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A NEW THEORY OF OSMOTIC PRESSURES OF BINARY SOLUTIONS OF NON-ELECTROLYTES

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A new theory of osmotic pressures of binary solutions of non-electrolytes

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A new theory of osmotic pressures is developed which applies to binary solutions of non-electrolytes separated by a semipermeable or a leaky membrane. Both solutions are assumed to be incompressible, one of these may be a pure solvent. Unlike the previous theories that are either empirical or stem from thermodynamic considerations, the present theory is based on the diffusion mechanism of osmosis and might therefore be termed 'mechanistic.' The general equations of this theory bring about a number of particular formulas for osmotic pressures covering all the possible combinations of the membranes (*semipermeable*, *leaky from one side*, *leaky from both sides*) and the pairs "A–B" of the solutions involved (among these "*concentrated* A–*concentrated* B," "*pure solvent* A–*concentrated* B," "*infinitely dilute* A–*infinitely dilute* B," "*pure solvent* A–*infinitely dilute* B"). The 'mechanistic' theory is validated by direct and indirect experimental data on osmotic pressures of aqueous solutions of sucrose and those of ethanol at all their feasible concentrations. In the case "*semipermeable membrane*" and "*pure solvent* A–*infinitely dilute solution* B," the present theory is reduced to the classical law of van't Hoff or Morse. In comparison with these and the other previous models of osmotic pressures, the proposed theory (i) holds for both ideal and non-ideal solutions, (ii) imposes no restrictions on the concentration of the mixtures, (iii) includes no adjustable parameters. The 'mechanistic' theory enables revealing the existence of an upper limit $\pi_{(+)}$ of osmotic pressure π, i.e. $\pi \leq \pi_{(+)}$, the limit $\pi_{(+)}$ depending on the molar volume of the solvent ($\pi_{(+)} \approx 1300$ atm for aqueous solutions). Information about the limits $\pi_{(+)}$ may be of importance to applications in biology, chemical engineering, etc. It is shown in particular that due to the limitation $\pi < \pi_{(+)}$, the life of marine animals in sea-water might be wiped out at the depths below approximately 13 km, should they exist. The present theory also brings about new expressions for the activity, the activity coefficient, and the chemical potential of solvent. In contrast to the similar classical laws, these expressions are in better agreement with physical reality and experimental data.

I. INTRODUCTION

Osmosis is a well-known phenomenon of a spontaneous flow of solvent molecules through a membrane separating two liquid solutions.[1-3] The flow is directed from a solution of higher solvent concentration (it may be a pure solvent) to a solution of lower solvent concentration. The membrane is generally assumed to be semipermeable, i.e., permeable to molecules of solvent but not to molecules of solute.

Osmosis gives rise to osmotic pressure that plays an important role in physical, chemical, and biological processes. In particular, it is a dominant driving force in biological systems moving various solvents and solutes through cell membranes.[4,5] Also, information about osmotic pressures is a main source of determining the molecular weights of solute macromolecules[6-9] and the equivalent radii of the membrane pores and channels.[10]

Although osmosis has been studied for more than a century, the underlying mechanisms are not yet fully understood.[10-12] Such a blind spot might have blocked the progress of any theory. Surprisingly enough, this has not happened, and a number of osmotic pressure theories have been developed that disregard any possible mechanisms of osmosis. A majority of these non-mechanistic theories (NMTs) are related to incompressible solutions of non-electrolytes separated by a semipermeable membrane, one of the solutions being binary, the other being a pure solvent. The most famous of the NMTs deal with the following categories of solutions:

1. Ideal dilute mixtures:

The van't Hoff equation[13]

$$\pi = RTC_2 \tag{1}$$

The Morse equation[14]

$$\pi = RTm_2' \tag{2}$$

Here π, R, T, C_2 and m_2' are the osmotic pressure, the gas constant, the absolute temperature, the molar and the volume molal concentrations of solute, respectively; m_2' is defined as

$$m_2' = m_2\overset{\circ}{\rho_1} \tag{3}$$

where m_2 is the solute molal concentration, $\overset{\circ}{\rho_1}$ is the density of a pure solvent at the given temperature T and pressure P.

2. Non-ideal dilute solutions:

The power ('virial') series[7-9,15,16]

$$\pi = RT(c_2/M_2 + A_2 c_2^2 + A_3 c_2^3 + \ldots) \tag{4}$$

Here M_2 is the solute molecular weight, $A_2, A_3,\ldots$ are the second, third, etc. virial coefficients, c_2 is the mass solute concentration (g of solute/liter of solution) expressed by

$$c_2 = C_2M_2 \tag{5}$$

3. Non-ideal concentrated solutions:

The logarithmic equation (Variant 1)

$$\pi = (RT/V_1^{\circ}) \ln (p_1^{\circ}/p_1) \tag{6}$$

where V_1° is the molar volume of a pure solvent, p_1° and p_1 are the vapor pressures of the pure solvent and of the solvent in the solution, respectively; both these pressures are taken at the same T and P, the vapor is assumed to obey Boyle's law. A logarithmic equation similar to (6) had first been established by van Laar,[17] then modified by the Earl of Berkeley and Hartley[18] and finally brought into the form (6) by some other contemporary authors.[19-22] Later on Eq. (6) was altered and amended by introducing adjustable parameters.[23-25]

The logarithmic equation (Variant 2)[11]

$$\pi = -(RT/V_1^{\circ}) \ln a_1 \tag{7}$$

Here $a_1 = \gamma_1 x_1$ is the activity of solvent in the solution, x_1 is the mole fraction of the solvent defined as

$$x_1 \equiv C_1/(C_1 + C_2) \equiv m_1/(m_1 + m_2) \equiv$$
$$m_1'/(m_1' + m_2') \tag{8}$$

γ_1 is the activity coefficient of the solvent measuring its departure from ideality. In general both γ_1 and a_1 depend on T, P and the mole fraction of solute $x_2 = 1 - x_1$:

$$\gamma_1 = \gamma_1(T, P, x_2) \tag{9}$$

$$a_1 = a_1(T, P, x_2) \equiv x_1\gamma_1(T, P, x_2) \tag{10}$$

In the case of ideal dilute mixtures, $x_2 \to 0$ and $x_1 \to 1$, so that $\gamma_1 \to 1$ and $a_1 \to x_1$. Given identities (8), Eq. (7) then reduces to Eq. (1) or (2). Also, in some derivations of Eqs. (6) and (7) the volume V_1° is substituted by the partial molar volume $\bar{V}_1$ of the solvent in the solution.[8,26]

