Osmosis

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INTRODUCTION

It has virtually become a truism that osmosis, and the inseparable array of related processes comprising ultrafiltration, diffusion, anomalous osmosis, etc., has found its final and lasting exposition to which anything can only be added by way of a few finishing touches. This view, as I shall attempt to show, is quite wrong, if for no other reason than that several of the different approaches to the problem are not complementary. We want two things: to gain an insight into the mechanisms operative in porous systems, and to derive equations which predict the flow rates from a minimal set of properties – if we can decide what these are. The purpose of this review is therefore twofold: to show that osmosis is a poorly understood phenomenon of considerable complexity, for which there is at present no fully acceptable theory; and to show that the widespread use of non-equilibrium thermodynamics has contributed little if anything to our understanding. Where osmosis is concerned the interpretation in terms of frictional coefficients has actually introduced several quite serious conceptual mistakes which render many of its conclusions invalid.
No apology is offered therefore, if the tone of this review seems rather negative and critical. In the last part I shall try to show that the central problem is to model osmotic flow realistically, and this requires a lot of physical insight at every stage of the argument. Some hydrodynamic treatments have modelled a somewhat arbitrary collection of flows and called it osmosis. Considerable progress towards a solution has been made however.

There are two major omissions here that do require some comment. Firstly, there is no discussion of the nature of osmotic pressure; this is a subject in itself with a long history (Hammel & Scholander, 1976). In a post-Gibbsian world however, the concept of water activity ($a_w$) and its counterpart the chemical potential of water ($\mu_w$) provide the essential framework for describing osmotic flows if not understanding osmotic pressure. Secondly, there is no attempt to treat cellular osmosis, as this is a vast field which relies almost entirely on the basic concepts of osmotic theory, and it is to the bare bones of the subject that attention is directed here – the mechanism of osmotic flow in membranes of variable porosity, from bimolecular lipid leaflets to pieces of paper.

**Flow equations**

A convenient way of approaching the general description of flows is to follow Kedem & Katchalsky (1958) in deriving equations for the volume and exchange flows from those representing the molar flows of solute and water; these can then be examined in detail.

The dissipation function $\Phi$ representing the entropy production rate per unit area of membrane is given by

$$\Phi = J_w \Delta \mu_w + J_s \Delta \mu_s,$$

(1)

where $J_w$ and $J_s$ are the molar flows of water and solute per unit membrane area, and $\Delta \mu_w$ and $\Delta \mu_s$ are the chemical potential differences of water and solute across the membrane. Using the expression for the chemical potential difference

$$\Delta \mu_i = \bar{V}_i \Delta P + RT \Delta \ln c_i,$$

(2)

we obtain the well-known expansions

$$\Delta \mu_w = \bar{V}_w \Delta P - \frac{RT \Delta c_s}{\bar{c}_s} = \bar{V}_w \Delta P - \frac{\Delta \Pi}{\bar{c}_s},$$

(3)

$$\Delta \mu_s = \bar{V}_s \Delta P + \frac{RT \Delta c_s}{\bar{c}_s} = \bar{V}_s \Delta P + \frac{\Delta \Pi}{\bar{c}_s},$$

(4)

where $\bar{c}_s = (c_1 - c_2)/\ln(c_1/c_2)$, reducing to $(c_1 + c_2)/2$ when $(c_1 - c_2)$ is
small. Substituted into (1) these expressions give

\[ \Phi = (J_w \vec{V}_w + J_s \vec{V}_s) \Delta P + (J_s / c_s - J_w / c_w) \]

\[ = J_v \Delta P + J_D \Delta \Pi, \quad (5) \]

which is an equation defining the volume flow \( J_v \) and the exchange flow \( J_D \), the latter representing the mean solute velocity relative to that of the water. The two terms \( J_v \Delta P \) and \( J_D \Delta \Pi \) thus represent the entropy due to viscous flow and to dilution. The two new flows can then be written as a pair of reciprocal equations which it has been claimed give an accurate and clear insight into the nature of osmotic flow:

\[ J_v = L_p \Delta P + L_{pD} \Delta \Pi, \quad (6) \]

\[ J_D = L_{DP} \Delta P + L_D \Delta \Pi. \quad (7) \]

Onsager reciprocity is assumed to hold, in which case \( L_{pD} = L_{DP} \). The coefficient \( L_{pD} \) is thus seen to be a cross-coefficient describing the osmotic permeability of the membrane. *Its physical meaning is apparent from the fact that on the one hand it characterizes the osmotic volume flow per unit osmotic gradient at \( \Delta P = 0 \), and on the other hand it represents the extent of ultrafiltration induced by mechanical pressure at \( \Delta \Pi = 0 \). Evidently in coarse non-selective membranes neither osmotic flow nor ultrafiltration take place, hence in this lower limiting case \( L_{pD} = 0 \)’ (Katchalsky, 1961). Another way of deriving equations (6) and (7) is to append transport coefficients to the two components of the chemical potentials given in equations (3) and (4)

\[ J_v = L_1 \vec{V}_w \Delta P - L_2 \frac{\Delta \Pi}{c_w}, \quad (8) \]

\[ J_s = L_3 \vec{V}_s \Delta P + L_4 \frac{\Delta \Pi}{c_s}, \quad (9) \]

and then rearrange them to obtain equations for \( J_v \) and \( J_D \) as given by equation (5). If we assume that the solution is dilute so that \( 1 / c_w = \vec{V}_w \), the result is

\[ J_v = (L_1 \vec{V}_w^2 + L_3 \vec{V}_s^2) \Delta P + \left( L_4 \frac{\vec{V}_s}{c_s} - L_2 \vec{V}_w^2 \right) \Delta \Pi, \quad (10) \]

\[ J_D = \left( L_3 \frac{\vec{V}_s}{c_s} - L_1 \vec{V}_w^2 \right) \Delta P + \left( L_4 \frac{1}{c_s} + L_2 \vec{V}_w^2 \right) \Delta \Pi, \quad (11) \]

from which it must be apparent that Onsager symmetry holds when \( L_1 = L_2 \) and \( L_3 = L_4 \).
Now an examination of equation (8) reveals two things: firstly, in a binary solution there can be no unique contribution of $\Delta \mu_s$ to the flow of water, for by the Gibbs–Duhem equation

$$\Sigma n_i d\mu_i = 0 \quad (T, P \text{ constant}) \quad (12)$$

$\Delta \mu_s$ can always be written as a function of $\Delta \mu_{ws}$ so that equation (8) completely defines the water flow, although the $L$'s may be concentration dependent; secondly, we know a priori that an osmotic pressure difference does not always produce the same water flow as an equivalent hydrostatic pressure difference, and so in general $L_1 \neq L_2$. This is in fact the observation upon which the whole problem of osmosis rests, if we are to go beyond Starling's law. When $L_1$ is not equal to $L_2$, the relationship between $L_3$ and $L_4$ must be

$$L_3 = L_4 + (L_1 - L_2) \frac{\bar{c}_i V^2_{w}}{V_s} \quad (13)$$

for $L_{PD}$ to equal $L_{DP}$. This equation can never be proved by thermodynamics. Thermodynamics merely shows that equation (13) is the necessary condition for Onsager symmetry to obtain; what is extremely puzzling about the description of osmosis given by equations (6) and (7) is why so much importance has been attached to the concept of Onsager symmetry in this connexion. Equation (13) can only be proved when we have a full description of osmosis in physical terms (hydrodynamic and kinetic), and then it may well turn out that osmotic volume flow and pressure-driven flow are essentially dissimilar processes between which no symmetry relations are intrinsically possible. One cannot but feel that the endless discussion about Onsager symmetry in this subject is a psychological problem, not a scientific one. We shall return to this problem in a later section.

