validity of the claim by Wilcox *et al.*, and to seek a physical explanation."

What does one conclude from all of the above? The results of the past century suggest that a certain caution would be very appropriate. The one statement that I would make with complete conviction is that this appears to be an interesting subject that should be vigorously pursued.

Summary

If there is indeed an effect of the variable sun on the weather, the physical cause for it remains quite elusive (*12*). We should keep in mind the possibility that there may be several causes and several effects. The situation may change through the 11-year sunspot cycle and the 22-year solar magnetic cycle, as well as on longer time scales.

Work is proceeding at a lively pace at the institutions mentioned in this article and at many others around the world. The Soviet Union has long had considerably more workers interested in this field than has any other country. A bilateral agreement between the Soviet Union and the United States has considerably increased the interactions between workers interested in this subject, including an exchange of extended visits between the two countries.

A detailed knowledge of solar causes of geomagnetic activity is only now beginning to emerge after many years of scientific efforts. This suggests that a possible successful solution to the sun-weather problem will require a similar magnitude of effort. We look forward with interest and optimism to the results of the next few years.

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Colligative Properties of a Solution

Enhanced tension in the solvent gives rise to alterations in solution.

H. T. Hammel

When a solute is added to a pure solvent to form a solution, some properties of the solvent are altered. In what way does the solvent in the solution differ from the pure solvent? To answer this question I shall examine here those properties of a solution which differ from those of the pure solvent and are known as the colligative properties. Four of these properties which can be measured experimentally are (i) the osmotic pressure, (ii) the lower vapor pressure, (iii) the lower melting temperature, and (iv) the higher boiling temperature. "Colligative" refers to those properties that depend on, or vary as a function of, the number of solute molecules in solution and not on the nature of the molecules. What reasonable physical explanation can be proposed for these changes which depend only on the number of molecules?

One virtue of thermodynamics is that it provides quantitative relationships between the colligative properties. This success, however, may have hindered the search for an explanation since thermodynamics describes relationships between pressures, volumes, temperature, and numbers and species of molecules in different phases without regard for the mechanisms underlying these relationships. Thus, from the first and second laws of thermodynamics one can, when dealing with homogeneous solutions, deduce that the chemical potential of the solvent depends on the temperature and external pressure to which the solution is subjected and upon the mole fraction of the solute. Suppose we ask what the change in chemical potential of a solvent is when the temperature is changed by dT, when the externally applied pressure is changed by dp, and when the mole fraction of solute is changed by dx_2 (the subscript 1 denotes solvent in solution, and the subscript 2 denotes solute). The basic thermodynamic statement that can be made about these changes is that the change in the chemical potential of the solvent, $d\mu_1$, in a homogeneous solution is given by

$$d\mu_1 = -\overline{S}_1 dT + \overline{V}_1 dp + \frac{\partial \mu_1}{\partial x_2} dx_2 \qquad (1)$$

where $\overline{S}_1$ is the partial molar entropy of the solvent, $\overline{V}_1$ is the partial molar volume of the solvent, and x_2 is the mole fraction of solute, which is the ratio of the number of moles of solute (N_2) to the number of moles of solute plus solvent ($N_2 + N_1$). Since we are here concerned only with changes induced by adding solute to a solvent, we can simplify this thermodynamic statement by limiting our attention to the situation in which the solvent is subjected to no change in T or p. Thus, we are left with the statement that the change in μ_1 in a homogeneous solution is given by

$$\Delta\mu_1 = \int_0^{x_2} \frac{d\mu_1}{dx_2} dx_2 \qquad (2)$$

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Equation 2 is a valid thermodynamic statement for a homogeneous solution, but it does not reveal what physical property of the solvent has changed. In many applications one may not wish to explain the change. However, as I shall demonstrate below, a reasonable explanation is provided by an elementary consideration of the thermal motion of the solute and solvent molecules. This kinetic explanation applies, at least in principle, to the colligative properties of real heterogeneous concentrated solutions of macromolecules. Furthermore, thermodynamic statements can be correctly applied to solutions only when one knows what property (or properties) of the solvent is altered by the introduction of solute.

In a solution composed of N_1 moles of solvent and N_2 moles of solute that do not dissociate or chemically combine with solvent molecules, the magnitude of each of the colligative properties varies with (N_2/N_1). For a dilute, ideal homogeneous solution the osmotic pressure (Fig. 1a) is

$$\Pi = \frac{RT}{\bar{V}_1}\,\frac{N_2}{N_1} \qquad (3)$$

where R is the gas constant and T is the absolute temperature; the vapor pressure (Fig. 1b) is lowered according to

$$\ell n\left(1 + \frac{\Delta p_{v\Pi}}{p_{v\ell}}\right) = -\,\frac{N_2}{N_1} \qquad (4)$$

where $\Delta p_{v\Pi} = p_{v\Pi} - p_{v\ell}$, and $p_{v\Pi}$ and $p_{v\ell}$ are the vapor pressures of the solution and the solvent, respectively. Corresponding equations for changes in the other colligative properties are discussed below. Even when the solute molecules dissociate into ions or hydrate, these equations remain valid if N_2 is defined as the number of moles of ions or hydrated solute molecules and N_1 is the number of moles of uncombined solvent molecules. As the concentration increases, and especially when macromolecules are involved, there is an accelerating increase in the colligative values which can become very large. But even so, quantitative relationships persist between all the colligative properties. For example, if the measured osmotic pressure, $\Pi_{\exp}$, greatly exceeds $(RT/\bar{V}_1)(N_2/N_1)$, one may accurately compute the other colligative properties by replacing (N_2/N_1) with $\Pi_{\exp}\bar{V}_1/RT$ in the above formulas. The simple fact that there are quantitative relationships between these four experimental properties of a solution under all conditions suggests that they have a common explanation.

Solvent Tension, the Crucial Point

In an effort to find this explanation, let us consider a thought experiment which Noyes proposed in 1900 (*1*). The essence of Noyes' experiment is revealed by comparing osmometers 1 and 2 in Fig. 2. The solute concentration in both osmometers is the same and is equal to $C_2' = (N_2/V_\ell)$. The molar concentration of the solute in this ideal solution is $C_2 = (N_2/V_s)$, where $V_s = V_\ell + V_2$ and where V_ℓ and V_2 are, respectively, the volumes of solvent and solute before combining. The rigid semipermeable membrane for osmometer 1 has been placed at the level $z = 0$, the level of the free surface of the pure solvent. The height of the column of solution shown in osmometer 1 is the equilibrium height h. The semipermeable membrane in osmometer 2 has been placed a small distance Δh below the level h. A column of pure solvent extends from the membrane to the basin below. The weight of the column between the membrane and $z = 0$ induces a tension $\Delta\tau_\ell$ in the pure solvent immediately below the membrane which is given by

$$\Delta\tau_\ell = \rho_\ell g(h - \Delta h) \qquad (5)$$

where g is the acceleration of gravity and ρ_ℓ is the density of the pure solvent. As Δh becomes negligible, $\Delta\tau_\ell$ at h becomes $\Delta\tau_\ell(h) = \rho_\ell gh$.