Besides Eqs. (1), (2) and (4), there are some less practicable NMTs of osmotic pressure of dilute solutions surveyed in books.[27-31]

Whatever their differences, all the NMTs result from one fundamental thermodynamic relation

$$\mu_1 = \mu_1^{\circ} + RT \ln a_1 \tag{11}$$

where μ_1° and μ_1 are the chemical potentials of a pure solvent and of the solvent in a solution, respectively. The law (11) is independent of any mechanisms of osmosis, and this remarkable feature is generally regarded as great advantage in building the osmotic pressure theories. Yet such a view does not seem quite impeccable, at least so far, because the use of Eq. (11) has imposed certain limitations on each NMTs.

The point is that there still is no comprehensive theory of liquid mixtures (including their chemical potentials) to be valid at any feasible temperature, pressure, and solute concentration.[32,33] The celebrated theories of non-ideal binary solutions[34-42] are restricted to particular types of mixtures and limited solute concentrations. Similar limitations are also inherent, to different degrees, in recently proposed theoretical developments.[43-48] To fit experimental data, all the mixture models involve *faute de mieux* adjustable parameters and are therefore called 'semitheoretical'.[49] As a result, up to now the key thermodynamic factors of non-ideal concentrated solutions—the activity a_1 by Eq. (10) and the chemical potential μ_1 by Eq. (11)—can only be expressed as empirical or semi-empirical functions of the arguments T, P, x_2.

Proceeding from semitheoretical expressions for a_1 and μ_1, the NMTs have a limited range of applicability. This range depends critically on the kind and concentration of solute molecules, i.e., on whether a real solution concerned may be considered as ideal or non-ideal, dilute or concentrated. The matter is aggravated by the fact that it is mostly difficult if not impossible to tell in advance the difference between these categories of solutions. Moreover, if a solution is sufficiently dilute, the difference between ideality and non-ideality can practically vanish, but the exact measure of this 'sufficiency' is also unknown beforehand.

In particular, the van't Hoff theory (1) is supposed to hold if a solution is both ideal and dilute (in terms of molarity C_2). Yet the theory fails for dilute and even very dilute solutions of hemoglobin,[30] insulin,[50] lysozime[51] and many other biological macromolecules. This simply means that such dilute solutions are non-ideal. On the other hand, at extremely low molarities some of these solutions exhibit ideal behavior. For instance, if the hemoglobin concentration $C_2 \leq C_2^* \approx$ 0.0005 moles/1000 ml, the van't Hoff theory proves to be quite satisfactory. Hence at $C_2 \leq C_2^*$ the non-ideal dilute solutions of hemoglobin become sufficiently dilute and may be treated as ideal mixtures. However, the van't Hoff law passes by the possible limits C_2^*, and so its range of applicability can be brought to light only by a direct comparison with experimental data. The same disadvantage is also peculiar to the Morse equation (2).

The more general virial theory (4), too, has weak points. One of them stems from the specific nature of the underlying virial coefficients A_2, A_3, etc. These coefficients, which depend on the kind of solution and represent its deviation from ideality, are usually and most reliably determined by osmometry.[8,52-55] This makes the virial theory semiempirical and deprives it of the ability to predict osmotic pressures before they have at least once been measured. Another weak point is associated with an upper limit of the solute molality m_2^*. The virial theory is based on the assumption that a solution is infinitely dilute, i.e., the molality $m_2^* \to 0$.[7] In fact the theory holds at $m_2^* >> 0$, but these real limits m_2^* do not enter into the virial equation (4) and are to be detected by experiments.

The logarithmic equations (6) and (7) are the most exact of all the NMTs. Yet they also have limitations. Due to the absence of a comprehensive theory of non-ideal concentrated solutions, there is no exact theory of the vapor pressures p_1 of those solutions either. Therefore the values of p_1 in Eq. (6) are to be determined empirically, with the help of direct measurements or, conversely, in terms of observed osmotic pressures. The second variant (7) is more general than the first one (6). Nevertheless, as noted above, the underlying activity a_1 by Eq. (10) still cannot be expressed as an exact theoretical function of x_2, T, P and is to be found empirically before being substituted in Eq. (7). Thus not only the virial theory (4) but also both the logarithmic equations (6) and (7) are semiempirical.

It is worth reminding one more weak point of the classical thermodynamic approach to osmotic problems. Classical thermodynamics is sufficient for dealing with semipermeable membranes, but if the membranes are leaky (permeable to solute), it fails. So do the NMTs. They can be amended if the osmotic pressures by these theories are multiplied by the reflection coefficient σ ($0 < \sigma < 1$) obtained in terms of irreversible thermodynamics.[56,57] Nevertheless, such a correction does not revise the essence of the NMTs and does not therefore eliminate their intrinsic shortcomings mentioned above.

The limitations of the NMTs and some mystery of osmotic mechanisms have long challenged the scientific community and in the last few decades led to revival of theoretical activity in the field of osmosis and osmotic pressure. The origin of osmosis was reconsidered from several angles to be touched upon in Sec. II. Here it suffices to note that these endeavors however inventive have neither shed new light on osmotic mechanisms nor resulted in an advanced theory of osmotic pressure.

Allowing for the above background, in this paper we try to develop a theory of osmotic pressure based on a mechanistic rather than on the thermodynamic consideration of osmosis. The aim of the study is to circumvent the limitations of the NMTs and provide a simpler and sufficiently precise technique for computing osmotic pressures. Our theory deals with incompressible binary solutions of non-electrolytes of any feasible concentrations. The solutions are separated by either a semipermeable or a leaky membrane. The underlying mechanism of osmosis is assumed to be diffusion of solvent molecules accompanied, for a leaky membrane, by diffusion of solute molecules.

The paper is organized as follows. In Sec. II we touch upon major hypotheses of osmotic mechanisms. Stemming then from the diffusion hypothesis, we set the stage for our model in Sec. III. The mechanistic theory of osmotic pressures for both semipermeable and leaky membranes is developed in Sec. IV. Particular cases of the theory are specified in Sec. V. In Sec. VI the theory is compared with the classical laws (1), (2) and verified by experimental data. Some significant features and consequences of the theory are discussed in Sec. VII.

