"activate" it to oxidize quite a number of hydroquinones, anilines, or even nitrite.

Experiment 6. To H_2O_2 in acetate buffer, *p*H 4.6, is added a trace of peroxidase: no effect. Benzidine is now added: blue coloring results.

Peroxidases occur here and there in animal material—for example, in leucocytes (verdoperoxidase, isolated in pure form by Kjell Agner in 1941) and in milk (lactoperoxidase, isolated by myself and Åkeson a year or so later).

In the living cells, both catalases and peroxidases function in the same way by using the hydrogen peroxide arising in connection with the reaction of oxygen with a number of autoxidable substances, such as flavins, ascorbic acid, and so forth, to oxidize otherwise difficultly combustible substrates. Especially interesting is Agner's observation that the verdoperoxidase in the leucocytes + H_2O_2, can detoxify, for example, tetanus and diphtheria toxins, which would of course explain one of the main functions of the leucocytes.

Catalases and peroxidases both give, with H_2O_2, first greenish complex compounds and then reddish ones. The study of these has presented immensely intricate problems, where we have had to use combinations of spectrophotometric and now very refined magnetic methods to try to elucidate the mechanism. Our American colleague Britton Chance, who in 1946–1948 worked at the Nobel Institute, has successfully carried investigations still further in this field.

Conclusion

What is the final goal of enzyme research? The first stage is to investigate the entire steric constitution of all enzymes—a nice little job! So far, we know only the most easily accessible sixth part of the smallest enzyme molecule, cytochrome *c*.

In the second stage, it is a matter of deciding how the enzymes are arranged in the cell structures. This implies, as a matter of fact, the filling of the yawning gulf between biochemistry and morphology.

Osmotic Pressure

Francis P. Chinard and Theodore Enns

Two recent articles, by Hildebrand (*1*) and Babbitt (*2*), have made evident some of the differences of opinion concerning the meaning of osmotic pressure. As is indicated by Hildebrand, the concept of osmotic pressure is of considerable importance in biological and physiological problems in which membranes are involved. Many physiologists have considered osmotic pressure to be the pressure exerted by solute molecules on a membrane permeable to the solvent but not to the solute. However, most, if not all, physical chemists and thermodynamicists consider osmotic pressure to be the pressure difference that must be imposed by the analyst across a membrane or barrier in order to establish equilibrium with respect to a substance that can cross the barrier. To some of the former group, osmotic pressure appears to be an intrinsic property of solute molecules. To the latter group, the determination of osmotic pressure is simply a convenient means of quantifying the effect of one constituent of a system on the properties of another constituent, just as determinations of freezing-point depression, boiling-point elevation, and vapor-pressure lowering are also measures of this effect.

We consider that the continued emphasis, in the physiological literature and occasionally in some of the more physicochemical contributions, on osmotic pressure as a property solely of solute molecules is unfortunate and misleading. We believe it is desirable, therefore, to set forth an elementary statement of the meaning of osmotic pressure (*3*). The following exposition presupposes some knowledge of the basic terms used. However, it may be noted here that the end-result as applied to physiological problems gives emphasis to the fact that the properties of *water* are affected by solutes. Consideration of the problem of capillary permeability by this approach has led to a reexamination of some fundamental physiological concepts (*4*).

To simplify the discussion, use is made of the concept of chemical potentials, which was introduced by Willard Gibbs (*5*). An elementary exposition of the concept will be found in W. Mansfield Clark's textbook (*6*). One of us (F.P.C.) has attempted a brief qualitative description (*7*).

Development

Consider a system comprised of two liquid phases, *A* and *B*, separated by a rigid membrane or barrier. Phase *A* contains only one constituent, denoted by the subscript 1, to which the barrier is permeable; phase *B* contains constituent 1 and another constituent, 2, to which the barrier is not permeable. Constituents 1 and 2 are soluble in each other. The pressure, *P*, is initially the same in the two phases. We wish to obtain a measure of the effects of constituent 2 on the properties of constituent 1. This effect will be expressed in terms of the chemical potential of constituent 1, in other words, in terms of the Gibbs free energy per mole of constituent 1. Under the initial conditions of equality of pressure in the two phases, equilibrium does not obtain with respect to constituent 1; experimentally there will be found net passage of constituent 1 from phase *A* to phase *B*; the chemical potential of constituent 1 in phase *A*, μ'_1, is greater than the chemical potential of constituent 1 in phase B, μ''_1.