Since $\Delta\tau_\ell$ below the membrane is in

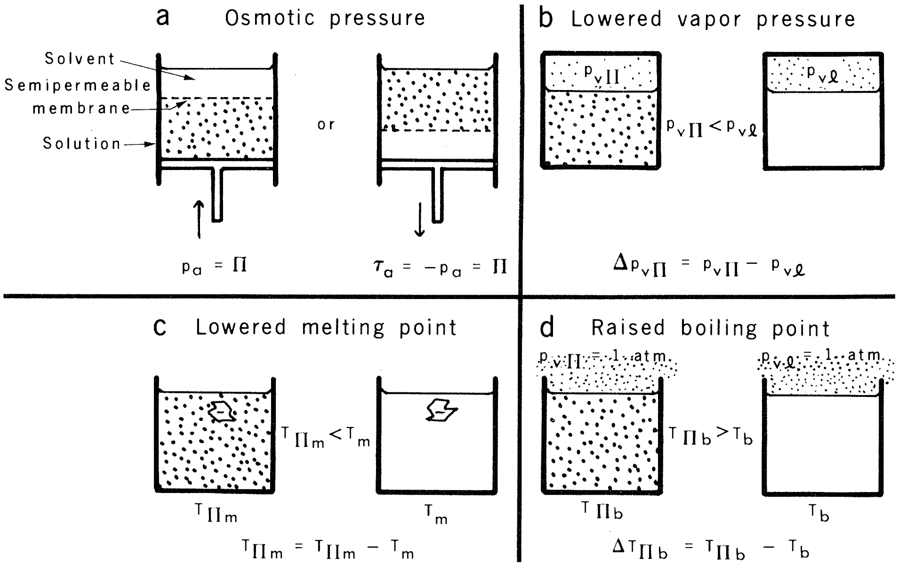

Fig. 1. Four colligative properties of a dilute, ideal homogeneous solution containing N_2 moles of solute in N_1 moles of solvent: (a) osmotic pressure, as given by Eq. 3, where p_a is the applied pressure and τ_a is the applied tension; (b) lowered vapor pressure $\Delta p_{v\Pi}$ as given by Eq. 4; (c) lowered melting temperature $\Delta T_{\Pi m}$, as given by Eq. 31; and (d) elevated boiling temperature $\Delta T_{\Pi b}$, as given by Eq. 32.

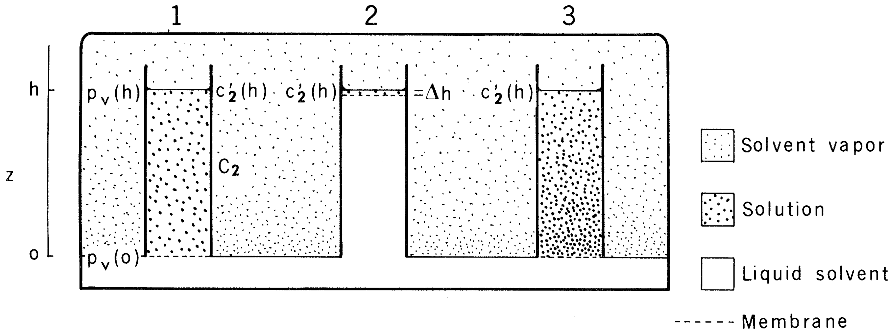

Fig. 2. The role of solute concentration at the free surface is indicated by the three osmotic columns at equilibrium in a gravitational field. The solutions are retained above a rigid, semipermeable membrane by an upright cylinder. The upper surfaces of the solutions are exposed only to the vapor pressure of the solvent; T is constant. At equilibrium the upper surface of the solution assumes a height h. For osmometers 1 and 3 the membrane is at the level of the pure solvent surface, and in osmometer 2 the membrane is located a distance Δh below the surface of the solution. The solutions in osmometers 1 and 2 are the same, and the solute distribution is homogeneous since $\rho_2 = \rho_1$. In solution 3, $\rho_2 \gg \rho_1$ and at equilibrium the osmotic concentration at h, $c_2'(h)$, is the same as $c_2'(h)$ for the solutions in osmometers 1 and 2. The solute concentration $c_2'(z)$ increases exponentially with decreasing z and is greatest at the membrane in osmometer 3 in a gravity field.

equilibrium with the thin layer of solution above the membrane, Π for this solution must be

$$\Pi = \Delta\tau_\ell(h) = \rho_\ell g h \qquad (6)$$

Furthermore, since $C_2' = (N_2/V_\ell)$ for osmometers 1 and 2, then Π in osmometer 1 must also be $\Pi = \rho_\ell g h$.

Should there be any doubt about this conclusion, one need only consider another important fact that Noyes included in his treatment (*1*). The Noyes experiment must be considered as an equilibrium experiment at constant T. There is no convection in the solvent vapor above the pure solvent in the basin or above the solution in osmometers 1 and 2. In this circumstance and in a gravity field there is a distribution of vapor above the pure solvent in the basin which is described by the Boltzmann distribution; that is, the vapor pressure at the distance z is

$$p_v(z) = p_v(0)\, e^{-\frac{m_1 g z}{kT}} \qquad (7)$$

where m_1 is the mass of a solvent molecule, k is the Boltzmann constant, and $p_v(0)$ is the vapor pressure of the pure solvent at $z = 0$ and temperature T. Now the vapor pressure of the solution at h and immediately above the solution in osmometers 1 and 2 must be exactly the same as

$$p_v(h) = p_v(0)\, e^{-\frac{m_1 g h}{kT}} \qquad (8)$$

If this were not true, there would be a continual net distillation of vapor between the solution surface and the pure solvent surface. This process is forbidden since, if it occurred, one could extract work from it as solvent would flow in a perpetual circuit. This conclusion about the vapor pressure at the surface of the solution has important implications.

I have deduced above that the solution in osmometer 2 is in equilibrium with pure solvent which is under a tension $\rho_\ell g h$ below the membrane. We now inquire how much this tension lowers p_v of the pure solvent at this level. The answer is given by a thermodynamic statement known as the Poynting relation (Fig. 3). The equilibrium vapor pressure of a liquid at a constant T is changed by a change in its tension $d\tau_\ell$, by an amount

$$\overline{V}_\ell d\tau_\ell = -\overline{V}_v dp_v \qquad (9)$$

where $\overline{V}_\ell$ is the molar volume of the liquid solvent, $\overline{V}_v$ is the molar volume of the solvent vapor, and dp_v is the change in vapor pressure. In the Noyes experiment, for osmometer 2 in Fig. 2, the change in tension in the pure solvent from $z = 0$ to h is $\tau_\ell(h) - \tau_\ell(0) = \rho_\ell g h$.

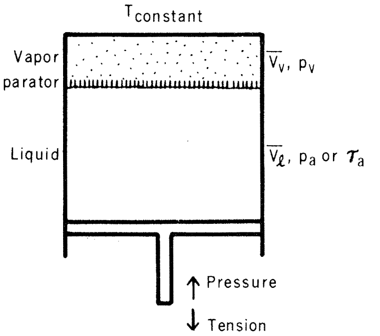

Fig. 3. The equilibrium vapor pressure of a liquid at constant T is changed by a change in the pressure, dp_ℓ, or a change in the tension, $d\tau_\ell = -dp_\ell$, of the liquid according to the Poynting relation (Eq. 9). The changes dp_ℓ or $d\tau_\ell$ are caused by changes in the applied pressure or tension dp_a or $d\tau_a$. The rigid separator in this apparatus is a liquid barrier but not a vapor barrier.

