Biophysical Chemistry 12 (1980) 223–233
© North-Holland Publishing Company

STATISTICAL-MECHANICAL THEORY OF PASSIVE TRANSPORT THROUGH PARTIALLY SIEVING OR LEAKY MEMBRANES *

L.F. del CASTILLO
Instituto de Investigaciones en Materiales, Universidad Nacional de Mexico, Mexico City

E.A. MASON
Brown University, Providence, Rhode Island 02912, USA

Received 23 January 1980

The basic equations for multicomponent transport through partially sieving or leaky membranes are discussed from a statistical-mechanical viewpoint. They have the same mathematical form as the corresponding equations for open membranes, but differ in a discontinuous way from the equations for semipermeable membranes (since a "leak" in a semipermeable membrane constitutes a discontinuous or singular perturbation). Partially sieving membranes can be made to mimic semipermeable behavior through the introduction of characteristic time scales. They may approximate semipermeable behavior at short times, but always deviate at longer times.

1. Introduction

We have previously used the basic principles of the statistical-mechanical theory of transport, plus a number of physical assumptions, to derive transport equations for open membranes [1] and for semipermeable membranes [2]. Open membranes allow all components of a mixture to pass through, whereas semipermeable membranes strictly prevent the passage of some components. Another class of membranes is often distinguished, known variously as leaky, partially sieving, or partially permselective membranes. Such membranes are usually regarded as intermediate, in some sense, between open and semipermeable membranes, in that they allow some components to pass only with difficulty. The notion of intermediate behavior is often formulated mathematically by introducing into the transport equations a term $\sigma\Delta\pi$, where σ is a phenomenological reflection coefficient and $\Delta\pi$ is the difference in osmotic pressure corresponding to true semipermeability [3,4]. Thus $\sigma = 1$ describes a semipermeable membrane and $\sigma = 0$ a "completely open" membrane.

The purpose of this paper is to show how the statistical-mechanical theory of membrane transport can handle the case of leaky or partially sieving membranes. We argue that, from the statistical-mechanical point of view, leaky membranes are just a subclass of open membranes. That is, the transport equations for leaky and open membranes have exactly the same mathematical form, and differ only in the relative magnitudes of some of the transport coefficients. This assertion is supported both by a careful review of the physical assumptions underlying the statistical-mechanical equations, and by a discussion of the known physical mechanisms of membrane sieving.

A conceptual problem arises in that it is impossible to get the statistical-mechanical transport equations for a leaky membrane to pass smoothly to the corresponding equations for a perfectly semipermeable membrane, in contrast to the way that some phenomenological equations behave by manipulation of the coefficient σ. The difficulty turns out to be that the equations should *not* be the same, because the equilibrium states for a leaky membrane and a semipermeable membrane are fundamentally different. That is, any leak, no matter how small, will eventually allow all the solute to pass through, and the final equilibrium

---

* Supported in part by U.S. National Science Foundation Grant ENG 76-07415.

state is the same as for a completely open membrane. Put another way, a tiny leak in an initially semipermeable membrane constitutes a singular, or discontinuous, perturbation. Such perturbations are well known in other fields, such as fluid dynamics [5] and quantum mechanics [6]. For example, the addition of even an infinitesimal viscosity to a fluid-dynamical problem changes the solutions of the equations for the flow field by a finite amount in the neighborhood of a surface.

The difficulty can be resolved by the introduction of characteristic time scales. At small times the *solutions* of the transport equations for leaky membranes can be made as close as desired to those for semipermeable membranes, simply by making certain transport coefficients very small. But at long times the solutions for leaky and semipermeable membranes diverge, and the equilibrium solution for the leaky membrane is the same as that for a completely open membrane. This behavior is illustrated by the analysis of an idealized osmotic experiment similar to that actually used in the "dynamic" method of measuring osmotic pressure [7,8].

2. Partially sieving membranes as a subclass of open membranes

We give first a brief critical review and extension of the statistical-mechanical derivation, in order to establish that nothing in the derivation puts any restrictions on the relative magnitudes of the coefficients that appear in the transport equations. We thereby infer that these equations are the same for partially sieving or leaky membranes as for open membranes. We check this inference by considering the known physical mechanisms of sieving behavior, and show that the transport equations properly describe these mechanisms.

2.1. Review and extension of statistical-mechanical derivation

The derivation can be divided into two parts: first, the passage from the statistical-mechanical Liouville equation to the equations of fluid dynamics for a flowing, diffusing multicomponent system; second, the passage from the equations of fluid dynamics to the equations of membrane transport. The first part was accomplished by Bearman and Kirkwood [9,10] and by Snell, Aranow, and Spangler [11]. Three essential assumptions are involved:

(1) The fluid can be described in terms of a local state.

(2) The local state deviates only slightly from a local equilibrium state, so that a first-order expansion of the distribution function about this local equilibrium state is valid. The first-order expansion leads to linear transport equations. (The choice of the reference equilibrium state is not unique, but this is not important for the application to membranes.)

(3) A quasicontinuum averaging is carried out over macroscopically small but microscopically large volume elements of the fluid.

The second part of the derivation was carried out by Mason and Viehland [1], and involves four further assumptions pertaining specifically to membranes, as follows:

(4) The membrane is taken as one component of the multicomponent mixture, constrained to be stationary in space, and making no contribution to the mixture viscosity.

(5) A local averaging or coarse-graining is carried out over the open volume of the membrane (e.g., over the cross-sectional area in the case of a cylindrical pore).

