5 November 1976, Volume 194, Number 4265 SCIENCE

Colligative Properties of Simple Solutions

Solutes simply dilute the solvent; they do not cause tension in the solvent.

Frank C. Andrews

In a recent article, Hammel (*1*) discusses the colligative properties of solutions with the goal of obtaining an intuitive, physical explanation of vapor pressure lowering, osmotic pressure, boiling point elevation, and freezing point depression. Hammel's view extends a picture painted in a number of papers by Scholander and his co-workers (*2*). Hammel argues that dissolving substance 2 (solute) in substance 1 (solvent) lowers the chemical potential μ_1 of the solvent by creating a negative pressure or tension that acts upon the solvent molecules. In this article I demonstrate that the conclusions Hammel draws from his thought experiments are by no means necessary. I show that the generally accepted molecular picture of pressure, vapor pressure, osmosis, boiling, and freezing in solutions is simple, intuitive, involves no mysterious solvent tensions, and explains the phenomena. The solute simply lowers the concentration of the solvent in the solution as compared to pure solvent. The colligative properties follow directly from this dilution of solvent by solute.

Thermodynamics of Colligative Properties

Hammel begins by observing that vapor pressure lowering, osmotic pressure, boiling point elevation, and freezing point depression are quantitatively related, which "suggests that they have a common explanation." Indeed, the thermodynamics of colligative properties is well known (*3*) and shows that they have precisely the same explanation:

The lowering of the vapor pressure of a solvent from $p_1{}^0$ to p_1 upon the addition of nonvolatile solute of mole fraction x_2 at constant temperature is given exactly by

$$\int_{p_1{}^0}^{p_1} [v_1{}^{\text{vap}}(p,T) - v_1{}^{\text{soln}}(x_2,p,T)]dp = \mu_1{}^{\text{solvent}}(p_1{}^0,T) - \mu_1{}^{\text{soln}}(x_2,p_1{}^0,T) \qquad (1)$$

Here $v_1{}^{\text{vap}}$ is the molar volume of solvent in the vapor, $v_1{}^{\text{soln}}$ is the molar volume of solvent in the solution, $\mu_1{}^{\text{soln}}$ is the chemical potential of solvent in the solution, $\mu_1{}^{\text{solvent}}$ is the chemical potential of pure solvent, and T is the temperature. Of course, one can often neglect $v_1{}^{\text{soln}}$ compared to $v_1{}^{\text{vap}}$ and use either the ideal gas law or some other simple empirical equation of state for $v_1{}^{\text{vap}}(p,T)$ to carry out the integration.

Osmosis involves the equilibrium between two phases of solute mole fractions x_2 and 0, through a membrane permeable to solvent only. The difference in μ_1 in the phases leads to solvent flux through the membrane into the solution, which flux can be halted by an excess pressure Π on the solution phase (in which the pressure is p^0). The equilibrium is governed exactly by the thermodynamic relation

$$\int_{p^0}^{p^0+\Pi} v_1{}^{\text{soln}}(x_2,p,T)dp = \mu_1{}^{\text{solvent}}(p^0,T) - \mu_1{}^{\text{soln}}(x_2,p^0,T) \qquad (2a)$$

Here a reasonable approximation is often to take $v_1{}^{\text{soln}}$ as independent of p (that is, an incompressible solution) and indeed to approximate it by the molar volume of pure solvent, $v_1{}^{\text{solvent}}$. If the solvent flux is halted instead by an excess negative pressure or tension Π applied to the solvent phase, the corresponding relation becomes

$$\int_{p^0-\Pi}^{p^0} v_1{}^{\text{solvent}}(p,T)dp = \mu_1{}^{\text{solvent}}(p^0,T) - \mu_1{}^{\text{soln}}(x_2,p^0,T) \qquad (2b)$$

The osmotic equilibrium is achieved locally, at the membrane, by the equality of μ_1 in the solutions immediately in contact with it.

The depression of the freezing point of a solution from T_0 to T at constant pressure p by the addition of solute of mole fraction x_2, which does not enter the solvent crystal, is given by

$$-\int_{T_0}^{T} \frac{\Delta h_1{}^{\text{fus}}}{T'} dT' = \mu_1{}^{\text{solvent}}(p^0,T) - \mu_1{}^{\text{soln}}(x_2,p^0,T) \qquad (3)$$

Here $\Delta h_1{}^{\text{fus}}$ is the molar heat of fusion of pure solvent at p^0 and T'. A reasonable approximation to the integrand in many cases is to take $\Delta h_1{}^{\text{fus}}$ as temperature-independent.