Let us now concentrate on the magnitude of the coefficient $L_{PD}$. It is convenient to deal with a generalized membrane represented by a slab, and to enquire later into its make-up. From the Gibbs–Duhem equation applied to a binary system we obtain the expression

$$\text{grad } \mu_w = -\frac{c_s}{c_w} \text{grad } \mu_s. \quad (14)$$

We now introduce partial molar frictional coefficients, which were first applied by Spiegler (1958) to membrane transport processes. Essentially these represent the coefficients of friction relating the velocities of two
components in the system to the driving force during steady-state flow. The gradients of chemical potential are the driving forces, and the velocities are given by

\[ v_i = \frac{J_i}{c_i}, \quad (15) \]

\( J_i \) being the molar flow of species \( i \) at a point where the concentration is \( c_i \). We therefore have

\begin{align*}
- \text{grad} \mu_s &= f_{sw} (v_s - v_w) + f_{sm} v_w, \quad (16) \\
- \text{grad} \mu_w &= f_{ws} (v_w - v_s) + f_{wm} v_w, \quad (17)
\end{align*}

where \( f_{sw} \) and \( f_{ws} \) are the frictional coefficients between solute and water which are related by

\[ c_s f_{sw} = c_w f_{ws}, \quad (18) \]

(Spiegler, 1958; Kedem & Katchalsky, 1961). Substituting for \( \text{grad} \mu_w \) in equation (17) from equation (14) gives

\[ \text{grad} \mu_w \frac{c_s}{c_w} = f_{ws} (v_w - v_s) + f_{wm} v_w, \quad (19) \]

and substituting for \( f_{ws} \) from equation (18)

\[ \text{grad} \mu_w \frac{c_s}{c_w} = f_{sw} \frac{c_s}{c_w} (v_w - v_s) + f_{wm} v_w \]

or

\[ \text{grad} \mu_w = f_{sw} \frac{v_w - v_s + f_{wm} c_w}{c_s}. \quad (20) \]

Adding (16) and (20)

\[ c_w v_w f_{wm} + c_s v_s f_{sm} = 0 \]

or

\[ J_w f_{wm} + J_s f_{sm} = 0. \quad (21) \]

The equation for volume flow

\[ J_v = J_w \bar{V}_w + J_s \bar{V}_s \quad (22) \]

becomes after insertion of \( J_w \) from (21)

\[ J_v = - J_s \frac{f_{sm}}{f_{wm}} \bar{V}_w + J_s \bar{V}_s. \quad (23) \]

Let us now consider a 'coarse non-selective' membrane composed of large aqueous pores separating pure water from a dilute solution of concentration \( c_s \). We may describe the apparent diffusion coefficients of
water and solute across this membrane by $D_w$ and $D_s$ respectively where

$$f_{sm} = \frac{RT}{D_s}, \quad f_{wm} = \frac{RT}{D_w}. \quad (24)$$

The values of $D_w$ and $D_s$ are close to, but not exactly equal to, their free-solution values $D_w^0$ and $D_s^0$. If we regard the solute diffusion through such a membrane as proceeding by Fick’s law

$$J_s = A \frac{D_s}{\Delta x} \Delta c, \quad (25)$$

where $A$ is the pore area and $\Delta x$ is the membrane thickness, then equation (23) becomes

$$J_v = -J_s \frac{D_w}{D_s} \bar{V}_w + J_s \bar{V}_s$$

or

$$J_v = -A \frac{\Delta c}{\Delta x} D_w \bar{V}_w + A \frac{\Delta c}{\Delta x} D_s \bar{V}_s \quad (26)$$

and the osmotic permeability given by equation (6) at zero pressure difference, $L_{pD} = J_v / RT \Delta c$, is

$$L_{pD} = \frac{A}{RT \Delta x} (D_s \bar{V}_s - D_w \bar{V}_w). \quad (27)$$

According to the accepted interpretation of equation (6) $L_{pD}$ should be zero for a coarse non-selective membrane, but it must be apparent that this is not so. Solute and water transfer occurs virtually entirely by diffusion in opposite directions, but because of the differences between the diffusion coefficients and the partial molar volumes, the net effect is a volume flow. It is of course true that (i) Fick’s law is not completely applicable here because volume flow is occurring counter to the solute flow, and (ii) the coefficients $D_s$ and $D_w$ must include the effects of frictional interaction with the pore-walls, although in large pores this becomes quite small; but neither of these considerations will reduce the right-hand side of equation (27) to zero, and may indeed have the opposite effect. When we use the term ‘coarse’ as applied to the membrane matrix it must therefore be evident that the osmotic permeability need not be zero; this is due to the fact that the membrane is water-filled, and this in itself imposes considerable specificity.

It might be argued that the volume flow will be very small, and can therefore be neglected, but even this is not so. Using diffusion coefficients
of 4.5 and 1.5 (x 10^{-5}\text{cm}^2\text{sec}^{-1}) for water and salt, and partial molar volumes of 18 and 16.6 (\text{cm}^3\text{mol}^{-1}) for these species, the value of $L_{pD}$ for a membrane 10^{-6}\text{cm} thick comes out at 10 \text{cm sec}^{-1}, if the pore area is 6\% of the membrane area. This is 100 times the osmotic permeability of a highly permeable lipid bilayer (House, 1974). If we consider the value of the reflexion coefficient, defined as the ratio of the osmotic permeability to the hydraulic conductivity

$$\sigma_s = \frac{L_{pD}}{L_p}$$

it must be apparent that this parameter is very small in the foregoing example, in fact approaching zero, due to the large hydraulic flow possible through a 'coarse' membrane. This example, seemingly trivial, highlights the growing tendency to replace the term 'reflexion coefficient' by its assumed equivalent 'osmotic permeability', to the detriment of scientific accuracy. 'Coarseness' applied to a membrane implies a low reflexion coefficient but says nothing about the osmotic permeability; 'non-selective', as we shall now show, is virtually impossible to define with any clear meaning.

If fluid is driven through a membrane by a pressure difference, the ratio of the solute to the volume flow will not in general be equal to the concentration in the bath from which the fluid comes: one of the components will be retarded with respect to the other. Staverman (1951) in fact defined the reflexion coefficient after considering such a situation, the solute being 'reflected' by the membrane. When the solute is not reflected, the membrane is said to be 'non-selective' and solution moves through the membrane unchanged in composition with respect to the bath of origin; in terms of equation (7) the coefficient $L_{DP}$ is zero. When the hydrostatic pressure difference is large compared to the osmotic difference we have from equations (6) and (7)

$$\frac{L_{DP}}{L_p} = \frac{J_D}{J_o} = \frac{J_s/\bar{c}_s - J_w/\bar{V}_w}{J_s\bar{V}_s + J_w\bar{V}_w} = \frac{J_s\left(1 + \bar{c}_s/\bar{V}_s\right)}{J_o\bar{c}_s} - 1$$

and when $\bar{c}_s/\bar{V}_s \ll 1$

$$L_{DP} = -L_p \left(1 - \frac{\theta}{\bar{c}_s}\right),$$

where $\theta = J_s/J_w$, representing the concentration of solution crossing the membrane. In the steady-state $\theta$ must of course be constant at any point
within the membrane to preserve continuity. Consider now a 'non-selective' membrane in which $L_{DP} = 0$, Fig. 1. This membrane will transport fluid of concentration $\theta = \tilde{\epsilon}_s$ under pressure. If, however, the two solutions bathing the membrane are not equal in concentration and flow occurs from a higher concentration $c_1$ to a lower $c_2$, the transported fluid will be hypotonic to $c_1$ as $\tilde{\epsilon}_s < c_1$. The membrane therefore discriminates against solute, and cannot be non-selective. If we reverse the flow the transported solution is now hypertonic to the bath of origin, because $\tilde{\epsilon}_s > c_2$, and the membrane now discriminates against water. Thus $L_{DP}$ cannot be solely a property of the membrane, but must also be a function of the concentration of the baths. The cardinal point is, of course, that $L_{DP}$ is defined with respect to $\tilde{\epsilon}_s$, which for small concentration differences is equal to the mean of the bathing concentrations, and the problem disappears in the limit when $c_1 \rightarrow c_2$. Failure to recognize this has led to disputes in the past concerning the applicability of equations (6) and (7). Bresler & Wendt (1969 a) have argued that for an open membrane $L_{DP} = 0$ and thus by equation (7) $J_D$ is not a function of $\Delta P$ across the membrane. If $\Delta \Pi$ is non-zero, however, there must be entropy production due to mixing, which is given by

$$\Phi = J_D \Delta \Pi$$  \hspace{1cm} (31)
and this dissipation rate is proportional to the applied pressure, which means that $J_D$ has to be non-zero; thus $L_{DP} \neq 0$ and Onsager symmetry is not possible (assuming that $\sigma_s$ is zero here). Bresler & Wendt conceive of solution at concentration $c_1$ (say) being forced through the membrane to mix with solution in the other bath at $c_2$. Their argument has been criticized by Smit & Stavermann (1970), who present experimental evidence showing that Onsager symmetry ($L_{DP} = L_{DP}$) is observed by porous membranes when the concentration differences are zero during ultrafiltration and small during osmotic flow, but these are precisely the conditions under which apparent reciprocity should be seen.