II. OSMOTIC MECHANISMS

As mentioned in Sec. I, the thermodynamic approach to osmotic problems is based on Eq. (11) for the chemical potential of solvent $\mu_1 \equiv \mu_1(T, P, x_2)$. Since this function is independent of an osmotic mechanism, a search for the latter has commonly been considered unessential and even needless. Such a mainstream opinion was first voiced in the early monograph on osmotic pressure[25] and later echoed in many works on physical and biophysical chemistry (see, for instance,[1,2,9,11,26,58-61]).

However popular, this view seems somewhat categorical. It implies an unconditional perfection of the thermodynamic approach and disregards its considerable limitation, the incapacity to yield the underlying function $\mu_1(T, P, x_2)$. Only if a system is ideal and dilute, the limitation is of no importance. In this particular case, the chemical potential is given by the relation

$$\mu_1 = \mu_1^\circ + RT \ln x_1 = \mu_1^\circ + RT \ln (1 - x_2) \qquad (12)$$

which results from Eq. (11) at $\gamma_1 = 1$ and leads to the limiting laws (1) and (2). In all other cases, the function $\mu_1(T, P, x_2)$ is unknown beforehand and has to be borrowed from additional sources: mixture theories, experiments, etc.

As a result of being incapable to furnish the underlying function $\mu_1(T, P, x_2)$, the thermodynamic approach is insufficient to solve osmotic problems for non-ideal and/or concentrated solutions. Although this fact is not new, it has not usually been emphasized. Meanwhile, it suggests an alternative technique that *per se*, in contrast to the thermodynamic approach, might be able to provide a comprehensive solution to osmotic problems by allowing for an osmotic mechanism.

The quest for this mechanism began in the 1850s and is still in progress stimulated mostly by biochemical needs.[4,5,10,12] Many hypotheses have been advanced to clear up what is behind the osmotic flow and osmotic pressure. An admirable review of early hypotheses is given in a treatise.[62] Several recent explanations of osmotic phenomena are proposed in articles.[63-69] All the hypotheses refer to the classical case of osmosis when a semipermeable membrane separates a pure solvent from a binary solution. The most remarkable of the osmosis explanations are as follows.

Kinetic hypothesis-1.[13] It stems from an analogy between solute molecules in dilute liquid solutions and the molecules of gases. Osmotic pressure is attributed to the bombardment of a semipermeable membrane by solute molecules.

Kinetic hypothesis-2.[70] Osmosis is ascribed to the bombardment of a semipermeable membrane by the molecules of solvent. Because there are more solvent molecules in the pure solvent than in the solution, the bombardment brings about an excess (osmotic) pressure exerted on the membrane. The pressure drives the solvent molecules into the solution and thus generates the osmotic flow.

Solubility hypothesis.[71-73] A semipermeable membrane is assumed to attract solvent molecules that are dissolved on one side of the membrane and given up on the other. The process leads to osmosis, i.e., to a net flow of the solvent into the solution where an additional hydrostatic pressure develops. The pressure builds up to a certain limit that is high enough to check the flow. This limit is called osmotic pressure.

Sieve hypothesis.[74-76] A semipermeable membrane is supposed to act as a sieve that permits the passage of small molecules of solvent but traps larger molecules of solute. Such an action results in a net flow of the solvent into the solution and thus gives rise to osmotic pressure in the same way as the solubility hypothesis explains.

Vapor pressure hypothesis.[23] A semipermeable membrane is assumed to be pierced by a multitude of dry capillaries. The capillaries retain both the liquid solvent and solution but pass vapor. Since the vapor pressure of the solvent is more than that of the solution, vapor diffuses through the capillaries from the solvent to the solution and then condenses there. The volume of the solution rises and so do its hydrostatic and vapor pressures until the latter becomes equal to the vapor pressure of the solvent. At this moment the hydrostatic pressure of the solution reaches its upper limit called osmotic pressure.

Surface tension hypothesis.[72,77-80] By this hypothesis, there is a positive difference in surface tensions of the solution and the solvent on both sides of the membrane. Due to the difference, a motive force springs up that drives (sucks) the whole body of solvent into the solution through the membrane capillaries and thus brings about the osmotic pressure.

Solvent tension hypothesis. It was first proposed in works[81,82] and then, in many years, reintroduced in articles.[63-66] The hypothesis ascribes osmotic pressure to the action of solvent tension which is defined as 'negative pressure' induced by the thermal motion of solute molecules. Also, the solvent tension is "attributable to the attractive forces between solvent molecules"[66] either in pure solvent or in a solution. Osmotic pressure is defined as the difference of the solvent tension in the solution and that in pure solvent. This explanation has been severely criticized.[83-88] One of the scathing remarks is as follows: "there is no need to introduce a solvent tension hypothesis that is more difficult to understand than the phenomena it is supposed to explain."[88]

There are some other comparatively new but also vague suggestions about osmotic mechanisms such as a pressure drop within the membrane at the membrane-solution interface,[67] solvent dilution by solute,[68] solvent cohesiveness, the interaction of solute particles with the semipermeable membrane or with the free surface of the solvent,[69] etc.

Diffusion hypothesis. In 1918 Haldane[89] put forward an idea of 'diffusion pressure' as explaining osmosis. A year later Kosakai stemming from his own osmotic experiments with boric acid, formaldehyde and carbamide[90,91] came to the conclusion that osmotic pressure is exerted by pure solvent "which has passed, by the process of unexplained diffusion, through a semipermeable membrane." Later on the diffusion origin of osmosis was arrived at by other researchers and in the long run the spontaneous diffusion of solvent has been accepted as the most plausible mechanism of osmotic pressure.[5,92-105] It has been adopted in a number of textbooks as the definition of osmosis[106-110] and applied in numerous theoretical works on the transport of molecules through natural and artificial membranes.

In the present paper we also take up the diffusion hypothesis and in the next Section discuss possible ways of its application to building a new theory of osmotic pressure.

