Five popular misconceptions about osmosis

Eric M. Kramer and David R. Myers

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Eric M. Kramer[a)]
Physics Department, Bard College at Simon's Rock, Great Barrington, Massachusetts 01230

David R. Myers
Chemistry Department, Bard College at Simon's Rock, Great Barrington, Massachusetts 01230

Osmosis is the flow of solvent across a semipermeable membrane from a region of lower to higher solute concentration. It is of central importance in plant and animal physiology and finds many uses in industry. A survey of published papers, web resources, and current textbooks reveals that numerous misconceptions about osmosis continue to be cited and taught. To clarify these issues, we re-derive the thermodynamics of osmosis using the canonical formalism of statistical mechanics and go on to discuss the main points that continue to lead to misunderstandings. © *2012 American Association of Physics Teachers.*
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I. INTRODUCTION

Osmosis is the flow of solvent across a semipermeable membrane from a region of lower to higher solute concentration. It is of central importance for growth and transport in plants, renal, and cardiovascular physiology in animals, and a range of industrial processes including recent attempts at commercial power generation.[1] Despite its importance, a range of surprising misconceptions about osmosis continue to appear in papers, web sites, and textbooks. Erroneous ideas about osmosis are especially common in educational materials aimed at students of chemistry and biology. Once learned, these errors influence the thinking of professionals throughout their careers. Popular misconceptions about osmosis center around the five questions listed below. In this paper, we present the correct answers to these questions and discuss the surprising persistence of the incorrect answers.

Five questions about osmosis. (Answers are summarized in Sec. V).

(1) Is osmosis limited to mixtures in the liquid state?
(2) Does osmosis require an attractive interaction between solute and solvent?
(3) Can osmosis drive solvent from a compartment of lower to higher solvent concentration?
(4) Can the osmotic pressure be interpreted as the partial pressure of the solute?
(5) What exerts the force that drives solvent across the semipermeable membrane, overcoming both viscous resistance and an opposing hydrostatic pressure gradient?

The canonical osmosis experiment is shown in Fig. 1. Two compartments are separated by a membrane that can pass molecular species A (the solvent) but not species B (the solute). Membrane semi-permeability is due to the presence of small pores, whose size and chemical affinity admit solvent but not solute molecules. One compartment (#1) contains a mixture of A and B, while the other compartment (#2) contains only A. The pressure in each compartment is controlled by a piston as shown. Mechanical equilibrium requires that the solution be maintained at a higher pressure than the pure solvent. The equilibrium pressure difference is called the osmotic pressure Π of the solution. If $P_1 < P_2 + \Pi$, then additional solvent will continue to flow across the membrane into the solution. If $P_1 > P_2 + \Pi$, then solvent will flow out of the solution and into the pure solvent. This process is thermodynamically reversible because an infinitesimal increase in P_1 from just below to just above $P_2 + \Pi$ will reverse the direction of solvent flow. There are two noteworthy features of osmosis. First, solvent will flow from a region of lower to a region of higher hydrostatic pressure as long as $P_1 < P_2 + \Pi$. Second, in the limit of a dilute solute, the osmotic pressure is equal to the pressure of an ideal gas with the same concentration as the solute, $\Pi = k_B T c_B$, where k_B is Boltzmann's constant, T is the absolute temperature, and c_B is the concentration of B. The equivalence between osmotic pressure and the ideal gas law was first published by van't Hoff in 1887 (Ref. 2) and is known as van't Hoff's law.

The correct thermodynamic theory of osmosis was first published by Gibbs in 1897 (Ref. 3) and can be found in many thermodynamics textbooks.[4] The mixture has a higher entropy per particle than the pure solvent due to the entropy of mixing, so entropy increase favors the flow of additional solvent into solution. Flow ceases when the hydrostatic pressure in the mixture exceeds that in the pure solvent by enough to make the solvent chemical potential in the two compartments equal.

Many of the current misconceptions about osmosis spring from the fact that Gibbs' theory provides little insight into the molecular kinetics of osmosis. That is, it offers no explanation for the flow in terms of interactions between solute molecules, solvent molecules, and the semipermeable membrane. An additional challenge is that the Gibbs free energy has the pressure, rather than the volume, as a natural coordinate, so the relationship between osmosis and solvent concentration is not readily apparent. The solvent concentration is central to discussions of the relationship (or lack thereof) between osmosis and diffusion, as discussed further in the following sections.