Therefore, the change in p_v of the pure solvent and also the difference between the vapor pressure at the surface of the solution and the vapor pressure at the surface of the pure solvent must be, according to the Poynting relation,

$$\int_{\tau_\ell(0)}^{\tau_\ell(h)} \overline{V}_\ell d\tau_\ell = -\int_{p_v(0)}^{p_v(h)} \overline{V}_v dp_v \qquad (10)$$

If $\overline{V}_\ell$ does not vary with τ_ℓ, the left integral is equal to $\overline{V}_\ell \rho_\ell g h$; since $\overline{V}_\ell \rho_\ell = m_1 N_A$, the left integral equals $m_1 N_A g h$, where N_A is Avogadro's number, the number of molecules per mole. To integrate the right side, let us assume that the solvent vapor obeys the ideal gas law, that is, $pV_v = NRT$, where V_v is the volume of the vapor and $R = kN_A$. According to this law, $\overline{V}_v$ is given by

$$\overline{V}_v = \frac{V_v}{N} = \frac{kN_A T}{p_v} \qquad (11)$$

and the right integral becomes

$$-kN_A T \int_{p_v(0)}^{p_v(h)} \frac{dp_v}{p_v} = - kN_A T \,\ell\text{n}\, \frac{p_v(h)}{p_v(0)} \qquad (12)$$

Therefore, according to the Poynting relation and only if $\Delta\tau_\ell$ at h is $\rho_\ell g h$, we can equate these two integrals and find that

$$p_v(h) = p_v(0)\, e^{-\frac{m_1 g h}{kT}}$$

This is precisely the same equation for the vapor pressure at h as that in Eq. 8, as indeed it must be. Noyes made the remarkable deduction that Π in osmometers 1 and 2 must equal $\Delta\tau_\ell$ in a column of pure solvent of height h; that is, $\Pi = \rho_\ell g h$. Moreover, only if Π is assigned this value will the p_v of the solution at the surface h exactly match $p_v(h)$. Even if the vapor is not an ideal gas, its effect upon the Poynting relation and the Boltzmann distribution will be the same so that the p_v of the solution at h always equals $p_v(h)$. If the solvent is compressible and $\overline{V}_\ell$ varies with pressure, h will be a little higher but the equality of the vapor pressures will remain the same.

Hulett, in 1902, used these deductions to suggest that the solvent in the solution in osmometer 2 was under the same $\Delta\tau$ as the pure solvent just on the other side of the membrane, that is, $\Delta\tau_1 = \Delta\tau_\ell(h)$ (*2*). He also suggested that this same $\Delta\tau_1$ applied to the solvent in the solution at h in osmometer 1 and, indeed, accounted for the appropriate lowering of the p_v at the surface of the solution. Hulett further suggested that the tension in the solution was induced by the thermal pressure of the solute molecules exerted at the surface of the solution. As we shall see later on, this latter suggestion of Hulett's requires clarification.

With rare exceptions (*3, 4*), Noyes' deductions regarding the colligative properties of a solution and Hulett's suggested explanations have been ignored or rejected as invalid. Perhaps the indifference to these important deductions can be attributed to the fact that for a homogeneous solution in osmometer 1 the density of the solution ρ_s may be the same as ρ_ℓ. For example, if $\rho_\ell = \rho_2$, and if $V_s = V_\ell + V_2$, then ρ_s and ρ_ℓ are equal so that Π becomes equal to $\rho_s g h$, but only for this special solution.

On the basis of the evidence presented above, one cannot decide whether the osmosis of an ideal homogeneous solution is to be attributed to the solute at the membrane or at the free surface. In a number of conventional hypotheses it has been suggested that the effect of the solute on the solvent at the membrane induces osmosis: (i) Solute molecules are said to have an affinity for solvent molecules (an association caused by strong long-range adhesive force between solute and solvent), and by virtue of this affinity solvent is drawn across the membrane until the hydrostatic pressure of the solvent above the membrane is sufficient to oppose this affinity. (ii) Solute molecules are said to lower the activity of the solvent so that the solvent diffuses from below the membrane, where its activity is higher, to above the membrane until the hydrostatic pressure of the solvent above the membrane fully opposes this diffusion down an activity gradient. (iii) Solute molecules are said to lower the concentration of the solvent above the membrane, and also in this case solvent diffuses down a concentration gradient until opposed by a hydrostatic pressure. In still other more sophisticated suggestions on how solute alters the solvent at the membrane it is assumed that the effect of the solute is proportional to the concentration of the solute at the membrane. Only Hulett (*2*) attributed osmosis to the concentration of the solute molecules at the free surface of the solution. Since the concentrations at the surface and at the membrane are equal in a well-stirred or homogeneous ideal solution, one can only state a preference from among an assortment of explanations for osmosis.

If the osmotic pressure of the solution in osmometer 3 (Fig. 2) is compared with that in osmometer 2, the choice of explanations for osmosis is narrowed. The concentration of the solution at h in osmometer 3 was chosen to be exactly the same as in osmometers 2 and 1, that is, $c_2'(h) = C_2'$. Since the solute concentration at the upper surface is the same in all three osmometers and since the upper surfaces of all solutions are at the same height h, they all must have the same Π and they all must have the same p_v at the surface, according to Noyes' deductions. The only difference between solutions 3 and 1 is that in solution 3 the solute molecules are much more dense than the solvent molecules, $\rho_2 \gg \rho_\ell$, so that in a gravity field the solute molecules at equilibrium are distributed according to Boltzmann's formulation

$$c_2'(z) = c_2'(0)\, e^{-\frac{m_2' g z}{kT}} \qquad (13)$$

where $m_2'g$ is the net weight of a solute molecule given by

$$m_2'g = m_2\left(1 - \frac{\rho_1}{\rho_2}\right)g \qquad (14)$$

where m_2 is the mass of a solute molecule. The solute concentration in osmometer 3 is least at h where it exactly equals the homogeneous concentration of solution 1, and it increases to its greatest concentration at the membrane. Of course, the total number of solute molecules is greater in osmometer 3 than in osmometer 1 and the number of solvent molecules is less. The solute concentration at h in osmometers 1 and 2 is unique; it is the only concentration at equilibrium that will (i) maintain the solution surface at h, (ii) lower p_v to the required value, and (iii) ensure that $\Pi = \rho_\ell g h$. Likewise, it is the only equilibrium solute concentration at height $z = h$ in osmometer 3 that will ensure that p_v above the surface of solution 3 equals the p_v above pure solvent at h. The fact that both Π and p_v of the solution in osmometer 3 must be the same as in osmometer 1 invalidates any explanation in which Π is attributed to the concentration of solute molecules at the membrane and at the same time the lowering of p_v is attributed to the solute concentration at the surface. Clearly, only the solute concentration at the free surface in all three osmometers relates proportionally to both the Π and p_v; and clearly the effect of the solute molecules upon the solvent at h has exactly the same effect upon p_v of the solution as would the application of a tension of $\Delta\tau = \Pi$ to the pure solvent, as Hulett clearly recognized (*2*).

There is still another argument which enhances the plausibility of Hulett's suggestion by rendering the alternatives implausible. Since p alters p_v of the solvent in a solution, it is the usual custom to state or imply that $p_v(h)$ is the solvent pressure at the surface of the solution. The solvent pressure then increases beneath the surface as $\rho_\ell g(h - z)$ in osmometer 1 of Fig. 2. This ignores the solvent tension of the surface; so it must be presumed that the p_v of the solvent in the solution is lowered by some other effect of the solute upon the solvent. Now all real solvents are compressible or expansible to some extent; therefore, the solvent in the solution in osmometer 1 would be compressed somewhat by its own weight. On the other hand, the pure solvent beneath the membrane in column 2 is subjected to increasing tension, $\rho_\ell g z$, and therefore it is expanded somewhat. If we compare columns of osmometers 1 and 2, we must conclude that column 2 is somewhat taller than column 1 because of the compression of the one solvent and the expansion of the other. But this leads us to the erroneous conclusion that two solutions of identical concentration can be at equilibrium with two different p_v values, a lower p_v above the solution in osmometer 2 than in osmometer 1. Hulett's suggestion avoids this difficulty by the simple expedient of assigning equal $\Delta\tau_1$ to the solvent in columns 1 and 2 and therefore equal expansion and equal lowering of p_v at all values of z. As I have shown above, this assignment of $\Delta\tau_1$ to the solvent also ensures an exact match with the p_v at any z above pure solvent in a gravitational field. The lesson to be learned from these considerations is that one cannot equate the $p_v(h)$ applied at the surface with the solvent pressure at the surface of the solution and then presume that the p_v of the solvent in the solution is lowered by some other effect of the solute upon the solvent. What follows is an attempt to develop Hulett's suggestion and to ascertain how $\Delta\tau_1$ is induced.

