Biophysical Chemistry 4 (1976) 229–236
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APPRAISAL OF EQUATIONS FOR NEUTRAL SOLUTE FLUX ACROSS POROUS SIEVING MEMBRANES

E.H. BRESLER
School of Medicine, Tulane University, and Veterans Administration Hospital, New Orleans, Louisiana 70146, USA

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

and

R.P. WENDT
Department of Chemistry, Loyola University, New Orleans, Louisiana 70118, USA

Received 2 February 1976

General transport equations, based on irreversible thermodynamics applied to membranes without regard to their structures, are compared with results based upon specific membrane models. It is pointed out that the range of validity of the general linear transport equations of irreversible thermodynamics may be extremely small, and that attempts to extend the range by thermodynamic considerations have always involved subtle assumptions of a nonthermodynamic nature. Simple membrane models are used as diagnostic tools to pinpoint such assumptions, with particular reference to the often-concealed assumption of membrane homoporosity. It is shown that it is not possible to write an exact equation for solute flux across an inert porous membrane only in terms of the three customary membrane parameters σ (reflection coefficient), P_s (permeability coefficient), and L_p (hydraulic conductivity), unless the membrane is strictly homoporous. Even in the linear range heteroporosity imposes a hidden condition of $\Delta p \gg \Delta\pi$ for such a three-parameter description to be valid. Useful results in the nonlinear regime require more detailed information on membrane structure than is contained in just three parameters.

1. Introduction

Despite a large body of literature on the subject, it is known that there are still difficulties in the description of transport across membranes. In particular, there is no general agreement on the limitations of accuracy and ranges of validity of various transport equations in use. In attempting to improve this situation, we believe there is merit in first discussing the simplest possible cases in order to clarify the essential difficulties, and in using these simple cases as the basis for generalization to the more complex cases of interest.

We first discuss several existing equations based on considerations of irreversible thermodynamics, in which all knowledge of solution and membrane structure is condensed into three overall parameters. By consideration of special detailed models we show that there are definite restrictions on the validity of applying such equations to membranes in general. In retrospect, it is apparent that difficulties have occurred because extra assumptions have been introduced, clothed in the language of irreversible thermodynamics, whose formal elegance has tended to obscure the fact that new physical information is involved. There is of course no error in the formal thermodynamic approach if applied strictly within its range of validity, but that range may be painfully restricted, and an extension of the range necessarily involves additional assumptions of an inherent physical nature.

In particular, three types of assumptions have occurred. The first involved the attempt to extend the strictly linear local transport equations to situations involving finite differences — that is, to perform an approximate integration of the linear differential equations. An assumption was introduced in the form of an apparent thermodynamic condition on entropy production, leading to a rather poor result. The second involved the assumption of mechanical equilibrium and the absence of viscous flow effects. The results are often applied successfully to cases where viscous flow is clearly involved, because the viscous effects can be absorbed into adjustable parameters; the consequences here are more subtle than in the first case, and can lead to errors in the physical interpretation of the transport coefficients. The third involved an assumption of membrane homogeneity that has sometimes served to conceal a more restrictive assumption of homoporosity, which can result in an extremely restricted range of validity.

In what follows we discuss some of the implications of these three assumptions, with emphasis on the assumption of homogeneity and homoporosity, since the others have been considered in some detail elsewhere. We proceed through simplified models of membrane structure, by which the consequences of the assumptions can be brought clearly into prominence, and show that the usual transport equations have a severely restricted range of applicability. In a following paper we show that, subject only to certain conditions, equations can nevertheless be derived that give a useful approximation to the correct result for a class of membranes of arbitrary structure within well-defined limits of uncertainty.

2. Equations from irreversible thermodynamics

Three independent parameters are required to characterize a system composed of a binary solution plus membrane. The defining equations indicate the experimental measurements to be made:

Hydraulic conductivity,

$$L_p = -(J_V/\Delta p)_{\Delta\pi=0}. \tag{1}$$

Reflection coefficient,

$$\sigma = (\Delta p/\Delta\pi)_{J_V=0}. \tag{2}$$

Permeability coefficient,

$$P_s = -(J_s^*/\Delta c_s^*)_{\Delta\pi, J_V=0}. \tag{3}$$

Here J_V is the volume flux density across the membrane, J_s is the solute flux density, Δp the pressure difference, $\Delta\pi = RT\Delta c_s$ is the osmotic pressure difference, where Δc_s is the difference in solute concentration, and the asterisks refer to a tracer for the solute.

