Osmotic Pressure in the Physics Course for Students of the Life Sciences

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Ideal gas models for equilibrium osmotic pressure and for nonequilibrium flow of solvent through an ideal semi-permeable membrane are presented. These models can easily be introduced in general physics courses for students of the life sciences. The models are justified in Appendices, which include a summary of the irreversible thermodynamics of flow through membranes. Some physiological examples are presented, including the Nernst equation and Gibbs–Donnan equilibrium.

INTRODUCTION

Osmotic pressure is central to physiologic processes in every living thing, yet it is not currently a fashionable topic in introductory physics courses. The result is that when a medical or biology student later encounters the phenomenon (for example, in physiology), he has no clear picture of the process involved, unless he has had a very good training in physical chemistry. Instead of being shown how to relate osmotic pressure in an ideal solution to whatever intuition he has developed about partial pressures in ideal gases, he is told that osmotic equilibrium occurs when "there is a balancing of osmotic and hydrostatic forces," or that the "hydrostatic pressure difference necessary to maintain the unequal concentration of total dissolved particles in the two solutions is equal and opposite to the osmotic pressure." While these statements are not incorrect, they are based on an understanding of osmotic pressure in terms of a driving force which is the gradient of a concentration-dependent chemical potential, a concept with which the student may have no experience.

The equations relating osmotic pressure to solute concentration for a dilute solution and an ideal membrane are analogous to those for an ideal gas; in fact, the concept of partial pressure can be applied to a dilute solution. For this reason semi-permeable membranes can be discussed along with ideal gases in the general physics course, to make the concept of osmotic equilibrium easier for our students to grasp in subsequent courses. While a real system can become quite complicated, this ideal model provides an initial understanding on which these details can later be based. The ideal gas model can also be used to consider the rate of transport of solvent in a system not in equilibrium; until recently this has been an area of disagreement among physiologists.

This paper discusses osmotic equilibrium and nonequilibrium flow at an elementary level using an ideal gas model. The justification for using such a simple model is given in the Appendices: Appendix I justifies the use of partial pressure in a dilute solution, and Appendix II reviews the irreversible thermodynamics of a semi-permeable membrane. Some physiological examples are included; these can be used in the physics course to maintain student interest.

OSMOTIC EQUILIBRIUM

The basic phenomenon with which we are dealing can be shown by a fairly simple lecture demonstration. The apparatus is shown in Fig. 1. A fine-bore tube is inserted through a one-hole rubber stopper, which is placed in one end of a cylinder of cellophane sausage casing; the other end is closed by a solid stopper. (String is tied around the cellophane to hold the stoppers in place.) The cylinder is filled with a sucrose solution colored with red ink for visibility. The cylinder is then immersed in water, and during the lecture

hour the red liquid will rise several feet in the capillary tubing.[1]

Let us try to understand this phenomenon by considering a similar experiment with ideal gases. (The justification for this model is given in Appendix I.) The situation we wish to consider is shown in Fig. 2. A box is divided into two compartments of volume V_1 and V_2 by a membrane which is permeable to gas atoms of species A but not to those of species B. If N molecules (M moles) of species A are introduced into either compartment, they will distribute themselves throughout the total volume of the box $V = V_1 + V_2$, with uniform concentration $n = N/V$ ($c = M/V$) and pressure $P_{1A} = P_{2A}$, as though the membrane were not there. Thus, since the membrane is permeable to A, equilibrium exists when the partial pressure of A is the same on both sides of the membrane. When molecules of species B are added to the first compartment they cannot pass through the membrane, so the pressure on that side is increased by the partial pressure of species B

$$P_B = n_B kT = c_B RT.$$

Transferring this result to the sucrose experiment, a solute concentration of c moles (n mole-
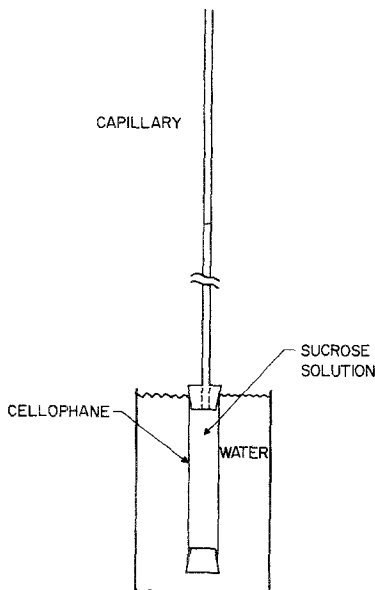