III. SETTING THE STAGE

Consider the arrangement in Fig. 1 where compartments A and B are separated by a rigid membrane M and contain liquid binary non-electrolyte solutions of the same names A and B, respectively. In what follows, molecules of solvent are denoted by $i = 1$ (species 1) and those of solute by $i = 2$ (species 2). We also suppose that the solutions are incompressible and the membrane M is in general leaky so that solvent and solute molecules can freely pass through it owing to their random thermal motion.[111]

In mixtures A and B, the partial molal volumes of species $i = 1, 2$ and their molar concentrations are respectively $\bar{V}_{i,\mathrm{A}}$, $\bar{V}_{i,\mathrm{B}}$ and $C_{i,\mathrm{A}}$, $C_{i,\mathrm{B}}$. The concentration difference is

$$\Delta C_i \equiv C_{i,\mathrm{A}} - C_{i,\mathrm{B}} \qquad (13)$$

Provided $\Delta C_1 > 0$ and hence $\Delta C_2 < 0$, the random motion of species 1 and 2 brings about two net diffusion flows (fluxes). One of them is a self-diffusion flux J_1 of solvent 1 from compartment A to compartment B and the other is an interdiffusion flux J_2 of solute 2 in the opposite direction from B to A (see Fig. 1), the dimension of the fluxes being $\mathrm{mol} \times \mathrm{m}^{-2} \times \mathrm{s}^{-1}$. The terms 'self-diffusion' and 'interdiffusion' originate from two kinds of the random motion of the species involved[112]: the motion of a solvent molecule through its identical twins ('self-diffusion'), and the motion of a solute molecule through the same solvent particles ('interdiffusion').

In addition to the fluxes J_1 and J_2, the diffusion process is characterized by the corresponding volume flows $J_1' \equiv \bar{V}_{1,\mathrm{A}} J_1$ and $J_2' \equiv \bar{V}_{2,\mathrm{B}} J_2$ ($\mathrm{m}^3 \times \mathrm{m}^{-2} \times \mathrm{s}^{-1}$). As J_1' and J_2' arise and keep passing the membrane M, in one of the two compartments (for instance B when $J_1' > J_2'$) the volume of the solution builds up and brings about an increasing hydrostatic pressure difference ΔP across M (see Fig. 1). This pressure gives rise to an increasing secondary bulk flow $J_\mathrm{P} \equiv J_3'$ of solution B as a whole. Both J_2' and J_3' counteract the prevailing osmotic flow J_1' and at a certain moment $t = t_{in} >> 0$ check it. Just at this moment, the net volume flow J' of all the molecules involved comes to zero, i.e.,

$$J' \equiv J_1' + J_2' + J_3' \equiv \bar{V}_{1,A} J_1 + \bar{V}_{2,B} J_2 + J_3' = 0 \qquad (14)$$

and the pressure difference ΔP reaches its maximum ΔP_{max} which is equal to osmotic pressure π by definition (see the solubility hypothesis in Sec. II).

It follows that the diffusion treatment of osmosis makes it possible to determine osmotic pressure π either directly, by measuring $\Delta P_{max} \equiv \pi$, or indirectly, in terms of the fluxes J_1', J_2', J_3' obeying Eq. (14). The first approach is empirical, the second one more theoretical and corresponding to the aim of our paper. To accomplish it, we must take into account some factors. Let us mention them.

First of all, diffusion is a process and hence the natural way to cope with the osmotic problem is to apply appropriate dynamic equations.

Also, before condition (14) takes place, i.e., at $0 < t < t_{in}$, the net volume flow $J' \equiv \bar{V}_{1,A} J_1 + \bar{V}_{2,B} J_2 + J_3'$ is developing as a time-dependent or nonstationary process. Time-dependent processes, especially rapid ones, are not easy to deal with. In the meantime, ample experiments show that the hydrostatic head ΔP indicating the rate of all the fluxes J_1', J_2', J_3' increases very slowly at $t < t_{in}$, stops at $t = t_{in}$ and then remains practically constant for a certain time interval $t \in [t_{in}, t_{out}]$. The problem may thus be facilitated by assuming that at $t \geq t_{in}$, the variables J_1', J_2', J_3' become time-independent or stationary (steady). This means that condition (14) will hold not only at the moment t_{in} but also thereafter, at $t > t_{in}$, when in addition to Eq. (14) we have

$$\Delta P = \Delta P_{max} \equiv \pi, \qquad t \in [t_{in}, t_{out}] \qquad (15)$$

Further in this paper we will consider only the steady state of osmosis which, in this Section, follows Eqs. (14) and (15).

It should also be kept in mind that osmosis is not an isolated phenomenon—it is developed as a combination of the coupled stationary flows J_1', J_2', J_3'. To deal with them, we need corresponding coupled stationary dynamic equations. The most appropriate phenomenological relations of this kind seem to be linear equations of nonequilibrium (irreversible) thermodynamics[113-115] that for our particular case take the form

$$J_1' = L_{11} X_1 + L_{12} X_2 + L_{13} X_3 \qquad (16)$$

$$J_2' = L_{21} X_1 + L_{22} X_2 + L_{23} X_3 \qquad (17)$$

$$J_3' = L_{31} X_1 + L_{32} X_2 + L_{33} X_3 \qquad (18)$$

Here X_1, X_2, X_3 are generalized forces, or gradients, producing the fluxes J_1', J_2', J_3', and L_{rs} (r, s = 1, 2, 3) are experimental quantities (phenomenological transport coefficients) obeying Onsager's reciprocal relations[116,117]

$$L_{rs} = L_{sr} \qquad (19)$$

The transport coefficients L_{rs} are independent of the forces X_r and may be split up into two groups. The first one consists of the coefficients L_{rr} that relate conjugate (similar) fluxes and forces $\{J_r', X_r\}$. The couples $\{J_r', X_r\}$ represent direct phenomena, i.e., reactions of the fluxes J_r' to the forces X_r acting right on J_r'. The second group includes the coefficients L_{rs} ($r \neq s$) that relate dissimilar fluxes and forces $\{J_r', X_s\}$. The couples $\{J_r', X_s\}$ stand for indirect (cross) phenomena, viz., reactions of the fluxes J_r' to the forces X_s acting straight on the other fluxes J_s'.

Equations (14)-(19) make up a certain mathematical model of osmosis and raise therefore a natural question: Is this model suitable for obtaining the required osmotic pressure π in terms of the concentration differences ΔC_1 and ΔC_2?