Kinetic Model for the Induction of Solvent Tension

My hypothesis is based on the fact that all molecules in a pure solvent as well as all molecules in a solution are in thermal motion. Binding forces exist between all molecules in the pure solvent and in the solution, and these forces are strong enough so that most of the molecules are retained in the liquid phase at room temperature. All molecules exert a force at any boundary when they are reflected, and this force is perpendicular to the boundary and equals the change of momentum perpendicular to the boundary per unit time. The extent of this force per unit area of boundary surface is the thermal pressure p, which, according to my hypothesis, is taken to be

$$p = CRT \qquad (15)$$

where C is the molar concentration of solute or solvent molecules.

In pure solvent, the pressure exerted by the thermal motion of those solvent molecules that are reflected from the free surface of the solvent is

$$p_\ell = C_\ell RT \qquad (16)$$

where C_ℓ is the molar concentration of pure solvent, that is, $C_\ell = (N_1/V_\ell)$, the number of moles of solvent in a unit volume of liquid solvent. Also C_ℓ is equal to the reciprocal of the molar volume of pure solvent, $C_\ell = (1/\bar{V}_\ell)$. For pure water p_ℓ would be 1260 bars at 0°C. Clearly something must be opposing this very large pressure. The binding forces between the solvent molecules oppose the thermal pressure. In other words, the pure solvent is under a tension at its surface equal to

$$\tau_\ell = \frac{RT}{\bar{V}_\ell} \qquad (17)$$

At any depth beneath the surface the tension would be less by the weight of the pure solvent per unit area. A gas bubble in the pure solvent would not expand, since τ_ℓ in the pure solvent is canceled by p_ℓ at the common boundary with the bubble. Indeed, if the radius of the bubble r is small, the gas in it will be under an additional pressure $(2\sigma_{\ell v}/r)$, where $\sigma_{\ell v}$ is the surface tension of the liquid with respect to the vapor in the bubble.

Next, we inquire about the pressures and the opposing tension in a homogeneous solution where N_2 moles of solute have been dissolved in N_1 moles of solvent. Before combining, the volume of N_1 moles of solvent was V_ℓ and the volume of N_2 moles of solute was V_2. After combination, the volume of the solution is $V_s = N_1\overline{V}_1 + N_2\overline{V}_2$. The molar concentration of the solute is $C_2 = (N_2/V_s)$, and the molar concentration of the solvent is $C_1 = (N_1/V_s)$. The thermal pressure exerted by the solvent molecules at the boundary of the solution is, according to the hypothesis presented here,

$$p_1 = C_1RT \tag{18}$$

and the pressure exerted by the solute molecules is $p_2 = C_2RT$. The total force exerted on a unit area of the solution surface is $(p_1 + p_2)$. Now we inquire about the τ_1 in the solvent which opposes this force. We shall assume that the solute molecules are not excluded from the surface zone of the solution. In this case, the fraction of a unit area of surface in a homogeneous solution that is pure solvent is the fraction of the total volume that is solvent, that is, $(N_1\overline{V}_1)/(N_1\overline{V}_1 + N_2\overline{V}_2)$. Therefore, the solvent tension in the solution is the force exerted on a unit area of solution divided by the fraction of the area that is solvent, or

$$\tau_1 = \frac{(p_1 + p_2)}{N_1\overline{V}_1/(N_1\overline{V}_1 + N_2\overline{V}_2)} = (C_1RT + C_2RT)\frac{V_s}{N_1\overline{V}_1} \tag{19}$$

An illustration may help to clarify this important conclusion.

Figure 4 is an instantaneous view of the positions of molecules in thermal motion: molecules in the surface zone of pure solvent are depicted in Fig. 4a, and molecules near the surface of the solution are shown in Fig. 4c. The binding forces between the molecules are also delineated. Solute molecules are similarly depicted in Fig. 4b. Imagine that the solute molecules, the solid circles in Fig. 4c, are near the surface but are constrained from exerting the force p_2 on a unit area of solution surface. Suppose that this imagined constraint renders $p_2 = 0$ so that τ_1 becomes simply $(RT/\overline{V}_1)$ or essentially the same as τ_ℓ in Fig. 4a. The mere presence of the solute molecules near the surface has no effect on the solvent or on τ_1 or p_v if $\overline{V}_1$ does not differ from $\overline{V}_\ell$. Now, when the solute molecules exert their thermal force p_2 on a unit area of solution surface, then τ_1 in the solution exceeds τ_ℓ in the pure solvent by

$$\Delta\tau_1 = \tau_1 - \tau_\ell = (C_1RT + C_2RT)\frac{V_s}{N_1\overline{V}_1} - C_\ell RT \tag{20}$$

from which we deduce that the enhanced solvent tension in a homogeneous solution is

$$\Delta\tau_1 = \frac{RT}{\overline{V}_1}\frac{N_2}{N_1} + \left(\frac{RT}{\overline{V}_1} - \frac{RT}{\overline{V}_\ell}\right) \tag{21}$$

In this derivation I have used the simplest assumption, namely, that the solute molecules are not excluded from the surface zone and that they are present there in the same proportion as the solvent volume is to the total volume in a homogeneous solution. If for any reason the solute molecules are near but excluded from the surface layer, then at the level below the surface where they are reflected they exert a force p_2 which sums with p_1. The tension induced in the solvent is this total force divided by the portion of a unit area at this level that is solvent. In this case as well, the enhanced tension is given by this same relation.

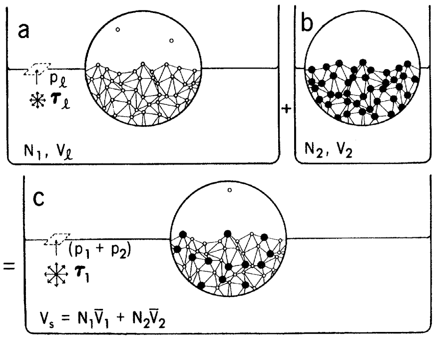

Fig. 4. Origin of the enhanced solvent tension in a solution, a thermal kinetic hypothesis. (a) Pure solvent, N_1 moles of volume V_ℓ; p_ℓ equals the force exerted by the thermal motion of the solvent molecules per unit area of surface; τ_ℓ is the opposing tension throughout the solvent where $\tau_\ell = p_\ell = C_\ell RT$ and $C_\ell = N_1/V_\ell$ is the molar concentration of the pure solvent. (b) Solute, N_2 moles of volume V_2. (c) Homogeneous solution with the assumption that solute molecules are not excluded from the surface zone; p_1 is the force exerted by the thermal motion of the solvent molecules per unit area of solution surface, $p_1 = C_1RT$, where $C_1 = N_1/V_s$, the molar concentration of solvent; p_2 is the force exerted by the thermal motion of the solute molecules per unit area of solution surface, $p_2 = C_2RT$, where $C_2 = N_2/V_s$. The total thermal force exerted by solute and solvent molecules per unit area of solution surface is $(p_1 + p_2)$. The tension in the solvent, τ_1, which opposes this force is the total force divided by the area of the solvent per unit area of solution surface. The fraction of the solution surface which is solvent is $[N_1\overline{V}_1/(N_1\overline{V}_1 + N_2\overline{V}_2)]$, that is, the volume fraction of the solution which is solvent. Thus, the solvent tension is given by Eq. 19, and the opposing enhanced tension in the solvent is given by

$$\Delta\tau_1 = \tau_1 - \tau_\ell = \frac{RT}{\overline{V}_1}\frac{N_2}{N_1} + \left(\frac{1}{\overline{V}_1} - \frac{1}{\overline{V}_\ell}\right)RT$$

If the molar volume of pure solvent, $\overline{V}_\ell$, equals the partial molar volume of solvent in the solution, $\overline{V}_1$, as in an ideal solution, then the enhanced solvent tension is given by Eq. 22.