The chemical potential of a given substance may be defined by the relationship

$$\mu = \mu^0 + RT \ln a \qquad (1)$$

where *R* is the gas constant, *T* is the absolute temperature, ln denotes natural logarithm, *a* is activity and μ^0 is a constant at any given set of values for *T* and *P*.

Under the initial conditions, the chemical potential of constituent 1 in phase *A* is

$$\mu'_1 = \mu^0 + RT \ln a'_1 \qquad (2)$$

and in phase *B* it is

$$\mu''_1 = \mu^0 + RT \ln a''_1 \qquad (3)$$

The difference between the chemical po-

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tentials of constituent 1 in the two phases is then

$$\mu'_1 - \mu''_1 = RT \ln \frac{a'_1}{a''_1} \qquad (4)$$

To obtain a measure of this difference of the chemical potentials, use is made of the experimental fact that when a certain pressure difference is imposed across the barrier there will be no net passage of constituent 1 from phase *A* to phase *B*. Experimentally, it is found that the pressure on phase *B*, P_B, must be greater than the pressure on phase *A*, P_A. Equilibrium is established with respect to constituent 1 in this manner, and the chemical potential, μ'_{1,P_A}, of constituent 1 in phase *A* at the pressure P_A is equal to the chemical potential, μ''_{1,P_B}, of constituent 1 in phase *B* at the pressure P_B.

We have now the relationships

$$\mu'_{1,P_A} = \mu^0_{1,P_A} + RT \ln a'_1 \qquad (5)$$

and

$$\mu''_{1,P_B} = \mu^0_{1,P_B} + RT \ln a''_1 \qquad (6)$$

But equilibrium obtains; hence,

$$\mu'_{1,P_A} = \mu''_{1,P_B} \qquad (7)$$

and

$$\mu^0_{1,P_A} + RT \ln a'_1 = \mu^0_{1,P_B} + RT \ln a''_1 \qquad (8)$$

From Eqs. 7 and 8 we have

$$\mu^0_{1,P_B} - \mu^0_{1,P_A} = RT \ln \frac{a'_1}{a''_1} \qquad (9)$$

where μ^0_{1,P_B} and μ^0_{1,P_A} are determined by temperature and pressure. The system is considered to be isothermal, and we need be concerned only with the variations of μ with *P*. This variation is given by

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \overline{V} \qquad (10)$$

where the subscripts *T* and *n* indicate that the temperature and composition remain constant, and where $\overline{V}$ is the partial molal volume of the constituent under consideration. For sufficiently small variations of *P*—that is, if P_A and P_B differ by a sufficiently small amount, and if the compressibility of the constituents may be neglected—we may write

$$\mu^0_{1,P_B} - \mu^0_{1,P_A} = \overline{V}_1(P_B - P_A) \qquad (11)$$

From Eq. 11 and Eqs. 4 and 9, there follows immediately

$$\mu'_1 - \mu''_1 = \overline{V}_1(P_B - P_A) = RT \ln \frac{a'_1}{a''_1} \qquad (12)$$

whence

$$P_B - P_A = \pi = \frac{RT}{\overline{V}_1} \ln \frac{a'_1}{a''_1} \qquad (13)$$

where π is the so-called osmotic pressure.

It is important to note that the osmotic pressure multiplied by the partial molal volume of the constituent under consideration is equal to the difference between chemical potentials that obtained when the pressures on the two phases were equal. Nowhere does "the pressure of solute molecules" enter.