To answer this question, we begin with reminding that the conjugate couple $\{J_3', X_3\}$ represents the bulk flow J_3' driven directly by the above hydrostatic head ΔP. Therefore the gradient $X_3 = \Delta P_{max} = \pi$, as follows from Eq. (15). Accordingly, the conjugate couple $\{J_1', X_1\}$ stands for the diffusion of solvent 1 through the membrane M, the flux J_1' being generated directly by the concentration gradient ΔC_1. Hence the force $X_1 = f_1(\Delta C_1)$. Analogously $X_2 = f_2(\Delta C_2)$. Since irreversible thermodynamics deals with linear processes, both $f_1(\Delta C_1)$ and $f_2(\Delta C_2)$ are to be linear functions, that is $f_1(\Delta C_1) \equiv b_1 \Delta C_1$ and $f_2(\Delta C_2) \equiv b_2 \Delta C_2$, where b_1 and b_2 are some constants to be found.

For this purpose, we invoke the key relation of irreversible thermodynamics[113]

$$\Lambda = J_1' X_1 + J_2' X_2 + J_3' X_3 \qquad (20)$$

where Λ is the local entropy production. In the model (14)-(19), all the fluxes J_1', J_2', J_3' are of the same dimension. Then, according to Eq. (20), all the forces X_1, X_2, X_3 must have another but also one and the same dimension. The generalized force X_3 is the osmotic pressure π whose dimension is, for instance, atm. Therefore the dimension of both $X_1 \equiv b_1 \Delta C_1$ and $X_2 \equiv b_2 \Delta C_2$ has to be atm as well. This requirement is satisfied if we take $b_1 \equiv b_2 = RT$.

As a result, the mathematical model (14)-(19) will include the following generalized forces:

$$X_1 = RT\Delta C_1 \qquad (21)$$

$$X_2 = RT\Delta C_2 \qquad (22)$$

$$X_3 = \pi \qquad (23)$$

We now suppose for simplicity that the membrane M in Fig. 1 is semipermeable. In this case, the flow of solute 2 across the membrane is forbidden so that

$$J_2' \equiv 0 \qquad (24)$$

Hence condition (14) takes the form

$$J' \equiv J_1' + J_3' \equiv \bar{V}_{1,\mathrm{A}} J_1 + J_3' = 0 \qquad (25)$$

Both identity (24) and Onsager's relations (19) require that

$$L_{2r} = L_{r2} \equiv 0 \quad (r = 1, 2, 3) \qquad (26)$$

In view of (19) and (26), Eqs. (16)-(18) reduce to

$$J_1' = L_{11} X_1 + L_{13} X_3 \qquad (27)$$

$$J_3' = L_{13} X_1 + L_{33} X_3 \qquad (28)$$

and owing to Eqs. (27) and (28), condition (25) changes to

$$(L_{11} + L_{13}) X_1 + (L_{13} + L_{33}) X_3 = 0 \qquad (29)$$

With regard to relations (21)-(23), Eqs. (27)-(29) become

$$J_1' = L_{11} RT\Delta C_1 + L_{13}\,\pi \qquad (30)$$

$$J_3' = L_{13} RT\Delta C_1 + L_{33}\,\pi \qquad (31)$$

$$(L_{11} + L_{13}) RT\Delta C_1 + (L_{13} + L_{33})\,\pi = 0 \qquad (32)$$

Equation (32) seems to bring about a solution to our problem. Indeed, if the forces $RT\Delta C_1$ and π were dependent, Eq. (32) would result in a desirable expression of osmotic pressure π:

$$\pi = -\,(L_{11} + L_{13})(L_{13} + L_{33})^{-1}\, RT\Delta C_1 \qquad (33)$$

Also, if $(L_{11} + L_{13})(L_{13} + L_{33})^{-1} \neq 0$, then relation (33) would differ from the van't Hoff equation $\pi = RT\Delta C_2$ and would therefore represent a new osmotic law.

In fact, however, solution (33) is incorrect because irreversible thermodynamics does not permit dependent forces[118] and fluxes.[119] Consequently, the generalized forces $RT\Delta C_1$ and π must be independent and Eq. (32) must hold at any values of these forces. This is possible only if the terms within the parentheses of Eq. (32) are identical zeroes:

$$L_{11} + L_{13} \equiv 0 \qquad (34)$$

$$L_{13} + L_{33} \equiv 0 \qquad (35)$$

Equations (34) and (35) reduce to

$$L_{11} = L_{33} = -\,L_{13} \qquad (36)$$

When inserted in Eq. (33), the coefficients L_{11}, L_{33}, L_{13} by (36) lead to an indeterminate form $\pi = 0/0$ and give us nothing.

It should be noted that there is a certain similarity between Eqs. (30)-(32) and the celebrated Kedem-Katchalsky theory of permeation across biological membranes.[120] If the generalized forces π and $RT\Delta C_1$ are substituted respectively by the equivalent pressure difference $\Delta p \equiv \Delta P_{max}$ and by the force $RT\Delta C_2$, then Eqs. (30)-(32) will in principle coincide with a particular case of the Kedem-Katchalsky theory when the membrane is semipermeable. Also, in that theory the generalized forces Δp and $RT\Delta C_2$ are assumed to be independent which brings about a relationship between the transport coefficients L_{rs} identical to Eq. (36).[5,95]

We thus see that the mathematical model (30)-(32) of two coupled fluxes J_1' and J_3' is unsuitable for finding the osmotic pressure π as a function of the concentration difference ΔC_1. We omit for brevity the proof that the model (14)-(19) of three coupled fluxes J_1', J_2', J_3' also fails to solve this problem. So do all other models of coupled fluxes if their number $n \geq 2$. Hence being a powerful technique for studying linear coupled processes, the phenomenological equations of irreversible thermodynamics (16)-(18), (27)-(28), (30)-(31) and the like are inapplicable to building a new osmotic pressure theory. This problem calls for a different approach to be dealt with in the next Section.

IV. DEVELOPMENT OF THE THEORY

In Sec. III we have seen that a solution to the osmotic pressure problem is infeasible if osmosis is considered as a set of $n \geq 2$ coupled diffusion fluxes. Thus nothing remains but to treat the osmotic phenomenon as a set of uncoupled diffusion flows. The term 'uncoupled' means here the following:

(i) for any solution involved, diffusion of solvent molecules is not isolated from that of solute molecules. Unlike Sec. III, these two processes are regarded together as one compound diffusion flow of the solution;

(ii) whatever the number of such compound flows, they all are treated separately as uncoupled fluxes.