This paper is organized as follows. In Sec. II, we derive the thermodynamics of binary mixtures using canonical statistical mechanics. In Sec. III, we derive van't Hoff's law and find a new expression for the solvent concentration difference across the membrane. In Sec. IV, we discuss the conditions under which the solvent is more concentrated in the solution compartment. In Sec. V, we answer the five questions posed above and discuss the misconception surrounding each of them. Readers wishing to avoid the more technical aspects of this paper may proceed directly to Sec. V. The paper is concluded in Sec. VI.
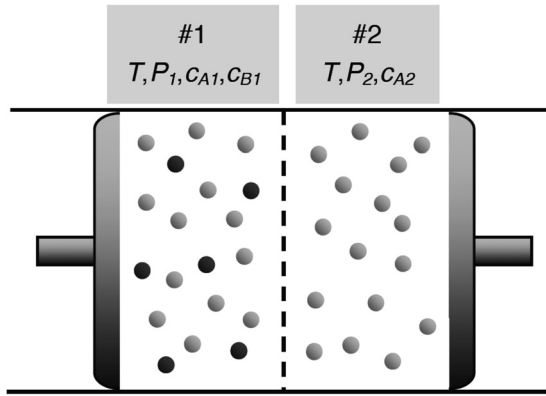
Fig. 1. The osmotic system: two compartments at temperature T are separated by a semipermeable membrane (dashed) that can pass solvent molecules of species A (gray) but not solute molecules of species B (black). Each compartment is maintained at constant pressure P_i by a piston. Symbols c_i denote concentrations.

II. THERMODYNAMICS OF A BINARY MIXTURE

Consider a binary mixture of molecular species with no nontrivial internal degrees of freedom (i.e., we neglect the energy of molecular vibrational and rotational modes). There are N_A molecules of species A and N_B molecules of species B. The particles interact via a pairwise potential $U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ that depends on the positions of the particles as well as their species. The total energy E of the mixture is then

$$E(\mathbf{r}_1 \dots \mathbf{r}_N; \mathbf{p}_1 \dots \mathbf{p}_N) = \sum_{i=1}^{N} \frac{p^2}{2m_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i \neq j}}^{N} U_{ij}(\mathbf{r}_i, \mathbf{r}_j), \quad (1)$$

where $N = N_A + N_B$, $\mathbf{r}_i$, and $\mathbf{p}_i$ are the position and momentum of particle i, and particles of type A are indexed before type B, so that the molecular mass m_i is m_A for $i = 1 \dots N_A$ and m_B for $i = (N_A + 1) \dots N$.

The semi-classical partition function for the mixture at temperature T in a volume V is[5]

$$Z(T, V, N_A, N_B) = \frac{1}{N_A! N_B!}\left(\frac{V}{\lambda_A^3}\right)^{N_A}\left(\frac{V}{\lambda_B^3}\right)^{N_B} Q, \quad (2)$$

where $\lambda_i = \hbar(2\pi/m_i k_B T)^{1/2}$ is the thermal wavelength of particle i ($\hbar$ being Planck's constant divided by 2π), and

$$Q(T, V, N_A, N_B) = \frac{1}{V^N}\int_V \mathbf{dr}_1 \dots \mathbf{dr}_N$$
$$\times \exp\left(-\frac{1}{2k_B T}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i \neq j}}^{N} U_{ij}(\mathbf{r}_i, \mathbf{r}_j)\right) \quad (3)$$

is the contribution to the partition function due to the potential energy. Using the Stirling approximation, the Helmholtz free energy is then

$$F(T, V, N_A, N_B) = -k_B T \ln(Z)$$
$$= N_A k_B T \ln\left(\frac{c_A \lambda_A^3}{e}\right)$$
$$+ N_B k_B T \ln\left(\frac{c_B \lambda_B^3}{e}\right) + V f(T, c_A, c_B), \quad (4)$$

where e is the base of natural logarithms, $c_i = N_i/V$ is the concentration of species i, and $f = -k_B T \ln(Q)/V$ is the contribution to the Helmholtz free energy per unit volume due to potential energy terms. The rightmost term is sometimes called the excess free energy because $f = 0$ corresponds to the case of an ideal gas mixture. In general, the integral represented in Eq. (3) cannot be solved, so the excess free energy cannot be expressed in closed form. For simple fluids, there are a range of empirical approximations available depending on the numerical accuracy desired in the equation of state. The simplest such approximation reproduces the van der Waals equation of state. The form of f is left arbitrary in the calculations that follow, and we require only that the mixture remains in a single, homogeneous phase.