(6) In the coarse-grained equations, the terms representing inertial effects are dropped, and those representing viscous effects are assumed to be nonseparative (i.e., not contributing to sieving behavior).

(7) The diffusion and thermal diffusion coefficients in the coarse-grained equations are taken to represent diffusion and thermal diffusion *within* the membrane.

Assumption (7) is generalized from its original form [1], in which the membrane was assumed to have only a space-filling role, so that diffusion coefficients within the membrane were proportional to the corresponding coefficients in free space. The original assumption was needlessly restrictive, being a holdover from gas theory [12], for which it is quite reasonable.

The important point is that none of the above assumptions restricts the possible magnitudes of any of the transport coefficients. If sieving behavior is considered to be caused by the relative ease with which various components of a mixture penetrate or pass through a membrane, then the statistical-mechanical equations can represent such behavior by manipulation of the magnitudes of the transport coefficients. This point can be emphasized by noting that it has been shown [1] that the statistical-mechanical equations are mathematically equivalent to various phenomenological equations (e.g., irreversible thermodynamics, frictional models) proposed for the specific purpose of describing leaky and partially sieving membranes. Only algebra is necessary to convert from one set of transport equations to another.

The transport equations obtained from the derivation outlined above are, for a mixture of ν components,

$$\sum_{j=1}^{\nu} \frac{c_j}{cD_{ij}} (\boldsymbol{u}_i - \boldsymbol{u}_j) + \frac{\boldsymbol{u}_i}{D_{i\mathrm{M}}} = -\frac{1}{RT} (\nabla_T \mu_i - X_i)$$

$$- \frac{B_\mathrm{o}}{\eta D_{i\mathrm{M}}} (\nabla p - cX) - \sum_{j=1}^{\nu} \frac{c_j}{cD_{ij}} D_{ij}^T \, \nabla \ln T, \qquad (1)$$

where c_j is the molar concentration of component j, $c = \Sigma c_i$ is the total molar concentration, $\boldsymbol{u}_i$ is the transport velocity of component i (flux density divided by concentration), $\nabla_T \mu_i$ is the chemical potential gradient of component i in an isothermal system with the same local state variables and concentration and pressure gradients as the real system, X_i is the external force per mole on component i, $X = \Sigma c_i X_i$ is the total external force per unit volume on the solution, and ∇p is the gradient of total pressure. The five types of transport coefficients appearing in eq. (1) are: D_{ij}, the diffusion coefficient of components i and j *within* the membrane in the presence of all the other components; $D_{i\mathrm{M}}$, the diffusion coefficient of i determined by direct interactions with the membrane, in the presence of the other components; B_o, a geometrical constant of the membrane that characterizes its viscous-flow properties; η, the viscosity of the solution within the membrane; and D_{ij}^T, a multicomponent thermal diffusion coefficient. The five sets of terms in eq. (1) have well-known physical meanings. The first set on the left-hand side (involving the D_{ij}) describes the interdiffusion of component i with all the other components, and the second set (involving $D_{i\mathrm{M}}$) describes the interdiffusion of i with the membrane. All the fluxes, $\boldsymbol{u}_i$ and $\boldsymbol{u}_j$, appear only the left-hand side of eq. (1). The three sets of terms on the right-hand side describe the "forces" that drive the fluxes. The first set (with the coefficient of RT) represents isothermal diffusion, including concentration diffusion, pressure diffusion, and forced diffusion. The second set (with B_o/η) represents viscous flow, which has been assumed to be nonseparative, and the third and last set of terms describes thermal diffusion. There are ν independent equations represented by (1), as i takes on values from 1 to ν.

A wide variety of behavior of solvents, solutes, and membranes is encompassed by eq. (1). To illustrate its wide applicability, we briefly mention a number of cases for which the validity of eq. (1) is not immediately obvious.

(1) *Time-dependent problems.* Strictly speaking, assumption 6 restricts eq. (1) to steady-state conditions at low Reynolds and Mach numbers [1]. The steady-state condition might appear quite restrictive, but a number of time-dependent phenomena can still be treated by a quasi-steady-state approximation, in which time variations are slow enough that eq. (1) is valid at any instant. A complete description of such phenomena then requires, in addition to eq. (1), the specification of conservation equations for mass and momentum, and of boundary and initial conditions. In some cases, a transport equation and a conservation equation for energy might also be needed. It seems likely that many, perhaps most, membrane problems can be handled by this technique. The case of membrane properties that change with time can be treated by essentially the same procedure, with the added complication that the transport coefficients within the membrane become time-dependent.

(2) *Heterogeneous and heteroporous membranes.* The coarse-graining procedure of assumption 5 implies that the membrane is homogeneous and homoporous, at least over the local scale of the coarse-graining. Membranes that are heterogeneous or heteroporous over a larger scale can be dealt with by considering them as built up of locally homogeneous and homoporous parts, to each of which eq. (1) applies separately. Solutions of the equations must then be matched at the boundaries of these local parts. In the limit, eq. (1) is applied to the whole membrane, but the transport coefficients depend explicitly on position. The resulting boundary-value problems may be very difficult to solve, either analytically or numerically, but the essential point is that the form of eq. (1) does not have to be changed.