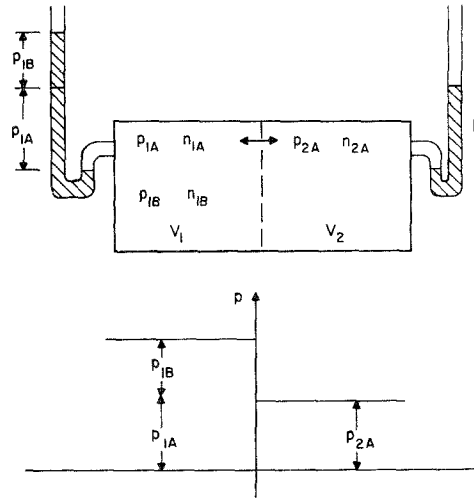FIG. 1. Demonstration of osmotic pressure.

FIG. 2. Ideal gas A can pass through the membrane separating the two compartments. Therefore $P_{1A} = P_{2A}$. The total pressure on the left exceeds that on the right by the partial pressure P_B.

cules) per unit volume will cause a partial pressure or osmotic pressure

$$\pi = nkT = cRT. \tag{1}$$

Since RT at room temperature is 22.4 liter–atm/mole, for a solvent concentration of 1 mole/liter, the osmotic pressure is 22.4 atm. The total pressure at the surface of the liquid in both the capillary and the outer container is one atmosphere. If the partial pressure of the sucrose inside the cylinder is π, the partial pressure of water in the cylinder must be π less than that outside. Thus, water will flow into the cylinder until the rise of water in the capillary has increased the total pressure in the cylinder by π.

The key to the ideal gas model discussed above is that molecules of gas A distribute themselves uniformly throughout both compartments, since they can pass freely through the membrane. Depending on the level of the course, this can be taken as self evident, or it can be derived using ideas from kinetic theory or thermodynamics. For example, equilibrium of gas A will exist when the number of molecules of A striking unit area of the membrane in unit time from each side is equal. This number is

$$n\langle v \rangle_{av}/4 = n(kT/2\pi m)^{1/2}, \tag{2}$$

so equilibrium requires that, $n_1 = n_2$, or, since $P = nkT$, $P_1 = P_2$. Alternatively, from a thermodynamic point of view, the classical entropy of an ideal gas is

$$S = Nk[\log V + (3/2) \log T + \text{const.}]. \quad (3)$$

This will be greatest when the gas fills the box.

Physiologists often speak of concentration work, the amount of work which must be done to concentrate a solute. While it is not directly related to osmotic pressure, it can also be discussed using the ideal gas model of a solution. Suppose that the membrane in Fig. 2 is a piston which is free to move. The excess pressure on side 1 will cause the piston to move to the right until compartment 1 occupies the entire volume. If an adjustable extra force is exerted on the piston so that it moves reversibly, the work done by the excess pressure of the gas on side 1 against this extra force is

$$W = \int_{V_1}^{V_1+V_2} \frac{M_B RT dV}{V} = M_B RT \log\left(\frac{V_1+V_2}{V_1}\right). \quad (4)$$

It would be necessary to do this work on the gas to move the piston back to its original position and reconcentrate species B.

OSMOTIC FLOW

There has been considerable controversy among physiologists about the nature of the flow which occurs when equilibrium does not exist. It is well known that the flow of solvent proceeds much more rapidly than would be expected for diffusion with the same concentration gradient,[2,3] but the explanation has been in dispute. The model of a semi-permeable membrane often used is a membrane pierced by pores which allow small solvent molecules to pass but which block larger molecules, such as proteins. Many workers in this field seem to have felt that bulk flow could not occur in small pores, though there is strong experimental evidence that it does.[3]