The correct answer to Bresler & Wendt's objection is that when $L_{DP} = 0$, $J_D$ is zero by definition. This can be easily shown. By equation (30) when $L_{DP} = 0$ the transported fluid will have a concentration equal to $\bar{c}_s$, and the volume transport rate will be $J_w/\bar{c}_s$. This is equivalent to $J_w/\bar{V}_w$, neglecting solute volume transport. (This assumption need not be made, and the argument can proceed perfectly well from equation (29).) Thus by equation (5) defining $J_D$

$$J_D = J_s = J_w/\bar{c}_s = J_w/\bar{V}_w = 0. \quad (32)$$

This is equivalent to saying that the decrease in entropy due to the separation of solution at a concentration $\bar{c}_s$ from $c_1$ is equal to the increase in entropy due to its mixing with $c_2$.

In reality a coarse 'non-selective' membrane does not behave in the above manner, and in this respect Bresler & Wendt are correct; but the equations are self-consistent too. The problem is that there is a mismatch between what the equations are generally assumed to represent in physical terms, and what they actually imply mathematically. They thus appear too treacherous, from a conceptual point of view, to be of any value.

Rearrangement of equation (30) leads to

$$-\frac{L_{DP}}{L_p} = \left(1 - \frac{\theta}{\bar{c}_s}\right) = \left(1 - \frac{J_s}{J_w/\bar{c}_s}\right) = \sigma_f$$

and so

$$J_s = (1 - \sigma_f)\bar{c}_s J_w, \quad (33)$$

where $\sigma_f$ is the drag reflection coefficient. This is an equation representing solute transfer by pressure-driven solvent drag, and we may add to it a component $\omega_s \Delta \Pi$ due to diffusion where $\omega_s$ is the solute osmotic
diffusion coefficient, to obtain the equations for solute and water flow known as the Kedem-Katchalsky equations, although they were first derived by Staverman (1951):

\[ J_v = L_p \Delta P + \sigma_s L_D \Delta \Pi, \tag{34} \]

\[ J_s = (1 - \sigma_f) \bar{\varepsilon}_s J_v + \omega_s \Delta \Pi. \tag{35} \]

These equations must now be seen in the light of the reservations discussed above. In view of their widespread and somewhat uncritical use we might note the following points:

(i) \( \bar{\varepsilon}_s \) is a mathematical function of the concentration in the two baths and has no clear physical meaning. It may be approximated to \((c_1 + c_2)/2\), the mean concentration between the baths when \( \Delta c \) is small by expanding \( \ln(c_1/c_2) \) as a series and dropping all but the first term, but whether or not this actually represents the concentration in the membrane depends upon the disposition of concentrations in the bathing solutions and the flow regime. There have been several amendments to the convective term which aim to give a more realistic description of the sieving process, either when \( \sigma_f = 0 \) (Bresler & Wendt, 1969b), or when \( \sigma_f \) is defined independently of any osmotic considerations but directly as a function of the sieving behaviour (Axel, 1976). These terms do not contain the term \( \bar{\varepsilon}_s \), whose ontogeny can be directly traced to the need to relate the osmotic pressure to the entropic part of the chemical potential

\[ \bar{\varepsilon}_s = \frac{\Delta \Pi}{\Delta \mu_s}. \tag{36} \]

From a pragmatic point of view they are important, but we are here concerned with ultrafiltration not as an independent process but as one related to osmosis, if not by a reciprocal coefficient, then by a pair of related coefficients \( \sigma_s \) and \( \sigma_f \).

(ii) There is no reason to assume \( \sigma_s \) and \( \sigma_f \) to be equal; they are derived from \( L_{pD} \) and \( L_{Dp} \) which we have seen from equations (10), (11) \textit{et seq.} are not in general equal, although Staverman, for example, assumed them to be so. A recent proof of their equality by Levitt (1975) will be discussed below.

(iii) The volume flow term \( J_v \) is ambiguous. As it appears here it represents a flow due to hydrostatic pressure differences, but it can be derived on more general terms in which there could presumably be
osmotic flow contributions. To what extent solute flow could be entrained
in the water flow set up by its own gradient is unclear, because we have no
clear picture of the relationship between the $\sigma'$s, $L_p$ and $\omega_s$; this is the
description of the osmotic process that we are in fact seeking.

The remainder of this review will therefore be concerned with dis-
cussing the progress that has been made in elucidating the two coefficients
$\sigma_s$ and $\sigma_f$ from equations (34) and (35).

Frictional Interpretations

The papers of Kedem & Katchalsky (1961), Katchalsky (1961), Dainty &
Ginzburg (1963) and Ginzburg & Katchalsky (1963) use the concept of
frictional coefficients familiar to the theory of diffusion, which have also
been applied by Spiegler (1958) to ionic diffusion through membranes,
as a basis for describing osmotic flow and ultrafiltration. The aim is to
provide an explanation of osmosis and related phenomena in terms of
friction, a concept of greater intuitive generality.

In free solution the molar friction coefficients $f_{ij}$, representing the
friction between a mole of $i$ and the component $j$, have a clear meaning.
When applied to membrane transfer by diffusion, the meaning becomes
slightly less precise due to the fact that many membranes are inhomo-
genous. In the case of osmosis the position becomes so complicated that
they are of little heuristic value. Firstly, however, it is necessary to outline
the description they provide.

The expression for the osmotic reflection coefficient

$$\sigma_s = 1 - \frac{\omega_s V_s}{L_p} - \frac{K_s f_{sw}}{\varphi_w (f_{sw} + f_{sm})}$$

(37)

is obtained by the method used in the previous section, i.e. by equating
the thermodynamic driving force with the friction forces in accordance
with Newton's 3rd law:

$$-\frac{d\mu_i}{dx} = f_{ij}(v_i - v_j).$$

(38)

The velocities $v_i$ and $v_j$ can be then expressed as flows of these two
components. Equation (37) may be interpreted in the following manner:
the first term indicates that osmotic flow would be maximal with $\sigma_s = 1$
were it not for the other terms; the second term represents the fraction of
osmotic flow which is due to volume transfer by the solute; the third term
describes the friction between the water and solute flows, which decreases the rate of osmotic flow across the membrane. If the third term is large enough, the reflexion coefficient can be zero or even negative.

The frictional description therefore assumes that in the absence of friction, osmotic flow occurs with virtually the same rate as pressure-driven flow. It must be apparent that frictional theory, in its very essence, cannot explain the phenomenon of osmosis because it gives no explanation of why the flow should be maximal, but accepts this fact as self-evident. If equation (37) is multiplied through by $\Delta \Pi L_p$, we obtain

$$
\sigma_s L_p \Delta \Pi = \Delta \Pi L_p - \Delta \Pi \omega_s \bar{V}_s - \frac{K_s f_{sw} \Delta \Pi L_p}{\phi_w (f_{sw} + f_{sw})}
$$

or

$$
J_v = J_{v(max)} - \frac{\bar{V}_w K_s f_{sw} \Delta \Pi}{f_{wm} (f_{sw} + f_{sm})} \Delta x
$$

(39)

in which use has been made of the relationships $J_s = \omega_s \Delta \Pi$ and $L_p = \phi_w \bar{V}_w / f_{wm} \Delta x$ (Kedem & Katchalsky, 1961). It is clear from this formulation that $J_{v(max)}$ receives no explanation in frictional theory. Friction with solute can only slow the water down; the problem really is to explain how it moves so fast.