In this Section we show that such an approach, despite some complications, results in a new osmotic pressure theory.

As stated above, we will now consider osmosis as a set of two uncoupled diffusion fluxes $\mathbf{J}_{\mathrm{A}\to\mathrm{B}}$ and $\mathbf{J}_{\mathrm{B}\to\mathrm{A}}$ (mol × m^{-2} × s^{-1}). Here $\mathbf{J}_{\mathrm{A}\to\mathrm{B}}$ ($\mathbf{J}_{\mathrm{B}\to\mathrm{A}}$) is the flux of a liquid binary solution A (B) to a liquid binary solution B (A) across a rigid membrane M of thickness h (Fig. 2). We also suppose that the diffusion process is isothermal, external forces are absent, both the membrane M and the non-electrolyte incompressible mixtures A and B are isotropic and homogeneous. Under such conditions, the diffusion of A and B is governed by Fick's laws[111,112,121]

$$\mathbf{J}_{\mathrm{A}\to\mathrm{B}} = -\,D_{\mathrm{A}}\ \mathrm{grad}\ C_{\mathrm{A}} \qquad (37)$$

$$\mathbf{J}_{\mathrm{B}\to\mathrm{A}} = -\,D_{\mathrm{B}}\ \mathrm{grad}\ C_{\mathrm{B}} \qquad (38)$$

$$\partial C_{\mathrm{A}}/\partial t = D_{\mathrm{A}}\ \mathrm{div\ grad}\ C_{\mathrm{A}} \qquad (39)$$

$$\partial C_B/\partial t = D_B \text{ div grad } C_B \tag{40}$$

where C_A and C_B are certain molar concentrations of the diffusible substances A and B (mol × m^{-3}) to be discussed later, D_A and D_B are the diffusion coefficients of the membrane (m^2 × s^{-1}) which are assumed to be independent of position but dependent on the concentrations C_A and C_B, i.e., $D_A \neq D_B$.

Before applying the general laws (37)-(40), we make them specific by additional assumptions:

1. The diffusion is a stationary process so that

$$\partial C_A/\partial t = 0 \tag{41}$$

$$\partial C_B/\partial t = 0 \tag{42}$$

2. The stationary process (41)-(42) may develop when the concentrations C_A and C_B are maintained at fixed values on both sides of the membrane M (see Fig. 2):

$$C_A = \langle C_A \rangle \text{ at } x = 0, \quad C_A = 0 \text{ at } x = h \tag{43}$$

$$C_B = 0 \text{ at } x = 0, \quad C_B = \langle C_B \rangle \text{ at } x = h \tag{44}$$

3. The stationary diffusion fluxes $\mathbf{J}_{A\to B}$ and $\mathbf{J}_{B\to A}$ are one-dimensional and directed along the x-axis. This means that

$$\mathbf{J}_{A\to B} = J_{A\to B}\mathbf{i} \tag{45}$$

$$\mathbf{J}_{B\to A} = J_{B\to A}\mathbf{i} \tag{46}$$

$$\text{grad } C_A = (dC_A/dx)\mathbf{i} \tag{47}$$

$$\text{grad } C_B = (dC_B/dx)\mathbf{i} \tag{48}$$

$$\text{div grad } C_A = d^2C_A/dx^2 \tag{49}$$

$$\text{div grad } C_B = d^2C_B/dx^2 \tag{50}$$

where **i** is the unit vector in the direction of positive x-axis, $|J_{A\to B}| \equiv |\mathbf{J}_{A\to B}|$, $|J_{B\to A}| \equiv |\mathbf{J}_{B\to A}|$.

In view of (41)-(42) and (45)-(50), Eqs. (37)-(40) take the form

$$J_{A\to B} = -D_A\, dC_A/dx \tag{51}$$

$$J_{B\to A} = -D_B\, dC_B/dx \tag{52}$$

$$d^2C_A/dx^2 = 0 \tag{53}$$

$$d^2C_B/dx^2 = 0 \tag{54}$$

The general solutions of Eqs. (53) and (54) are

$$C_A = r_{1A}x + r_{2A} \tag{55}$$

$$C_B = r_{1B}x + r_{2B} \tag{56}$$

The arbitrary constants r_{1A}, r_{2A}, r_{1B}, r_{2B} can be determined by the boundary conditions (43)-(44) to yield the final solutions of Eqs. (55) and (56)

$$C_A = \langle C_A \rangle (1 - x/h) \tag{57}$$

$$C_B = \langle C_B \rangle x/h \tag{58}$$

On substituting C_A and C_B from Eqs. (57)-(58) into Eqs. (51)-(52), we have

$$J_{A\to B} = D_A h^{-1} \langle C_A \rangle \tag{59}$$

$$J_{B\to A} = -D_B h^{-1} \langle C_B \rangle \tag{60}$$

Now we may define a net diffusion flux $J_D \equiv J_{A\to B} + J_{B\to A}$. In view of Eqs. (59)-(60), this flux is

$$J_D = D_A h^{-1} [\langle C_A \rangle - \xi \langle C_B \rangle] \tag{61}$$

where $\xi \equiv D_B/D_A$. Relation (61) is a key to the forthcoming analysis and is therefore to be discussed closely.

It is obvious that Eq. (61) makes sense if the concentrations $\langle C_A \rangle$ and $\langle C_B \rangle$ refer to *identical* molecules. For instance, if we studied interdiffusion of solute molecules (species 2), then $\langle C_A \rangle$ and $\langle C_B \rangle$ would be the molar concentrations $C_{2,A}$ and $C_{2,B}$, respectively (see Sec. III). On the other hand, if we dealt with self-diffusion of solvent molecules (species 1), then $\langle C_A \rangle$ and $\langle C_B \rangle$ would equal the molar concentrations $C_{1,A}$ and $C_{1,B}$.