It does not seem to be widely recognized that the interaction of the transported molecules with other transported molecules so that they move collectively causes solvent flow to be more rapid

than the diffusion of a dilute solute. We can make this distinction clear in the general physics course. An analogy to the problem at hand is well known for the gaseous case: the distinction between self-diffusion and hydrodynamic flow in a tube. In each case there are many molecules, so that the mean free path for collision with some other molecule is much less than the tube radius. In the first case, self diffusion, there is no net flow. A few of the molecules are "tagged" and are in unequal concentration at either end of the tube. This is analogous to the diffusion of ions or small molecules through pores in a membrane. The net number of tagged molecules per second moving to the right through area πa^2 is given by[4]

$$dN/dt = -\Gamma_d \pi a^2 (dP/dx), \quad (5)$$

where $\Gamma_d = \langle v \rangle_{av} \lambda / 3kT$; Γ_d represents a diffusion coefficient in which the units on each side of the equation differ. The rate of transport is proportional to the area of the tube because the diffusing molecules, though they frequently strike the other molecules of the gas, are moving independently of each other. The second case is viscous hydrodynamic flow obeying Poiseuille's law.[5] Expressing it in the present notation for a tube of radius a and using the kinetic theory expression for the viscosity of an ideal gas we have

$$dN/dt = -(3\pi a^4/8m\langle v \rangle_{av}\lambda)(dP/dx). \quad (6)$$

Putting this in the same form as the previous equation, we get $\Gamma_h = (a/m\langle v \rangle_{av})(3a/8\lambda)$. The ratio is (using $\langle v \rangle_{av}^2 = 8kT/\pi m$)

$$\Gamma_h/\Gamma_d = \pi(3a/8\lambda)^2. \quad (7)$$

The hydrodynamic flow is much greater than the diffusive flow, being proportional to the square of the tube area, because all the molecules are involved in the transport process. They undergo frequent collisions with one another and move collectively. In diffusion, the molecules having a concentration gradient collide with one another infrequently, although their mean free path for collisions with water molecules is small. Appendix II summarizes thermodynamic arguments which show the similarity of osmotic and hydrostatic

pressure differences in causing bulk flow, as well as the difference between bulk flow and diffusion. A model for the liquid case is also presented.

BIOLOGICAL EXAMPLES

A few examples of situations in physiology where osmosis is important are given in this section, as a source for lecture examples or homework problems. While these are well known to physiologists, they are not usually accessible to physics teachers.

Swelling of a Cell in a Hyptonic Solution

Suppose that an ideal membrane which is permeable to solvent A encloses a volume containing both solvent A and solute B. Further suppose that this apparatus is immersed in a bath of solvent A. The pressure in the interior volume will always be greater than the pressure outside by an amount $\pi = C_B RT$; the bath is said to be hypotonic. The interior volume will expand until the membrane bursts or provides sufficient force to maintain the pressure difference. This is seen in physiology: For example, red blood cells placed in water will swell until they burst, because the cell membrane is impermeable to many of its constituent molecules.[6]

Plasma Flow Through a Capillary Wall.

Osmotic pressure is important in the transfer of oxygen from the blood to the cells of the body and in the collection of carbon dioxide by the blood. The transfer takes place as the blood flows through capillaries, which are very fine (about the diameter of a red cell). The blood cells move in plasma, which consists of water, electrolytes, small molecules such as glucose and dissolved oxygen, and larger molecules, such as proteins. The wall of the capillary is permeable to the water and small molecules; these together we will call "solvent." Outside the capillaries is the interstitial fluid which bathes the cells. Osmotic pressure is responsible for the flow of solvent from the capillary to the interstitial fluid at the arterial end and back into the capillary at the venous end. The flow is shown schematically in Fig. 3(a). Typical pressures, relative to atmospheric, are shown. The total pressure is P, and the osmotic pressure is π. The partial pressure of the solvent is therefore $P - \pi$. The total gauge pressure along the
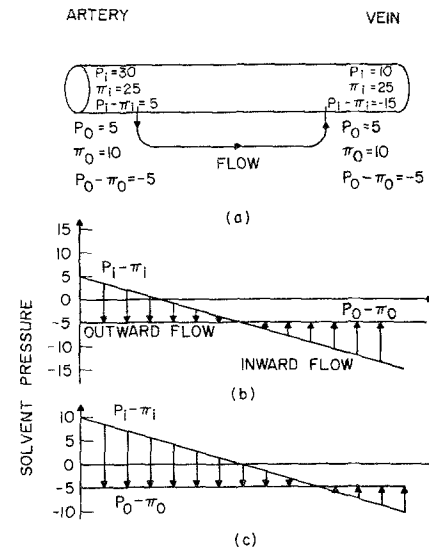