Although equation (37) has been derived in a fairly direct way from thermodynamic fundamentals, there must be room for re-examination of steps in the argument leading to equation (37). $f_{wm}$ is worthy of attention because it represents in a single parameter what must be a complex phenomenon under diverse conditions.

We start by examining the relationship between $f_{wm}$, hydraulic flow and diffusive flow. The water flow through a membrane under a driving force is

$$
- \frac{d \mu_w}{dx} = f_{wm} v_w = f_{wm} \frac{J_w}{c_w} = \frac{J_w \bar{V}_w f_{wm}}{\phi_w},
$$

(40)

where the volume fraction $\phi_w$ and concentration $c_w$ of water in the membrane are related by $\phi_w = c_w \bar{V}_w$, and solute is absent. Integrating equation (40) across the thickness of the membrane leads to

$$
\bar{V}_w \Delta P = \frac{J_w f_{wm} \Delta x}{\phi_w}
$$

(41)

when only a pressure gradient is present. This rearranges to

$$
J_v = \frac{\bar{V}_w \phi_w \Delta P}{f_{wm} \Delta x}
$$

(42)
which by analogy with equation (6) leads to

\[ L_p = \frac{V_w \phi_w}{f_{wm} \Delta x} \]  

(43)

This derivation is to be found in greater detail in section 10.4.1. of Katchalsky & Curran (1965). If we develop equations (40) and (41) for a concentration difference of water across the membrane we obtain

\[ RTV_w \Delta c = \frac{J_w V_w f_{wm}}{\phi_w} \]  

(44)

rearranging to give

\[ J_w = \frac{RT \phi_w \Delta c}{f_{wm} \Delta x} \]

which by analogy with Fick's law leads to an expression for \( P_w \), the membrane permeability to water

\[ P_w = \frac{RT \phi_w}{f_{wm} \Delta x} \]  

(45)

Now the relationship between \( P_w \) and \( L_p \) in a system where water crosses the membrane solely by diffusion has been derived by several authors and is generally given as

\[ L_p = P_w \frac{V_w}{RT} \]  

(46)

when there is no molecular filing present, although this only has to be considered when labelled water is used to follow \( P_w \) and is irrelevant here. Considering equations (43) and (45) it is obvious that \( L_p \) and \( P_w \) are indeed related by equation (46). For porous membranes, however, where the radius of the channels is appreciably larger than that of the water molecules, equation (46) does not hold and \( L_p \) and \( P_w V_w/RT \) can differ by a large factor; this discrepancy has of course been made the basis of much work to determine the radii of channels in porous membranes, and whatever the explanation of the discrepancy in certain specified systems, it is theoretically quite sound. It stems from the fact that pressure-flow occurs by bulk or viscous flow, whilst concentration-driven flow occurs by diffusion. The ratio of the two quantities

\[ \beta = \frac{L_p}{P_w V_w/RT} \]  

(47)

is often called the 'bulk-to-diffusive' flow ratio, and ranges from unity
upwards. It must therefore be apparent that the frictional treatment culminating in equations (43) and (45) will always give a $\beta$-value of one, no matter what the membrane is like; there is no provision for changes in $f_{wm}$, which is regarded as a constant for any particular membrane. The next step is to examine what $f_{wm}$ could represent.

In Fig. 2 is shown a membrane pore separating two baths in which the frictional constraints on a water molecule during passage through the pore are broken into two components

$$f_{wm} = f'_{wm} + f''_{wm}$$

which represent frictional interaction with the wall and with the water in the pore. This point has been realized by Mikulecky (1972) who has extended the wall friction to water molecules in the pore which are not in contact with the wall; this is very difficult to visualize in physical terms, but it does emphasize that $f_{wm}$ has a complex internal structure. The two components would be rather difficult to define clearly, particularly in terms of kinetic theory, but they will serve to make the point in a qualitative fashion. When a water molecule traverses the pore under conditions of pure diffusion, the relative magnitude of the components is determined by the pore dimensions; when the flow is laminar, however, the components assume different magnitudes, $f'_{wm}$ remaining approximately the same, but $f''_{wm}$ decreasing in accordance with the fact that internal friction is at a minimum in liquids undergoing steady-state viscous flow. Thus the value of $f_{wm}$ for a given membrane will change along with changes in the
flow regime, and cannot be regarded as a constant under all conditions.

The magnitude of the changes in \( f_{wm} \) will now be considered. If the wall friction is small compared to that encountered in the core, which will be true for anything but very small pores, then substitution of equations (43) and (45) into equation (47) shows that the water-membrane frictional coefficients for diffusive flow, \( f_{wm}^d \), and pressure-driven flow, \( f_{wm}^b \), are related by

\[
\frac{f_{wm}^d}{f_{wm}^b} = \beta.
\]

(49)

This requires some comment. The \( \beta \)-value of equation (49) is not that measured by following the diffusive flow with labelled water, but rather the 'true' value that would be calculated from Fick's law, Poiseuille's law (say), and the pore geometry. When the pores are small \( \beta \) is thus equal to one, for water traverses the pores by a diffusive mechanism whatever the nature of the driving force.

The fact that \( f_{wm} \) has two components as shown in equation (48) has not been taken into account in any of the frictional theories of osmosis, but it has made a brief appearance where isotopic flows are considered. To illustrate the confusion to which this subject is prone we might consider the formula derived by Kedem & Katchalsky (1961) and Essig (1966) to describe \( \beta \) as measured by bulk flow and labelled water diffusion,

\[
\beta = \frac{f_{D0} + f_{Dm}}{f_{wm}},
\]

(50)

where \( f_{D0} \) and \( f_{Dm} \) are the interaction of labelled water with the pore-water and the pore-wall, and \( f_{wm} \) is the bulk water-membrane coefficient. This has been simplified to

\[
\beta = 1 + \frac{f_{D0}}{f_{wm}}
\]

(51)

by making the assumption that \( f_{Dm} = f_{wm} \), based on the assumed equality of frictional interaction between labelled and unlabelled water. Using equation (51) Essig has concluded that in non-porous membranes where water crosses only by diffusion, \( \beta \) need not be one, in contradiction of the thermodynamic derivation. This must apply also to the transfer of unlabelled water, because no account of molecular filing is contained in the analysis. Equation (51) is incorrect, however, because it is derived by equating a component of diffusive transfer (the pore-wall friction, \( f_{Dm} \))
with the whole bulk frictional coefficient (pore-wall friction + pore-water friction). By equation (48) the two components \( f_{D0} \) and \( f_{Dm} \) are equal to an overall coefficient representing labelled water transfer

\[
f_{D0} + f_{Dm} = f_{Dm}^{\beta}
\]

and so equation (50) becomes

\[
\beta = \frac{f_{Dm}^{\beta}}{f_{um}}, \quad (53)
\]

which is equivalent to equation (49); it merely defines \( \beta \) as the ratio of two frictional coefficients, which are equal (by definition) when the membrane only allows diffusional flow. It may appear peculiar that the two components of \( f_{um} \) have been seen to apply to tracer diffusion but not to net water flow.

What relevance has all this to osmosis? If we consider what we have established concerning osmotic flow in porous systems it must be apparent that its rate varies from that of diffusive flow to that of pressure-driven flow (\( \sigma_s = 1 \)). Thus the value of \( f_{um} \) which characterizes osmosis (\( f_{um}^{*} \)) can vary from \( f_{um}^{b} \) to \( \beta f_{um}^{b} \). When osmotic flow is set up the value of \( f_{um} \) is a function of the flow regime established in the pore. We can see that the derivation of equation (37) has been made without regard for this point, and it is therefore of great interest to derive an equation for \( \sigma_s \) without assuming the constancy of \( f_{um} \) under all flow regimes.