Some insight into the thermodynamics of osmosis can be gained by considering the entropy S and the internal energy U of the mixture, given by

$$S(T, V, N_A, N_B) = -\frac{\partial F}{\partial T}$$
$$= -N_A k_B \ln(c_A \lambda_A^3) - N_B k_B \ln(c_B \lambda_B^3)$$
$$+ \frac{5}{2}k_B(N_A + N_B) - V\frac{\partial f}{\partial T}, \quad (5)$$

and

$$U(T, V, N_A, N_B) = F + TS$$
$$= \frac{3}{2}k_B T(N_A + N_B) + V\left(f - T\frac{\partial f}{\partial T}\right). \quad (6)$$

As expected, the logarithmic terms in the free energy are strictly entropic in origin. We will see in Sec. III that the solute entropic term $\ln(c_B)$ is the formal source of the osmotic pressure. The reader should not think of this as the "solute entropy," however, because entropy is only defined for the mixture considered as a whole.

III. OSMOSIS

In this section, we consider an osmotic system. Because van't Hoff's law arises in the case of a dilute solute ($c_B \ll c_A$), it is helpful to Taylor expand the excess free energy to first order in c_B as

$$f(T, c_A, c_B) = g(T, c_A) + c_B h(T, c_A) + O(c_B^2), \quad (7)$$

where g is the excess free energy of the pure solvent and $h = (\partial f/\partial c_B)_{c_B=0}$ is a measure of how the excess free energy changes under an exchange of A for B (and not to be confused with Planck's constant). The pressure P and the chemical potentials μ_i are then

$$P = -\frac{\partial F}{\partial V} = k_B T(c_A + c_B) - g + c_A g' + c_A c_B h' + O(c_B^2), \quad (8)$$

$$\mu_A = \frac{\partial F}{\partial N_A} = k_B T \ln(c_A \lambda_A^3) + g' + c_B h' + O(c_B^2), \quad (9)$$

$$\mu_B = \frac{\partial F}{\partial N_B} = k_B T \ln(c_B \lambda_B^3) + h + O(c_B), \quad (10)$$

where primes denote derivatives with respect to c_A. Note that the chemical potential of the solvent μ_A, which controls the flux of solvent, includes the solute explicitly via a term that derives from the energy of interaction between A and B, $h' = (\partial^2 f / \partial c_A \partial c_B)_{c_B=0}$. A sufficiently strong attraction between A and B will give $h' < 0$. We will see below that this condition is sufficient for the solvent concentration in the mixture to exceed that in the pure solvent. Note also that the solute entropic term $\ln(c_B)$ contributes to the pressure as $k_B T c_B$. This term will become the osmotic pressure.

Now consider the osmotic system shown in Fig. 1. Two compartments are separated by a membrane permeable to solvent A but not to solute B. The solution compartment (#1) contains species A and B at concentrations c_{A1} and c_{B1}, respectively. The pure solvent compartment (#2) contains only A at concentration c_{A2}. The compartments are maintained in equilibrium by pistons exerting pressures P_1 and P_2, respectively. At equilibrium, the solvent chemical potentials are equal across the membrane, $\mu_{A1} = \mu_{A2}$. Substituting Eq. (9) for the chemical potential, this becomes

$$k_B T \ln(c_{A1}\lambda_A^3) + g'(T, c_{A1}) + c_{B1}h'(T, c_{A1})$$
$$= k_B T \ln(c_{A2}\lambda_A^3) + g'(T, c_{A2}). \tag{11}$$

In the dilute-B limit, the solvent concentrations in compartments 1 and 2 are approximately equal. Defining the solvent concentration difference $\Delta c_A = c_{A1} - c_{A2}$, we substitute $c_{A2} = c_{1A} - \Delta c_A$ into the right hand side of Eq. (11) and expand around c_{1A}. Keeping terms to first order in c_{1B} and Δc_A, Eq. (11) simplifies to

$$\frac{\Delta c_A}{c_{A1}} = -\kappa_T h' c_{A1} c_{B1}, \tag{12}$$

where $\kappa_T = [c_{A1}(k_B T + c_{A1}g'')]^{-1}$ is the isothermal compressibility. The solvent concentration difference is proportional to the solute concentration, but the sign may be positive or negative depending on particle interactions. If $h' < 0$, then $\Delta c_A > 0$ and the concentration of solvent is higher in the mixture than in the pure solvent.

