Table 2. Mean percentage variabilities.

Point on loudness scale	Computed from loudness values	Computed from decibel values
25	8.3	11.8
50	9.9	8.5
75	7.9	3.9

approximate the average of the loudness values by the following procedure.

1) Divide each decibel value by 3.
2) Find the antidecibel values.
3) Average these values.
4) Find the decibel value corresponding to this average.
5) Multiply this decibel value by 3.

This procedure will undo the skewness caused by a cube-root relation between loudness and intensity. For other mathematical relations an analogous procedure can be applied.

Of course, since there are other causes of skewness than the one that concerns us here, the foregoing procedure is no panacea. For some kinds of experimental data the arithmetic mean is a poor measure of central tendency, not because the measurements are made on other than an interval or a ratio scale, but simply because out-sized errors sometimes occur in one direction or another. The resulting skewness can usually best be coped with by resort to medians (*3*).

References and Notes

1. For a fuller discussion of these scales, see S. S. Stevens, "On the theory of scales of measurement," *Science* **103**, 677 (1946); S. S. Stevens, "Mathematics, measurement and psychophysics," in S. S. Stevens, Ed., *Handbook of Experimental Psychology* (Wiley, New York, 1951), chap. 1. For other discussions of these scales, see F. B. Silsbee, "Measure for measure: some problems and paradoxes of precision," *J. Wash. Acad. Sci.* **41**, 213 (1951); C. H. Coombs, H. Raiffa and R. M. Thrall, "Some views on mathematical models and measurement theory," *Psychol. Rev.* **61**, 132 (1954); and J. P. Guilford, *Psychometric Methods*, (McGraw-Hill, New York, ed. 2, 1954).
2. Prepared under contract N5ori-76 between Harvard University and the Office of Naval Research, U.S. Navy (project NR142-201, report PNR-155).
3. See, for example, E. C. Poulton and S. S. Stevens, "On the halving and doubling of the loudness of white noise," *J. Acoust. Soc. Amer.*, in press.

Osmotic Pressure

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OSMOTIC pressure no longer occupies the central role in the theory of solutions that it did a half-century ago, but in biology it retains, nevertheless, its importance as a concept, by reason of the membranes existing in living organisms. It has become evident from questions put to me that the theories of solution upon which many, if not most, biologists were brought up are now so old-fashioned that I might perform a service to the large biological clientele of this journal by presenting the subject in modern terms, emphasizing primarily the concepts involved.

The first important step in developing a theory of solutions was that made by van't Hoff, 1887, who derived the relationship that the osmotic pressure of a substance in sufficiently dilute solution is equal in magnitude to the pressure it would have if it existed as a gas in the volume occupied by the solution. This made it possible to determine the molecular weight of a nonvolatile solute by measuring its osmotic pressure in a solution of known concentration. Using this "van't Hoff law" in Carnot cycles, he derived equations relating molecular weight to the lowering of the freezing temperature and the rise in boiling temperature of the solvent. These relationships became the heart of the physical chemistry of a half-century ago. Nernst discussed electrode potentials in terms of balance between emf, solution pressure of an electrode and osmotic pressure of its ion. Every textbook of physical chemistry expounded osmotic pressure at some length, and some investigators made great efforts to measure it with precision.

But this quasi-gas model of solutions, like the first Wright airplane, with the rudder in front, proved to be a poor basis for further progress. It treated the solvent only as providing volume for the quasi-gaseous solute. It is strictly true, as van't Hoff himself pointed out, only at infinite dilution, but many investigators overlooked the restriction and applied it at concentrations where even gases cease to follow the gas laws. One enthusiast determined the freezing temperatures of concentrated solutions of calcium chloride and ascribed all deviations from the formula to the removal of part of the water from its role as solvent. The water of hydration thus calculated exceeded all the water in the vessel. He was, of course, deeply humiliated when a critic pointed this out.

