is useful, although not unique.

We can dramatize the non-uniqueness of any identification of osmotic flow by algebraic manipulation of eq. (25) to eliminate the viscous-flow terms. The resulting equations look like the Stefan-Maxwell equations for pure diffusion, but the permeability coefficients P_{ij} and $P_{i\mathrm{M}}$ are modified and contain contributions from viscosity. We follow the same method as used for open membranes [1,10], multiplying eq. (25) by c_i, summing over all species i, and using the Gibbs-Duhem relation in the form,

$$\Delta p = \sum_{i=1}^{\nu} c_i \Delta_{\mathrm{T}}\mu_i + \sum_{k=\nu+1}^{\nu+\tau} c_k \Delta_{\mathrm{T}}\mu_k = \sum_{i=1}^{\nu} c_i \Delta_{\mathrm{T}}\mu_i + \Delta p_{\mathrm{eq}} . \tag{33}$$

The terms involving P_{ij} and P_{ij}^{T} sum to zero and the resulting equation can be solved for the quantity $(\Delta p - \Delta p_{\mathrm{eq}} - c\Delta\Phi)$, which is substituted back into eq. (25) and the result manipulated into the form,

$$\sum_{j=1}^{\nu} \frac{c_j}{cT_{ij}}(u_i - u_j) + \frac{u_i}{T_{i\mathrm{M}}} = -\frac{1}{RT}(\Delta_{\mathrm{T}}\mu_i - \Delta\Phi_i) - \sum_{j=1}^{\nu} \frac{c_j}{cP_{ij}} P_{ij}^{\mathrm{T}} \Delta \ln T . \tag{34}$$

The thermal diffusion terms are unchanged, but the permeability coefficients P_{ij} and $P_{i\mathrm{M}}$ are transformed into "effective" permeability coefficients or transmission coefficients, defined as

$$T_{i\mathrm{M}} \equiv P_{i\mathrm{M}} \left(1 + \frac{\bar{B}_0 RT}{\eta^0} \sum_{j=1}^{\nu} \frac{c_j}{P_{j\mathrm{M}}}\right) , \tag{35}$$

$$\frac{1}{T_{ij}} \equiv \frac{1}{P_{ij}} + \frac{cB_0RT}{\eta^0 T_{i\mathrm{M}} P_{j\mathrm{M}}} . \tag{36}$$

The characteristic indication of osmotic flow, namely the term Δp_{eq}, has disappeared. The only clue that eqs. (34)–(36) might refer to a semipermeable membrane is that the summations run over only the permeant components and omit the impermeant ones. The equations for an open membrane [1] in the Stefan-Maxwell form look exactly like eqs. (34)–(36), but the summations run over all components.

Eq. (25), with explicit viscous-flow terms, is mathematically the same as eq. (34), in which viscosity appears only in the coefficients. Which form to use is a matter of taste or convenience, as is our identification of osmotic flow through the term Δp_{eq}. If there is some advantage in discussing viscous flow or osmotic flow separately in a particular problem, then eq. (25) is useful; if a unified treatment of both open and semipermeable membranes is desired, then eq. (34) might be preferable because it has the same form for both cases.

Adopting our identification of osmotic flow for purposes of discussion, we now inquire about the mechanism involved in producing such flow. This apparently irrelevant question is in fact connected with two problems; the validity of one-dimensional descriptions of membrane transport, and the validity of a local averaging or coarse-graining over the open volume of a membrane, which is an essential feature of our statistical-mechanical approach. Anderson and Malone [5] have made detailed calculations of osmotic flow for a model membrane consisting of a system of long parallel cylindrical pores, with a model solution consisting of a dilute suspension of spherical particles in a continuum Newtonian fluid. They find that an essential feature of their results is the force exerted by the pore wall on the solution. Since this force is *perpendicular* to the direction of transport, there is an implication that one-dimensional treatments of transport may be inadequate [5], and that coarse-graining assumptions may discard important information [15]. These are valid points, and it is of course obvious that something must have been discarded by such assumptions.

The matter can be clarified by consideration of the specific case of osmotic flow. According to the work of Anderson and Malone, the driving force for osmotic flow is a pressure gradient inside the pores, which arises because the pore walls exert forces on the solute particles perpendicular to the transport direction. However, our derivation in Sec. III shows that the osmotic effects in semipermeable membranes, including an internal pressure gradient, can be accounted for by assuming only that *some* force exists that prevents the transport of the impermeant species. The origin and nature of this force are not relevant to the general problem of finding the correct form of the transport equations. In other words, our statistical-mechanical approach yields the form of the transport equations regardless of the detailed mechanism or mechanisms involved on a microscopic scale. The information lost is knowledge about the transport coefficients thermselves — they appear in the theory as undetermined quantities that must be measured experimentally or calculated from a detailed microscopic model.

We thus conclude that course-graining and one-dimensional treatments are safe as long as the transport coefficients are handled empirically. They are certainly likely to be inadequate for relating the coefficients to specific properties of the membrane and the solution, a conclusion in complete agreement with Anderson and Malone.

6. Continuous membrane model

In our results so far we have used finite differences across the membrane, and treated the membrane as a surface of discontinuity. We have thereby dodged all questions involving the structure of the membrane and the mechanisms for producing osmotic effects, in order to concentrate on the problem of the form of the transport equations in general. The penalty for this generality is that we are restricted to small differences across the membrane, so that the linear transport equations will be accurate. To escape this limitation to the linear regime we need to formulate local differential equations (rather than finite-difference equations), which can be integrated across a membrane of nonzero thickness. We must therefore construct a model of a semipermeable membrane that has nonzero thickness and is continuous in the sense that it is reasonable to imagine integrating a differential equation across it.