(3) *Anisotropic membranes.* Most real cases can probably be handled by allowing the transport coefficients to depend on position and/or the direction of flow, in a manner similar to case (2) above. If this pro-

cedure is not satisfactory, then eq. (1) must be changed. The nature of the reformulation of eq. (1) that would be needed is clear, but the results are mathematically complex – for instance, diffusion coefficients become second-order tensors instead of scalars, so that terms like $D\nabla\mu_i$ must be changed to $\mathbf{D}\cdot\nabla\mu_i$. This situation arises for gaseous ions in strong electric fields [13], but let us hope not for real membrane problems.

(4) *Deformable membranes.* Assumption 4 might seem to imply that the membrane must be rigid, but eq. (1) can treat deformable membranes straightforwardly by allowing the transport coefficients to depend on the membrane deformation. A complete description of the problem then requires an additional relation that gives the membrane deformation in terms of variables such as the pressure [14]. Again, the resulting mathematics may be complicated, but no change in the mathematical form of eq. (1) is required.

(5) *Solution membranes.* A solution membrane is one in which the components first dissolve, and then diffuse as in a liquid. A stationary liquid layer can act as a solution membrane, as can certain types of rubber sheets. The generalization given in assumption 7 allows solution membranes to be described simply in terms of the transport coefficients within the membrane. In addition, boundary conditions may need to be changed to allow for the effects of distribution coefficients. In other words, eq. (1) applies within the membrane, but transport coefficients and boundary conditions must be used that apply to the interior of the membrane rather than to external conditions.

(6) *"Tight" membranes.* By this name we mean to suggest membranes in which behavior at a molecular level is paramount, and a continuum description of transport supposedly breaks down. An example would be single-file diffusion in biological membranes [15]. Our contention is that assumption 5 on coarse-grain averaging over the membrane allows a continuum description, namely eq. (1), to be used. The problem of describing the possible peculiar behavior of a tight membrane is then transferred to the transport coefficients and boundary conditions, just as for a solution membrane. For example, a single-file membrane might require a strongly composition-dependent diffusion coefficient for its description [15]. Such a membrane might also require replacement of the groups $B_0/\eta D_{iM}$ in eq. (1) by a more empirical coefficient, since the concept of a continuum viscosity would probably be inapplicable. A more likely prospect, however, is that the whole viscous-flow term in eq. (1) would be negligible. As another example, energy-barrier models for membrane transport have been shown to be consistent with a continuum description [16].

(7) *Carrier-facilitated transport.* This case involves a transport mechanism in which the transported component reacts with a carrier molecule at one surface of the membrane to form a complex, the complex moves through the membrane to the other surface where it dissociates, and then the free carrier moves back to the first surface to react again and repeat its circuit [17]. Clearly, eq. (1) still applies within the membrane, but the transported species need to be correctly identified. That is, the i, j subscripts in eq. (1) must include the free carrier and the complex. The only question remaining is how to introduce the reaction rates for formation and decomposition of the complex. The answer is well known – reactions are described by adding source-sink (or creation-destruction) terms to the mass conservation equations for the various species. Thus, although the net effects of carrier-facilitated transport can be very large [17], no change in the form of eq. (1) is required.

In summary, the form of the transport equations does not need to be changed in order to describe a wide variety of cases. It may be necessary to let the transport coefficients depend on position, or time, or external variables, or to include modifications to the accompanying conservation equations or boundary conditions, but eq. (1) remains unaltered in form.

However, there are several situations where eq. (1) is likely to be inadequate. Perhaps the most obvious is the case of so-called active transport, in which "pumps" within the membrane act selectively on some of the transported species. Since the mechanism of such transport is at present unknown, it is not even clear how it should be described mathematically, and it seems futile to even speculate on possible modifications to eq. (1) at this point. Another obvious inadequacy must occur in principle for fast transients, since inertial terms have been dropped in deriving eq. (1). Whether or not this will cause any difficulties in practice is not yet known. Finally, the phenomenon of diffusion along internal surfaces of the membrane has been ignored. Surface diffusion can be included in the format of eq. (1) if it can be described as a noninteracting parallel pathway for diffusion, but otherwise the entire formulation of the problem would need to be reconsidered.

2.2. Mechanisms of sieving

We now wish to check explicitly that eq. (1) is capable of describing all the known steady-state mechanisms of sieving. These mechanisms are as follows:

(1) Membrane mosaic structures.
(2) Long-range forces.
(3) Kinetic entrance effects.
(4) Steric entrance effects.
(5) Internal hydrodynamic drag.

For each of these mechanisms, we show that the statistical-mechanical transport equations are applicable, provided only that transport coefficients and boundary conditions are properly interpreted. It should be noted that steady-state operation requires that net sieving must occur at the membrane surface, where rejected species can be removed by stirring or rapid by-flow [18]. That is, a steady state cannot be reached unless a removal mechanism coexists with the rejection mechanism.

(1) *Membrane mosaic structures.* In this simple picture (sometimes known as a "two-pipe model"), part of the membrane is completely open and part is perfectly semipermeable. Such a mechanism is obviously describable by our transport equations — the open-membrane equations apply to the open portions, the semipermeable-membrane equations (described in the next section) apply to the other portions, and the solutions of the equations are combined as already discussed for heteroporous membranes.

(2) *Long-range forces.* The usual long-range forces relevant to membranes are the electrostatic ones due to fixed charges within the membrane, although other possibilities can at least be imagined (e.g., magnetic forces). These forces appear directly in eq. (1) as the X_i, and the treatment of the problem in this way is well understood in principle [19,20]. A further equation describing the relation between the electrical forces and the charge distributions must now be included (e.g., the Poisson-Boltzmann equation). The mathematical solution of the resulting set of equations may be difficult to obtain, even by numerical methods [19,20], but there is no question about the applicability of eq. (1).