If we consider an ideal solution, one for which $V_s = V_\ell + V_2$, then $\overline{V}_1 = \overline{V}_\ell$ and $\Delta\tau_1$ is

$$\Delta\tau_1 = \frac{RT}{\overline{V}_1}\frac{N_2}{N_1} \tag{22}$$

If for any reason the solute molecules exert a force in addition to their thermal force, $\Delta\tau_1$ may exceed $(RT/\overline{V}_1)(N_2/N_1)$ in an ideal solution. For example, if the solute molecules are very large or are highly concentrated, they may exert a mechanical force on the boundary as well. Or, if each solute molecule were an electric (or a magnetic) dipole, then in an electric (or magnetic) field gradient of appropriate sign each solute molecule would exert a force in addition to the thermal force at the surface and $\Delta\tau_1$ may exceed the magnitude given in Eq. 22.

Osmotic Pressure

The development presented above has led to the deduction that the thermal motion of solute molecules in a dilute, ideal homogeneous solution induces no effect on the solvent other than to enhance the tension in the solvent by an amount given in Eq. 22. Now the question arises, is $\Delta\tau_1$ a reasonable explanation for the four colligative properties of the solution?

Indeed, I have already shown that only an explanation in which Π and p_v of the solution are attributed to the concentration of the solute molecules at its free surface, at equilibrium, can be valid. Furthermore, I have shown that the Π of a solution (Fig. 1a) must exactly equal an opposing $\Delta\tau$ in the pure solvent below the membrane. Therefore, it is only necessary to state that Π, at equilibrium, equals $\Delta\tau_1$ induced in the solvent by the thermal force or other force exerted at the surface of the solution. So for an ideal homogeneous solution, as in osmometer 1, Eq. 3 holds if a thermal force is exerted at the surface. In this equation N_2/N_1 is the mole ratio of solute molecules, ions, colloidal particles, or whatever other solute, to solvent molecules, all in unrestricted Brownian motion. Now $N_1\overline{V}_1$ is the volume of the solvent, V_ℓ in the ideal solution. I shall define the osmotic concentration of the solution, C_2', to be $C_2' = N_2/V_\ell$, the number of moles of solute in a liter of solvent. For an aqueous solution, this definition approximates the definition of a molal solution since a liter of water weighs nearly a kilogram and $\Delta\tau_1$ and Π in a dilute aqueous solution are proportional to the molal concentration. If the solution is not ideal, for example, $V_s < V_\ell + V_2$ as is often the case for an aqueous solution, then $N_2\bar{V}_2$ may be much less than V_2 even though $N_1\bar{V}_1$ may be more than V_ℓ, that is, $\bar{V}_1 > V_\ell$. In this case $\Delta\tau_1$ and Π will be less than for an ideal solution and will be proportional to some concentration between a molal and a molar concentration.

Vapor Pressure

The Poynting relation for p_v (Fig. 1b) for the solvent in a solution is like Eq. 9, that is,

$$\bar{V}_1 d\tau_1 = -\bar{V}_v dp_v$$

For a dilute, ideal homogeneous solution, the integral of the left side of the Poynting relation is

$$\int_{\tau_\ell}^{\tau_1} \bar{V}_1 d\tau_1 = RT\frac{N_2}{N_1} \tag{23}$$

If the vapor behaves like an ideal gas, then

$$RT\frac{N_2}{N_1} = -RT\int_{p_{v\ell}}^{p_{v\Pi}} \frac{dp_v}{p_v} \tag{24}$$

where $p_{v\ell}$ is the vapor pressure of the pure solvent and $p_{v\Pi}$ is the vapor pressure of the solution, and

$$\ell n\frac{p_{v\Pi}}{p_{v\ell}} = -\frac{N_2}{N_1} \tag{25}$$

Equation 25 was derived by assuming that the $\Delta\tau_1$ in the solvent of the solution is the cause of the lowered vapor pressure of the solution, $\Delta p_{v\Pi}$. Since $\Delta p_{v\Pi} = p_{v\Pi} - p_{v\ell}$, Eq. 25 is the same as Eq. 4, and the lower p_v of the solution is to be attributed to $\Delta\tau_1$.

One interpretation of an ideal solution is that the forces between the like and unlike molecules are the same magnitude so that $V_s = V_\ell + V_2$. In an ideal solution for which both solute and solvent are volatile, the ratio of the molar amounts of solvent vapor to solute vapor above the solution may be the same as the ratio in the solution, that is, N_1/N_2. In this case,

$$p_{v_1}/p_{v_2} = N_1/N_2 \tag{26}$$

Also in this case, the vapor pressure of the pure solvent, $p_{v\ell}$, will be the same as the vapor pressure of the pure solute. Likewise, in this case

$$p_{v\ell} = p_{v_1} + p_{v_2} \tag{27}$$

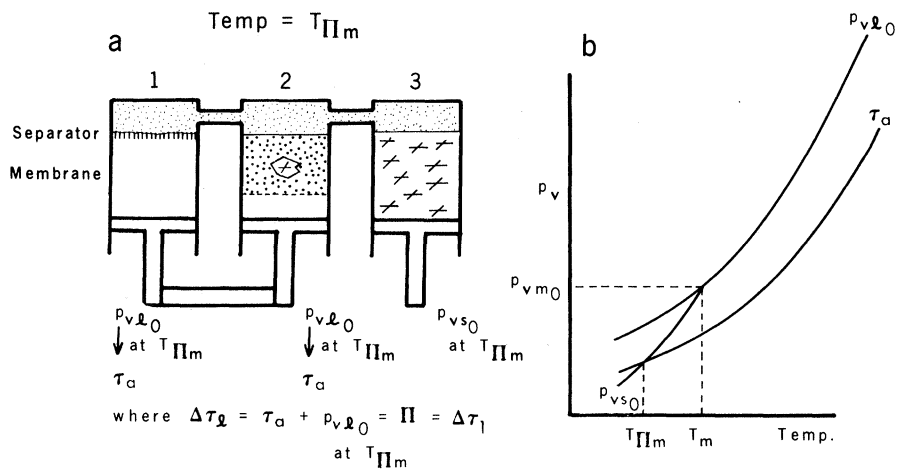

Fig. 5. Melting temperature lowered by solvent tension. Cylinder 1 contains water separated from its vapor by a rigid porous membrane. Cylinder 2 contains solution with a free surface and separated from the solvent by a semipermeable membrane. Cylinder 3 has a fixed ice surface. The three cylinders are connected and have the same vapor pressure. Solvents in cylinders 1 and 2 are under applied tension τ_a. At the freezing point the vapor pressure from the tensile water matches that of the ice.