Such a model is quite easy to construct. Since impermeant species cannot enter the membrane, it is reasonable to represent the membrane front surface as a plane that is impermeable to some species and permeable to others, and the body of the membrane as permeable to the species that can pass the front surface. In other words, we model a finite semiperemable membrane as a semipermeable surface of discontinuity plus an open membrane. From an element such as this, very complicated models of finite membranes can be constructed by combining different elements in series and parallel.

Across the surface of discontinuity we use eq. (25) or eq. (34), and in the body of the membrane we use the corresponding differential equations for an open membrane, which are [1]

$$\sum_{j=1}^{\nu} \frac{c_j}{cD_{ij}}(u_i - u_j) + \frac{u_i}{D_{i\mathrm{M}}} = -\frac{1}{RT}(\nabla_{\mathrm{T}}\mu_i - X_i) - \frac{B_0}{\eta D_{i\mathrm{M}}}(\nabla p - cX) - \sum_{j=1}^{\nu} \frac{c_j}{cD_{ij}} D_{ij}^{\mathrm{T}} \nabla \ln T\,, \qquad (37)$$

or

$$\sum_{j=1}^{\nu} \frac{c_j}{cE_{ij}}(u_i - u_j) + \frac{u_i}{E_{iM}}$$
$$= -\frac{1}{RT}(\nabla_{\mathrm{T}}\mu_i - X_i) - \sum_{j=1}^{\nu} \frac{c_j}{cD_{ij}} D_{ij}^{\mathrm{T}} \nabla \ln T , \qquad (38)$$

where the X's are external forces, the D's are diffusion coefficients, and the E's are effective diffusion coefficients related to the D's by the same set of equations that relate T's to P's for a discontinuous membrane, namely, eqs. (35) and (36).

A further simplification may often be possible, if the open portion of the membrane element is thick enough to be rate-limiting for the fluxes. Then the permeant species will be essentially in equilibrium across the discontinuous surface, and eqs. (25) and (34) can be replaced by equations for the continuity of the chemical potentials, e.g., $\Delta\mu_i = 0$. If the external potentials are not continuous across the surface ($\Delta\Phi_i \neq 0$), then the total potentials must be continuous, $\Delta\mu_i - \Delta\Phi_i = 0$. This condition on the continuities of chemical potentials across membrane surfaces in general was proposed some time ago by Kirkwood [16], and has often been used since. Of course, there will always be a pressure discontinuity across the surface if any impermeant species are present, but this will be equal to Δp_{eq} and can be calculated from eq. (26) if Δc_k and $\Delta_{\mathrm{T}}\mu_k$ are small. If they are not small, then Δp_{eq} should be calculated from the usual equation for osmotic equilibrium, obtained by integration of the Gibbs-Duhem relation,

$$\Delta p_{\mathrm{eq}} = \sum_{k=\nu+1}^{\nu+\tau} \int_{c_k'}^{c_k''} c_k \, \mathrm{d}\mu_k \, . \qquad (39)$$

In other words, we use equilibrium conditions across the impermeable surface of discontinuity to establish the boundary conditions just within the membrane surface, and then treat the rest of the problem as a matter of integration of the transport equations for an open membrane through the body of the membrane.

A schematic diagram of such a finite membrane element is shown in fig. 2. The internal pressure gradient, whose importance has been emphasized by Mauro [3,4] and by Anderson and Malone [5] among others, shows up clearly on this diagram. Membrane models of this sort have been proposed and used by many workers, and we make no pretense of originality here. Our only aim is to show how this model can be used to escape the restriction to linear finite-difference transport equations that is imposed by the representation of the entire membrane as a surface of discontinuity.

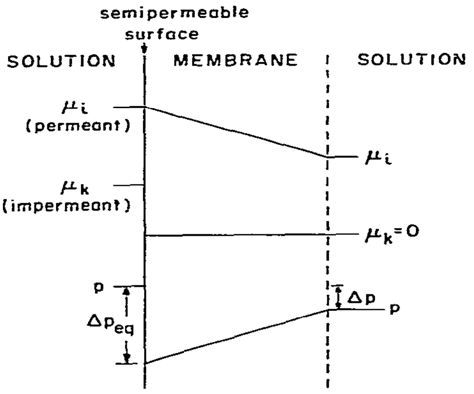

Fig. 2. Schematic diagram of an element for a continuous model of a semipermeable membrane, showing surface discontinuities and internal gradients.

7. Discussion

The present results, as far as we are aware, represent the first general formulation of transport equations for semipermeable membranes. This contrasts with the previous results for open membranes, in which essentially known equations were put on a better fundamental basis. Two new results that arise with semipermeable membranes are the so-called mixed solvent effect in osmosis, and the identification of osmotic flow, including a demonstration that such identification cannot be unique, however useful it might be.

Problems involving detailed structure of the membrane have been deliberately avoided. They are separated off into problems concerning the determination of the transport coefficients, or the integration of the transport equations subject to given boundary conditions. By concentrating on just the general mathematical form taken by the transport equations, we have sacrificed the ability of calculate any transport coefficients or to discuss detailed mechanisms of transport. The answers to such problems must come from another sort of theory entirely.

The reader may wonder whether we could have mimicked semipermeability by manipulating magnitudes of the transport coefficients in the equations for an open membrane, instead of introducing fictitious external forces to keep the impermeant species from crossing the membrane. This trick does not work because the final equilibrium states are different when a species cannot pass a membrane at all and when it can pass it only slowly and with great difficulty. That is, if a species has a nonzero probability of crossing the membrane, it will eventually do so, no matter how small the probability is made. This latter situation applies to the problem of transport through sieving or "leaky" membranes, which we hope to treat in future work.

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