(3) *Kinetic entrance effects.* In this mechanism a relative separation occurs because more of one species than of another enters the membrane per unit time [21]. This is the major mechanism for gas (isotope) separation by diffusion across porous barriers, but it is doubtful whether it is ever of importance for liquid solutions. At any rate, no example of it has even been demonstrated experimentally. The effect occurs in gases because the mean molecular speed is greater for light molecules than for heavy ones, and is quite properly described by equations of the form of eq. (1) [12, 21]. The coefficients in eq. (1) that account for the separation are the D_{iM}, which are Knudsen diffusion coefficients in the case of gases. Thus the D_{iM} can have two functions — to describe how fast species i passes through the membrane, and also how fast it enters. Only the latter effect leads to steady-state sieving.

(4) *Steric entrance effects.* This mechanism is usually discussed in the context of a hydrodynamic model involving a rigid-sphere solute suspended in a continuum solvent, moving through a membrane consisting of straight cylindrical pores in a rigid plate. Ferry [22] long ago pointed out that partial sieving can occur when the solute diameter is comparable to, but less than, the pore diameter, because the region near the pore wall is inaccessible to solute particles of nonzero size. The effective pore area is thereby reduced by a factor of $(1-\lambda)^2$, where λ is the ratio of solute to pore diameters. A further discrimination against the wall region occurs if the solution is flowing, because the flow velocity is zero at the pore wall and maximum on the axis. This produces a further reduction in effective pore area by a factor of $[2-(1-\lambda)^2]$. The subject has been discussed by Bean [23] and by Anderson and Quinn [24], among others. Some authors classify these two effects as two separate mechanisms [25], but the distinction is unimportant for our purposes. There has never been any doubt that a standard transport equation, such as eq. (1), was applicable, but there has been discussion as to whether these steric effects should appear as modifications to diffusion coefficients, or as changed boundary conditions representing effective distribution coefficients. The question appears to be resolvable by consideration of an entrance Peclet number [25], but this is irrelevant from our point of view — all that matters is that eq. (1) is applicable, not that there may be some questions regarding how it is applied in detail.

(5) *Internal hydrodynamic drag.* The same model as used for (4) above applies here. A solute particle moving through a fluid suffers a greater drag force when near a solid wall than when in the unbounded

fluid. This wall-drag effect is customarily interpreted as reducing the solute diffusion coefficient within the membrane, and increasing the overall rejection coefficient, by factors which depend on the diameter ratio λ [23–26]. Thus there is no problem as far as the use of eq. (1) is concerned; the form remains the same, and only some coefficients are changed. Nevertheless, a somewhat subtle conceptual difficulty arises, which requires a short digression at this point. The diffculty is that wall drag is a frictional effect *within* the membrane, and yet it produces a rejection effect at the *surface* of the membrane at steady state. How is this physically possible? A slowing down of particles should only produce a greater internal concentration at steady state, not a rejection. Part of the answer has to do with rapid diffusive equilibrium at the pore entrance [25], so that some particles come back out of the entrance, but another explanation is required when convective flow is dominant. In that case the question can be put rather more starkly: how can the hydrodynamic drag on a particle within a pore send a signal back to the pore entrance to tell another particle not to enter? Somewhat surprisingly, a signal *can* be sent back, by way of the continuum solvent. The explanation is fairly easy to grasp by analogy with the case of the long-range electrostatic forces. There the charges set up an electric field that can be felt by a charged particle attempting to enter the pore. Moreover, any change in the internal charge distribution is instantly signaled to the electric field everywhere. (Strictly, there is a slight delay due to the finite speed of light, but this effect is negligible in the present context.) In the hydrodynamic case, there is a flow field that plays the same role as the electric field, and the equation for this flow field allows for the propagation of signals, limited only by the speed of sound (effectively infinite for our purposes). Thus the particles within a pore can indeed send a signal via the flow field back to the pore entrance, and there is no contradiction between sieving behavior and steady-state operation.

In summary, all the criteria available support the position that partially sieving or leaky membranes are in no essential way different from open membranes. In the next section we show in what sense the behavior of partially sieving membranes can approach that of perfectly semipermeable membranes.

3. Relation to semipermeable membranes

We first show that the transport equations for partially sieving (i.e., open) membranes cannot be put into the same form as the equations for semipermeable membranes by simply manipulating the magnitudes of the transport coefficients, unless a drastic physical assumption is made. It must be assumed that the viscous-flow term of eq. (1) (the term involving B_o/η) is negligible for all times of interest; this is equivalent to setting the reflection coefficient σ of the phenomenological transport equations equal to unity. However, even this equivalence of the two sets of transport equations proves to be illusory, as we next show by considering a simple dynamic osmotic experiment, in which the pressure difference across a membrane is followed as a function of time. No matter how small the viscous-flow term is taken to be, the pressure-time curve for a partially sieving membrane eventually deviates from the corresponding curve for a semipermeable membrane, unless the viscous-flow term is made *exactly* zero. This example also shows the need to introduce a characteristic time scale in comparing partially sieving and semipermeable membranes.