Now we can confirm that this approach gives the correct expression for the osmotic pressure. Substituting Eq. (8) into $\Pi = P_1 - P_2$ and expanding c_{A2} around c_{A1} as above gives

$$\Pi = k_B T(c_{B1} + \Delta c_A) + (\Delta c_A)c_{A1}g'' + c_{A1}c_{B1}h'. \tag{13}$$

On substituting Eq. (12) for the concentration difference, this reduces to van't Hoff's law $\Pi = k_B T c_{B1}$, as expected. We see that terms depending on the interaction between particles all cancel to leading order, and the osmotic pressure originates with the solute entropic term $\ln(c_B)$. Thus, van't Hoff's law is independent of the state of the mixture and applies to liquids, gases, and supercritical fluids.

In Sec. IV, we examine further the conditions under which $\Delta c_A > 0$.

IV. THE CONCENTRATION DIFFERENCE

A. Gases

Although one does not usually think of gaseous mixtures when considering osmosis, we have already seen that van't Hoff's law is independent of the phase of the mixture. In this section, we consider both ideal and real gases.

There are no interactions between particles in an ideal gas mixture, so $h = 0$ and Eq. (12) becomes $c_{A1} = c_{A2}$. At equilibrium, the solvent concentrations in the two compartments are exactly equal.

For a mixture of dilute real gases, the excess free energy may be described using a virial expansion in powers of the concentration (see, for example, Ref. 5, Sec. 704) giving

$$f(T, c_A, c_B) = k_B T[(B_{AA}c_A^2 + 2B_{AB}c_A c_B + B_{BB}c_B^2) + O(c^3)], \tag{14}$$

so $g(T, c_A) = k_B T B_{AA} c_A^2$ and $h(T, c_A) = 2k_B T B_{AB} c_A$. Equation (12) then becomes

$$\Delta c_A = -2B_{AB}c_{A1}c_{B1} + O(c^3), \tag{15}$$

so the sign of the solvent concentration difference is determined by the mixed second virial coefficient B_{AB} (positive when $B_{AB} < 0$). The mixed second virial coefficient can in turn be related to the pairwise interaction potential between solute and solvent U_{AB}, using the cluster expansion[5]

$$B_{AB} = \frac{1}{2}\int d\mathbf{r}(1 - e^{-U_{AB}(\mathbf{r})/k_B T}). \tag{16}$$

A negative potential will tend to make the virial coefficient negative and a positive potential will tend to make the virial coefficient positive. In real gases at room temperature, the dominant contribution to the integral is the weakly attractive van der Waals force between molecules, so B_{AB} is typically negative (e.g., $B_{N_2O_2} = -11.9$ cm^3/mole at T $= 298$ K [Ref. 6]). Thus, an osmotic system with gaseous species will usually have $\Delta c_A > 0$.

B. Liquids

To understand the solvent concentration difference in a liquid osmotic system, we begin by asking what transformations are necessary to convert an isolated system of pure solvent at T, P_2, and c_{A2} into an isolated dilute binary mixture at T, P_1, c_{A1}, and c_{B1}. One can accomplish this by a sequence of two quasi-static, isothermal steps. First, increase the pressure on the pure solvent from P_2 to P_1. Second, exchange some of the solvent molecules for an equal amount of solute while maintaining the pressure constant at P_1. The first process will compress the solvent and increase its concentration, although the effect is typically small for a system far from its liquid-vapor critical point. The reader might guess that the second process, in replacing solvent by solute, will always yield a decrease in the solvent concentration. Surprisingly, this is not the case. If there is a sufficiently large attraction between solvent and solute, the isobaric exchange is accompanied by a decrease in the system volume and a corresponding increase in the concentration of the remaining solvent. The commonly tabulated quantity that describes isobaric volume change under solute-solvent exchange is called the *partial molar volume* of the solute.[7] If the partial molar volume of a solute is negative, then solvent concentration increases under the exchange. This indeed occurs for many aqueous ionic solutions because cations organize adjacent water molecules into a hydration layer that is denser than the relatively open hydrogen bond network that connects water molecules.[8,9]

As an example, consider sodium fluoride (NaF), a salt that dissociates to Na^+ and F^-. The partial molar volume of the compound is the sum of the two ionic partial molar volumes, which in this case is -3.3 cm^3/mol.[8] We thus see that there are both liquid and gaseous mixtures for which osmosis can drive solvent from a region of lower to higher solvent concentration.