On the assumption that the membrane is homogeneous and that mechanical equilibrium prevails, Kedem and Katchalsky [1,2] gave the following expression as a general equation for the solute flux density:

$$J_s = J_V(1-\sigma)\bar{c}_s - P_s\Delta c_s, \tag{4}$$

where the mean concentration $\bar{c}_s$ is

$$\bar{c}_s = \Delta c_s/\Delta \ln c_s, \tag{5}$$

which is supposed to be completely valid within the realm of linear flux-force relations. A variation suggested as an approximation to eq. (5) is [1–3]

$$\bar{c}_s = \tfrac{1}{2}(c_s' + c_s''), \tag{6}$$

where c_s' and c_s'' are the solute concentrations on each side of the membrane. The corresponding equation for volume flux density is, in both cases,

$$J_V = -L_p(\Delta p - \sigma\Delta\pi). \tag{7}$$

It has been shown elsewhere [4,5] that eq. (6) is not just a special case of eq. (5), but in fact gives a wider range of validity to the transport eq. (4), and that the supposedly thermodynamic result of eq. (5) can cause the transport eq. (4) to give poor results.

The cause of this peculiar situation has been traced to an inaccurate assumption in the thermodynamic treatment, a concealed assumption of a non-thermodynamic nature [5]. To demonstrate this, we consider the local differential transport equation for the membrane [12],

$$J_s = J_V(1-\sigma)c_s - D\partial c_s/\partial z, \tag{8}$$

where D is the solute–solvent diffusion coefficient in the membrane. Although c_s depends on position z, we can nevertheless perform a formal integration and write a result identical in form to eq. (4). No error occurs at this point, for we have merely used the mean value theorem. No problem arises with the average coefficient defined as P_s, since this is to be determined experimentally according to eq. (3). The real problem lies in the determination of the average concentration $\bar{c}_s$. The average defined by eq. (5) is chosen to give the correct overall entropy production [1,2]; the *assumption* is that this average also gives an accurate transport equation. There is no thermodynamic necessity for this result, and no reason why the same average concentration should appear in both the entropy production equation and a transport equation; consideration of just the transport suggests the use of the average $\bar{c}_s$ given by eq. (6), and both theory and experiment show that this is a superior choice [5].

Regarding the second type of assumption, the omission of viscous flow terms in the thermodynamic treatment is often not serious, since viscous contributions to flow can be absorbed in the parameter L_p, which must be determined experimentally. Difficulties arise only when a physical interpretation of the transport coefficients is attempted, and the prediction of their dependence on variables such as composition, pressure, and temperature. This problem has already been discussed in detail elsewhere [6], although more in the language of the equivalent frictional-model equations, and need not be further considered here.

The assumption of homogeneity is more serious. Statements to the effect that the irreversible thermodynamic treatment of membrane transport views the membrane as a black box imply that the results are general and independent of membrane structure. But the notion of homogeneity clearly refers to at least one aspect of membrane structure. Moreover, the term "homogeneous" is never precisely defined, and it is not at all clear whether or not homoporosity is the same as homogeneity. The ambiguity here seems to be related to the degree of coarse-graining thought to be tolerable in the definition of homogeneity. That is, if homogeneity is taken to mean that each small section of a membrane behaves the same as any other small section, the difficulty comes in deciding on the permissible size of such small sections. At one extreme, requiring the sections to be of molecular dimensions would virtually limit the results to membranes of the solution type. Toward the other extreme, of requiring the section to be large enough to manipulate in laboratory practice, a dimension as small as a micron could still permit a heteroporosity that would certainly vitiate the thermodynamic results, as shown later by specific examples. For instance, using the assumption of homogeneity (among others), Patlak et al. [7] performed an exact integration of the local differential eq. (8) across the membrane and obtained