To simplify matters it is convenient to derive an expression for \( \sigma_s' \), the reflexion coefficient in the absence of solute volume transfer.

\[
\sigma_s = \sigma_s' - \frac{\omega_s \bar{V}_s}{\bar{E}_p}.
\]

When there is only a hydrostatic pressure difference across the membrane (\( \Delta \Pi = 0 \)) the balancing of driving forces and frictional forces in the steady-state leads to

\[
-\Delta \mu_w = -\bar{V}_w \frac{\Delta P}{\Delta x} = f_{um}(v_{w0} - v_s) + f_{um}^{b} v_{w0}
\]

\[
= v_{w0} \left( f_{um}^{b} + \frac{c_s \bar{V}_w f_{um}^{b}}{\phi_w} \right) - \frac{v_s C_s \bar{V}_w f_{um}^{b} \phi_w}{\phi_w},
\]

where use has been made of the reciprocal equation (18) and of the definition of the membrane water content, \( \phi_w = c_w \bar{V}_w \), where \( c_w \) is the
water concentration in the membrane; the relationship for solute flow is

\[-\Delta \mu_s = -\bar{V}_s \frac{\Delta P}{\Delta x} = f_{sw}(v_s - v_w) + f_{sm} v_s = v_s(f_{sm} + f_{sw}) - v_w f_{sw}.\]  

(56)

When there is only an osmotic pressure difference (\(\Delta P = 0\)) the corresponding expressions for water and solute are

\[-\Delta \mu_w = \bar{V}_w \frac{\Delta \Pi}{\Delta x} = v_m \left( f_{wm}^* + \frac{c_s \bar{V}_{ws} f_{sw}}{\phi_w} \right) - v_s c_s \bar{V}_{ws} f_{sw} \phi_w \]  

(57)

and

\[-\Delta \mu_s = -\frac{1}{\bar{c}_s} \frac{\Delta \Pi}{\Delta x} = v_s(f_{sm} + f_{sw}) - v_w f_{sw}.\]  

(58)

If we now substitute for \(v_s\) between equations (55)-(56) and (57)-(58) and solve the resulting equations for \(v_w(\Delta \Pi = 0)\) and \(v_w(\Delta P = 0)\) respectively, the ratio is equal to the reflecson coefficient

\[\sigma' = \frac{v_w(\Delta P = 0)}{v_w(\Delta \Pi = 0)}\]

or

\[\sigma'_s = \left[ \frac{f_{sm} + f_{sw} - \frac{c_s f_{sw}}{\bar{c}_s \phi_w}}{f_{sm} + f_{sw} + \bar{V}_s c_s f_{sw} \phi_w} \right] \left[ \frac{c_s \bar{V}_{ws} f_{sw}^2}{\phi_w} - (f_{sm} + f_{sw}) \left( f_{wm}^* + \frac{c_s \bar{V}_{ws} f_{sw} \phi_w}{\phi_w} \right) \right].\]  

(59)

If we put \(c_s/\bar{c}_s\) equal to \(K_s\), the distribution coefficient of solute, where \(c_s\) is the solute concentration at any point within the membrane and \(\bar{c}_s\) is the mean bath concentration for dilute solutions, and note that \(\bar{V}_s c_s \ll 1\), equation (59) becomes

\[\sigma'_s = \left[ 1 - \frac{K_s f_{sw}}{\phi_w(f_{sw} + f_{sm})} \right] \left[ \frac{c_s \bar{V}_{ws} f_{sw}^2}{\phi_w} - (f_{sm} + f_{sw}) \left( f_{wm}^* + \frac{c_s \bar{V}_{ws} f_{sw} \phi_w}{\phi_w} \right) \right],\]  

(60)

where \(f_{wm}^*\) is the frictional coefficient for water transfer during osmotic flow. It is evident the usual expression for \(\sigma'_s\) (see equation (37)) given by the first bracketed term, is obtained only when \(f_{wm}^* = f_{wm}^b\); this can only be true when \(\sigma'_s = 1\), but we cannot know this in advance.

Perusal of equation (60) reveals the barrenness of the frictional interpretation of osmosis. From the four coefficients of equations (34) and (35) it takes three, by equating \(\sigma_s\) and \(\eta_j\); it then claims that these can be translated into three frictional coefficients \(f_{sw}, f_{sm}\) and \(f_{wm}\) which are
'amenable to physical interpretation'. We can see that this is quite incorrect however, for in reality four coefficients are required, one of which, \((f_{wm}^*)\), is intractable. In fact, the whole physics of the problem lies in predicting how \(f_{wm}^*\) differs from \(f_{wm}^b\). Any attempt to interpret equation (60) relies on an interpretation of the magnitude of \(f_{wm}^*\), which ends in a tautology. Two examples will make this clear: (i) when \(f_{sw} \to 0\) equation (60) reduces to

\[
\sigma_s' = \frac{f_{wm}^b}{f_{wm}^*}, \tag{61}
\]

which is not necessarily one, but if we write that \(f_{wm}^* = f_{wm}^d\), this is equivalent to presuming that \(\sigma_s' = 1\); there is no independent way of comparing \(f_{wm}^*\) and \(f_{wm}^d\) available to frictional theory; (2) if \(1/\sigma_{sw} \to 0\), which is equivalent to saying that the membrane is semipermeable \((\sigma_8 = 1)\), then

\[
\sigma_s' = \frac{f_{wm}^b + [(c_s P_s f_{sw} f_{sw})]}{f_{wm}^* + [(c_s P_s f_{sw})/\sigma_{sw}]}, \tag{62}
\]

which is equal to unity when \(f_{wm}^* = f_{wm}^b\), an assumption which again we can only make once we already know that \(\sigma_s' = 1\). As the essential nature of the difference between \(f_{wm}^*\), \(f_{wm}^b\) and \(f_{wm}^d\) is unobtainable from frictional theory, it cannot yield a formula for \(\sigma_s\) in terms of independent parameters. The derivation of \(\sigma_s\) for electrolytes is more complicated but is open to the same objections. The interpretation of anomalous osmosis in terms of \(\sigma_s\) is dealt with later.

HYDRODYNAMIC THEORIES

The term ‘hydrodynamic’ should be understood here as denoting theories which try to describe the forces acting on the fluid which moves during osmotic flow, forces which may be electrical, mechanical or diffusive in nature, and vary within the membrane pore. Any kinetic theory should be able to give some answer to the following questions. (i) Is \(\sigma_s\) equal to \(\sigma_f\)? (ii) How does \(\sigma\) vary with pore size? (iii) Why is there apparent bulk flow during osmosis, i.e. why is the maximum rate near to that of pressure-driven flow? (iv) In respect of (iii), are the rates equal, or merely similar, i.e. does \(\sigma_s\) really rise to be 1? The capacity to describe anomalous osmosis, or as we shall see, to discriminate between specific contributions to anomalous osmosis, is an additional constraint to any theory.

In answer to the first question, Levitt (1975) has set out to show on general hydrodynamic grounds that \(\sigma_s = \sigma_f\), without assuming any particular form for the drag coefficients. His elegant analysis considers
the drag exerted on solute particles by a fluid passing with a creeping-flow (regime) through a pore, and thereby obtains an expression for $\sigma_f$. When it comes to the osmotic coefficient $\sigma_s$, however, the analysis has nothing to do with osmosis. The expression for $\sigma_s$ is derived by assuming that values of $\sigma_s$ less than unity arise by the drag exerted on solvent moving with viscous flow alone by solute particles, and in this respect Levitt's analysis is merely a restatement in hydrodynamic terms of Kedem and Katchalsky's frictional theory of osmosis; the problem is to explain the nature and the rate of volume transfer during osmotic flow, and there is no reason to assume that the flow regime pertaining then is similar to that generated by a pressure gradient, nor that osmosis is simply a frictional phenomenon. Levitt has in fact merely produced a similar equality to equation (18), which is to say that solvent-solute friction is a reciprocal phenomenon when the flow regime is constant even in systems of relatively complicated geometry.