The matter under discussion is, however, quite different because diffusion of solvent and solute molecules is now considered as one compound diffusion flow. It follows that the corresponding compound concentrations $\langle C_A \rangle$ and $\langle C_B \rangle$ are neither of the above quantities and must be some combinations of them. The simplest ones are linear functions $\langle C_A \rangle = C_{1,A} + C_{2,A}$ and $\langle C_B \rangle = C_{1,B} + C_{2,B}$. There may be a number of other plausible combinations, but it is not clear in advance which one of them is true. This uncertainty sets up a substantial obstacle. To overcome it, we should 'homogenize' (in a specified sense) solvent and solute molecules and on this basis find such tenable functions $\langle C_A \rangle$ and $\langle C_B \rangle$ of the underlying molar concentrations $C_{1,A}$, $C_{2,A}$ and $C_{1,B}$, $C_{2,B}$ that would

(i) *apriori* stem from a molecular consideration of the solutions involved and

(ii) *aposteriori* result in a new osmotic pressure theory to be borne out experimentally over any real range of the solute concentrations $C_{2,A}$ and $C_{2,B}$ or $m_{2,A}'$ and $m_{2,B}'$.

To begin with, we consider solution A and suppose for a moment that it consists of a pure solvent 1 only. If we took one liter of A (or $m_{1,A}'$ moles of the solvent) and added in it $m_{2,A}'$ moles of the same solvent, we would get $V_{A(1,1)} = 1 + m_{2,A}'/m_{1,A}'$ liters of the same one-component solution A. In reality, however, solution A is binary, i.e., made by dissolving $m_{2,A}'$ moles of solute 2 in each liter of solvent 1, so that instead of one liter of species 1 we obtain $V_{A(1,2)} = \bar{V}_{1,A} m_{1,A}' + \bar{V}_{2,A} m_{2,A}'$ liters of the real solution A, the partial molal volumes $\bar{V}_{1,A}$ and $\bar{V}_{2,A}$ depending on the mole fraction of solute $x_{2,A} = m_{2,A}'/(m_{1,A}' + m_{2,A}')$.

The above relations will apply to mixture B if subscripts A are replaced by B. Also, the volume molal concentrations $m_{1,A}'$ and $m_{1,B}'$ refer to one liter of the same solvent 1 and are therefore independent of the kind of solution, i.e., $m_{1,A}' \equiv m_{1,B}' \equiv m_1'$. As a result, we will have

$$V_{A(1,1)} = 1 + m_{2,A}'/m_1' \tag{62}$$

$$V_{B(1,1)} = 1 + m_{2,B}'/m_1' \tag{63}$$

$$V_{A(1,2)} = \bar{V}_{1,A} m_1' + \bar{V}_{2,A} m_{2,A}' \tag{64}$$

$$V_{B(1,2)} = \bar{V}_{1,B} m_1' + \bar{V}_{2,B} m_{2,B}' \tag{65}$$

Now we introduce dimensionless parameters

$$\lambda_A = V_{A(1,2)}/V_{A(1,1)} \tag{66}$$

$$\lambda_B = V_{B(1,2)}/V_{B(1,1)} \tag{67}$$

that are some measures of similarity between molecules of solute 1 and solvent 2. Indeed, either of these parameters equals unity if species 1 and 2 are identical, and departs from unity if these species are different.

More precisely, the parameters λ_A and λ_B refer to the 'volume' response of one liter of pure solvent 1 to dissolving in it respectively $m_{2,A}'$ and $m_{2,B}'$ moles of solute 2 in lieu of the same amounts of solvent 1. For instance, λ_A shows by how much one liter of pure solvent increases if instead of dissolving in it $m_{2,A}'$ moles of species 1, we dissolve the same $m_{2,A}'$ moles of species 2. It follows that $m_{2,A}'$ moles of solute 2 are equivalent in volume to and may be substituted by $\lambda_A m_{2,A}'$ moles of solvent 1. The same holds if subscripts A are replaced with B.

Thus, we may suppose both solutions A and B to be *homogeneous* mixtures consisting of volume-identical species 1 and having the following compound *molal* concentrations:

$$\langle m_A' \rangle = m_1' + \lambda_A m_{2,A}' \tag{68}$$

$$\langle m_B' \rangle = m_1' + \lambda_B m_{2,B}' \tag{69}$$

Relations (68)-(69) enable us to obtain the compound *molar* concentrations $\langle C_A \rangle$ and $\langle C_B \rangle$:

$$\langle C_A \rangle \equiv \langle m_A' \rangle / V_{A(1,2)} = (m_1' + \lambda_A m_{2,A}')/V_{A(1,2)} \tag{70}$$

$$\langle C_B \rangle \equiv \langle m_B' \rangle / V_{B(1,2)} = (m_1' + \lambda_B m_{2,B}')/V_{B(1,2)} \tag{71}$$

In view of the identities

$$C_{1,A} \equiv m_1'/V_{A(1,2)} \tag{72}$$

$$C_{2,A} \equiv m_{2,A}'/V_{A(1,2)} \tag{73}$$

$$C_{1,B} \equiv m_1'/V_{B(1,2)} \tag{74}$$

$$C_{2,B} \equiv m_{2,B}'/V_{B(1,2)} \tag{75}$$

equations (66)-(67) and (70)-(71) can be rewritten as follows:

$$\lambda_A = V_{A(1,2)}/(1 + C_{2,A}/C_{1,A}) \tag{76}$$

$$\lambda_B = V_{B(1,2)}/(1 + C_{2,B}/C_{1,B}) \tag{77}$$

$$\langle C_A \rangle = C_{1,A} + \lambda_A C_{2,A} \tag{78}$$

$$\langle C_B \rangle = C_{1,B} + \lambda_B C_{2,B} \tag{79}$$

It should be noted that Eqs. (68)-(71), (78)-(79) are not final. They have to be modified by taking account of the membrane selectivity to different molecules. Indeed, solute molecules are usually 'reflected' from the membrane— completely or partially—whereas solvent molecules do not. Thus only a fraction of species 2 may pass the membrane. We denote this fraction by $\tau_{2,A}$ for species 2 in compartment A and by $\tau_{2,B}$ for species 2 in compartment B (see Fig. 2). The introduction of $\tau_{2,A}$ means that of $m_{2,A}'$ moles of the solute in A only $\tau_{2,A} m_{2,A}'$ can diffuse to B. The same is true for the fraction $\tau_{2,B}$ if one replaces A by B.