$$J_s = J_V(1-\sigma)c_s' - J_V(1-\sigma) \times \left(\frac{\Delta c_s}{\exp[J_V(1-\sigma)/P_s] - 1}\right), \qquad (9)$$

the corresponding volume flux equation still being eq. (7). We shall show that eq. (9) is strictly valid only for the special case of homoporous membranes. Parenthetically, it is interesting that series expansion of eq. (9) for small values of J_V leads to eq. (6) for $\bar{c}_s$, not to eq. (5) [3]. It may be that there is no completely safe way out of this coarse-graining dilemma as far as irreversible thermodynamics is concerned, and that some recourse to detailed models will always be necessary. We believe the examples in this and a following paper serve to reinforce this view.

3. Derivation of model equations

In the preceding section we have commented on the flaws introduced into apparently rigorous results from irreversible thermodynamics by the introduction of hidden assumptions involving the integration of local linear differential equations and the neglect of viscous effects, and alluded to possible flaws introduced by the assumption of homogeneity and homoporosity. In this section we investigate this last point in more detail through special models. These models are not intended to mimic closely any real membranes, but rather are intended as diagnostic probes of theories that are supposed to be general, in order to determine whether they contain concealed assumptions or conditions. We first consider a simple, well-defined model of a membrane system, and then investigate to what extent variations in the model geometry erode the accuracy of simple transport equations based on irreversible thermodynamics. It takes very little complexity in membrane geometry to destroy the strict applicability of the thermodynamic results. But in somewhat surprising compensation for this loss, it turns out that the inaccuracies introduced by membrane geometry variation are contained within fairly narrow mathematical bounds, as is shown in a following paper.

3.1. Classes of membranes

The membrane is considered to consist of an array of cylindrical pores of the same length, parallel and noninterconnecting. The solute and solvent molecules are considered to be spheres of definite diameters, with the solvent diameter much smaller than the solute diameter. Several possibilities exist for such a system.

(1) The pore diameters are all smaller than the solute diameter, but larger than the solvent diameter. Such a membrane is semipermeable and solute flux across it is zero.

(2) All pore diameters are much larger than the solute diameter. Such a membrane is completely open and exhibits no sieving properties.

(3) The pores are of a size intermediate between (1) and (2) above, so that they offer steric hindrance to the passage of solute but allow relatively unhindered passage of solvent. The action of such pores has been termed "statistical sieving" by Ferry [8,9], who first proposed the mechanism in a quantitative manner. Others have described it as sieving on a "steric" basis.

(4) Some pores are as described in (1), and some as in (2). Such a bimodal distribution of pore sizes will result in partial sieving of the solute.

3.2. *Equations for homoporous membranes*

We first suppose that all pores have the same constant diameter. The semipermeable membrane is of little interest in connection with binary solutions, since only solvent passes through it, and we do not discuss it further.

The local differential transport equation for a pore i of the completely open membrane is

$$J_s^{(i)} = J_V^{(i)} c_s - D^{(i)} \partial c_s/\partial z, \tag{10}$$

where $D^{(i)}$ is the solute–solvent diffusion coefficient in the pore. Integrating across the thickness l of the membrane, multiplying by the fractional area weighting factors, a_i, and summing over all pores, we obtain

$$J_s = J_V c_s' - \frac{J_V \Delta c_s}{\exp(J_V/P_s) - 1}, \tag{11}$$

where $P_s = \Sigma_i a_i D^{(i)}/l$ is the permeability coefficient for the whole membrane. The equation for J_V is

$$J_V = -L_p \Delta p. \tag{12}$$

These results are the same as eqs. (7) and (9) based on irreversible thermodynamics, with $\sigma = 0$. It is apparent that eq. (11) will not be so simple if there is a distribution of pore sizes, a point discussed in the following section.