FIG. 3. Pressure relations along a capillary from the arterial to the venous end. Pressures are in Torr. (a) Typical pressures at the end of a capillary. (b) Pressures along capillary, assuming a constant gradient. When the partial pressure of the solvent is greater inside than outside, there will be outward flow; in the converse case there will be inward flow. (c) Initial situation (before P_0 has increased) in hypoproteinemia.

capillary drops from 30 Torr to 10 Torr because of the viscous resistance to flow. The osmotic pressure in the capillary is about 25 Torr because of protein molecules which are too large to pass through the pores in the capillary wall. The total pressure in the interstitial fluid outside the capillary is about 5 Torr above atmospheric because of the elasticity of the tissues. (There is currently some debate about the exact value.) There is some protein in the interstitial fluid, giving an osmotic pressure of about 10 Torr. The solvent partial pressure $P - \pi$ is plotted in Fig. 3(b). In the first half of the capillary the flow is outward; in the last half it is inward.

In several diseases, such as malnutrition, intestinal or liver disease, the patient experiences hypoproteinemia, a lowering of the concentration of protein in the blood. Thus π_i is reduced. If π_i were suddenly reduced by 5 Torr the curve for $P_i - \pi_i$ would be elevated, as shown in Fig. 3(c). This would cause a net migration of fluid from the capillary, which in turn would raise P_0 due to tissue distension, until the amount of fluid leaving the capillary was equal to that entering.
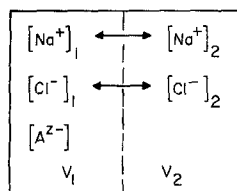
Fig. 4. Distribution of species when a potential difference exists across the membrane.

This accumulation of fluid outside the capillaries between the cells is called edema. Edema can also be caused by failure of the right side of the heart, which causes P_i on the venous side of the capillary to rise. This also raises the partial pressure of solvent in the capillary compared to the partial pressure outside.

Equilibrium with a Potential Energy Difference: The Nernst Equation

In the considerations of an ideal gas above, we have assumed that the concentration of the species which can pass through the membrane is the same on both sides. This will not be true if the molecules are charged and a potential difference exists across the membrane. Concentrations will differ by a Boltzmann factor because of the potential energy difference. In physiology this is usually written as the Nernst equation (F is the Faraday and z the valence):

$$V_2 - V_1 = (RT/zF) \log(n_1/n_2)$$
$$= (RT/zF) \log(c_1/c_2). \quad (8)$$

There are several ways to derive this equation. The most direct is to use the Boltzmann factor. If that has not been discussed in the physics course, one can use the analogy between the electrical potential energy difference of an ion of charge ze, which is $ze(V_2 - V_1)$, and the gravitational potential energy difference of a molecule, $U_2 - U_1 = mgh$. The concentration of gas in the atmosphere varies with height, even if the temperature is constant, because of the variation of potential energy. Macroscopic consideration of the pressure on a volume of gas and the ideal gas equation can be used to obtain the barometer equation[7]:

$$P_2/P_1 = n_2/n_1 = c_2/c_1 = \exp[-(U_2 - U_1)/kT]. \quad (9)$$

Solving this equation for the potential difference gives

$$U_2 - U_1 = kT \log(c_1/c_2). \quad (10)$$

The potential energy difference in the electrical case is

$$U_2 - U_1 = ze(V_2 - V_1). \quad (11)$$

Then Eq. (10) becomes

$$V_2 - V_1 = (kT/ze) \log(n_1/n_2). \quad (12)$$

Multiplying numerator and denominator on the right by Avogadro's number and introducing the definition of the Faraday as charge per mole of electrons completes the proof. One may also derive Eq. (11) by considering the work necessary to concentrate the gas. As the gas moves to a region of lower potential energy, work is done on it by the force giving rise to the potential energy. If the gas remains at the same temperature, this work is just that required to make the gas more concentrated [see Eq. (4)]. If the potential energy of each molecule changes by $U_2 - U_1$ and there are N molecules, the total energy change is equal to the concentration work.

$$N(U_2 - U_1) = NkT \log(V_2/V_1)$$
$$(U_2 - U_1) = kT \log(n_1/n_2).$$

In the case of a liquid, this equation can be obtained directly, but not at the level of an introductory course. We are dealing with diffusion or Brownian motion of particles under the influence of a constant external force. This is described by the Smoluchowski equation,[8] which has Eq. (9) as its steady state solution.