One of van't Hoff's explicitly stated assumptions in deriving the equation for osmotic pressure was that the solute in dilute solution is described by Henry's law, namely, that its partial pressure is proportional to its molar concentration. This had been abundantly verified for dilute solutions of gases, and it is, indeed, almost a logical necessity; the effects of dissolved molecules too far apart to affect one another must be proportional to their number. What was not appreciated in those days was that all the relationships derived from the expression for osmotic pressure could have been obtained directly jointly from Henry's law and the "Gibbs-Duhem" equation connecting the partial vapor pressures of the two components, which is pure thermodynamics, based upon the fact that a solution may be diluted either by distilling out reversibly a certain amount of solute as vapor or by distilling in an equivalent amount of solvent, and that the free energy change is the same for both. An important consequence of this relationship is that in the range of concentration in which the solute follows Henry's law the solvent follows Raoult's law (*1*).

In *Theoretische Chemie* (ed. 3, 1900) by Nernst, the great physicochemical authority of a half-century ago, one may find Raoult's law derived from van't Hoff's law, a roundabout way, as we now see, of getting it from Henry's law.

The foregoing considerations should not be interpreted as implying any lack of respect for men of the caliber of van't Hoff and Nernst. My purpose is only to point out that the approach to solution theory in the books and courses from which at least the older among my readers doubtless studied is far from being as enlightening and adequate as is now possible.

Vapor pressure and osmotic pressure. Let us begin with the purely thermodynamic relationship between the vapor pressure of the component we will call the solvent and the osmotic pressure of the solute against a membrane permeable only to the solvent. This is easily derived by aid of the principle that the change in free energy involved when pure solvent is transferred into a solution reversibly, under equilibrium conditions, is the same whether the transfer takes place by isothermal distillation through the vapor phase or by passage through a membrane against the osmotic pressure. The relationship is

$$\Pi_2 \bar{v}_1 = -RT \ln f_1/f_1^\circ, \qquad (1)$$

where Π_2 is the osmotic pressure of the solute, $\bar{v}_1$ is the partial molar volume of the solvent—the increase in volume of the solution when 1 mole of solvent is added to an infinitely large volume of solution —and f_1° is the fugacity of the pure solvent; f_1 is its fugacity from the solution. The term *fugacity*, or escaping tendency, introduced by G. N. Lewis, is essentially the pressure the vapor would have if it were an ideal gas. Omitted from this equation is a comparatively small term expressing the change in free energy involved in compressing the solution to the hydrostatic pressure Π_2 before adding solvent through the membrane.

Equation 1 shows that osmotic pressure is far larger in magnitude than the corresponding difference in vapor pressure between solvent and solution and is the better property to measure when investigating very dilute solutions. A solution so dilute that the vapor pressure of the solvent would be lowered only 0.1 mm of Hg from 100 mm would, assuming $v_1 = 100$ ml, have an osmotic pressure of 186 mm.

The ideal solution. Equation 1, as it stands, is useless for calculating osmotic pressure from composition, or vice versa. Such a relationship is very simply derived for a solution whose two species of molecule have the same intermolecular forces and volumes, the two liquids mixing with no changes in temperature or volume. In that case the escaping tendency of a single molecule is the same in pure liquid and solution, hence the fugacity of that species is proportional to its fraction of the total number of molecules present. Designating the number of moles of solvent and solute by N_1 and N_2, respectively, we write

$$\frac{f_1}{f_1^\circ} = \frac{N_1}{N_1 + N_2} = x_1 \text{ and } \frac{f_2}{f_2^\circ} = \frac{N_2}{N_1 + N_2} = x_2. \qquad (2)$$

This is the modern expression of Raoult's law for an "ideal solution," discovered empirically by Raoult in 1887. He expressed it in terms of the lowering of vapor pressure

$$(p_1^0 - p_1)/p_1^0 = N_2/N_1,$$

a form that failed to suggest its theoretical significance. The osmotic pressure of an ideal solution can now be expressed in terms of composition.