The results for sieving membrane of the Ferry type are still simple. The local transport equation for a single pore i is

$$J_s^{(i)} = S_F J_V^{(i)} c_s - S_D D^{(i)} \partial c_s/\partial z, \tag{13}$$

where S_F and S_D are geometric constants that are functions of the ratio of the solute diameter to the pore diameter. The precise expressions for S_F and S_D do not matter here; we integrate across the membrane thickness, multiply by the weighting factors, and sum to obtain

$$J_s = S_F J_V c_s' - \frac{S_F J_V \Delta c_s}{\exp(S_F J_V l/S_D D) - 1}. \tag{14}$$

Identifying S_F and S_D in terms of experimental quantities as $S_F = 1 - \sigma$ and $S_D D/l = P_s$, we transform eq. (14) to

$$J_s = J_V(1-\sigma)c_s' - J_V(1-\sigma) \times \left(\frac{\Delta c_s}{\exp[J_V(1-\sigma)/P_s] - 1} \right), \tag{15}$$

which is the same as eq. (9) from irreversible thermodynamics. The expression for volume flow is also as given by irreversible thermodynamics, eq. (7). But, as for the open membrane, a dispersion of pore sizes will cause complications.

3.3. *Equation for heteroporous membranes*

The simplest heteroporous membrane is the bimodal distribution. For this distribution we consider the two types of pores separately and the combine the results. Let superscript (1) denote the large pores and (2) the small pores; a_1 is the fraction of total membrane area occupied by large pores, and a_2 is the fraction occupied by small pores (the sum $a_1 + a_2 \leqslant 1$).

Since the solute flux occurs only through the large pores, we can write

$$J_s = J_s^{(1)} a_1 = a_1 J_V^{(1)} c_s' - \frac{a_1 J_V^{(1)} \Delta c_s}{\exp(J_V^{(1)}/P_s^{(1)}) - 1}. \tag{16}$$

The volume fluxes are

$$J_V^{(1)} = -L_p^{(1)} \Delta p, \tag{17}$$

$$J_V^{(2)} = -L_p^{(2)} (\Delta p - \Delta \pi). \tag{18}$$

Since $J_V^{(1)}$, $J_V^{(2)}$, $L_p^{(1)}$, and $L_p^{(2)}$ are not individually observable, we wish to express them in terms of $L_p = a_1 L_p^{(1)} + a_2 L_p^{(2)}$ and $\sigma = (\Delta p/\Delta\pi)_{J_V=0}$. After multiplying eqs. (17) and (18) by their respective weighting factors, a_1 and a_2, and adding, we obtain

$$J_V = -L_p [\Delta p - (L_p^{(2)} a_2/L_p)\Delta\pi], \tag{19}$$

from which the expression for σ follows from its definition, [eq. (2)],

$$\sigma = a_2 L_p^{(2)}/L_p. \tag{20}$$

These results are the same as eq. (7) for J_V based on irreversible thermodynamics. The result for J_s, however, is different; solving for $J_V^{(1)}$ we find

$$\begin{aligned} a_1 J_V^{(1)} &= J_V - a_2 J_V^{(2)} = -L_p(1-\sigma)\Delta p \\ &= J_V(1-\sigma)(1-\sigma\Delta\pi/\Delta p)^{-1}, \end{aligned} \tag{21}$$

so that eq. (16) becomes

$$\begin{aligned} J_s = J_V \left(\frac{1-\sigma}{1-\sigma\Delta\pi/\Delta p}\right) c_s' - J_V \left(\frac{1-\sigma}{1-\sigma\Delta\pi/\Delta p}\right) \\ \times \left(\frac{\Delta c_s}{\exp[J_V(1-\sigma)/P_s(1-\sigma\Delta\pi/\Delta p)] - 1}\right), \end{aligned} \tag{22}$$

where P_s, the overall measured diffusive permeability, is equal to $a_1 P^{(1)}$.

This is *not* the same as eq. (9) from irreversible thermodynamics unless $\Delta p \gg \Delta\pi$. Thus the result from irreversible thermodynamics is not strictly applicable even to such a simple model as the bimodal pore distribution. A dispersion of pore sizes will cause additional complications.