Similarly, the elevation of the boiling point of a solution from T_0 to T at constant pressure p^0 brought about by the addition of nonvolatile solute of mole fraction x_2 is given by

$$\int_{T_0}^{T} \frac{\Delta h_1{}^{\text{vap}}}{T'} dT' = \mu_1{}^{\text{solvent}}(p^0,T) - \mu_1{}^{\text{soln}}(x_2,p^0,T) \qquad (4)$$

Here $\Delta h_1{}^{\text{vap}}$ is the molar heat of vaporization of pure solvent at p^0 and T'. In this case also, the approximation that $\Delta h_1{}^{\text{vap}}$ is independent of T is often made.

The right-hand sides of Eqs. 1 through 4 have exactly the same form; thus, for a given solution, the left-hand sides must all be equal. The "common explanation" of these four phenomena lies therefore in the decrease in μ_1 upon the dissolving of solute in the solution, thus diluting the solvent. It is precisely this decrease that I will explore here, following Hammel's arguments so far as possible. In the process I will also have occasion to consider the effects of positive and negative pressures on solutions.

The author is professor of chemistry at the University of California, Santa Cruz 95064.

Hammel's Thought Experiment

Hammel first introduces the following thought experiment, shown in Fig. 1 [figure 2 in (*1*)]: Pure liquid solvent fills a closed chamber to a height 0. Three upright cylinders equipped with fixed membranes permeable only to solvent stand with their bases beneath the solvent surface. The chamber above the solvent and cylinders is filled with solvent vapor.

Cylinder 1 has the membrane at height 0 and is filled with a solution made from a solute whose partial molar volume is the same as that of the solvent, so that the solution density does not change with height from that of the pure solvent. The height h at which the solution stands above the solvent level is determined by solution concentration so that the osmotic pressure Π is exactly $\rho g h$ (ρ is the density of pure solvent and g is the acceleration of gravity) plus the difference in vapor pressure at the two heights:

$$\Pi = \rho g h + p^{\mathrm{vap}}(h) - p^{\mathrm{vap}}(0) = \rho g h + p^{\mathrm{vap}}(0)(e^{-M_1 gh/RT} - 1) \qquad (5)$$

where M_1 is the molecular weight of solvent and R is the gas constant. The validity of the term $\rho g h$ for hydrostatic head and the barometric formula used in Eq. 5 are well known (*4*). The second term on the right-hand side of Eq. 5 is usually negligible compared to $\rho g h$.

Cylinder 2 has the membrane just below height h. On top of the membrane is a very thin layer of the same solution that fills cylinder 1. Beneath the membrane is pure solvent. This solvent has the same density as the solution filling cylinder 1 (*5*), so that the solvent just below the membrane in cylinder 2 is at a pressure of $p^{\mathrm{vap}}(0) - \rho g h$. In this case, the column of solvent is supported from the top by the membrane, so that the weight of liquid below leads to negative pressure which becomes less negative as one goes down the column. The negative pressure works in the same way as the negative of a positive pressure in establishing osmotic equilibrium, as shown by Eq. 2b. The solution just above the membrane has the pressure $p^{\mathrm{vap}}(h)$, and so Eq. 5 for the osmotic equilibrium is satisfied.

Cylinder 3 has its membrane at height 0 and is filled to height h with a solution of a different solute in the same solvent. The concentration of solution is chosen so that μ_1^{soln} at height h equals the value of μ_1^{soln} at height h in the other columns [and of course $\mu_1^{\mathrm{vap}}(h)$ as well], so that all three liquid surfaces exposed at h are mutually in equilibrium with each other through the vapor. The solute molecules in cylinder 3 are chosen to be much denser than those in cylinders 1 and 2. Thus the solvent concentration is lower at height 0 in column 3 than it is in column 1. However, there is a larger hydrostatic head in column 3 because the solution is denser, and the effects of greater head and smaller concentration cancel precisely, as they must, to assure equilibrium across the membrane at the base of the column.