The limiting law, or van't Hoff law, of osmotic pressure is derived from Eq. 13 by the use of simplifying assumptions. The activity, *a*, is the product of the mole fraction, *N*, and the mole fraction activity coefficient, *f*. We may then write for Eq. 13

$$\pi = \frac{RT}{\overline{V}_1} \ln \frac{N'_1 f'_1}{N''_1 f''_1} \qquad (14)$$

The convention that the activity of constituent 1 in phase *A* is unity is now applied. Equation 14 reduces to:

$$\pi = \frac{RT}{\overline{V}_1} \ln \frac{1}{N''_1 f''_1} = -\frac{RT}{\overline{V}_1} \ln N''_1 f''_1 \qquad (15)$$

If constituent 2 is present in sufficiently small concentrations, it may be assumed that $N''_1 f''_1$ approaches N''_1 in value. In the present simplified system, we have $N''_1 + N''_2 = 1$. Hence, $N''_1 f''_1$ may be replaced by $(1 - N''_2)$. We now have

$$\pi = -\frac{RT}{\overline{V}_1} \ln (1 - N''_2) \qquad (16)$$

The logarithmic portion is expressed as a series to give

$$\pi = -\frac{RT}{\overline{V}_1}\left[-N''_2 - \tfrac{1}{2}(N''_2)^2 - \tfrac{1}{3}(N''_2)^3 - \cdots\right] \qquad (17)$$

It is now assumed that all terms in the expansion of degree higher than 1 may be neglected. Thus

$$\pi = \frac{RT}{\overline{V}_1} \cdot N''_2 \qquad (18)$$

But

$$N''_2 = \frac{n''_2}{n''_1 + n''_2} \qquad (19)$$

where *n* denotes number of moles. But n''_2 is small compared with n''_1; therefore, we may write $N''_2 = n''_2/n''_1$. We then have

$$\pi = \frac{RT}{n''_1 \cdot \overline{V}_1} \cdot n''_2 \qquad (20)$$

But $n''_1\overline{V}_1$ is simply the volume occupied by constituent 1 and may be written V_1. Then n''_2/V_1 is the molal concentration of constituent 2 and is denoted by C''_2. We have finally

$$\pi = C''_2 RT \qquad (21)$$

This is van't Hoff's limiting law of osmotic pressure. It is an approximation. It does no more than indicate the approximate relationship between the concentration of constituent 2 and the pressure difference that must be imposed in the present system in order to establish equilibrium with respect to constituent 1.

Conclusions

The relationship is analogous in form to the simple gas law. However, this *analogy* does not require that the pressure difference π, experimentally determined, be the "bombardment pressure of the solute molecules against the barrier." Indeed, if this were the case, the pressure "exerted" by the solute molecules against the barrier would have to be a *negative* bombardment pressure in order to account for the passage at equal hydrostatic pressures of the solvent from the pure solvent phase to the solution phase. It may be pointed out that there is no justification or basis for the concept of *negative* pressure: pressure approaches zero as the molecular density approaches zero, but pressure does not and cannot assume negative values.

Use of the term *osmotic pressure* in the sense of the "pressure of the solute against a membrane permeable only to the solvent" cannot be justified either on theoretical or on experimental grounds (see, for example, *6, 8, 9*).

On occasion, the convenient operational designations, "solvent" and "solute," have been used with the implications of fundamental differences in properties. It will be noted that these designations have been avoided in the derivation given here. In a system such as is considered here, "solvent" would designate constituent 1 and "solute" constituent 2. But the meaning of such designations would be simply that the barrier is permeable to constituent 1 and not permeable to constituent 2. The designations would be reversed if a barrier permeable to constituent 2 but not to constituent 1 were used. A system frequently considered in physiology is that formed by the plasma, the capillary walls, and the interstitial fluid. In a simplified form of the system, water would be the solvent, the plasma proteins the solute, and the capillary walls the barrier. In such a simplified system, the osmotic pressure of the plasma as determined in the laboratory provides a measure of the effect of the proteins on the properties of water.