Gibbs–Donnan Equilibrium

A difference in concentration of charged ions can be passively maintained across a membrane if there is one charged species which cannot cross the membrane. Such an equilibrium situation is called Gibbs–Donnan equilibrium and provides an example of applying the Nernst Equation. Assume that one has a positive ion (Na^+) and two anions, one of which can pass through the membrane (Cl^-) and one of which cannot (A^{z-}), as shown in Fig. 4. Usually A^{z-} is a protein

TABLE I. Gibbs–Donnan equilibrium of plasma and interstitial fluid.

	Plasma	Interstitial fluid
Protein concentration	1.0×10^{-3} mole/liter	0
Protein charge	$-18e$	
Chloride concentration	146.25×10^{-3} mole/liter	155×10^{-3} mole/liter
Sodium concentration	164.25×10^{-3} mole/liter	155×10^{-3} mole/liter
Total ion concentration	311.5×10^{-3} mole/liter	310×10^{-3} mole/liter
Pressure excess in plasma	29 Torr	
Potential of plasma with respect to interstitial fluid	-1.5×10^{-3} V	

with a valence of about -18. Let the membrane potential difference be $V_2 - V_1$. If we let the chemical symbol in brackets represent the concentration of each substance, we have, from the Nernst equation or Eq. (9)

$$[\text{Na}]_2/[\text{Na}]_1 = \exp[-e(V_2 - V_1)/kT],$$

and

$$[\text{Cl}]_2/[\text{Cl}]_1 = \exp[e(V_2 - V_1)/kT],$$

from which

$$[\text{Na}]_2/[\text{Na}]_1 = [\text{Cl}]_1/[\text{Cl}]_2. \tag{13}$$

Since the solution must be electrically neutral (except for a thin layer of charge at each surface of the membrane), we can write two additional equations:

$$[\text{Na}]_1 = [\text{Cl}]_1 + [zA]$$
$$[\text{Na}]_2 = [\text{Cl}]_2. \tag{14}$$

These can be combined with Eq. (13) to determine the various concentrations and hence $V_2 - V_1$. It is then interesting to insert typical numbers for the concentrations and membrane thickness to determine the charge per unit area on the membrane. Typical values[9] for a simplified model of plasma and interstitial fluid are shown in Table I; the temperature is assumed to be 310°K. The difference in total concentrations of all species on each side of the capillary wall can then be used in Eq. (1) to find the equilibrium pressure difference. Assuming a membrane thickness of 3×10^{-7} m,

the electric field is 5000 V/m, which requires a charge density of 4.5×10^{-8} C/m^2 on each side of the membrane. This would correspond to an excess charge on 1 out of every 10^{11} atoms in a layer 3×10^{-7} m thick.

CONCLUSION

The main features of osmotic pressure and osmotic flow are the same whether one speaks of a gas or a dilute solution. A discussion of equilibrium and nonequilibrium effects in the general physics course can be helpful to students in the life sciences. Some equilibrium examples from physiology are given.

ACKNOWLEDGMENTS

APPENDIX I. RELATION OF A DILUTE SOLUTION TO AN IDEAL GAS

One may well wonder why the equation for an ideal gas has any relevance to a dilute solution. The discussion has been couched in these terms for two reasons: (1) The expressions for the energy, entropy, free energy, and partial pressure of a dilute solution have the same dependence on concentration as they do in an ideal gas; (2) the

TABLE II. Comparison of thermodynamic quantities for an ideal gas with those for a dilute solution; N_i =molecules of species i, M_0 =moles of solvent, and M_i =moles of solute.