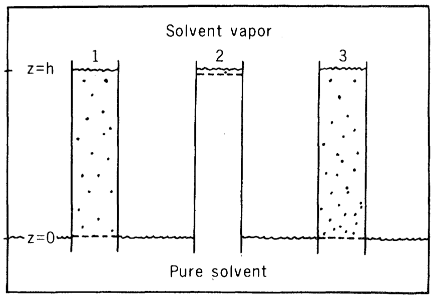

Fig. 1. Three columns fitted with membranes permeable to solvent only, immersed in solvent, filled with liquids, exposed to solvent vapor: A thought experiment employed by Hammel (*1*).

At this point, Hammel draws a series of conclusions reminiscent of speculations of Noyes (*6*) and Hulett (*7*). However, there is no mystery about the states of the columns, the vapor pressure over them, or the osmotic equilibria within them. It is well known (*4*) that equilibrium in the presence of g is governed by the equation

$$\mu_i + M_i g z = \text{constant} \qquad (6)$$

as opposed to the same expression without the $M_i g z$ term in the absence of gravity. Here M_i is the molecular weight of substance i, and z is the height.

From Eq. 6 we can conclude the following: For any equilibrium system in the earth's gravitational field which can be viewed as a set of subsystems, consider the group of all subsystems free to exchange substance i among themselves, however or wherever in the system this interchange can occur. These subsystems may contain any number of walls, phase transitions, semipermeable membranes, or other substances dissolved therein. At any fixed height z in the system at equilibrium, μ_i will have the same value in each subsystem into which it is possible for substance i to get. Across each membrane permeable to i, the equilibrium will be governed by the equality of μ_i on each side. Across each phase boundary the equilibrium will be governed by the equality of μ_i in each phase. The value of μ_i depends only on z and not on the choice of subsystem. Equilibrium is maintained in each small region of a subsystem; it depends on local properties and not on properties in a distant part of the subsystem.

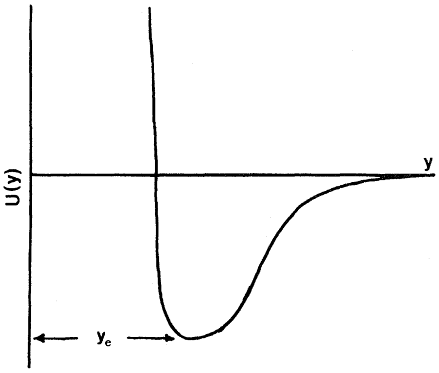

Fig. 2. Potential energy of interaction $U(y)$ between a molecule and the test surface as a function of the distance y between molecule and surface.

This conclusion from thermodynamics eliminates any sense of mystery or wonder from Hammel's thought experiment. He compares columns 1 and 3 and says they invalidate any explanation in which Π is attributed to the concentration of solute molecules at the membrane and simultaneously in which the vapor pressure lowering is attributed to the solute concentration at the surface. Yet those are precisely the causes to which they must be attributed. The larger Π across the membrane at the bottom of column 3 as compared to column 1 is required by the greater solute concentration at the membrane in column 3 and is maintained by the greater density of the solution in column 3. It is true, of course, that subjecting solvent to a tension of Π, as just below the membrane in column 2, permits an osmotic equilibrium with the layer of solution under its vapor pressure just above the membrane. But there is no suction on the solution above the membrane from the solvent below. The purpose of the membrane is precisely to eliminate such suction. Pressure differences are sustained by the membrane, whereas diffusive flow of solvent is permitted through it. Just because adding solute to solvent affects μ_i the same way as a negative pressure (tension) on the solvent would is no reason to believe that the solute creates a tension.

Next, Hammel considers the question of whether one can equate the vapor pressure at the surface of the solution with the solvent pressure at the surface. The difficulty with this question is that there is really only a pressure in the solution as such—it is caused by both solvent and solute—and it compresses both solvent and solute alike. It is artificial to attempt to distinguish between solvent pressure and solute pressure. In his attempt to do this, Hammel concludes that dissolving solute in water somehow creates a tension on the water molecules, a conclusion that is inconsistent with the carefully refined quantum mechanical model of molecules and how they interact with each other, and with the statistical mechanical model of how these interactions give solutions their unique properties. I now briefly summarize the intuitive picture painted by statistical mechanics of liquids, their pressures and tensions, vapor pressures, osmotic pressures, boiling points, and freezing points.