The term *osmotic pressure* is in itself misleading. It is probable that this has contributed to the confusion surrounding the meaning of the term. As we have noted, osmotic pressure as experimentally determined is a pressure *difference* and not an absolute pressure. The experimental implications have been retained in, for example, the terms *freezing-point depres-*

sion and *boiling-point elevation*; there is no connotation of absolute measurements but only of relative measurements. The freezing point of a pure solvent is, in effect, that temperature at which a liquid phase and a solid phase can coexist without change of mass of the individual phases. The freezing point of a solution is that temperature at which a solid, pure-solvent phase can coexist with a liquid-solution phase without change of mass of the individual phases. The difference between these two temperatures is the freezing-point depression. In other words, the temperature of a *solution* and of the pure solvent must be decreased below the freezing point of the pure solvent in order to establish equilibrium with respect to the solvent between the solvent in the solution and solvent in the pure solid phase. Similar remarks apply to boiling point elevation. Osmotic pressure is then simply the pressure *increment* that must be imposed on a solution in order that pure solvent phase and solution phase, separated by an appropriate barrier permeable only to the solvent, can coexist without change of mass of the individual phases. In other words, osmotic pressure as a pressure *difference* is similar to the freezing-point *depression* and to the boiling-point *elevation.*

This should provide an adequate negative answer to the often asked question: "Does osmotic pressure exist as such in a solution?" A negative answer is also provided from the derivations we have given. It may be pointed out, in addition, that Gibbs referred to the "so-called osmotic pressure" and indicated clearly that the pressure calculated by the laws of Boyle, Charles, and Avogadro for the solute in the space occupied by the solution was *calculated* and not experimentally found (*10*). Pressure can be measured in a single phase, just as temperature can. But just as the determination of freezing point or boiling point requires the coexistence of *two* phases, so does the determination of osmotic pressure require the coexistence of two phases (*11*).

One does not subtract freezing-point depression from the actual temperature of a solution to calculate an "effective temperature." No more should one subtract osmotic pressure from the actual pressure of a solution to calculate an "effective pressure."

It is recognized, as Haldane pointed out a number of years ago (*12*), that the concept of osmotic pressure as something which exists in solutions even when no external pressure is applied is firmly entrenched. It is hoped, nonetheless, that this discussion may help to clarify the meaning of osmotic pressure and that the concept of osmotic pressure as the bombardment pressure of solute molecules against an impermeable barrier will eventually be abandoned.

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World-Wide Travel of Atomic Debris

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For centuries meteorologists have thought of exploring large-scale atmospheric circulations by means of tracers. The literature describes how man has successfully tracked fluorescent particles to a distance of 100 miles (*1*), used radioactive tracers across the United States (*2*), and followed volcanic ash and forest fire smoke over distances of the order of 1000 miles (*3*). Only the dust from a major volcanic eruption, such as Krakatao, has been tracked on a truly global scale.

During two of the nuclear test periods in the Pacific Proving Grounds of the U.S. Atomic Energy Commission, sufficient radioactive debris was thrown into the atmosphere to be deposited in both hemispheres. Measurements of the deposited radioactivity were obtained from exposed sheets of gummed film. The details of the network and the sampling and measurement techniques have been described by Eisenbud and Harley (*4*). It should be noted, however, that the deposition of particles on the adhesive surface depends either on the presence of precipitation or, in dry weather, on turbulence to assist the impaction of the particles on the horizontal surface of the paper. It is thus possible to have a cloud of radioactive particles pass two stations simultaneously and have only the station with rain note the presence of the particles overhead. The gummed-film method of collection is recognized as being as crude as it is simple.

The nuclear explosions are treated in this article, the Mike shot on 1 November 1952 and the Bravo shot on 1 March 1954. The shots were similar in that both are described as having had energy in the megaton range, both were detonated at or near the earth's surface on a coral island, and both had atomic clouds that penetrated into the stratosphere. To the meteorologist, the main difference of interest between the two events is the season.

Winds

The winds acting on the two atomic clouds at the time of detonation are illustrated in Fig. 1. The wind structure has been estimated, when necessary, from observations at nearby locations and times. On both days the tropopause was found at an altitude of about 55,000 feet, and it separated winds blowing from different directions. The easterly winds

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