Quantity	Gas	Dilute Solution
E_i	$(3/2)N_i kT$	$M_i e_i(T)$
S_i	$N_i s_i(T) - N_i k \log(N_i/V)$	$M_i s_i'(T) - M_i R \log(M_i/M_0)$
F_i	$N_i f_i(T) + N_i kT \log(N_i/V)$	$M_i f_i'(T) + M_i RT \log(M_i/M_0)$
G_i	$N_i g_i(T) + N_i kT \log(N_i/V)$	$M_i g_i'(T) + M_i RT \log(M_i/M_0)$

derivation of the equations for the dilute solution is too complicated for the general physics course. The results of a careful discussion[10] will be summarized here.

Consider M_0 moles of solvent with total energy $E_0(T, P)$, volume $V_0(T, P)$, and entropy $S_0(T, P)$. Let there be M_i moles of dissolved substance A_i. Then, if $M_i/M_0 \ll 1$ for all such substances, one obtains expressions for the energy, E_i, entropy, S_i, Helmholtz free energy, F_i, and Gibbs free energy, G_i, which are compared to those for an ideal gas[11,12] in Table II. To find the effect of the solutes on the pressure in the solution, one uses the fact that

$$P = (\partial F/\partial V)_E, \qquad (15)$$

where F is the Helmholtz free energy. Fermi evaluates this derivative by letting the membrane move to the right. He shows that the excess pressure is given by

$$P = (RT/V)\Sigma M_i = \Sigma P_i. \qquad (16)$$

This is the same result as in Eq. (1) for the ideal gas. Since the total pressure is the pressure of the solvent P_0 plus the sum of these osmotic pressures, we may speak of the partial pressure of the solvent and of each solute.

APPENDIX II. FLOW OF LIQUIDS THROUGH MEMBRANES

The treatment given in terms of an ideal gas model is of course only an idealization. The thermodynamics for real fluids has been worked out[13] and will be summarized here. Suppose that one has a pressure difference ΔP and an osmotic pressure $\Delta\pi = RT\Delta c_s$ across a membrane, where Δc_s is the concentration difference of solute in

moles per unit volume. The velocity of the water (solvent) across the membrane is v_w and the velocity of the solute is v_s. One can write phenomenological relationships between these variables, assuming small values of ΔP and $\Delta\pi$, so that the relations are linear and introducing four phenomenological coefficients, L. The correct velocity variables turn out to be

$$v_w \approx v_w + \langle c_s \rangle_{av} \langle V_s \rangle_{av} v_s = L_P \Delta P + L_{PD} \Delta\pi$$

$$v_s - v_w = L_{DP} \Delta P + L_D \Delta\pi. \qquad (17)$$

The first equation represents the total volume flow across the membrane; the second represents the net motion of water and solute. Two other symbols have been introduced in Eqs. (17). The first $\langle c_s \rangle_{av}$, is the concentration (moles/liter of solution) of the solute averaged over both sides of the membrane. The molar volume $\langle V_s \rangle_{av}$ is the volume increase of the solution when one mole of solute is added. For an ideal solution it is nearly the volume of one mole of solute. The product is therefore the volume of solute per unit volume of solution. It is usually very small, but in certain cases it cannot be neglected. Requiring that the entropy of the system not decrease leads to the Onsager relations:

$$L_{PD} = L_{DP}$$

$$L_P L_D \geq L_{DP} L_{PD}.$$

For an ideal membrane such as the one considered in the body of this paper, there can be no flow of solute through the membrane: $v_s = 0$. In that case one can show that $L_P = L_D = -L_{PD}$, and both Eqs. (17) become

$$v_w = L_P(\Delta P - \Delta\pi).$$

If $\Delta\pi = 0$ and there is a pressure difference, we see that there will be a flow of water. If $\Delta P = 0$, a difference in osmotic pressure (solute concentration) will cause a flow of water in the opposite direction. There will be no flow of water when $\Delta P = \Delta\pi$.