Pressure and Tension in Pure Liquids

Suppose one wants to measure the pressure in a pure liquid solvent. This requires insertion of a test surface of known area into the liquid in the region of interest. The force exerted by the solvent molecules on the surface in the direction normal to it is measured. The pressure in the liquid is this force divided by the area of the test surface. Each solvent molecule interacts with the test surface through a potential energy, $U(y)$, where U changes with distance y from the surface in the manner shown in Fig. 2. The force exerted by the molecule on the surface is the negative of the slope of this curve, and so, at separation distances less than y_e, molecules exert a positive force on the surface (that is, they push on it); at distances greater than y_e, molecules exert a negative force on the surface (that is, they pull on it). At any instant one obtains the total force on the test surface from the y values of all the neighboring molecules by summing the forces (slopes) obtained from Fig. 2.

In most conditions where the pressure is positive, the forces from molecules whose $y < y_e$ outweigh the forces from molecules whose $y > y_e$. Although there is a greater number of the latter, their attractive forces are smaller than the repulsive forces of the former, and so the pressure is positive (*8*).

In conditions like that prevailing in the solvent of column 2 (Fig. 1) where pressure is negative, solvent molecules are pulled apart a bit from each other and the surface. Even a very tiny expansion of the liquid changes the weighted average distance separating the molecules from just less than y_e to just greater than y_e. This change leads to a negative, rather than positive, net force on the wall and thus to a negative pressure (tension).

Pressure and Tension in Solutions

Now suppose one adds solute molecules to the solvent. These solute molecules interact with each other, with solvent molecules, and with the test surface through potentials shaped generally like that in Fig. 2, but with different well depths, different y_e values, and other minor differences. The force on the test surface now arises from both solvent and solute molecules. Nothing is changed except that there are two kinds of molecules, each contributing to the total pressure. This is true regardless of whether that pressure is positive or negative. Any part of the solution (solvent or solute) is under an average pressure which is this total pressure of the solution. There is no way to distinguish between solvent pressure, solute pressure, or total pressure in the solution. They are the same. This is important enough to emphasize: The average pressure on any small portion of the solution equals the average pressure on a solvent molecule in that portion equals the average pressure on a solute molecule in that region equals the macroscopic pressure as measured in that region of the solution. There is no way that particles interacting through intermolecular potentials such as those of Fig. 2 can sustain different pressures on solute and solvent in fluids at equilibrium.

Vapor Pressure of Solutions

If pure solvent is sealed into an evacuated chamber, some tiny fraction of the molecules in the surface acquire enough thermal energy through random motion to break out of the potential wells of their neighbors and enter the vapor. As the pressure in the vapor increases, the rate at which vapor molecules collide with the surface and stick increases. Eventually, the rates of evaporation and condensation become equal, and the equilibrium pressure is the vapor pressure of the solvent at this temperature.

Now, suppose we add nonvolatile solute to the solvent. In an ideal (Raoult's law) solution, solute molecules occupy the same fraction of the surface as their mole fraction (in a Henry's law solution, these fractions are not necessarily the same but they are proportional). The rate of evaporation of solvent is reduced by the mole fraction of solute. For the moment, however, nothing has changed in the vapor, and so it continues to condense at the same rate as before the addition. Thus, the pressure decreases until a new equilibrium is reached in which the rate of condensation is also reduced by the mole fraction of the solute. Since the rate of condensation is proportional to pressure (*9*), the final vapor pressure is also reduced by the solute mole fraction (for ideal solutions and ideal vapor).

Another way to view this situation is that the solute molecules dilute the solvent, thus decreasing μ_1^{soln}. Since μ_1^{soln} is a measure of the driving force for the molecular transport of solvent, a lower concentration of solvent must lower the value of μ_1^{soln}. The only change of pressure in the solution on the addition of solute comes from the decreased vapor pressure, which has a trivial effect on μ_1^{soln}. Were the pressure on the solvent to be drastically decreased as well, there would be two causes for μ_1^{solvent} to drop—the dilution of solvent and the decreased solvent pressure. There is no need to postulate a solvent tension; there is, to my knowledge, no mechanism whereby solvent tension is consistent with molecular theory, and solvent tension would lead to twice the actual decrease of μ_1^{solvent} observed for solutions.

Osmotic Pressure

Suppose a solvent-filled vessel is divided into two parts (A and B) by a membrane permeable to solvent only. Solvent flows at equal rates through the membrane from A into B and from B into A. Now suppose we add solute to B. At any given time, the fraction of the pores or channels through the membrane from B which are blocked by solute and thus cannot pass solvent is x_2. Thus the flow from B to A is cut by x_2. However, there is no change in A, and so the flow from A to B continues at the same rate. A net flow from A to B results, and, if the pressures remain equal on the two sides, this flow will continue at a decreasing rate as the solution in B is enriched in solvent.