Before we discuss other heteroporous membranes, it is worth noting that sieving membranes of the bimodal and homoporous Ferry types are experimentally distinguishable in principle. For instance, one could measure the sieving coefficient $\phi \equiv (J_s/J_V)/c_s' = c_s''/c'$ in a hyperfiltration experiment as a function of c_s' at a fixed value of J_V. According to eq. (15) the value of ϕ is

$$\phi = \frac{1-\sigma}{1-\sigma\exp[-J_V(1-\sigma)/P_s]}, \tag{23}$$

which is a constant independent of c_s' for fixed J_V. However, the corresponding result according to eq. (22) is

$$\phi = \frac{1-\sigma}{\{\alpha + (1-\alpha)\exp[-J_V(1-\sigma)/\alpha P_s\} - \sigma\exp[-J_V(1-\sigma)/\alpha P_s]},$$

where (24)

$$\alpha \equiv 1 - \sigma\frac{\Delta\pi}{\Delta p} = \frac{J_V}{J_V + \sigma L_p RT c_s'(1-\phi)}. \tag{25}$$

Although this is a transcendental equation for ϕ and cannot be solved explicitly, it is clear that ϕ depends on c_s' through the occurrence of c_s' in α. The numerical magnitudes for available membranes are such that the effect should be experimentally observable if concentration polarization at the membrane face can be removed.

Distribution of pore diameters causes difficulties for all the membrane models under discussion except the semipermeable membrane, for which no difficulty arises as long as all the pores are smaller than the solute molecules. The essential nature of the problem is most easily illustrated for the membrane consisting of a parallel array of completely open pores. If we integrate across the membrane for each pore, multiply by the factors a_i, and the sum over all pores, we obtain

$$\begin{aligned} J_s = \sum_i a_i J_s^{(i)} = c_s' \sum_i a_i J_V^{(1)} \\ - \Delta c_s \sum_i \frac{a_i J_V^{(i)}}{\exp(J_V^{(i)} l/D^{(i)}) - 1}, \end{aligned} \tag{26}$$

which is obviously different from the result obtained for a homoporous membrane. Somewhat surprisingly, it turns out that the last summation can usually be replaced by a single term to a good approximation. This fact can be made plausible by the following considerations. If $J_V^{(i)} l/D^{(i)}$ is either very large or very small, the expression for J_s has the same mathematical form as for a homoporous membrane. For large values the last term in eq. (26) vanishes and the result is

$$J_s = c_s' \sum_i a_i J_V^{(i)} = c_s' J_V, \tag{27}$$

the same as for the homoporous case. For small values the exponential in the last term of eq. (26) can be expanded in a power series, to yield

$$J_s = (c_s' + \tfrac{1}{2}\Delta c_s) \sum_i a_i J_V^{(i)} - \Delta c_s \sum_i a_i D^{(i)}/l + \cdots,$$

$$= J_V \left(\frac{c_s' + c_s''}{2}\right) - P_s \Delta c_s. \qquad (28)$$

Thus the only place the curve of J_s versus J_V for a heteroporous open membrane can differ from that for a homoporous one with the same value of P_s is in the curved intermediate region between high and low values of J_V/P_s. Mathematical bounds on the size of the difference can be established by consideration of the nature of the mathematical functions involved. This question is taken up in detail in a following paper.[1]

We note that heteroporosity causes no difficulty with the equation for volume flow, since it is linear; in other words, eq. (7) remains valid.

It is important to show that the nonlinear portion of a J_s versus J_V curve can be of experimental interest. Some numerical estimates on this point are given in the appendix.

The foregoing results establish that the proper linear flux equation from irreversible thermodynamics, namely eq. (4) used with the correct $\bar{c}_s$ given by eq. (6), holds in the limit that J_V/P_s is small, *provided* that the previously hidden condition of $\Delta p \gg \Delta\pi$ is met. What is not obvious is how much the domain of utility of the linear flux equation can be constricted by the nature of the pore size distribution. This is illustrated in fig. 1, where we show a dimensionless plot of $J_s/c_s'P_s$ versus J_V/P_s with $\Delta c_s/c_s' = -1$ for two open membranes, one homoporous and the other bimodal. The bimodal distribution consists of a few large pores and a large number of small pores, such that the volume flow through one large pore is much greater than that through one small pore, but most of the open membrane area consists of the small pores. The domain of utility of the linear flux equation is so small for this heteroporous membrane as to be virtually useless.