In the non-ideal case, one can write $L_{DP} = L_{PD} = -\sigma L_P$, so that the three independent parameters are L_P, σ and L_D. The equations are then

$$v_w + \langle c_s \rangle_{av} \langle V_s \rangle_{av} v_s = L_P (\Delta P - \sigma \Delta\pi)$$

$$v_s - v_w = \sigma L_P \Delta P + L_D \Delta\pi. \qquad (18)$$

In this case, no volume flow occurs if $\Delta P = \sigma\Delta\pi$, a hydrostatic pressure which is less than that calculated in the ideal case. (Reference 13 shows that $\sigma < 1$ and that σ may in fact be negative in special cases.) To discuss flow of water or solute, it is most convenient to calculate the flux. The solute flux, J_s (moles/area-sec), will be given by the molar concentration times the velocity: $J_s = \langle c_s \rangle_{av} \langle v_s \rangle_{av}$. This can be obtained by adding Eqs. (17) and assuming that $\langle c_s \rangle_{av} \langle V_s \rangle_{av} \ll 1$:

$$J_s = \langle c_s \rangle_{av} L_P (1-\sigma) \Delta P + c_s (L_D - \sigma L_P) \Delta\pi. \quad (19)$$

The water flux is $\langle c_w \rangle_{av} \langle V_w \rangle_{av}$, which is approximately

$$J_w = \langle c_w \rangle_{av} L_P (\Delta P - \sigma \Delta\pi). \qquad (20)$$

[Actually, multiplying the first of Eqs. (18) by $\langle c_w \rangle_{av}$ shows that the left-hand side of Eq. (20) should be $J_w + \langle V_s \rangle_{av} \langle c_w \rangle_{av} J_s$, which is proportional to the total volume flux through the membrane.[14]] If a hydrostatic pressure $\Delta P = \sigma\Delta\pi$ is applied, there will be no net volume flow (which is approximately no water flow); but there will be diffusion:

$$J_s = \langle c_s \rangle_{av} (L_D - \sigma^2 L_P) \Delta\pi. \qquad (21)$$

This is often written in terms of a new coefficient, ω, the coefficient of permeability at zero volume flow:

$$J_s = \omega \Delta\pi,$$

$$\omega = \langle c_s \rangle_{av} (L_D - \sigma^2 L_P). \qquad (21a)$$

The second of the Onsager relations assures that ω will be positive and that the solute will not diffuse against the concentration gradient. The statement above that essentially no water flow occurs when $\Delta P = \sigma\Delta\pi$ is analogous to the statement which was made for the gaseous model: a species will have no osmotic flow if its partial pressure is the same on both sides of the membrane.

We are now in a position to understand the point of controversy. Physiologists were at one time surprised that an osmotic pressure difference causes a greater water flow than one would expect for discussion of tagged water under the same concentration gradient.[2,3] We can now show that one would expect no simple relationship between the two cases. The water flux for a given concentration difference ($\Delta\pi = RT\Delta c_s$) and no pressure difference is

$$J_w = \langle c_w \rangle_{av} \sigma L_P \Delta\pi. \qquad (22)$$

The coefficients L_P and σ refer to a particular combination of nonpermeant solute and membrane. For diffusion of tagged water through the membrane, one has a completely different set of coefficients with tagged water being the solute. If the membrane cannot distinguish between tagged and untagged water, there can be no net movement of solvent and solute under a pressure gradient, so $\sigma = 0$. Then Eqs. (19) and (20) become

$$J_w' + \langle V_s' \rangle_{av} \langle c_s' \rangle_{av} J_s' = \langle c_w' \rangle_{av} L_P' \Delta P$$

$$J_s' = \langle c_s' \rangle_{av} L_P' \Delta P + \langle c_s' \rangle_{av} L_D' \Delta\pi. \qquad (23)$$

Primes have been added to emphasize that these coefficients are different from those for the case of a nonpermeant solute. If there is no ΔP, we will have zero volume flow but there will be diffusion of tagged water:

$$J_s' = \langle c_s' \rangle_{av} v_s' = c_s' L_D' \Delta\pi = \omega' \Delta\pi. \qquad (24)$$

This is clearly different from the flux of Eq. (22)

In order to obtain further details we must use a model. The simplest is a series of $\mathfrak{N}$ pores per unit area through the membrane, whose radii, R, are

large compared to molecular size. One then assumes that the flow is laminar, so that Poiseuille's law can be applied. The volume of water transported through a single pore in one second will be $\pi R^4 \Delta P / 8\eta \Delta x$, where η is the viscosity of the water and Δx the membrane thickness. This is multiplied by $\langle c_w \rangle_{\mathrm{av}}$ to get the flow in moles per second. For the $\mathfrak{N}$ pores per unit area, the total flow is

$$J_w = \langle c_w \rangle_{\mathrm{av}} L_P \Delta P = (\langle c_w \rangle_{\mathrm{av}} \mathfrak{N} \pi R^4 / 8\eta \Delta x) \Delta P, \quad (25)$$

from which

$$L_P = \mathfrak{N} \pi R^4 / 8\eta \Delta x. \quad (26)$$

Note that L_P is independent of the solute concentration.