3.1. Comparison of equations

Suppose that a membrane is made impermeable to τ of the ν components of a mixture. Then in place of eq. (1) we obtain the results for a semipermeable membrane [2],

$$\sum_{j=1}^{\nu-\tau} \frac{c_j}{cD_{ij}}(u_i-u_j)+\frac{u_i}{D_{iM}}=-\frac{1}{RT}(\nabla_T\mu_i-X_i) \qquad (2)$$

$$-\frac{B_o}{\eta D_{iM}}(\nabla p-\nabla p_{eq}-cX)-\sum_{j=1}^{\nu-\tau}\frac{c_j}{cD_{ij}}D_{ij}^T\,\nabla\ln T,$$

where we have written gradients instead of the more proper finite differences in order not to complicate the notation unduly. It is surely no surprise to find τ terms missing from each of the two summations in this expression as compared to eq. (1), nor to find that eq. (2) represents only $\nu-\tau$ equations instead of ν equations. The essential difference between the two cases is the term ∇p_{eq} in eq. (2), defined as

$$\nabla p_{eq}\equiv\sum_{k=\nu-\tau+1}^{\nu} c_k\nabla_T\,\mu_k, \qquad (3)$$

which is related to an osmotic pressure difference, although not in an obvious way in the case of multicomponent solutions [2]. Thus the transport equations for the semipermeable membrane differ from those for the sieving membrane by the effective pressure difference, $(\nabla p - \nabla p_{eq})$ instead of ∇p, that drives the viscous component of the flow. One way that the two sets of equations could become equivalent would be for the viscous flow to be negligible, so that the whole term involving B_0/η could be dropped (as well as dropping all terms and equations referring to the τ impermeant components). Physically, this would correspond to a very "tight" membrane, in which diffusive transport *always* dominated over viscous transport. Although this condition solves the problem of transforming the transport equations for sieving membranes into those for semipermeable membranes, it is an unacceptably restrictive condition.

Since the difficulty in transforming one set of transport equations into the other lies in the terms involving B_0/η, perhaps we could suppress these terms by mathematical manipulation instead of simply dropping them. A transformation that suppresses the viscous-flow terms by absorbing them into "effective" diffusion coefficients is known [1,2]; the results can be written for both partially sieving and semipermeable membranes in the form,

$$\sum_{j=1}^{N} \frac{c_j}{cE_{ij}} (u_i - u_j) + \frac{u_i}{E_{iM}}$$

$$= -\frac{1}{RT} (\nabla_T \mu_i - X_i) - \sum_{j=1}^{N} \frac{c_j}{cD_{ij}} D_{ij}^T \ \nabla \ln T, \qquad (4)$$

where

$$E_{iM} = D_{iM} \cdot \left(1 + \frac{B_0 RT}{\eta} \sum_{j=1}^{N} \frac{c_j}{D_{jM}}\right), \qquad (5)$$

$$\frac{1}{E_{ij}} = \frac{1}{D_{ij}} + \frac{cB_0 RT}{\eta D_{iM} D_{jM}} \left(1 + \frac{B_0 RT}{\eta} \sum_{j=1}^{N} \frac{c_j}{D_{jM}}\right)^{-1}, \qquad (6)$$

$$N = \begin{cases} \nu \quad : & \text{partially sieving} \qquad (7a) \\ \nu - \tau : & \text{semipermeable.} \qquad (7b) \end{cases}$$

The thermal diffusion terms remain unchanged in eq. (4), but the diffusion coefficients D_{ij} and D_{iM} are transformed into the coefficients E_{ij} and E_{iM}, which contain the viscous-flow factor B_0/η. The only indication that eqs. (4)–(6) might refer to a semipermeable membrane rather than to a partially sieving membrane is the fact that the summations omit the impermeant components in the semipermeable case and include all components in the sieving case. We can rationalize the omission of fluxes in eq. (4) as applied to semipermeable membranes, on the grounds that they should be zero for impermeant components, so that eq. (4) appears to pass smoothly from the sieving case to the semipermeable case. This is true as far as the *form* of eq. (4) is concerned, but the coefficients E_{iM} and E_{ij} do not behave properly in trying to make a partially sieving membrane appear to act like a semipermeable one. Specifically, suppose that we try to make a partially sieving membrane appear semipermeable by assuming that the ν-th component can pass only with very great difficulty. Although eq. (4) behaves properly, the coefficients E_{iM} and E_{ij} misbehave because the term involving $D_{\nu M}$ in the summations of eqs. (5) and (6) refuses to disappear. In fact, it comes to dominate the sums because the only physical way to express the fact that component ν passes the membrane with difficulty is to make $D_{\nu M}$ small compared to the other D_{jM}.

The foregoing difficulties can be avoided only by making B_0/η small enough that the summation terms in eqs. (5) and (6) can be neglected. But the neglect of terms involving B_0/η was the same drastic treatment needed to make eq. (1) pass smoothly into eq. (2). Thus the transformation that produced eq. (4) and hid the viscous terms in the effective diffusion coefficients has availed nothing.