Combining these two equations, we obtain

$$p_{v_1}/p_{v\ell} = \frac{N_1}{N_1 + N_2} \equiv x_1 \tag{28}$$

This statement is Raoult's law. A standard solution is defined as one that obeys Raoult's law. Thus, an ideal solution for which $V_s = V_\ell + V_2$ will also be a standard solution, when $p_{v_1}/p_{v_2} = N_1/N_2$, and will obey Raoult's law.

Melting Point

An understanding of the lowered melting point (Fig. 1c) is based on the effects of T and p upon the vapor pressures of the liquid and solid phases of the solvent, $p_{v\Pi\ell}$ and $p_{v\Pi s}$, respectively, in the solution. These effects are precisely determined by thermodynamic statements. The effect of p at constant T is given by the Poynting relation, and the effect of T is given by the Clapeyron equation. If the vapor of the solvent behaves like an ideal gas, then the effect of temperature upon $p_{v\Pi\ell}$ and $p_{v\Pi s}$ in the solution is given by the Clausius-Clapeyron equation. For equilibrium between the liquid and its vapor, the relationship is

$$\frac{d\,\ell n\,p_v}{dT} = \frac{\Delta\bar{H}_{\ell v}}{T^2} \tag{29}$$

where $\Delta\bar{H}_{\ell v}$ is the molar enthalpy from liquid to vapor, that is, the heat of vaporization per mole. A similar relation applies to the solid phase where $\Delta\bar{H}_{sv}$ is the molar enthalpy from solid to vapor, that is, the heat of sublimation per mole.

The conditions required to establish an equilibrium between the p_v of the solid phase and the liquid phase of the solvent in the solution contained in cylinder 2 above the rigid semipermeable membrane are shown in Fig. 5a. One condition for equilibrium is that a downward force be applied to the frictionless pistons in cylinders 1 and 2 such that solvent will not flow through the membrane in the middle cylinder and such that the vapor pressure of the solvent in cylinder 1, $p_{v\ell}$, will match $p_{v\Pi}$. The downward forces on these two pistons must be the same for all temperatures. The resulting change in p from the vapor pressure of the pure solvent subject only to its own vapor pressure, $p_{v\ell_0}$, must be the negative value of the osmotic pressure of the solution, that is,

$$\Pi = \tau_a + p_{v\ell_0} = \Delta\tau_1 = \frac{RT}{\bar{V}_1}\frac{N_2}{N_1} = -\frac{RT}{\bar{V}_1}\ell n\frac{p_{v\ell}}{p_{v\ell_0}} \tag{30}$$

where τ_a is the downward tension applied by the pistons, and $p_{v\ell}$ is the vapor pressure of the solvent in the solution and the pure solvent in both cylinders subject to the applied tension τ_a.

The other condition for equilibrium is that the T of the solution and all phases of the solvent must be that at which p_{vs_0}, the vapor pressure of the frozen solvent, subject only to its own vapor pressure, in cylinder 3, equals $p_{v\ell}$ in cylinder 1. This is a unique T, that at which a crystal of solvent in the solution is also at equilibrium with the solution. Figure 5b indicates graphically how this T can be predicted. The line labeled $p_{v\ell_0}$ is the integral form of the Clausius-Clapeyron equation for liquid solvent subject to its own p_v only. The line labeled τ_a is the vapor pressure of the pure solvent as a function of T and subject to a tension τ_a. This line, of course, applies to the pure solvent in cylinder 1 as well as to the solvent below the membrane in cylinder 2; the line also applies to the solvent in the solution, which is, by my hypothesis, under an enhanced tension $\Delta\tau_1 = \Pi$ which opposes the p of the solute molecules exerted at the surface of the solution. The line labeled p_{vs_0} applies to the frozen solvent in cylinder 3 and also to the crystal in the solution. There the crystal is subject to the same p from the combined thermal motion of the solute and solvent molecules as it would be in pure solvent where its melting temperature is T_m. The unique temperature $T_{\Pi m}$, illustrated graphically, is the only temperature at which the vapor pressure of the crystal equals the vapor pressure of the solvent in the solution subject to the enhanced tension Π. Therefore, $T_{\Pi m}$ is the melting point of the solution and is lower than T_m by the amount

$$T_{\Pi m} = \frac{T_m}{1 + \dfrac{RT_m}{\Delta \bar{H}_{\ell s}} \dfrac{N_2}{N_1}} \qquad (31)$$

where $\Delta \bar{H}_{\ell s}$ is the molar enthalpy for the phase transition from liquid to solid, that is, the heat of fusion per mole. For one mole of a solute which does not dissociate or hydrate in 1000 milliliters of water, $\Delta T_{\Pi m} = T_{\Pi m} - T_m = 1.8556°\text{K}$. Thus, the lowering of the melting point, like the other colligative properties, is attributable to the enhanced tension in the solvent induced by the thermal pressure of the solute molecules exerted at the free surface of the solution.

In this derivation of the melting temperature of a crystal of frozen solvent in a solution, it has been assumed that all radii of curvature at the surface of the crystal are large, that is, much greater than a micrometer, and it has also been assumed that $(p_2 + p_1)$ does not differ from p_ℓ so that the crystal could be treated as though it were a large bubble or outside the solution. The only additional pressures to which the crystal is subjected are the pressure of the vapor above the solution and the gravity pressure of the solvent, both of which may be only a few centimeters of water or millibars. If the radius of curvature of an edge of the crystal were small, a condition that could develop if T should drop below $T_{\Pi m}$ so that growth at an edge is started, then there is an added pressure applied to the crystal edge which is $2\sigma_{\ell s}/r$, where r is the radius of the growing surface and $\sigma_{\ell s}$ is the surface tension of the liquid with respect to the solid phase of the solvent. For water and ice, $\sigma_{\ell s} \simeq 20$ dynes per centimeter at 0°C. For a growing surface whose radius is 1 micrometer, the applied surface pressure would be 0.4 bar. At this surface the pressure would be $p_{vs_0} + 0.4$ bar, which would raise the vapor pressure of the ice and thereby lower $T_{\Pi m}$ by 0.034°C. In other words, if the T of a solution whose melting temperature is $T_{\Pi m}$ were lowered by 0.034°C, then the growth of the ice crystal would proceed at the edges where the radius of curvature would become 1 micrometer. Another application of these considerations would be to apply a net around the ice crystal such that growth could occur only through the openings in the net. If the openings in the net had radii of 0.06 micrometer, then the growing surfaces would acquire this radius and the surface pressure applied to the crystal surface would lower the equilibrium melting or freezing temperature by 0.55°C. Kuhn (*5*), Kuhn *et al.* (*6*), and Bloch *et al.* (*7*) have shown that a structurally caused freezing point depression can be demonstrated in artificial gels and in muscle.

Another effect of pressure on the melting temperature of real solutions which cannot be overlooked is that $(p_1 + p_2)$ will not always exactly equal p_ℓ. In fact, often $(p_1 + p_2) < p_\ell$ so that $T_{\Pi m}$ is not the temperature at which the curve labeled p_{vs_0} intersects the curve labeled τ_a in Fig. 5b but rather the temperature at which the latter curve intersects a curve slightly below the former curve, that is, at a slightly higher $T_{\Pi m}$.