$$\Pi_2 v_1 = RT \ln \frac{(N_1 + N_2)}{N_1}. \qquad (3)$$

The term $(N_1 + N_2)/N_1$ may be written as $1 + N_2/N_1$ and the logarithm expanded:

$$\ln\left(1 + \frac{N_2}{N_1}\right) = \frac{N_2}{N_1}\left[1 + \frac{1}{2}\frac{N_2}{N_1} + \frac{1}{3}\left(\frac{N_2}{N_1}\right)^2 + \dots\right].$$

With dilute solutions, N_2/N_1 is small, and neglecting higher powers we may write,

$$\Pi_2 v_1 = \frac{N_2}{N_1} RT. \qquad (4)$$

Substituting the concentration, $c_2 = N_2/N_1 v_1$, we obtain the original van't Hoff form of the "law,"

$$\Pi_2 = c_2 RT. \qquad (5)$$

We see from the derivation the various assumptions involved, few if any of which would be strictly valid for the systems dealt with by biologists. Thus one obviously should be chary about ascribing causes to the deviations from Eq. 5 that are found for such systems as the biologist studies.

Mechanism of osmotic pressure; role of entropy. There was formerly a great deal of discussion of the cause of osmotic pressure, whether it should be ascribed to attractive forces or to thermal bombardment of the semipermeable membrane by the solute molecules. We now see that it is primarily a consequence of the tendency of two different liquid species, under the impulse of thermal agitation, to achieve a state of maximum disorder by any available path, and that the route via osmosis is no more significant theoretically than one via the vapor state or the solid state. Indeed it makes no difference whether the composition of a solution is changed by adding solvent or by removing the equivalent amount of solute. A dissolved electrolyte might be removed by electrolysis.

The thermodynamic measure of molecular disorder is entropy, therefore it may be asserted that osmotic pressure is primarily related to entropy. But entropy is a concept that many persons treat as did a certain engineering instructor who could only say, in reply to a student's question, "I don't know what entropy is; nobody knows what it is; you just use it; that's all." Let us try to do better than this for our particular purpose.

We may illustrate the assignment of a numerical value to the disorder of a mixture by considering, first, the two-dimensional system of checkers. If black checkers are put on one-half of a checkerboard and red ones on the other half, and the board is shaken, the pieces will soon be randomly distributed, and the chance that, on repeated shaking, the original segregation will reappear is almost vanishingly small. After most shakings, the ratios of red to black on the two halves of the board will be nearly equal. The mixing results from the shaking only; no attractive forces are involved. Of course, if the black pieces were made of steel, magnetized, and the red of copper, the former would resist mixing, and the degree of randomness would depend upon the violence of shaking.

The amount of entropy involved in mixing n_1 and n_2 molecules of equal size to form a completely random mixture can be formulated in terms of the number of possible ways of arranging the two sorts in the spaces of the instantaneous configuration of the mixture. This need not be a regular lattice. It is exactly like calculating the number of ways in which n_1 black pieces and n_2 red pieces can be arranged upon a board with $n_1 + n_2$ spaces that are not equal squares. It is $(n_1 + n_2)!/n_1!n_2!$. Because entropy should be additive with respect to disorder, we express it as proportional to the logarithm of this expression,

$$S = k \log [(n_1 + n_2)!/n_1!n_2!].$$

Using Sterling's theorem and taking $n_1 + n_2$ equal to the Avogadro number, we obtain for the increase in entropy upon mixing $N_1 + N_2$ moles,

$$\Delta S^{\mathrm{M}} = -R(N_1 \ln x_1 + N_2 \ln x_2). \tag{6}$$

The entropy of transferring 1 mole of component 1 from pure liquid, where its entropy is $\mathrm{s}_1°$, to solution of composition x_1, where its partial molal entropy is

$$\overline{\mathrm{s}}_1 - \mathrm{s}_1° = -R \ln x_1. \tag{7}$$

If the molecules are not of the same size, the entropy of mixing is larger. An approximate formula was derived independently by Flory (*2*) and by Huggins (*2*) by considering that one component is a linear polymer, whose units are strung like beads on the sites of an imaginary lattice, the monomer molecules of the solvent occupying the remaining sites. I found that it could be derived also without that restriction (*2*). The equations are

$$\Delta S^{\mathrm{M}} = -R[N_1 \ln \phi_1 + N_2 \ln \phi_2] \tag{8}$$

and

$$\overline{\mathrm{s}}_1 - \mathrm{s}_1° = -R \left[\ln \phi_1 + \phi_2 \left(1 - \frac{\mathrm{v}_1}{\mathrm{v}_2}\right)\right]. \tag{9}$$