A treatment which assumes equality of $\sigma_f$ and $\sigma_s$ is that of Durbin, Frank & Solomon (1956), which combined with expressions for the area 'available' to either solutes or water for membrane transfer (Renkin, 1954) leads to an expression for $\sigma$. Here again the approach is founded upon ultrafiltration and not osmosis. From equation (30) it is clear that

$$\frac{L_{DP}}{L_p} = 1 - \frac{\theta}{\bar{c}_s} = \sigma_f,$$

where $\theta$ is the concentration of the transported solution during ultrafiltration, $\bar{c}_s$ being the bath concentration when $c_1 = c_2$. It is considered that the ratio of these concentrations is equal to the effective areas for filtration (under a pressure difference) of water and solute; thus

$$\sigma_f = 1 - \frac{A_s}{A_w}.$$  \hspace{1cm} (63)

The effective areas $A$ are in fact complex functions of the solute, water and pore radii comprising (i) an entrance effect and (ii) a frictional interaction within the pore wall. The final expression, which is discussed in detail by House (1974), is

$$\sigma_f = 1 - \frac{\{2(1 - \lambda_s)^2 - (1 - \lambda_s)^4\}(1 - 2 \cdot 104 \lambda_s + 2 \cdot 09 \lambda_s^3 - 0 \cdot 95 \lambda_s^5)}{\{2(1 - \lambda_w)^2 - (1 - \lambda_w)^4\}(1 - 2 \cdot 104 \lambda_w + 2 \cdot 09 \lambda_w^3 - 0 \cdot 95 \lambda_w^5)},$$  \hspace{1cm} (64)

in which the two right-hand terms are truncated series. This equation
has been shown to fit data for $\sigma$ as a function of $\lambda_g$ reasonably well, although its validity (when applied to $\lambda_g$) hangs completely upon Onsager reciprocity, and disregards transfer by salt migration. A remarkable aspect of the widespread use of equation (64) is that it contains no provision whatsoever for interaction between salt and water flows, in spite of the fact that this interaction has often been assumed to be at the heart of osmosis; there is no effect of solute radius on the effective area for water $A_{w}$, which might be related to the frictional term $f_{sw}$. We shall return to (64) later.

Those theories which consider the nature of the flow during osmosis will now be considered, the true osmotic models. In the model of Mauro (1957) and Ray (1960) the exclusion of salt from the pore is considered to lead to hydrostatic pressure gradients along the pore axis, and these create a bulk flow of water at the same rate as would be produced by an equivalent pressure gradient applied across the membrane in the absence of salt; thus $\sigma = 1$. This situation is shown in Fig. 3(a), where the osmotic pressure $\Pi$ falls to zero at the pore mouth over a very short distance which we may call the reflexion zone.

On the assumption that the difference in water potential is zero or very small over this region ($\Delta \mu_{w} \rightarrow 0$) there must be a fall in pressure ($P_{0} - P_{1}$) to maintain this state of affairs; as there is no pressure-difference over the membrane as a whole (in this special case) the pressure must rise again over the remaining pore-length. The pressure is assumed to be at a minimum at the inner end of the reflexion zone, and there is thus a pressure gradient

$$\frac{dP}{dx} = \frac{P_{0} - P_{1}}{l}$$

(65)

in the pore, where $P_{0} - P_{1} = \Delta \Pi$. Both Ray (1960) and Dainty (1965) have described the process in qualitative kinetic terms. At the pore mouth, water molecules jump preferentially into the bath (containing salt) and create a drop in water concentration in this pore region. Water in the pore moves to equalize the concentration and this results in a linear pressure gradient along the pore. Water molecules leave the pore by diffusion at the same rate as bulk flow of water occurs along the pore because diffusion is very rapid over the reflexion zone owing to its very short length.

In the presentations of Mauro, and of Dainty, there is no treatment of the penetration of salt into the pore although there is a problem associated with this particular point: if the zone is small but finite then the drop in
hydrostatic pressure must be smaller than the drop in osmotic pressure or water will not leave the pore, but how much smaller? Obviously this one-dimensional approach must provide a more quantitative picture of salt penetration into the pore to be intellectually satisfying.

In Ray's treatment of a membrane permeable to salt the concentration in the pore is artificially divided into two regions, one of which seems to be controlled by unilateral exchange of salt with the bath, whilst the other, which extends across the pore, seems to be linear although bulk flow is presumed to occur in this zone (Fig. 3a). In fact whereas for the impermeant salt Ray has correctly calculated the pressure drop in the pore, for the permeant case he has assumed a particular biphasic solute gradient in the pore, and then inserted into this a value for \((P_o - P_i)\), the pressure drop in the pore, derived for the impermeant case. The pressure-drop,
however, must be calculated as a function of the salt gradients in the pore, and there is no a priori reason to postulate a biphasic reflexion zone when solute can move throughout the pore.

In the treatment by Hill (1972) a reflexion zone of finite length is set up in a purely arbitrary manner, i.e. it is not generated by any property of the salt-pore interaction, and the consequences are investigated of varying its length from zero to 1 (the pore length). The underlying assumption is that the pressure drop in the pore is minimal at the inner end of the zone, which is common to Ray's treatment, but this has to be proved and is by no means certain. When the zone extends across the pore $\sigma_s$ falls to a value which is equal to $\beta^{-1}$, due to the fact that there is no pressure gradient within the pore and water is traversing the pore by diffusion only. A serious drawback of this approach is that the permeation problem is not directly confronted because when the reflexion zone extends over the pore length the salt is still 'reflected' and its velocity is zero; the contribution of salt flow to volume flow, $\vec{V}_s \cdot J_s$, is neglected and so is the salt-water friction term $f_{sw} \cdot v_s$. Thus in both papers the treatment of the permeant case is rather unsatisfactory.

Before considering the permeation process in more detail it is necessary to make a somewhat lengthy digression to discuss a group of pore theories which fall naturally into a class and which purport to give a more detailed and thorough examination of the nature of osmotic flow in pores. These are the models of Manning (1968), Anderson & Malone (1974) and Marshall (1977). The first of these is a one-dimensional model similar to that of Ray (1960), although it relies on different principles; the other two are concerned with showing that one-dimensional models fail to give an adequate description of osmosis because the critical interaction occurs at the pore-wall resulting in both axial and radial gradients of concentration and pressure. The paper of Anderson and Malone proposes that there is a 'wall exclusion layer' in which salt is at a lower concentration than the pore core due to a repulsive field set up by the pore wall. This field may be due to electrical, steric or other forces. The potential characterizing this field is $V_{(r)}$, which varies along a radius. As there is radial thermodynamic equilibrium in long pores the chemical potentials of salt and water are constant (radially not axially), and as the salt potential is given by

$$\mu_s = \mu^0_s RT \ln c + \bar{V}_s P + \Psi$$

(66)

it follows that the solute concentration profile at any point on the radius ($x = r$) is

$$c_r = c_0 e^{-(V_{(r)} - V_{(0)})}$$

(67)
where \( c_0 \) is the concentration on the pore axis \((x = 0)\) and \( V \) is the dimensionless wall potential, \( V = \Psi/RT \). The effect of pressure on \( \mu_s \) is neglected.

As \( \Delta \mu_w \) is constant radially, it follows that

\[
P_r - \Pi_r = P_0 - \Pi_0 \tag{68}
\]

and so

\[
P_r = P_0 - \Pi_0 (1 - e^{-V_{(r)}r - V_{(r)}a}) \tag{69}
\]

The pressure drop at the wall is \( \Pi \)-dependent, and as \( \Pi \) varies along the pore from one bath to the other so does the pressure at the wall, driving the fluid through the pore from the bath of lowered osmotic pressure to the higher. This can be combined with a non-slip condition at the wall to give a plug flow similar to that predicted for electro-osmosis (Fig. 4).

Several predictions immediately follow from this analysis. Firstly, the absence of any specific force between salt and pore wall will give rise to osmosis as described above due to steric factors: the centre of mass of solute particles is obviously excluded from a region adjacent to the wall from \((r_p - a)\) where \( r_p \) is the pore radius and \( a \) the solute radius, and this appears as a discontinuous \( V_{(r)} \)-function. Secondly, when the force between pore wall and salt is attractive, the flow is reversed, i.e. negative
osmosis results. This result is mildly surprising in view of the preponderance of attractive forces (van de Waals) between molecules, for it is shown that steric hinderance can never completely mask the negative osmosis. Thirdly, the application of pressure to counteract the osmotic flow results in an abolition of net flow, but leads to water circulation within the membrane pore; this is because the flow is driven by axial pressure gradients which vary with radial position. Again this is similar to electro-osmosis (Wyman & Kostin, 1973).