It thus appears that a partially sieving membrane cannot be made to behave like a semipermeable membrane by manipulation of the coefficients in the transport equations, unless the viscous-flow terms are discarded. As a check on this conclusion, and to make contact with a more conventional formulation of membrane transport, we consider the simple case of an ideal dilute binary solution, and see what is involved in setting the phenomenological reflection coefficient σ equal to unity, in terms of the present statistical-mechanical equations. We recall how σ is defined in the treatment of membrane transport by irreversible thermodynamics, as formulated by Kedem and Katchalsky [4,27],

$$J_V = L_p \nabla p - L_{pD} \nabla \pi \tag{8a}$$

$$= - L_p(\nabla p - \sigma \nabla \pi). \tag{8b}$$

Here J_V is the so-called volume flux, and L_p and L_{pD} are Onsager coefficients. Denoting solute by subscript s and solvent by subscript w, we write the definitions of J_V and σ as

$$J_V \equiv c_s u_s \bar{V}_s + c_w u_w \bar{V}_w, \tag{9}$$

$$\sigma \equiv - L_{pD}/L_p, \tag{10}$$

where $\bar{V}$ is partial molar volume. For a dilute ideal solution we also have

$$\nabla \pi = RT \nabla c_s. \tag{11}$$

Specializing eq. (1) or eq. (4) to this case, we can compare coefficients and find the relations [1],

$$L_p = D_{wM}/cRT + B_o/\eta, \tag{12}$$

$$L_{pD} = \frac{D_{sw}}{RT}\left(\frac{\bar{V}_s D_{sM} - \bar{V}_w D_{wM}}{D_{sw} + D_{sM}}\right), \tag{13}$$

from which σ is found to be

$$\sigma = \left(1 - \frac{\bar{V}_s}{\bar{V}_w}\,\frac{D_{sM}}{D_{wM}}\right)\left(1 + \frac{D_{sM}}{D_{sw}}\right)^{-1}\left(1 + \frac{cB_oRT}{\eta D_{wM}}\right)^{-1} \tag{14}$$

To pass to the semipermeable limit of $\sigma = 1$, we see that it is necessary not only to make the passage of solute difficult by taking $D_{sM} \ll D_{wM}, D_{sw}$, but also to make the viscous flow negligible by taking $B_o/\eta \ll D_{wM}/cRT$. Thus our previous conclusion is confirmed. It is interesting to note that this point never arose before in connection with the treatment by irreversible thermodynamics, because viscous flow was improperly omitted at the very beginning [1,21].

3.2. *Example: pressure-time curves in a dynamic osmotic experiment*

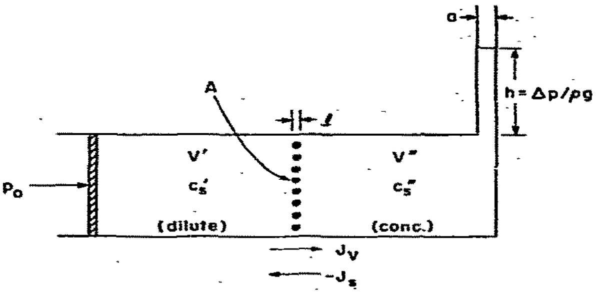

Fig. 1. Schematic diagram of a dynamic osmotic experiment, to illustrate the discontinuous difference between a sieving and a semipermeable membrane, and to show the need for a characteristic time scale. The areas of the membrane and capillary rise tube are A and a, respectively, and the membrane thickness is l.

To illustrate the discontinuous difference between a sieving and a semipermeable membrane, and to show the necessity of introducing characteristic time scales, we consider a simple idealized experiment. A membrane separates two similar binary solutions of different concentration; the pressure on the more dilute solution is held constant, and the pressure of the more concentrated solution is followed as a function of time (e.g., by observing the rise and fall of liquid in a capillary connected to the more concentrated solution, as shown in fig. 1). This arrangement is an idealized osmometer, such as is used in dynamic osmotic pressure measurements [7,8]; instead of limiting observations to early times, however, we follow the pressure difference to equilibrium between the two solutions. The notation of irreversible thermodynamics is particularly convenient for this discussion. We need the transport equations giving the volume flux J_V and the solute flux J_s; the first is given by eq. (8), and the second is given by [4,27],

$$J_s = - (L_p + L_{Dp})\, c_s \nabla p - (L_{pD} + L_D)\, c_s \nabla \pi \tag{15a}$$

$$= - L_p(1 - \sigma)\, c_s \nabla p - (L_D - \sigma L_p)\, c_s \nabla \pi, \tag{15b}$$

in which we have assumed that the solutions are dilute and ideal. The new transport coefficients introduced here are $L_{Dp} = L_{pD}$ (Onsager reciprocity) and L_D, which is related to the coefficients of the statistical-mechanical theory by [28]

$$L_D = \frac{D_{wM}}{cRT}\left(\frac{c}{c_s}\,\frac{D_{sM}}{D_{wM}} - 1\right)\left(1 + \frac{D_{sM}}{D_{sw}}\right)^{-1}. \tag{16}$$

The −1 in the first parentheses was neglected in ref. [1] because $c_s \ll c$ for a dilute solution, but this approximation is not permitted when we wish to consider the limit $D_{sM}/D_{wM} \to 0$, as we do here.