The simplest model of diffusion is somewhat more difficult. It was first given by Einstein in his papers on Brownian motion.[15] These papers are well worth reading, since osmosis, diffusion, and Brownian motion are all intimately related. We will consider diffusion through large pores in which the solute is unimpeded, and for which σ is therefore zero, so that Eq. (24) applies. We will further assume that the particles are spherical, have radius r, and that the pores are large enough so that we can neglect interactions of the particles with the walls. Each sphere will experience a force due to the surrounding water and a force exerted by collisions with the other spheres. Instead of considering the microscopic details, we will consider only the average effects. We will assume the force due to the surrounding water is given by a viscous drag $f = 6\pi\eta rv$ on each sphere, where v is the velocity of the sphere relative to the water. There will be a force exerted by other spheres only if there is a concentration gradient. To calculate this, imagine two planes perpendicular to the axis of the cylindrical pore, at x and at $x + \Delta x$. The partial pressure of solute to the left of the plane at x will exert a positively directed force across the plane equal to $\pi(x) \pi R^2$. The net force on the enclosed volume $\pi R^2 \Delta x$ is

$$- (\pi R^2)(d\pi/dx) \Delta x,$$

so that the force per unit volume due to the

osmotic pressure gradient is $- (d\pi/dx)$. This is the force of solute molecules on other solute molecules. To see this, imagine an infinitely thin piston at x, which is free to move, and which is completely permeable to water but impermeable to the spheres. It will move along with the spheres as they drift, experiencing a force due to spheres on its left and transmitting that force to spheres (not to water) on its right. If N_A is Avogadro's number, there are $\langle c_s \rangle_{\mathrm{av}} N_A$ solute spheres per unit volume, and the force per sphere is

$$- (\langle c_s \rangle_{\mathrm{av}} N_A)^{-1} d\pi/dx.$$

The solute spheres acquire a terminal velocity when this is balanced by viscous drag:

$$v = \Delta\pi / \langle c_s \rangle_{\mathrm{av}} N_A 6\pi\eta r \Delta x.$$

If the membrane again has $\mathfrak{N}$ pores per unit area, the total flux will be

$$J_s' = (\mathfrak{N} R^2 / 6N_A \eta r \Delta x) \Delta\pi, \quad (27)$$

from which

$$L_D' = (\mathfrak{N} R^2 / \langle c_s \rangle_{\mathrm{av}} 6N_A \eta r \Delta x). \quad (28)$$

The ratio of hydrodynamic flow to self diffusion through the pores when $\Delta P = \Delta\pi$ is then

$$g = J_w / J_s' = 3\pi \langle c_w \rangle_{\mathrm{av}} N_A r R^2 / 4. \quad (29)$$

If we use $\langle c_w \rangle_{\mathrm{av}} = 1/18$ mole/cm³, and $r = 2 \times 10^{-8}$ cm, we have

$$g = J_w / J_s' = (R/2.5 \times 10^{-8} \text{ cm})^2. \quad (30)$$

According to this, the hydrodynamic flow will be 100 times the diffusive flow for $R = 25 \times 10^{-8}$ cm. The ratio will increase as R^2, as in the gaseous model of Eq. (7). Of course, for pores this small, the assumptions of the model are quite questionable. Corrections to the model have been made by Kedem and Katchalsky[16] and by Bean.[17] Bean quotes experiments by Kauffman and Leonard[18] on the diffusion of various sugars through cellophane. He applies a refined model to their data

and obtains pore diameters of 20–40 Å; other workers obtain 60–80 Å for cellophane. A typical value of g for cellophane is 80; on the other hand there are membranes for which $g = 1$. Bean reviews the existing work on fine pores, where our assumptions break down, and concludes that there is room for improvement.

[1] This cannot be made a quantitative experiment because the cellophane is not perfectly impermeable to the sucrose; after a time the liquid in the capillary will begin to fall. The rate of the effect is enhanced by using a small bore capillary and a large area of cellophane.

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