V. ANSWERS TO THE QUESTIONS

Here, we provide the correct answer to each of the questions posed in Sec. I, as well as the popular misconception that contradicts each answer. We then discuss each answer in detail, paying particular attention to the likely reasons that the wrong answer remains popular.

Answers to questions presented in Sec. I.

(1) The phenomenology of osmosis is the same for gases, liquids, and supercritical fluids. The misconception is that osmosis is limited to liquids.
(2) Osmosis does not depend on an attractive force between solute and solvent. The misconception is that osmosis requires an attractive force.
(3) Osmosis can drive solvent from a lower to a higher solvent concentration compartment. The misconception is that osmosis always happens down a concentration gradient.
(4) The osmotic pressure cannot be interpreted as the partial pressure of the solute. The misconception is that it can.
(5) The semipermeable membrane exerts the force that drives solvent flow. The misconception is that no force is required to explain the flow.

A. The state of the mixture

In Sec. III, we showed that van't Hoff's law, and the phenomenology of osmosis more generally, is the same whether the mixture is a liquid, gas, or supercritical fluid.

The misconception. Numerous chemistry educational websites, and many chemistry textbooks, imply or state explicitly that osmosis is limited to liquids. There are two reasons for this. First, common experimental demonstrations of osmosis use a liquid solvent, typically water. Second, when van't Hoff's law is taught to students, it is invariably grouped together with a collection of other laws collectively called the colligative properties of dilute solutions (historically, the word "colligative" was chosen to describe those properties that are *bound together* by a shared, linear dependence on solute concentration). There are good reasons to group the colligative properties together, namely, they all derive from the same solute contribution to the free energy.[4] However, two of the colligative properties are explicitly applicable only to liquids: the elevation of the boiling point by added solute, and Raoult's law for the vapor pressure above a solution. Thus, students and professionals often infer that van't Hoff's law is similarly applicable only to liquid mixtures.

B. The interaction between solute and solvent

In Sec. III, we showed that osmosis is independent of the interactions between solute and solvent. There is no restriction on the shape of the interaction potentials other than the general requirement that the pure solvent and the mixture each exist as a single, homogeneous phase.

The misconception. The central question of osmosis is why additional solvent will flow into the solution compartment despite the fact that it is held at a higher hydrostatic pressure. Below, we will see that there is a force that drives solvent into the solution, but the explanation is subtle and not generally known outside the field of physics. Instead, some authors favor the incorrect view that the solute must exert an attractive force on the solvent to somehow "pull" it across the membrane (e.g., Refs. 10 and 11). This idea has the advantage of simplicity and is readily tied to the idea that the solute be miscible in the solvent.

C. Solvent flow and solvent concentration

In Sec. IV, we showed that osmosis can drive solvent flux from a region of lower to higher solvent concentration. This observation was published at least as early as 1969,[12] yet it continues to surprise many professionals.

The misconception. Students in biology and chemistry are typically taught that osmosis is a special case of simple diffusion. The idea is that solute molecules displace the solvent and thereby decrease the solvent concentration. Then, it is argued that osmotic flow is simply the diffusion of solvent through the pores of the membrane. Many textbooks offer an equivalent kinetic argument stating that solvent molecules arrive at a membrane pore with greater frequency from the pure solvent side (e.g., Refs. 13 and 14). The confusion of osmosis with simple diffusion dates to the turn of the 20th century. For example, in his 1904 textbook *Theoretical Chemistry*,[15] Walter Nernst wrote (p. 157), "the diffusion of cane sugar in water…obviously involves the same expansive force which we have learned to call the osmotic pressure."