In the model of Manning, the potential is unattenuated across the whole pore radius, and there is no radial gradient of anything. This serves to convert the system to a problem in one-dimension, but one in which the pressure drop along the pore axis is also created by the axial fall in solute concentration within a potential field due to the wall. Bulk-flow is therefore generated, but by quite different physical principles from those in Ray's model.

Marshall's model is by far the most detailed, and considers the interaction of two ions of a uni-uni salt with a pore wall containing fixed charges, as well as steric effects. The solution requires a coupling of the inertia-free Navier–Stokes equations with the Nernst–Plank equations, and relies also on the concept of the 'wall exclusion layer' of Anderson and Malone. It predicts an expression for the reflexion coefficient of non-electrolytes which reduces to that of Anderson and Malone for non-electrolytes when the charges on the pore wall disappear.

These theories, sophisticated as they are, are all open to two serious criticisms which we shall now consider in detail.

(1) When salt is excluded completely from the pore by total steric hinderance, these models should predict that $\sigma_s = 1$. This is a fundamental prerequisite of any osmotic theory. From the expressions for $\sigma_s$ derived therein it can in every case be shown that when the wall repulsion potential $V_r$ becomes very large, $\sigma_s$ tends to unity, and this is taken to mimic salt exclusion from the pore. However it takes little sophisticated mathematics to see that when salt is absent from the pore there are no concentration gradients, no pressure gradients, and no flows! In all these models there is a failure to recognize the fact that it takes both $\sigma$ and $\Delta \Pi$ to create an osmotic volume flow, and when the pore contains only water there is no gradient of $\Pi$ or $P$ to set up the bulk flow. It might be argued that $\Delta \Pi$ between the two baths is unchanged, which of course is true, but there is then no machinery inherent in these models for generating an internal pressure gradient along the pore.
(2) A far worse criticism is that the very concept of pressure gradients in a 'wall exclusion layer' is almost certainly illusory. Let us consider the junction between a surface and a solution where a repulsive potential acting on the salt $V_s(x)$ exists, falling off with distance (Fig. 5).

The effect of the surface field is to raise the activity coefficient of the salt; this in turn leads to a redistribution of salt as shown, so that the activity of the salt is constant with distance from the surface. This is the fundamental condition of equilibrium. As the osmotic pressure is given by

$$\Pi = RTa_s,$$

(70)

where $a_s$ is the activity of solute, and not by

$$\Pi = RTc_s,$$

(71)

we can see that there is no change in $\Pi$ on approaching the wall, and therefore no compensatory change in pressure. The effect of $V_s(x)$ on $\gamma_s$, the activity coefficient, has precise parallels in many situations but for
an example we might choose the Debye–Hückel theory of electrolytes. Here it is possible to compute an electrostatic potential, $\xi$ around an ion of charge $Q$/mol, which (in this case) lowers the activity coefficient of the salt according to the relation

$$\ln \gamma_s = \frac{1}{RT} \int_0^Q \xi \cdot dQ$$

(72)

where $\mu_s = \mu_s^0 + RT \ln c_s + RT \ln \gamma_s$. In our case we have the similar relationship

$$\ln \gamma_{s(\phi)} = \frac{1}{RT} \int_0^r \Psi' \cdot dx$$

(73)

where $\Psi' = RT \frac{dV}{dx}$.

Substitution of this equation, which is equivalent to $\gamma_{s(\phi)} = e^{\Psi(\phi)}$ together with equation (67) into

$$a_s = \gamma_s c_s$$

(74)

leads to $a_s = \text{const}$. Anderson and Malone have claimed the pressure gradient can be deduced from the Gibbs–Duhem equation by including $dV$ as a term (their equation (8)), but this is impossible because $dV$ is not an intensive state function, i.e. a thermodynamic property of the system, but a specific potential related to only one component of the solution. The Gibbs–Duhem equation at constant $T$

$$- V \frac{dP}{dT} + n_s \Delta \mu_s + n_w \Delta \mu_w = 0$$

(75)

leads to $dP = 0$, when both $\Delta \mu_s$ and $\Delta \mu_w$ are zero.

The only way in which pressure can be generated is by a vectorial force field acting on all components irrespective of their chemical nature, such as gravity on liquid mass. In view of these considerations we shall not pursue these theories any further as their very basis seems to have been removed, and assume that there is still progress to be made with one-dimensional models.

When solute is excluded totally from a pore on grounds of molecular size, there exists a situation which is qualitatively different from the permeant case. In an equilibrium situation where the bathing solutions are identical the water in the pore is in thermodynamic equilibrium with that in the baths and must therefore be under reduced hydrostatic pressure. If the pores are salt-permeable there are both steric and interactive forces associated with the wall to be considered, but for reasons outlined above these do not affect the activity of solute in the membrane, only its
concentration; there is consequently a gradient of activity along the pore axis set up under conditions of osmotic disequilibrium. The assumption which underlies so many treatments of osmosis, and the hydrodynamic approach in particular, that there is no essential difference between the impermeant and permeant cases and that the former can be simply modelled by increasing the pore-wall interactions of the latter until the solute is 'squeezed out', may well be wholly incorrect.

Inherent in the hydrodynamic approach is another peculiarity, which ultimately can be traced to a combination of factors: the failure to consider diffusive water flow during osmosis and the preconception that \( \sigma_s = 0 \) when solute can pass freely through the pore. We have seen in a previous section that when the pore radius is large (compared to solute) there is nothing to prevent osmotic water transfer by diffusion. This point can be enlarged upon: a pore might possess a bulk-to-diffusive flow ratio (\( \beta \)) in a particular solvent very near unity, owing to high viscosity (decreasing \( L_p \)) and high partial molar volume (equation (47)), but be large enough to be solute-permeant; if we now visualize the size of the solute species as being very small (\( \lambda_s \rightarrow 0 \)) it must be obvious that solvent will cross the pore at least as fast as by diffusion, which owing to the low value of \( \beta \) is comparable with the bulk flow rate when \( \sigma_s = 1 \). Thus \( \sigma_s \) for a small salt in theory need not even be small, let alone zero. It can be argued that in reality the finite size of the solvent molecules will set an upper limit to \( \sigma_s \) when the salt is small, but we can see that this is ancillary to most hydrodynamic treatments which consider the solvent to be a continuum and ignore its diffusional flow. The expressions for \( \sigma_s \) of Renkin (equation (64)), Levitt (1975), Anderson & Malone (1974), and Marshall (1977), the two latter being

\[
\sigma_s = \left(1 - (1 - \lambda_s)\beta\right)^2
\]

for uncharged systems where \( \lambda_s \) is the ratio of solute radius to pore radius, all become zero when \( \lambda_s \) is small.

To conclude, it is important to point a way to a possible solution. The problem is to calculate the reflexion coefficients from the parameters of the solute, solvent and the geometry of the pore, indeed to determine from any theory rich enough to encompass most osmotic phenomena, what minimum set of parameters are required to do this. When osmotic models are restricted to an interpretation in terms of frictional coefficients they are truly unidimensional because the resistances to flow are proportional to the \( f_{ij} \), these being merely lumped coefficients which
have not been derived in any way from the properties of the constituents. Models which involve a consideration of bulk flow are really quasi-unidimensional models because they must introduce a hydraulic conductivity \( L_p \) which is dependent upon the solvent-wall interaction, leading to velocities which vary with radial position; Poiseuille flow is a special case of this. The problem then resolves itself into one of calculating the water conductance of the pore \( (\beta, L_p, f_{wm}, \text{or whatever}) \) as a function of the driving forces at any point. This is because the conductance is in reality a function of the flow regime, and the latter is dependent upon the driving forces (frictional, osmotic, or hydrostatic). Thus if the combination of forces changes along the pore, so does \( f_{wm} \).