Boiling Point

The elevated boiling point of a solution (Fig. 1d) is also explained by the enhanced tension in the solution. I shall assume that the Clausius-Clapeyron equation is a good approximation for the vapor pressure of a solvent near T_b, the temperature at which the p_v equals 1 atmosphere. The enhanced tension in the solvent of the solution will lower the vapor pressure of the solution to below 1 atmosphere, according to Poynting's relation, so that the solution will no longer boil at T_b. The increase in temperature required to restore p_v of the solution to 1 atmosphere is $\Delta T_{\Pi b}$, where

$$T_{\Pi b} = \frac{T_b}{1 - \dfrac{RT}{\Delta \bar{H}_{\ell v}} \dfrac{N_2}{N_1}} \qquad (32)$$

and $\Delta \bar{H}_{\ell v}$ is the molar enthalpy for vaporization. Thus in this case also it is the enhanced tension in the solvent of the solution which precisely and uniquely accounts for the elevated boiling point of a solution.

Chemical Potential

Finally, we return to the thermodynamic statement which describes the change in chemical potential of the solvent in a homogeneous solution. If T and p are constant and if we assign the value $-\bar{V}_1 d\tau_1$ to the last term in the statement, that is,

$$d\mu_1 = \frac{\partial \mu_1}{\partial x_2}\, dx_2 = -\bar{V}_1 d\tau_1 \qquad (33)$$

then the decrease in μ_1 due to increasing x_2 is fully accounted for by the $\Delta\tau_1$ induced by the thermal force of the solute molecules exerted at the surface of the solution. Thus, with the addition of N_2 moles of solute to N_1 moles of solvent x_2 in a homogeneous solution changes from 0 to $N_2/(N_1 + N_2)$ and $\Delta\mu_1$ is changed by

$$\Delta\mu_1 = \int_0^{x_2} \frac{\partial \mu_1}{\partial x_2}\, dx_2 = -\bar{V}_1 \Delta\tau_1 \qquad (34)$$

For a heterogeneous solution this is not a valid statement, and only if the integration is from 0 to the x_2 at the surface where $\Delta\tau_1$ is induced does the integral become valid. For example, in a heterogeneous solution such as that in osmometer 3 in Fig. 2, $\Delta\mu_1$ of the solvent is

$$\Delta\mu_1 = \int_0^{x_2(h)} \frac{\partial \mu_1}{\partial x_2}\, dx_2 = -\bar{V}_1 \Delta\tau_1 \qquad (35)$$

which also equals $-RT[N_2(h)]/[N_1(h)]$. Therefore, as stated above, it is essential to know what property of the solvent is altered and how it is altered by the solute in order to apply thermodynamic statements to the solvent in a solution.

Significance and Conclusion

One might ponder whether this reasonable explanation of the colligative properties of a solution has any merit other than its theoretical interest. The answer is probably affirmative since understanding osmosis is essential for understanding the behavior and function of living cells. Although no living cell is ever in equilibrium, it seems unlikely that nonequilibrium osmotic processes can be understood without first understanding equilibrium osmosis. Furthermore, the hydraulic permeability of a porous cell membrane will depend on the property (or properties) of the water that has been altered by the solutes. If, as I contend, the μ_1 of the water is lower on one side of a membrane because solute molecules enhance τ_1 in the water, then the movement of water through the pores will be attributed to mass flow and not to diffusion. In addition, the hydraulic permeability of a porous membrane will be orders of magnitude greater than if the water were to diffuse down an "activity" or "water concentration" gradient. On the other hand, if the cell membrane is not sufficiently porous to permit the mass flow of water through it, then the permeability will be the same whether the water tension is enhanced or the "water concentration" is lowered across the membrane.

When considering the pressure exerted by the thermal motion of solvent molecules as they reflect from their boundary, I postulated this pressure to be $p_\ell = C_\ell k N_A T$ in pure solvent, where $C_\ell = N_1/V_\ell$. This postulate seems reasonable if the molecules of the solvent do not cluster, polymerize, or fractionate to any extent, that is, if there are always N_A molecules in a mole of solvent which independently share the thermal energy at temperature T. As I further postulated for pure solvent (Eq. 17), this thermal pressure p_ℓ induces an equal and opposing tension in the binding force between the molecules of solvent

$$\tau_\ell = \frac{N_1 k N_A T}{V_\ell} = \frac{k N_A T}{\overline{V}_\ell} \qquad (36)$$

A change in temperature dT will change the tension in such a solvent by

$$\frac{d\tau_\ell}{dT} = \frac{k N_A}{\overline{V}_\ell} \qquad (37)$$

Since the definitions of the coefficients of thermal expansion (α) and expansibility (κ) are, respectively,

$$\frac{dV}{V} = \alpha dT \qquad (38)$$

and

$$\frac{dV}{V} = \kappa d\tau \qquad (39)$$

then

$$\frac{d\tau}{dT} = \alpha/\kappa \qquad (40)$$

For a solvent of N_A independent molecules per mole, we may expect that

$$\frac{\alpha}{\kappa} = \frac{k N_A}{M\nu} \qquad (41)$$

where M is the molecular weight of the solvent and ν is the specific volume of the solvent (in cubic centimeters per gram). If no external pressure is applied to this solvent, then its chemical potential μ_ℓ will change by

$$d\mu_\ell = -\overline{S}_\ell dT \qquad (42)$$

when the temperature changes by dT. Since this change in T alters the internal τ_ℓ, we may infer that the change in μ_ℓ is also

$$d\mu_\ell = -\overline{V}_\ell d\tau_\ell = -k N_A dT \qquad (43)$$

For a liquid whose molecules do not cluster or dissociate and remain as N_A independent molecules per mole, we conclude that its molar entropy is

$$\overline{S}_\ell = k N_A = \frac{\alpha M \nu}{\kappa} \qquad (44)$$

where α is in reciprocal degrees Kelvin, M is in grams per mole, and κ is in square centimeters per dyne. These relationships do not apply well to water, although at 20.5°C it does happen that

$$\frac{\alpha M \nu}{\kappa} = \frac{(211.14 \times 10^{-6}) \times 18.02 \times 1.00}{45.84 \times 10^{-12}}$$

$$\frac{\alpha M \nu}{\chi} = 83.14 \times 10^{6} \text{ dyne cm mole}^{-1}$$
$$^{\circ}\text{K}^{-1} = k N_A$$

The virtual or "thermal" entropy of liquid water in the standard state at 25°C is 69.9×10^6 dyne cm mole^{-1} °K^{-1}, which is significantly less than would be expected (83.1) at this T.

The thermal and elastic properties of a real solvent are not fully explicable in terms of my elementary treatment of the p_ℓ of its molecules and the opposing τ_ℓ in the binding force between them. Polymerization of molecules in a liquid may diminish their independence in thermal motion and reduce their pressure. Polymerization may also alter ρ, $\overline{V}$, and α by rendering less random the configuration of molecules in a liquid. Perhaps also the polarization of molecules contributes an electrostatic force to the thermal force exerted by these molecules as they are reflected at a free surface of the liquid. Other complex properties of real solvents may alter their thermal pressure, thermal properties, and elasticity. Nevertheless, the compelling argument that solute molecules induce an effect on the solvent which equates with $\Delta\tau_1$ may suggest another approach to a study of the properties of liquids. These considerations of the effects of molecular cluster formation, atomic or ionic dissociation, and polarization upon the solvent tension do not invalidate the computation presented here of $\Delta\tau_1$ induced by the thermal motion of solute in a solution. For dilute solutions, at least, we may reasonably suppose that the extent to which the thermal pressure p_ℓ in pure solvent differs from $(N_1 k N_A T)/V_\ell$ is nearly the same as the extent to which p_1 differs from $(N_1 k N_A T)/V_s$ so that $\Delta\tau_1$ remains equal to $(RT/\overline{V}_1)/(N_1/N_2)$ as a good approximation.