The difference between Eqs. 6 and 8, or 7 and 9, is small when v_1 and v_2 do not differ by a factor of more than 2 or 3, but it becomes enormous if one component is a high polymer. Let us see, next, how such differences would affect the lowering of vapor pressure and the osmotic pressure. This requires resort to the second law of thermodynamics, and I shall give a very elementary, rather intuitive derivation, for the purpose of emphasizing the three concepts involved.

Entropy, energy, and free energy. Certain forms of energy, including kinetic, potential, electric, magnetic, can be, at least in principle, reversibly transformed into one another. But if any of them generate heat, it cannot be quantitatively reconverted into the others. The kinetic energy of, say, a piece of lead moving through space at 0°K would represent an orderly movement of its atoms in parallel paths; but if the object were suddenly stopped by a hard meteorite, its temperature would rise, the orderly motion of the atoms would become disordered, and the probability that they would all suddenly move together as before would be infinitesimal. Any process that is accompanied by an increase in molecular disorder has less capacity for doing work, less free energy, the higher the temperature at which it occurs. Designating the change of free energy and entropy of the system by ΔF and ΔS, respectively, we may translate that statement into mathematical form, writing

$$[\partial(\Delta F)/\partial T]_p = -\Delta S. \tag{10}$$

Also, the heat absorbed in a process will not all be available for doing work if the process involves an increase in molecular disorder, as it does when a gas is liberated, and the excess of ΔH over ΔF should be proportional to the increase in entropy. The proportionality constant is the absolute temperature, and we may write

$$\Delta H - \Delta F = T\Delta S. \tag{11}$$

These are two expressions of the second law of thermodynamics. This way of getting them shows, I trust, why the concept of entropy is necessary and reasonable. It is not a proper derivation, but a good many of our most important concepts, principles and laws have been perceived as hunches and only later derived by the stricter logic of the textbook. I am a strong believer in the desirability of beginning with the concepts rather than a series of mathematical steps.

Let us now pursue our subject by writing under each term of Eq. 11 its value for an ideal solution:

$$\begin{aligned} \overline{\mathrm{F}}_1 - \mathrm{F}_1^0 &= \overline{\mathrm{H}}_1 - \mathrm{H}_1^0 - T(\overline{\mathrm{S}}_1 - \mathrm{S}_1^0), \\ RT \ln (f_1/f_1^0) &= 0 - T(-R \ln x_1). \end{aligned} \tag{12}$$

It follows that $f_1/f_1° = x_1$ (and, of course, $f_2/f_2° = x_2$) and we thus obtain Raoult's law by a more rigid treatment of molecular disorder than the one given earlier.

If we are dealing with components whose molar volumes are unequal but that nevertheless mix "athermally," then Eq. 9 becomes appropriate. Let us see the effect upon osmotic pressure of using a not very high polymer with $\mathrm{v}_2 = 10^3\mathrm{v}_1$. Suppose 1 mole of solvent is transferred into a solution where $x_2 = 10^{-3}$ and $x_1 = 0.999$. If $\mathrm{v}_1 = \mathrm{v}_2$, the entropy of transfer per mole is from Eq. 7, 0.00197 cal/deg. If the solute is a polymer, with $v_1 = 100$ ml and $v_2 = 10^3 v_1$, Eq. 9 gives 0.39 cal/deg. With $T = 298°\mathrm{K}$, the values of $RT \ln(f_1{}^\circ/f_1)$ are 0.024 lit atm and 4.7 lit atm, and the osmotic pressures, by Eq. 1, are 0.24 and 47 atm, respectively, an enormous difference.