The conservation equations giving Δp and $\Delta \pi = RT\,\Delta c_s$ as a function of time are

$$\mathrm{d}\Delta p/\mathrm{d}t = \alpha_1 J_V, \tag{17a}$$

$$\mathrm{d}\Delta c_s/\mathrm{d}t = \alpha_2 J_s, \tag{17b}$$

where $\Delta c_s = c_s'' - c_s'$, and α_1 and α_2 are geometrical and physical parameters of the membrane-solution system (fig. 1),

$$\alpha_1 = \rho g(A/a), \tag{18a}$$

$$\alpha_2 = A(1/V' + 1/V''). \tag{18b}$$

If we write the transport equations in finite-difference form, we can combine the transport and conservation equations to yield

$$\mathrm{d}\Delta p/\mathrm{d}t = -\lambda_1\Delta p + \lambda_2\Delta\pi, \tag{19a}$$

$$\mathrm{d}\Delta\pi/\mathrm{d}t = -\lambda_3\Delta p - \lambda_4\Delta\pi, \tag{19b}$$

where

$$\lambda_1 = \alpha_1 L_p/l, \qquad \lambda_2 = \sigma\lambda_1,$$

$$\lambda_3/\lambda_1 = RT(\alpha_2/\alpha_1)\,\bar{c}_s(1-\sigma),$$

$$\lambda_4/\lambda_1 = RT(\alpha_2/\alpha_1)\,\bar{c}_s[(L_D/L_p) - \sigma]. \tag{20}$$

A special case of this problem, with $\lambda_3 = 0$, was discussed much earlier by Laidler and Shuler [29].

It is easy to solve eqs. (19) if the λ's are taken as constant (a reasonable approximation if $\Delta c_s/\bar{c}_s$ is small). For initial conditions ($t = 0$) of $\Delta p = 0$ and $\Delta\pi = (\Delta\pi)_0$, the solution can be written as

$$\Delta p = \sigma(\Delta\pi)_0\,(\lambda_1\tau_1)\,(1 - \mathrm{e}^{-t/\tau_1})\,\mathrm{e}^{-t/\tau_2}, \tag{21}$$

where

$$\tau_1^{-1} = [(\lambda_1 - \lambda_4)^2 - 4\sigma\lambda_1\lambda_3]^{1/2}, \tag{22a}$$

$$\tau_2^{-1} = \tfrac{1}{2}(\lambda_1 + \lambda_4) - \tfrac{1}{2}\tau_1^{-1}. \tag{22b}$$

As the membrane is made less and less permeable to solute, eq. (19b) shows that $\lambda_3, \lambda_4 \to 0$, whereby the relaxation times become

$$\tau_1^{-1} \to \lambda_1, \qquad \tau_2^{-1} \to \lambda_4 + \sigma\lambda_3, \tag{23}$$

Notice that the initial slope of Δp versus t is equal to $\sigma(\Delta\pi)_0\lambda_1$ and so gives σ directly, which is the basis of dynamic osmometry [7,8].

It is clear from eq. (21) that the non-semipermeable, or "leaky", character of the membrane resides in the factor $\exp(-t/\tau_2)$, which eventually forces Δp back to zero at sufficiently large t. The curve of Δp versus t mimics true semipermeable behavior at all finite t only in the limit $\tau_2 \to \infty$. This limiting behavior requires $\lambda_3, \lambda_4 = 0$. To make $\lambda_3 = 0$ we must have $\sigma = 1$ according to eq. (20), and we have already seen from eq. (14) that this requires $D_{sM}/D_{wM} = 0$, $D_{sM}/D_{sw} = 0$, and $cB_0RT/\eta D_{wM} = 0$. To make $\lambda_4 = 0$ requires only the first of these three conditions, since the factor $[(L_D/L_p) - \sigma]$ in λ_4 is found to be

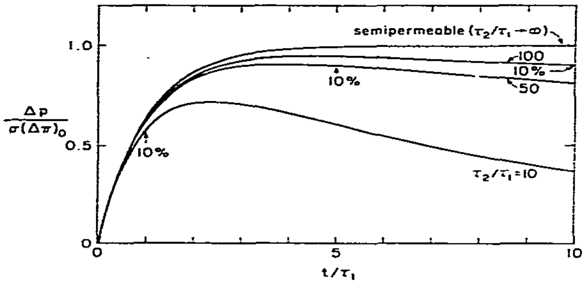

Fig. 2. Pressure-time curves for the experiment of fig. 1, showing how semipermeable behavior can be approximated by a sieving membrane only within a certain time scale. The short arrows mark the time limits for approximation within 10% for three curves of different degrees of sieving behavior.

$$\frac{L_D}{L_p} - \sigma = \frac{c}{c_s}\frac{D_{sM}}{D_{wM}}\left(1 + \frac{D_{sM}}{D_{sw}}\right)^{-1}\left(1 + \frac{cB_0RT}{\eta D_{wM}}\right)^{-1}. \tag{24}$$

Thus our earlier contention is demonstrated — unless the viscous-flow term is zero, λ_3 will not vanish, and Δp will eventually fall to zero no matter how closely it may approach the semipermeable plateau limit of $(\Delta\pi)_0$ at earlier times. (Notice in eq. (21) that $\sigma \to 1$, $\lambda_1\tau_1 \to 0$ when $\lambda_3, \lambda_4 \to 0$.)

However, it is also clear from eq. (21) that a partially sieving membrane can approximate semipermeable behavior within a time scale that is set by the magnitude of τ_2. For example, to stay within about 10% of semipermeable behavior, we would require that $t \lesssim \tau_2/10$, to stay within 5% would require $t \lesssim \tau_2/20$, and so on.

The character of Δp versus t curves for several values of τ_2 is illustrated in fig. 2 (where for simplicity we have chosen $\lambda_1\tau_1 = 1$). As long as t remains within its prescribed limit, a partially sieving membrane approximates the behavior of a semipermeable membrane, even if $\sigma \neq 1$. (Notice that σ has been included as part of the normalization factor of Δp in fig. 2.) However, beyond this limit the behaviors diverge; ultimately Δp approaches $(\Delta\pi)_0$ for a semipermeable membrane, but approaches zero for a partially sieving membrane.