However, if through any mechanism the pressure is allowed to increase in B, solvent molecules are pushed into the membrane with the extra force represented by the steeper slope (Fig. 2) for $y < y_e$. This increases the rate of solvent flow from B into A. Eventually an equilibrium is reached in which the decrease of flow caused by pore blockage by solute is exactly balanced by the increase of flow caused by increased pressure. This excess pressure is Π. This is what happens in columns 1 and 3 of Hammel's example.

Similarly, instead of increasing the pressure in B, we could decrease the pressure in A or even turn it into a tension. This would pull the solvent molecules in A away from the membrane with forces represented by the attractive region of Fig. 2 ($y > y_e$). This tension decreases the rate of solvent flow from A to B and can also lead to an equilibrium (as happens in column 2 of Hammel's example). As before, the pressure in B is higher than that in A by Π; the pressure difference is simply achieved by a tension on A rather than a pressure on B.

The above phenomenon could have been discussed in terms of the effect of concentration and pressure on μ_1^{soln}. Increased pressure increases the driving force for the flow of solvent and thus increases μ_1^{soln}, and decreased pressure similarly decreases μ_1^{soln}.

Boiling Point Elevation

No liquid is stable at finite temperature in the absence of an applied pressure that holds it together. Indeed, whenever the applied pressure on a liquid is less than the equilibrium vapor pressure of the liquid at the given temperature (vapor pressure as measured above), the liquid structure is unstable and the liquid will boil. Thus the boiling point is the temperature at which the vapor pressure of a liquid equals the applied pressure on the liquid.

Consider pure solvent under a fixed external pressure p^0. At its boiling point, T_0, the vapor pressure of the solvent will be p^0. If we now add nonvolatile solute, the vapor pressure of the resulting solution is lowered, as we saw above. The temperature T_0, which was the boiling point of the pure solvent, is now below the boiling point of the new solution. So long as the pressure stays fixed at p^0, the solution must be heated to a temperature above T_0 in order for its vapor pressure to become equal to what it was before the addition of solute. Thus T_0 increases when nonvolatile solute is added to solvent.

Freezing Point Depression

At the freezing point of pure solvent, $\mu_1^{\text{solid}} = \mu_1^{\text{liquid}}$; this is the condition for which the rate at which molecules are leaving the solid for the liquid exactly balances the rate at which molecules are leaving the liquid to enter the solid. Now let us add solute to the liquid, the solute being of such nature that it does not enter the solvent crystal structure, that is, the solute is incompatible with the crystal lattice and thus is excluded from it. The solute in no way affects the solid solvent, and so the rate of molecules leaving the solid for the liquid is unchanged. The solute, as before, dilutes the solvent in the liquid. Solvent bathes only a fraction of the crystal surface, and so the rate of molecules leaving the solution for the solid is decreased. The net result is a melting of the solid, which will disappear completely if temperature remains fixed. The melting of the solid, however, removes thermal energy from the system and lowers the temperature until a new equilibrium is achieved. Thus the freezing point of a solution is depressed over that of pure solvent.

Entropy of Solution

One can obtain an intuitive picture of the entropy change ΔS_{soln} that occurs upon formation of an ideal solution by using Boltzmann's expression, $k\ell\text{n}W$, for entropy [for example, see (*9*), p. 59]. Here k is Boltzmann's constant and W is the degeneracy of the thermodynamic state. The solution of N_1 solvent molecules and N_2 solute molecules has one source of degeneracy that the pure solvent and pure solute do not. That is the fact that of the $(N_1 + N_2)$ sites of molecules in the solution, N_1 of these are occupied by solvent and N_2 by solute. The number of different ways of assigning $(N_1 + N_2)$ sites into groups of N_1 and N_2 is

$$\frac{(N_1 + N_2)!}{N_1!\ N_2!}$$

This feature, the dilution of solvent by solute and solute by solvent, contributes

$$\Delta S_{\text{soln}} = k\ \ell\text{n} W_{\text{soln}} = k\ \ell\text{n}\ \frac{(N_1 + N_2)!}{N_1!\ N_2!} \qquad (7)$$