This analogy between osmosis and simple diffusion is not valid. In addition to our comments about solvent concentration we can offer a second objection. Unlike osmosis, diffusion is not a thermodynamically reversible process. There is no small change in the external conditions of a diffusing system that will reverse the flux of solute and solvent. Osmosis and simple diffusion are distinct phenomena. Not surprisingly, the analogy also fails to make quantitatively correct predictions. Experiments have repeatedly shown that the water flux during osmosis is too large to be accounted for by Fick's law for diffusion.[16–19]

As for why the analogy between osmosis and diffusion has persisted up to the present, the reasons seem to be simplicity and pedagogic utility. The osmosis-diffusion analogy treats both the membrane and the solute as passive components whose only role is steric. Then, by making the analogy with diffusion, no additional concepts are required. The analogy is pedagogically useful in that it reinforces the idea that osmotic water transport, like diffusion, is a passive process; a cell does not need to metabolize ATP to drive the flux.

D. Osmotic pressure and partial pressure

The pressure of an ideal gas mixture may be formally written as the sum of the ideal gas pressures of each species separately, in which case the terms in the sum are called the partial pressures.[4,5] For an osmotic system of ideal gases, the pressure in the mixture compartment is $P_1 = k_B T c_{A1} + k_B T c_{B1}$ and one can say the first term on the right is the partial pressure of the solvent and the second term is the partial pressure of the solute. Comparing this to van't Hoff's law, $\Pi = k_B T c_{B1}$, we see that the osmotic pressure is equal to the

partial pressure of the solute. However, this only applies to a mixture of ideal gases, where the particles do not interact.

For a mixture of interacting particles, the concept of partial pressure ceases to be valid. For example, the virial expansion for the pressure of a binary mixture, to second order in the concentrations, is[5]

$$P = k_B T[(c_A + c_B) + (B_{AA}c_A^2 + 2B_{AB}c_A c_B + B_{BB}c_B^2)$$
$$+ O(c^3)], \qquad (17)$$

where the B_{ij} are the second virial coefficients at temperature T. The nonzero cross-term means that the pressure is no longer expressible as a sum, $P \neq P_A(c_A) + P_B(c_B)$. Therefore, the concept of partial pressure is only well-defined for an ideal gas mixture and not for interacting systems. In general, one cannot describe the osmotic pressure as the partial pressure of the solute.

From the perspective of molecular kinetics, the idea of partial pressure is appealing because it lets one understand the pressure in a compartment as being due to the bombardment of each molecular species independently against the walls. However, in the case of interacting systems, solute and solvent particles are continuously exchanging momentum through their mutual forces of interaction. The pressure of the system cannot be divided among the species in any meaningful way. To our knowledge, this point was first made in the context of osmosis in Ref. 20.

The misconception. The idea that osmotic pressure is the partial pressure of the solute has a long and controversial history. Superfically, it seems to offer a simple explanation for the symbolic equivalence between van't Hoff's law and the ideal gas law. However, when carried to its logical conclusion, it leads to a bizarre and unsupportable view of osmosis called the *solvent tension theory*.[21–24] The solvent tension theory assumes that the hydrostatic pressure in a fluid can be treated as the sum of a piece strictly due to the solute and a piece strictly due to the solvent, $P = P_A(c_A) + P_B(c_B)$. Then the osmotic pressure is assigned *ad hoc* to the solute, $P_B = k_B T c_B$. This division is supposed to explain osmotic flow as follows. Consider a beaker of water, open to the air at room temperature and 1.0 atm of pressure. Next, dissolve enough sugar in the water to create an osmotic pressure of 2.0 atm. Equating the osmotic pressure of the solution to the "partial pressure" of the sugar, mechanical equilibrium at the air-water interface would require the water to be at a "partial pressure" of -1.0 atm (i.e., in tension). The solvent tension model goes on to suggest that this "tensile water," brought into contact with a supply of pure water across a semipermeable membrane, will exert a tensile force that draws additional solvent into the solution. The solvent tension theory reached its greatest influence in the 1970's, including several publications in high-profile journals[24] before being discredited.[20]

E. The force driving osmotic flow

Unlike the preceding four misconceptions, the question of the force driving osmotic flow is not made clear by the usual thermodynamic treatments. In Sec. III, we discussed the fact that van't Hoff's law derives from a term in the entropy that can be assigned to the solute, but it is not immediately apparent how this entropic force acts on the solvent. To make progress, we turn to the molecular kinetic theory of osmosis.