4. Discussion

The present results show how the behavior of partially sieving or leaky membranes can be encompassed within results obtained earlier for open membranes and for semipermeable membranes. It is argued that the statistical-mechanical equations for transport through partially sieving membranes are of exactly the same form as the corresponding equations for open membranes, differing only in the relative magnitudes of the transport coefficients occurring in the equations. The argument is supported by a critical analysis of the assumptions underlying the statistical-mechanical theory, and further buttressed by consideration of all the known specific mechanisms of membrane sieving. The transport equations for partially sieving or leaky membranes do not, in general, pass continuously into the equations for semipermeable membranes, unless a drastic physical assumption is made, namely that viscous flow is *always* negligible. The reason for this lack of continuous behavior is that any "leak" in a semipermeable membrane, no matter how small, constitutes a discontinuous perturbation.

The discontinuity between partial sieving and semipermeable behavior can be handled by the introduction of suitable time scales, as illustrated by an idealized dynamic osmotic experiment. At short times on such a scale, a partially sieving membrane can approximate semipermeable behavior, but large deviations occur at longer times. Although a single time scale was sufficient for the simple example discussed here, it is probable that more complicated cases could require the introduction of multiple time scales. In the case of steady-state experiments, in which time does not enter explicitly, time scales would appear indirectly through contact or residence times (that is, as a distance divided by a velocity).

The present results complete the task, begun earlier [1,2], of formulating the general equations that describe passive transport through membranes, without restrictions on the nature of the fluids involved or the number of components therein, on the basis of well-founded statistical-mechanical arguments. The only questions remaining within the framework of this theory pertain to possible alternative (but equivalent) forms of the transport equations that may be useful to the experimenter. An example might be a formulation that introduces reflection coefficients in the general multicomponent case, without the current restriction to either binary or to dilute multicomponent solutions [4]. However, questions involving the calculation of transport coefficients or the elucidation of detailed transport mechanisms cannot be answered by the present methods, and require a different theoretical approach.

References

[1] E.A. Mason and L.A. Viehland, J. Chem. Phys. 68 (1978) 3562.

[2] L.F. del Castillo, E.A. Mason and H.E. Revercomb, Biophys. Chem. 10 (1979) 191.

[3] A.J. Staverman, Rec. Trav. Chim. 70 (1951) 344.

[4] A. Katchalsky and P.F. Curran, Nonequilibrium thermodynamics in biophysics (Harvard University Press, Cambridge, Mass., 1967), Chap. 10.

[5] M. Van Dyke, Perturbation methods in fluid mechanics (Academic Press, New York, 1964), pp. 16–17.

[6] J.K. Klauder, Science (Wash. D.C.) 199 (1978) 735.

[7] Earl of Berkeley and E.G.J. Hartley, Proc. Roy. Soc. B82 (1909) 271.

[8] E. Heyer, A. Cass and A. Mauro, Yale J. Biol. Med. 42 (1970) 139.

[9] R.J. Bearman and J.G. Kirkwood, J. Chem. Phys. 28 (1958) 136.

[10] R.J. Bearman, J. Chem. Phys. 31 (1959) 751.

[11] F.M. Snell, R. Aranow and R.A. Spangler, J. Chem. Phys. 47 (1967) 4959.

[12] E.A. Mason, A.P. Malinauskas and R.B. Evans, III, J. Chem. Phys. 46 (1967) 3199.

[13] E.W. McDaniel and E.A. Mason, The mobility and diffusion of ions in gases (Wiley, New York, 1973), Chap. 1.

[14] J.M. Guerrero and L.F. del Castillo, Desalination 26 (1978) 141.

[15] R.F. Abercrombie, Am. J. Phys. 46 (1978) 425.

[16] L.F. del Castillo, E.A. Mason and L.A. Viehland, Biophys. Chem. 9 (1979) 111.

[17] E.L. Cussler, Multicomponent diffusion (Elsevier, Amsterdam, 1976), Chap. 8.

[18] E.H. Bresler, R.P. Wendt and E.A. Mason, Science (Wash. D.C.) 172 (1971) 858.

[19] G. Jacazio, R.F. Probstein, A.A. Sonin and D. Yung, J. Phys. Chem. 76 (1972) 4015.

[20] G.D. Mehta and T.F. Morse, J. Chem. Phys. 63 (1975) 1878.

[21] M.H. Daneshpajooh, E.A. Mason, E.H. Bresler and R.P. Wendt, Biophys. J. 15 (1975) 591.
[22] J.D. Ferry, Chem. Rev. 18 (1936) 373.
[23] C.P. Bean, in: Membranes: a series of advances, Vol. I, ed. G. Eisenman (Marcel Dekker, New York, 1972), Chap. 1.
[24] J.L. Anderson and J.A. Quinn, Biophys. J. 14 (1974) 130.
[25] W.D. Munch, L.P. Zestar and J.L. Anderson, J. Membrane Sci. 5 (1979) 77.
[26] A. Verniory, R. DuBois, P. Decoodt, J.P. Gassee and P.P. Lambert, J. Gen. Physiol. 62 (1973) 489.
[27] O. Kedem and A. Katchalsky, Biochim. Biophys. Acta 27 (1958) 229.
[28] E.A. Mason, R.P. Wendt and E.H. Bresler, J. Chem. Soc. Faraday Trans. II 68 (1972) 1938.
[29] K.J. Laidler and K.E. Shuler, J. Chem. Phys. 17 (1949) 856.