to the entropy of the solution. Use of Stirling's approximation for the large factorials yields

$$\Delta S_{\text{soln}} = k\ \ell\text{n}\left[\left(\frac{N_1 + N_2}{e}\right)^{N_1 + N_2}\left(\frac{e}{N_1}\right)^{N_1}\left(\frac{e}{N_2}\right)^{N_2}\right] \qquad (8)$$

$$\Delta S_{\text{soln}} = k\ \ell\text{n}\left[\left(\frac{N_1 + N_2}{N_1}\right)^{N_1}\left(\frac{N_1 + N_2}{N_2}\right)^{N_2}\right] \qquad (9)$$

$$\Delta S_{\text{soln}} = -\ N_1 k\ \ell\text{n}\ x_1 - N_2 k\ \ell\text{n}\ x_2 \qquad (10)$$

where x_1 is the mole fraction of solvent. For the formation of ideal solutions, this is the only contribution to ΔS. A property of ideal solutions is that they form without heat evolution; thus ΔH_{soln} (the enthalpy change) = 0 [for example, see (*3*), p. 191]. Thus, for the solution process,

$$\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}} = N_1 kT\ \ell\text{n}\ x_1 + N_2 kT\ \ell\text{n}\ x_2 \qquad (11)$$

The Gibbs free energy G of any equilibrium system is [for example, see (*3*), chapter 13]

$$G = \sum_i n_i \mu_i \qquad (12)$$

where n_i is the number of moles of i and μ_i is the partial molar Gibbs free energy. Thus, if we choose pure solvent and pure solute ($x_1 = 1$, $x_2 = 1$) as the standard states for them, the concentration dependence of μ_1 can be expressed simply by

$$\mu_1 = \mu_1^0 + RT\ \ell\text{n}\ x_1 \qquad (13)$$

where μ_1^0 is equal to the molar Gibbs free energy of pure solvent and $R = N_0 k$, where N_0 is Avogadro's number.

The entire decrease in μ_1 on dissolving solute in solvent to form an ideal solution is due to the dilution of the solvent by the solute. This dilution does not affect H or p. It simply increases the randomness by offering a larger number of sites for solvent molecules than were present in the pure solvent. This increases the S of the solvent, which in turn decreases μ_1^{soln}.

Ascent of Sap in Trees

Just because solutes do not exert tension on solvents does not mean that solutions cannot be under tension, for example, in living systems. The data of Scholander and his co-workers (*2*) or Plumb and Bridgman (*10*) suggest that columns of water exist under tension in some plants. But the cause of sap flow in such plants is simpler than the solvent tension model of Hammel. We can liken the columns in Fig. 1 to three trees. If the solvent vapor above them were any less dense, solvent would evaporate from their surfaces (leaves). This would lower μ_1^{soln} at the surfaces. Since μ_1^{solvent} at the bases of the columns (roots) is unaffected and so is the gravitational potential, solvent is driven up the columns (trees). In column 2, this would occur through a general bulk flow up the column, driven by an increase in tension as solvent moves upward. In columns 1 and 3, there would also be upward bulk flow of solution, driven by the decreasing pressure. Since this flow would drag solute along, the solute would have to keep diffusing back against the flow in order to maintain its previous equilibrium distribution, which is undisturbed by the evaporation of solvent. Other modes of transport could also be imagined. The entire flow of solvent, or the flow in parts of the tree, could be diffusive. The tree or such regions of it would then resemble a very thick osmotic membrane. Solutes could be encountered by the solvent in various parts of the tree, separated from the rest by membranes. Such regions could resemble parts of columns 1 or 3 of Fig. 1. Negative pressure could exist in regions of the sap, rather than in all of it, if those regions were properly separated from the rest by membranes. Such a region would resemble part of column 2.