This theory was developed gradually in the first half of the 20th century with contributions from many authors[25–30] and was first published in modern form in the 1950's.[31–34]

Osmotic flow is properly described as a bulk or hydrodynamic flow through the pores of the membrane. However, because viscous drag would rapidly bring any spontaneous flow to a stop, one must seek a force that continuously drives solvent through the pores into the solution. The force is exerted on the solvent by the semi-permeable membrane. A simple thought-experiment illustrates how this happens. Consider an idealized semipermeable membrane as a force field that repels solute but has no effect on the solvent.[25,27,31] The Brownian motion of the solute molecules bring them into occasional contact with this field, at which time they receive some momentum directed away from the membrane. Viscous interactions between solute and solvent then rapidly distribute this momentum to the solvent molecules in the neighborhood of the membrane. In this way, the membrane exerts a repulsive force on the solution as a whole. Since additional pure solvent can freely cross our idealized membrane, it flows into the solution compartment, gradually increasing the hydrostatic pressure in the solution. Thus, a pressure gradient builds up across the thickness of the membrane. This pressure gradient exerts a second force on the solution, capable of counteracting the membrane force. Quantitative treatments[31,32] show that the pressure difference required to stop solvent flow into a dilute solution is exactly $\Pi = k_B T c_B$. Nelson has aptly called the mechanism by which the membrane drives fluid flow the *rectification* of Brownian motion.[34]

The same force-balance argument can be applied to the case of a membrane with pores. In one popular approximation, semi-permeability is established by steric effects: solvent molecules are small enough to pass through the pores while solute molecules are too large.[32] A more realistic example is the movement of water molecules single-file through the hydrophilic channel of an Aquaporin (AQP) or other integral membrane protein.[19,35] In either case the pore or channel aperture defines a region that repels solute but not solvent, approximating the idealized case described in the previous paragraph. The basic features of the kinetic model are unchanged.

The misconception. The reader may notice that in the previous subsection we stated that the osmotic pressure could not be interpreted as the partial pressure of the solute, while here we are claiming that the force driving flow derives from the random thermal motions of the solute. The fact that both statements are true is at the heart of the difficulty some people have with osmosis. The rectified Brownian motion model requires two momentum transfers: first from membrane to solute, and then from solute to solvent. Those people desiring a simpler explanation will be inclined to make incorrect inferences. Notably, the failure of the concept of partial pressure in the mixture has been taken by some researchers to mean that the kinetics of the solute are entirely irrelevant for osmosis. They are then inclined to accept the incorrect idea that the role of the solute is simply to dilute the solvent, and proceed from there to an analogy between osmosis and diffusion.

VI. CONCLUSION

In this paper, we re-derive the thermodynamics of an osmotic system and discuss five misconceptions about osmosis

that continue to appear in textbooks, websites, and occasional published papers. These misconceptions are surprisingly robust. Nearly all have been discussed by other authors during the long history of osmotic research, and yet they continue to find adherents in each generation of professionals. The main reasons for the continued popularity of various misconceptions are their simplicity, their pedagogic utility, and the appeal of an analogy with more easily explained phenomena (in particular, solvation and simple diffusion). Part of the challenge facing those of us interested in improving the situation lies with disciplinary insularity. While authors in physics and biophysics have generally settled on the correct understanding of osmosis, these ideas have not penetrated into the fields of chemistry and biology. We suggest that improved communication between the disciplines on this topic would be beneficial.

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[a]Electronic mail: ekramer@simons-rock.edu

[1]S. E. Skilhagen, "The power of osmosis," Int. Water Power Dam Constr. **62**, 20–23 (2010).

[2]J. van't Hoff, "The function of osmotic pressure in the analogy between solutions and gases," Philos. Mag. **26**, 81–105 (1888).

[3]J. W. Gibbs, "Semi-permeable films and osmotic pressure," Nature **55**, 461–462 (1897).

[4]H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley and Sons, New York, 1985).

[5]R. Fowler and E. Guggenheim, *Statistical Thermodynamics* (Cambridge U.P., London, 1965).

[6]K. R. Hall and G. A. Iglesias-Silva, "Cross second virial coefficients for the systems $N_2 + O_2$ and $H_2O + O_2$," J. Chem. Eng. Data **39**, 873–875 (1994).

[7]A. F. Fucaloro, Y. Pu, K. Cha, A. Williams, and K. Conrad, "Partial molar volumes and refractions of aqueous solutions of fructose, glucose, mannose, and sucrose at 15.00, 20.00, and 25.00 C," J. Sol. Chem. **36**, 61–80 (2007).