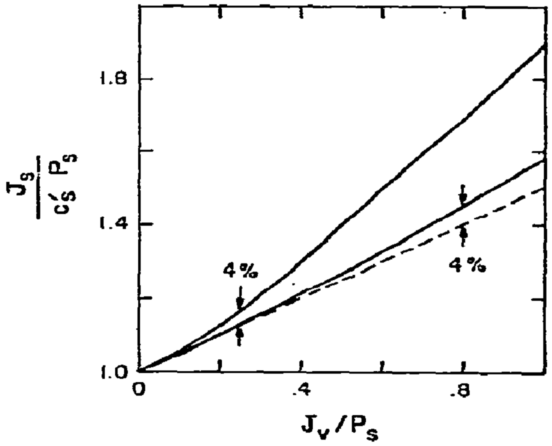

Fig. 1. Effect of membrane heteroporosity on the range of utility of the thermodynamic linear flux equation, shown as dimensionless solute flux as a function of dimensionless volume flux with $\Delta c_s/c_s' = -1$. The dashed straight line is the thermodynamic linear relation, and the lower solid curve is for a homoporous membrane. The uppermost curve is for a heteroporous membrane consisting of many small pores and a few large pores (10 percent of the membrane open area is large pores), with each large pore carrying 1000 times the volume flow of a small pore. Both membranes have exactly the same values of overall transport parameters.

3.4. Effect of individual pore nonuniformity

So far we have considered only uniform parallel-pipe pores. We now wish to consider how the results can be altered by variations in the geometry of an individual pore. Our discussion is based on one fundamental assumption: the flow inside the membrane can be regarded as one-dimensional in some locally averaged sense, even though the flow is undoubtedly three-dimensional on a true microscopic scale. This assumption is almost always made, at least implicitly, in studies of membrane transport. It then follows that the pore cross section does not have to be circular, or even particularly regular. We may therefore hope to mimic pore geometry by a series combination of pore segments of various lengths and cross sections. Two cases can be distinguished for the series pore-segment model: the solute concentration varies monotonically from one end of the pore to the other (no internal concentration polarization), or the pore exhibits internal concentration polarization (accumulations of solute such as are caused by local steric hindrances within the pore).

The case of series of pore segments without internal concentration polarization gives a surprisingly simple result — the curve of J_s versus J_V has exactly the same form as for a uniform pore, eq. (11). This result is proved in a following paper. It is also clear that the equation for J_V as a function of Δp is the same as for a uniform pore, eq. (12), since the equation is linear. Moreover, Ferry sieving at the entrance to the *first* pore segment does not change the result, so that eq. (15) for J_s and eq. (7) for J_V hold exactly for the case of pore segments in series, with the reflection coefficient

σ representing strictly an entrance effect. These results, plus the mathematical bounds established for parallel arrays of pores, can then be used to establish bounds for any series–parallel combination of pore segments of various lengths and cross sections, with any amount of internal connectivity, as shown in a following paper.

The case of internal concentration polarization raises very serious problems. None of the theorems on bounds proved in the following paper then holds, and it seems likely that useful approximate transport equations cannot in general be written. For instance, the equation for volume flow is no longer linear in the hydrostatic and osmotic pressure differences, and the defining eqs. (1) and (2) for hydraulic conductivity and reflection coefficient are no longer useful inasmuch as both coefficients become strongly flow-dependent. We do not discuss these complex phenomena further here, but only mention as an example the situation described by Teorell [10], where two membranes are in series with an intervening compartment containing a solute to which both membranes are impermeable. It can be appreciated that the effects described by Teorell as occurring with this arrangement do not require the presence of two anatomically distinct membranes with an intervening compartment, but may be observed in a single membrane with the proper pore geometry.