Conclusion

The colligative properties at equilibrium in a solution with an unrestrained surface can be attributed to the thermal, mechanical, and electrostatic forces exerted by the solute and solvent molecules at this surface. Very simply, the sum of these forces divided by the area of the solvent portion of the unrestrained solution surface is equal to a tension in the solvent that is greater than that in the pure solvent, and this enhanced tension lowers the vapor pressure of the solvent, raises its boiling temperature, lowers its melting temperature, and gives rise to osmotic pressure of the solution. This explanation of the colligative properties of a solution at equilibrium has been known for more than 70 years. Perhaps this revised account of Hulett's explanation (*2*) combined with experimental evidence obtained by Scholander (*4*) will lead to its acceptance as an admissible explanation (*8*).

The next important step will be to apply this explanation to the osmotic processes of living systems which are never at equilibrium, sometimes in steady state, and often irreversible. Water, the life solvent on earth, flows between cells and the fluid medium in which they are bathed. The membrane at the boundary of the cell and membranes around organelles within the cell are permeable to water and less permeable (in varying degree) to other molecules and ions. The thermal motions and electrical charges of these molecules and ions exert forces at the boundaries where they are reflected. When subjected to a pressure difference across the membrane, the boundary will move as water flows freely through the membrane transporting other permeable substances. These fluxes change the volume and the concentrations of the solution bounded by the membrane, and conversely they change the volume and concentrations of the bathing fluid. Furthermore, molecules and ions may be actively transported and may be reactants and products of cellular chemistry, and they vary greatly in size and in their diffusion coefficients. Nevertheless, treating the osmotic process as outlined in this article should increase understanding of osmotic processes in living systems.

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8. The enhanced tension in the solvent of a homogeneous ideal solution is

$$\Delta\tau_1 = \frac{RT}{\bar{V}_1}\frac{N_2}{N_1}$$

This can also be written

$$\Delta\tau_1(V_s - N_2\bar{V}_2) = N_2RT$$

which is in the form of an equation of state of N_2 moles of solute molecules occupying a volume of $N_2\bar{V}_2$ in the solution whose volume is V_s; $\Delta\tau_1$, the additional tension in the solvent induced by and opposing the thermal motion of the solute molecules, is analogous to the wall pressure exerted by the container of N_g moles of real gas occupying a volume $N_g\bar{V}_g$ in a container of volume V. The wall pressure, p_w, induced by and opposing the thermal motion of the real gas is

$$p_w(V - N_g\bar{V}_g) = N_gRT$$

which is the equation of state of a real gas for which the pressure exerted by the gas is proportional to its molar concentration,

$$p_g = C_gRT \quad \frac{N_gRT}{V}$$

The opposing pressure exerted by the containing wall is greater than p_g by the ratio $V/(V - N_g\bar{V}_g)$. These considerations applied to a solution ensure that the two methods illustrated in Fig. 1a give the same value of Π. In the left cylinder the wall pressure, as measured by p_a, is equal to π and equals $N_2RT/(V_s - N_2\bar{V}_2)$. In the right cylinder the applied tension in the pure solvent below the membrane equals the enhanced solvent tension in the solution, that is,

$$\pi = \tau_a = \Delta\tau_1 = \frac{N_2\ RT}{N_1\ \bar{V}_1}$$

thus assuring that both methods give the same value of π. I would also like to suggest that the concentrations $(N_2/N_1\bar{V}_1)$ and $(N_1/\bar{N}_1\bar{V}_1)$ be designated as the tensile concentrations of the solute and the solvent, respectively, in the solution.

9. Provocative discussions with Prof. P. F. Scholander since 1960 have led to the thesis formulated in this essay. Discussions with Drs. Y. C. Fung, A. R. Hargens, A. B. Hastings, E. A. Hemmingsen, D. A. Krueger, J. Steen, C. B. Wenger, and A. A. Yayanos have also contributed importantly to my understanding of the phenomenon. My investigations of water relations in plants have been supported, in part, by National Science Foundation grant GB8343 (from the Division of Biomedical Science), grant GA-19604 (from the Office of Polar Programs), and by National Institutes of Health grant NS11704.

Early Man at Holly Oak, Delaware

Paleoenvironmental studies in Delaware suggest alternate times of habitation by early man.

John C. Kraft and Ronald A. Thomas

A reevaluation of an association of early man in northern Delaware with the woolly mammoth (*Mammuthus* or *Elephas* sp.) suggests a time from the early to middle Holocene epoch (8000 to 4000 B.C.) or, alternatively, an extremely early association in the early Wisconsin and late Sangamon ages. Stratigraphic and palynological analyses identify thin sedimentary layers as representing paleoenvironments of the late Holocene epoch and early Wisconsin and Sangamon ages in the northern Delaware region at the boundary between the piedmont and coastal plain geomorphic provinces. These sediments are closely associated with occurrences of abundant Archaic and Paleo-Indian artifacts and a carving of the woolly mammoth. Below, we discuss the probability of association of these artifacts of early American man with the woolly mammoth as well as with the mastodon in either the early to middle Holocene epoch (5,000 to 10,000 years ago) and the very latest Wisconsin age or early Wisconsin and late Sangamon ages (60,000 to 100,000 years ago).

The Holly Oak Pendant

An interesting discovery pertaining to early man in the New World occurred in 1864 when H. T. Cresson and W. L. de Suralt found a number of artifacts associated with some peats near the Holly Oak railroad station in northern Delaware. Among the items found was a pendant carved from a fossil whelk shell, into which was incised the image of a woolly mammoth (Fig. 1). Needless to say, great excitement ensued concerning this evidence of early American man.

Unfortunately, the story of the exact location of discovery of the pendant is somewhat in doubt. One report states that it was found amidst some peat being dug from a "deep" hole on the Delaware River plain opposite the Holly Oak station of the Pennsylvania Railroad (*1*). The farmers are said to have been digging peat for use as fertilizer. Another account (*2*), reports that the Holly Oak pendant was found amidst some peat already spread on a farmer's field near the Holly Oak station of the Wilmington and Baltimore Railroad. The peat was said to have been taken from a "fallen forest layer in one of the adjoining estuaries of the Delaware River."

From 1864 until his death in 1894, Cresson pursued a career as an archeologist and continued to search the northern Delaware piedmont and coastal plain area for further evidences of early man in America. By 1880, he and a few associates had found more than 1000 artifacts, including logs with evidence of cutting, stone sinkers, arrowheads, spearheads, stone knives, hammerstones, splinters of bone, potsherds, stone axes, celts, chips of argillite, quartz, quartzite, flint, jasper, shell beads, a mastodon tooth, human teeth, bone implements, and other remains. Many of these artifacts were ultimately deposited in the Peabody Museum, Yale University, and in the National Museum of Natural History, Smithsonian Institution. Figure 2 shows some of the associated artifacts and human remains. This conglomeration of tools, carvings, bones, teeth, and beads is indeed puzzling. Much of the association appears to be from the Archaic period (8000 to 2000 B.C.). However, the bone implements and the mammoth carved on the Holly Oak pendant suggest a possible Paleo-Indian origin (before 8000 B.C.). Obviously, a great deal of reevaluation needs to be done with regard to the discoveries of Cresson and his associates in northern Delaware.

Cresson's work ranged along the relatively narrow coastal plain adjacent to the fall zone and piedmont of northern Delaware (Fig. 3). Some of the artifacts are reported to have been dug from a rock shelter near the town of Claymont. Many others were found in a layer of peat under the tidal mud that extended under the bed of Naaman's Creek at its confluence with the Delaware River (*3*). Unfortunately, detailed records of the stratigraphy of the sites and of precise locations of the discoveries were not maintained. Interestingly, during the same part of the late 19th century, other discoveries were being made in North America of remains of

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