[8]Y. Marcus, "Thermodynamics of solvation of ions. Part 6. The standard partial molar volumes of aqueous ions at 298.15 K," J. Chem. Soc., Faraday Transactions **89**, 713–718 (1993).

[9]B. Hille, *Ion Channels of Excitable Membranes*, 3rd ed. (Sinauer, Sunderland, Mass, 2001).

[10]F. Kiil, "Molecular mechanisms of osmosis," Am. J. Physiol. Regulatory Integrative Comp. Physiol. **256**, R801–R808 (1989).

[11]K. N. Frayn, *Metabolic Regulation: A Human Perspective*, 2nd ed. (Wiley-Blackwell, Oxford, 2003).

[12]F. B. Salisbury and C. Ross, *Plant Physiology* (Wadsworth Publishing, Belmont, 1969).

[13]T. E. Brown, H. E. H. LeMay, and B. E. Bursten, *Chemistry: The Central Science*, 9th ed. (Prentice-Hall, London, 2003).

[14]J. W. Moore, C. L. Stanitski, and P. C. Jurs, *Principles of Chemistry: The Molecular Science* (Brooks Cole, Belmont, CA, 2010).

[15]W. Nernst, *Theoretical Chemistry*, 4th ed. (Macmillan and Co., New York, 1904).

[16]A. Mauro, "Nature of solvent transfer in osmosis," Science **126**, 252–253 (1957).

[17]C. V. Paganelli and A. K. Solomon, "The rate of exchange of tritiated water across the human red cell membrane," J. Gen. Physiol. **41**, 259–277 (1957).

[18]R. Villegas, T. C. Barton, and A. K. Solomon, The entrance of water into beef and dog red cells, J. Gen. Physiol. **42**, 355–369 (1958).

[19]F. Zhu, E. Tajkhorshid, and K. Schulten, "Theory and simulation of water permeation in Aquaporin-1," Biophys. J. **86**, 50–57 (2004).

[20]H. Soodak and A. Iberall, "Osmosis, diffusion, convection," Am. J. Physiol. Regulatory Integrative Comp. Physiol. **235**, 3–17 (1978).

[21]G. A. Hulett, "Beziehung zwischen negativem druck und osmotischem druck," Z. Phys. Chem. **42**, 353–368 (1903).

[22]H. Hammel and P. Scholander, *Osmosis and Tensile Solvent* (Springer-Verlag, New York, 1976).

[23]H. Hammel and W. M. Schlegel, "Osmosis and solute-solvent drag," Cell Biochem. Biophys. **42**, 277–345 (2005).

[24]H. Hammel, "Colligative properties of a solution," Science **192**, 748–756 (1976).

[25]H. Lorentz, "Zur molekulartheorie verdunnter losungen," Z. Phys. Chem. **7**, 36–54 (1891).

[26]A. Einstein, *Investigations on the Theory of Brownian Movement* (Dover, New York, 1956).

[27]P. Ehrenfest, "On the kinetic interpretation of the osmotic pressure," Proc. K. Ned. Akad. Wet. **17**, 1241–1245 (1915).

[28]P. Debye, "Theorie cinetique des lois de la pression osmotique que des electrolytes forts," Recl. Trav. Chim. Pays-Bas **42**, 597–604 (1923).

[29]A. Eucken, E. R. Jette, and V. K. LaMer, *Fundamentals of Physical Chemistry* (McGraw-Hill, New York, 1925).

[30]E. Fermi, *Thermodynamics* (Dover, New York, 1956).

[31]G. Joos and I. M. Freeman, *Theoretical Physics*, 2nd ed. (Hafner Publishing, New York, 1951).

[32]G. B. Benedek and F. M. H. Villars, *Physics With Illustrative Examples From Medicine and Biology, Vol. 2. Statistical physics*, 1st ed. (Addison-Wesley, Reading, MA, 1974).

[33]G. Oster and C. C. Peskin, "Dynamics of Osmotic Fluid Flow," in *Mechanics of Swelling: From Clays to Living Cells and Tissues*, edited by T. Karalis (Springer-Verlag, New York, 1992) pp. 731–742.

[34]P. Nelson, *Biological Physics* (W.H. Freeman, New York, 2007).

[35]D. Gomes, A. Agasse, P. Thibaud, S. Delrot, H. Gers, and F. Chaumont, "Aquaporins are multifunctional water and solute transporters highly divergent in living organisms," Biochim. Biophys. Acta **1788**, 1213–1228 (2009).