Ray’s model, for all its defects, is the bravest attempt to pursue a unidimensional model to the end, and it is clear that there is a need to continue this approach, using not a linear combination of diffusive and bulk flows as does Ray, but with a theory which calculates \( f_{wm} \) as a function of the forces operating on the water at any point. To take an example, it is impossible linearly to combine the bulk and diffusional flows due to opposed hydrostatic and osmotic forces when the direction of net flow is determined by the diffusional field, for in this case no bulk flow regime could properly be said to exist. Until this fundamental problem has been solved, or rather decided, it is premature to conclude that quasi-unidimensional models have failed to give a reasonable comprehensive account of osmosis. In this connection it is very surprising to see, considering the importance of osmotic theory in biophysics, how scanty and piecemeal is the experimental data against which any theory can be measured.

In view of the uncertainties surrounding the precise derivation of an expression for \( \sigma_s \), and taking into consideration that theoretical approaches like those of Levitt (1975) and Anderson & Malone (1974) have differed as to whether \( \sigma_s \) departs significantly from \( \sigma_f \), it is impossible at this point in time to give a definite statement as to the existence of symmetry. Marshall (1977) has pointed out that the mathematical procedures used in their derivation, such as series truncation, may themselves obscure any differences between the coefficients.

One can see that it must be true, however, that if \( \sigma_s \) is not equal to \( \sigma_f \), then the two must be related by a subsidiary equation, in addition to (34) and (35). Osmosis and ultrafiltration must be related phenomena, but not necessarily in the naive way assigned to them by thermodynamics which assumes they are merely reciprocal.
ANOMALOUS OSMOSIS AND ELECTRO-OSMOSIS

Anomalous osmosis is net volume flow from the high concentration to the low. There are basically two mechanisms that could give rise to this flow. The first is that volume transfer by the salt can exceed that due to the water. This requires no more theoretical basis than is contained in equation (54): if the last term is big enough then the overall reflexion coefficient reverses sign. Such a membrane has in fact been constructed by Weinstein & Caplan (1968) from a mosaic of ion exchangers, and it is possible to calculate from the data that the volume flow (which is minute) is due to the salt. Such an effect has been discussed by Schlägl (1955) and Kedem & Katchalsky (1961, section 9). It is only in charged membranes that the salt permeability can attain very high values and so this effect is virtually confined to charged membranes permeated by electrolytes.

In this latter paper it is very difficult to disentangle this effect from another arising from frictional interaction between salt and water which constitutes the second mechanism mentioned above. Reference to equation (59) shows that if $f_{sw}$ becomes quite large, then

$$\sigma_s \rightarrow (1 - K_s) \quad (77)$$

and if $K_s$ exceeds 1 then $\sigma_s$ reverses sign. This effect can be developed for a charged membrane in which case $K_s$ is a complex function of membrane charge and salt concentration in the baths. The basic effect, however, is that water can be driven towards the more dilute bath by friction with salt moving in the same direction.

For a deeper understanding of anomalous osmosis it is necessary to consider the potential gradients set up within a pore separating two salt baths at different concentrations but equal potentials. It then becomes clear that there is an electro-osmotic component involved in the volume flow created by the internal potential gradients, which in fact must always be considered when the membrane is charged. Electro-osmosis, i.e. volume-flow in response to an applied trans-membrane potential difference, is due to the fact that the pore fluid (or some region of it) possesses a net charge arising from the repulsive force exerted by the fixed charge system of the pore wall on ions of similar charge; the potential gradient thus exerts a force on the ions in this region which results in a body force on the water by virtue of the frictional coupling. This effect, although treated in a simple manner by Helmholtz &
Smoluchowski, has been given a more rigorous analysis by Wyman & Kostin (1973) who have coupled the Navier–Stokes and Nernst–Planck equations in open charged pores, to give an account of the radial velocity profile, and under certain conditions the axial profile, which can lead to circulation within the pore. Wyman and Kostin do not consider the effect of ion convection due to viscous flow on the Navier–Stokes equations, and this omission is of uncertain effect (to me), but may be small. Thus anomalous osmosis in charged membranes and electro-osmosis can be treated by the same methods according to whether the baths are potential-clamped or concentration-clamped respectively. In this connexion Marshall (1977) has pointed out that the fixed membrane charges have an effect on the ion concentrations in the baths adjacent to the pore mouths so that concentration-clamping holds only at infinity in real situations; his model should be consulted for its many interesting details, but the electro-osmotic drag factor he uses is so intimately bound up with the concept of the ‘wall exclusion layer’ to which serious objection has been raised that it unfortunately cannot be considered in isolation.

In both anomalous osmosis and electro-osmosis the computed radial velocity profile is not that of Poiseuille flow, and indeed it is not yet clear whether it is so in osmotic flow. Thus hydrostatic, osmotic or potential differences, resulting as they do in volume flow in one and the same pore, must give rise as a first approximation to flows which are susceptible of linear combination by an equation of the form

\[ J_v = L_p \Delta P + \sigma_s L_p \Delta \Pi + P_e \Delta E. \] (78)

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**Symbols used in the text**

- \( a_s \) Solute activity (equation (74)).
- \( A_s, A_w \) Effective area for filtration of solute, water.
- \( c_i, c_s, c_w \) Concentration of the \( i \)th species, salt, water.
\( \bar{c}_s \) Concentration function equal to the mean concentration of solute in the membrane when \( \Delta c \to 0 \) (equation 36).

\( c_1, c_2 \) Solute concentrations in the two baths.

\( D_s, D_w \) Diffusion coefficient of solute, water.

\( \Delta E \) Transmembrane potential difference.

\( f_{ij} \) Overall partial molar frictional coefficient between the \( i \)th and \( j \)th components (equations (16, 17)).

\( f'_{ww}, f'_{wm} \) Frictional coefficient between water and pore-water, pore-wall.

\( f_{wm}^{d}, f_{wm}^{b} \) Overall frictional coefficient between water and membrane during diffusive flow, bulk (viscous) flow (equation (49)).

\( f_{Dw}, f_{Dm} \) Frictional coefficient between diffusing labelled water and pore-wall (equation (50)).

\( f_{Dm}^{d} \) Overall frictional coefficient between diffusing labelled water and membrane (equation (52)).

\( f_{wm}^{*} \) Overall frictional coefficient between water and membrane during osmotic flow (equation 57).

\( J_i, J_s, J_w \) Molar flow of \( i \)th species, solute, water.

\( J_v \) Transmembrane volume flow rate.

\( J_D \) Transmembrane exchange flow (equation (6)).

\( K_w \) Distribution coefficient of solute in the membrane.

\( L_p \) Hydraulic conductivity.

\( L_{pD}, L_{DP}, L_D \) Phenomenological coefficients relating to osmosis, ultrafiltration, and exchange diffusion (equations (6, 7)).

\( L_{1,2,3,4} \) Phenomenological transport coefficients (equations (8, 9)).

\( l \) Pore length.

\( n_s, n_w \) Moles of solute, water.

\( P \) Hydrostatic pressure.

\( P_e \) Electro-osmotic permeability (equation (78)).

\( P_w \) Membrane permeability to water.

\( V \) Volume.

\( V_i, V_s, V_w \) Partial molar volumes of the \( i \)th species, solute, water.

\( V_p \) Repulsive wall potential varying with pore-radius.

\( v_i, v_s, v_w \) Velocity of the \( i \)th species, solute, water.

\( \beta \) Bulk-to-diffusive flow ratio (equation (47)).

\( \gamma_s \) Activity coefficient of solute (equation (74)).

\( \theta \) Concentration of filtrate during ultrafiltration (equation (39)).

\( \lambda_s, \lambda_w \) Ratio of solute, water radius to pore radius.
$\mu_i, \mu_s, \mu_w$  
Chemical potential of $i$th species, solute, water (equation 1).

$\Pi$  
Osmotic pressure.

$\sigma, \sigma'$  
Osmotic reflexion coefficient in presence, absence of volume transfer by solute (equations (28, 54)).

$\sigma_f$  
Ultrafiltration or drag reflexion coefficient (equation (33)).

$\Phi$  
Dissipation function.

$\phi_w$  
Volume fraction of water in the membrane (equation (40)).

$\omega_s$  
Solute osmotic diffusion coefficient (equation (35)).

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