4. Discussion

The foregoing simplified detailed models for membrane transport serve to clarify several aspects of the applicability of irreversible thermodynamics. It is easy to devise pore models for which the range of validity of the linear transport equations of irreversible thermodynamics is almost vanishingly small. Attempts to extend the range by means of arguments of a general thermodynamic character always seem to involve subtle assumptions that are fundamentally nonthermodynamic, such as the condition of $\Delta p \gg \Delta\pi$ for eq. (9), or the use of the equation for finite entropy production to define an average concentration by eq. (5). In other words, it is not possible to write an exact equation for finite J_s without more information on membrane structure than is contained in the parameters P_s, σ, and L_p. Thus the only way to be assured of the complete generality that one expects from a thermodynamic discussion is to remain strictly within the range of local linear transport equations, which may be a very limited range indeed. However, it should be remembered that the linear laws are not derived from irreversible thermodynamics, but are *assumed* by it. The only physical content of linear irreversible thermodynamics resides in the Onsager reciprocal relations for the off-diagonal transport coefficients. In the present context of combined solute diffusion and convection this corresponds to substitution of $(1-\sigma)$ for the sieving coefficient S_F in the equation for solute flux. But as we have shown, by means of a specific model having a bimodal pore size distribution, this substitution cannot be made in the general case unless $\Delta p \gg \Delta\pi$. Even when this hidden condition is satisfied, a further surprise awaits – the range of validity of the relation $S_F = 1 - \sigma$ usually turns out experimentally to be much greater than the range of validity of the linear laws. This suggests that the relation may be based on some principle or some feature of real membranes other than the general principles of near equilibrium and microscopic reversibility that underlie the Onsager reciprocal relations. It is in fact easy to conceive of a special model for which this is the case, involving a kinetic picture of the development of osmotic pressure by impacts of solute molecules on the membrane surface along the lines suggested long ago by van 't Hoff [11], but we shall not pursue this subject further here.

To put matters in as stark a light as possible: although irreversible thermodynamics provides a useful context and notation for describing membrane transport, the range of applicability for its strict general validity is extremely small; further nonthermodynamic information on membrane structure is required. The primitive structural models discussed in the present paper may serve to indicate the directions a suitable detailed theory might take. In a following paper we discuss the mathematical bounds that can be put on transport equations for membranes of arbitrary structure, and the relation of these bounds to the problem of inferring structural information on membranes from macroscopic transport measurements.

Acknowledgement

We are grateful to the late M.H. Daneshpajooh for many useful discussions. This research was supported in part by U.S. Veterans Administration medical research funds, and by a National Science Foundation Grant to Brown University.

Appendix: Numerical estimate of nonlinear region of J_s versus J_V

Here we present a rough numerical estimate to determine whether or not the nonlinear portion of a J_s versus J_V curve lies in an experimentally interesting region. We use eq. (15) for a Ferry-type sieving membrane, and take the group $J_V(1-\sigma)l/D$ as the figure of merit. It is only for values of this group greater than about unity that deviations from linearity become appreciable. To estimate J_V we use Poiseuille's law,

$$J_V = \frac{r^2}{8\eta}\frac{\Delta p}{l}, \tag{A1}$$

where r is the pore radius and η the solution viscosity. We estimate D from the Stokes–Einstein formula,

$$D = \frac{kT}{6\pi\eta a}, \tag{A2}$$

where a is the solute radius. We express r in terms of a through an approximate steric-effect expression,

$$1-\sigma \approx [1-(a/r)]^2. \tag{A3}$$

Combining these expressions, we obtain

$$\frac{J_V(1-\sigma)l}{D} \approx \frac{3\pi(1-\sigma)a^3\Delta p}{4kT[1-(1-\sigma)^{1/2}]^2}. \tag{A4}$$

As an example, for $a = 5$ Å and $\Delta p = 1$ atm, we find the result at 300 K to be 0.042 for $\sigma = 0.5$, and 2.5 for $\sigma = 0.1$. The first is in the linear region, but the second is in the nonlinear. Note that this analysis assumes homoporosity; heteroporosity causes nonlinearity to set in even sooner.

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[12] Although this is a local and internal equation, c_s is defined as an external concentration throughout this paper. A similar local equation not incorporating $1-\sigma$ explicitly and written in terms of the internal concentration, $\hat{c}_s$, within the membrane could be readily converted to eq. (8) by assuming $\hat{c}_s = (1-\sigma)\,c_s$ and $\hat{D}$ (internal diffusion coefficient) $= D/(1-\sigma)$. The former assumption implies $1-\sigma$ is identical with the solute partition coefficient between the external solution phase and the membrane phase. Rather than enter into the controversy about the validity of this assumption we simply accept eq. (8) as a useful working equation for the diagnostic purposes of this paper.