Indeed, in theory, water transport may occur in plants by various means. The overall constraint governing passive flow (as opposed to active transport) is always Eq. 6, which in this case takes the form

$$\mu_{\text{root}} + Mgh_{\text{root}} = \mu_{\text{leaf}} + Mgh_{\text{leaf}} \tag{14}$$

Suppose, in order to find the maximum height to which the sap might rise, we take h_{root} to be zero and let the roots stand in a pool of water. In this case μ for water at the root is the same as μ for water vapor in saturated air, since those two phases would be in equilibrium with each other. If p_0 is the vapor pressure of water at the temperature of interest and rp_0 is the actual partial pressure of water vapor in the air, then r is the relative humidity. We may use the expression

$$\mu^0 + RT\ell\text{n}\, p$$

to express μ for a dilute gas [for example, see (*3*), p. 181] where μ^0 is μ of the pure gas at a pressure of 1 atmosphere. Then Eq. 14 becomes

$$\mu^0 + RT\,\ell\text{n}\, p_0 = \mu^0 + RT\,\ell\text{n}\,(rp_0) + Mgh \tag{15}$$

Thus the maximum height to which water may be driven up a tree is

$$h = \frac{RT}{Mg}\,\ell\text{n}\left(\frac{1}{r}\right) \tag{16}$$

At 25°C, this is $1.40 \times 10^4\ \ell\text{n}\ (1/r)$ meters, which, for example, is 1475 meters at $r = 90$ percent. This value is the same regardless of whether the mechanism of flow of water up the tree is pressure-driven bulk flow or diffusive flow or any combination of the two. The value is, of course, reduced if the tree stands in moist soil as opposed to a pool of water.

Summary

Vapor pressure lowering, osmotic pressure, boiling point elevation, and freezing point depression are all related quantitatively to the decrease in μ_1^{soln} upon the addition of solute in forming a solution. In any equilibrium system, regardless of whether it is in a gravitational field or whether it contains walls, semipermeable membranes, phase transitions, or solutes, all equilibria are maintained locally, in the small region of the equilibrium, by the equality of μ_1^{soln}. If there are several subsystems in a gravitational field, at any fixed height, μ_i will have the same value in each subsystem into which substance i can get, and $\mu_i + M_igh$ is constant throughout the entire system.

In a solution, there is no mechanism by which solvent and solute molecules could sustain different pressures. Both the solvent and solute are always under identical pressures in a region of solution, namely, the pressure of the solution in that region. Since nature does not know which component we call the solvent and which the solute, equations should be symmetric in the two (acknowledging that the nonvolatile component, if any, is commonly chosen to be solute).

Simple molecular pictures illustrate what is happening to cause pressure (positive or negative) in liquids, vapor pressure of liquids, and the various colligative properties of solutions. The only effect of solute involved in these properties is that it dilutes the solvent, with the resulting increase in S and decrease in μ_1^{soln}.

Water can be driven passively up a tree to enormous heights by the difference between its chemical potential in the roots and the ambient air. There is nothing mysterious about the molecular bases for any of these phenomena. Biologists can use the well-understood pictures of these phenomena with confidence to study what is happening in the complicated living systems they consider.

References and Notes

1. H. T. Hammel, *Science* **192**, 748 (1976).
→ P. F. Scholander, H. T. Hammel, E. D. Bradstreet, E. A. Hemmingsen, *ibid.* **148**, 339 (1965); → P. F. Scholander, A. R. Hargens, S. L. Miller, *ibid.* **161**, 321 (1968); P. F. Scholander, *Proc. Natl. Acad. Sci. U.S.A.* **55**, 1407 (19 → *Science* **156**, 67 (1967); *Microvasc. Res.* **3**, 215 (1971).
3. For example, see F. C. Andrews, *Thermodynamics: Principles and Applications* (Wiley-Interscience, New York, 1971), equations 29-22, 29-10, 29-15, and their derivations.
4. F. C. Andrews, *Science* **178**, 1199 (1972).
5. Actually, the compression of solution in column 1 and the expansion of solvent in column 2 causes the fluid density in column 1 to exceed that in column 2. Nevertheless, the osmotic pressures as given by Eqs. 2a and 2b in that case are not quite equal, since v_1^{soln} in the compressed column 1 is smaller than v_1^{solvent} in the expanded column 2.
6. A. Noyes, *Z. Phys. Chem.* **38**, 707 (1900).
7. G. A. Hulett, *Acta Phys. Chem.* **42**, 353 (1902).
8. Use of a potential with an infinitely hard core, as Hammel apparently chose, requires a bit of time-averaging in order to obtain the pressure, as opposed to the instantaneous measurement permitted by use of a more realistic continuous potential. However, such a choice in no significant way changes any of the arguments made herein.
9. F. C. Andrews, *Equilibrium Statistical Mechanics* (Wiley-Interscience, New York, ed. 2, 1975), p. 201.
10. R. C. Plumb and W. B. Bridgman, *Science* **176**, 1129 (1972).