But most solutions are far from ideal, by reason not only of unequal molar volumes but of unequal intermolecular forces: van der Waals, dipole, hydrogen bonding, acid-base, and ionic. These introduce not only changes in configuration, disorder, and therefore entropy but also changes in heat content. No longer can one assume that the entropy of mixing will be correctly predicted by the foregoing equations or that the heat of mixing will be zero. It is worth mentioning, however, that the heat term in Eq. 12 is a quadratic function of the concentration of the solute and, hence, disappears in the limit. For a solution, in which thermal agitation suffices to give random mixing, this term is given approximately by the expression,

$$\bar{H}_1 - H_1{}^\circ = v_1\phi_2{}^2(\delta_2 - \delta_1)^2,$$

where the δ's are "solubility parameters" expressing the intermolecular forces of solute and solvent. To deal with all these factors is far beyond the scope of so limited a treatment as this, which is intended only to remove some of the mystery that often beclouds the subject and to warn against the drawing of too simple inferences from deviations that may be encountered from the primitive equation, $\Pi = c_2RT$. The emphasis upon the role of entropy in modern solution theory is in striking contrast to its neglect during the period when the theory was based upon osmotic pressure. In Nernst's *Theoretische Chemie,* there is but one reference to entropy. It is in small type and consists of an argument for not using it! Today, no physical or natural scientist can afford to be utterly ignorant of entropy.

References

1. For derivations, see J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes* (Reinhold, New York, 1950).
2. For references and detailed discussion, see reference 1, Chapters VI and XX; also J. H. Hildebrand *J. Chem. Phys.* **15**, 225 (1947).

The European Oyster in American Waters

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THE common European oyster, *Ostrea edulis* L., which occurs along the Atlantic Coast of Europe from Norway to Spain, in the British Isles, and the western part of the Mediterranean, may propagate at a somewhat lower temperature than our native oyster, *Crassostrea virginica* Gmelin. We thought, therefore, that the European oyster might be introduced into this country (*1*) to occupy eventually a definite ecologic niche in areas where the water is too cold for the successful propagation of our native oyster but is still sufficiently warm to be within the propagating temperature range of *O. edulis.* Among such areas are certain bodies of water along the shoreline of Maine and some well-protected bays and harbors of our Pacific Coast states.

The oysters were shipped to us from the Oosterschelde, Holland, by P. Korringa late in September 1949 and were placed in Milford Harbor on 11 October. The shipment consisted of approximately 9000 oysters representing 3 year-classes, that is, the 1947, 1948, and 1949 sets. Because of the long trip approximately 13 percent died soon after arrival, the mortality being heaviest among the youngest year-class.

The oysters were intended chiefly for studies to determine whether they would survive and propagate under the ecologic conditions to which they would be subjected in this country. Simultaneously with these studies, observations were also made on the seasonal gonadal changes of the oysters kept in different localities, their rate of growth, artificial propagation, and several other aspects of their biology.

Some of the oysters were left in Milford Harbor, but the others were transplanted to four localities of Maine, including Boothbay Harbor. The oysters grew well in all regions. Their mortality in Milford did not exceed, in general, that of the native oyster living in the same environment. Each winter since their arrival from Europe the oysters have lived under a layer of ice, at least for some time. In Milford Harbor, an estuary strongly affected by river discharge, the oysters were subjected, especially in the spring, to prolonged periods of low salinity but, nevertheless, survived, a fact indicating that they possess good tolerance in this respect.

The European oysters were noticeably affected if the turbidity of the water, whether caused by silt or high concentrations of microorganisms, was relatively high. We even witnessed cases of abortion of embryos and immature larvae by gravid females that had been exposed to a dense concentration of dinoflagellates belonging to the genera *Prorocentrum* and *Gymnodinium.* The larvae were expelled in pseudofeces imbedded in mucus along with masses of dinoflagellates. The abortion was usually complete, removing all larvae from the mantle cavity where they are nor-