The above reasoning has a direct bearing on Eqs. (68)-(71), (78)-(79) in which the terms $m_{2,A}'$ and $m_{2,B}'$ are to be supplanted by $\tau_{2,A} m_{2,A}'$ and $\tau_{2,B} m_{2,B}'$, respectively. We thus obtain

$$\langle m_A' \rangle = m_1' + \lambda_A \tau_{2,A} m_{2,A}' \tag{80}$$

$$\langle m_B' \rangle = m_1' + \lambda_B \tau_{2,B} m_{2,B}' \tag{81}$$

$$\langle C_A \rangle = (m_1' + \lambda_A \tau_{2,A} m_{2,A}')/V_{A(1,2)} \tag{82}$$

$$\langle C_B \rangle = (m_1' + \lambda_B \tau_{2,B} m_{2,B}')/V_{B(1,2)} \tag{83}$$

$$\langle C_A \rangle = C_{1,A} + \lambda_A \tau_{2,A} C_{2,A} \tag{84}$$

$$\langle C_B \rangle = C_{1,B} + \lambda_B \tau_{2,B} C_{2,B} \tag{85}$$

In Eqs. (80)-(85), both the fractions $\tau_{2,A}$ and $\tau_{2,B}$ are limited and related to the corresponding Staverman reflection coefficients $\sigma_{2,A}$ and $\sigma_{2,B}$ by

$$\tau_{2,A} = 1 - \sigma_{2,A} \qquad (0 \le \tau_{2,A} \le 1) \tag{86}$$

$$\tau_{2,B} = 1 - \sigma_{2,B} \qquad (0 \le \tau_{2,B} \le 1) \tag{87}$$

If the membrane under discussion is completely leaky, it permits all the solute molecules to pass through so that

$$\tau_{2,A} = \tau_{2,B} = 1 \quad \text{and} \quad \sigma_{2,A} = \sigma_{2,B} = 0 \tag{88}$$

On the contrary, if the membrane is semipermeable, we have

$$\tau_{2,A} = \tau_{2,B} = 0 \quad \text{and} \quad \sigma_{2,A} = \sigma_{2,B} = 1 \tag{89}$$

Relations (88)-(89) show that the fractions $\tau_{2,A}$, $\tau_{2,B}$ are opposite in a sense to the reflection coefficients $\sigma_{2,A}$, $\sigma_{2,B}$ and may therefore be called the permeation coefficients.

We now return to the underlying equation (61) and find the unknown function $\xi \equiv D_B/D_A$ using Eqs. (84)-(85) and (88). Equation (61) states that

$$\xi = \langle C_A \rangle / \langle C_B \rangle \quad \text{if} \quad J_D = 0 \tag{90}$$

According to (90), the function ξ is wholly determined by those concentrations $\langle C_A \rangle$ and $\langle C_B \rangle$ that correspond to the zero net flux $J_D = 0$.

It is clear that $J_D = 0$ if the mixtures at hand A and B are identical. In this case, all the solution characteristics with subscripts A are equal to those with subscripts B, viz., $C_{1,A} = C_{1,B}$, $C_{2,A} = C_{2,B}$, etc. Consequently, $\langle C_A \rangle = \langle C_B \rangle = \langle C \rangle$ and Eq. (61) reduces to $J_D = D_A h^{-1} \langle C \rangle (1 - \xi)$. Taking $J_D = 0$, we get $\xi = 1$, in conformity with Eq. (90).

The above example is almost trivial. It has, however, some reason because of raising an important question: Is there a solution to Eq. (90) when the mixtures A and B are not identical but different? In other words: If $J_D = 0$, is it possible that $\langle C_A \rangle \neq \langle C_B \rangle$ and $\xi \neq 1$?

To answer this question, we consider a completely leaky membrane M obeying Eq. (88). Now, if we take one liter of each solution A and B, these equal volumes will have the compound molar concentrations $\langle C_A \rangle$ and $\langle C_B \rangle \neq \langle C_A \rangle$ by Eqs. (78)-(79) to which the general equations (84)-(85) reduce at $\tau_{2,A} = \tau_{2,B} = 1$, in accordance with (88). Since the membrane M is completely leaky, any fraction of the above liter of solution A diffusing through M to compartment B will be counterbalanced by an equal volume fraction of solution B diffusing through M in the opposite direction, to compartment A. As a result, the net flux J_D will be zero. We thus come to the conclusion that

$$J_D = 0 \quad \text{if} \quad \langle C_A \rangle \text{ and } \langle C_B \rangle \neq \langle C_A \rangle \text{ obey Eqs. (78)-(79)} \tag{91}$$

Combining this condition with Eq. (90), we have

$$\xi = \langle C_A \rangle / \langle C_B \rangle \tag{92}$$

where $\langle C_A \rangle$ and $\langle C_B \rangle$ follow Eqs. (78)-(79). Given these equations, relation (92) takes the final form

$$\xi = (C_{1,A} + \lambda_A C_{2,A})/(C_{1,B} + \lambda_B C_{2,B}) \tag{93}$$

Substituting ξ from (93) into Eq. (61) and taking account of Eqs. (84)-(85), we obtain

$$J_D = D_A h^{-1} \psi \tag{94}$$

where

$$\psi \equiv C_{1,A} + \lambda_A \tau_{2,A} C_{2,A} - (C_{1,B} + \lambda_B \tau_{2,B} C_{2,B}) \times$$
$$(C_{1,A} + \lambda_A C_{2,A})/(C_{1,B} + \lambda_B C_{2,B}) \tag{95}$$

If the membrane M is not completely leaky, then according to Eq. (94)-(95) there will be a net diffusion flux $J_D \neq 0$. It may be directed either from compartment A to compartment B and be positive, $J_D > 0$, or vice versa and be negative, $J_D < 0$. Without loss of generality we take $J_D > 0$. Then J_D will be the current of solution A (solvent and solute molecules together!) across the membrane M to compartment B with a stationary velocity v_A = constant. This flux has the 'homogeneous' concentration $\langle C_A \rangle$ and may be represented as[122]

$$J_D = \langle C_A \rangle \, v_A \tag{96}$$

where the velocity v_A is determined by

$$v_A = b_A X_A \tag{97}$$

Here b_A is the mechanical mobility of a particle[121,122] (the solvent or solute molecule of solution A), X_A is the force driving the particle through the membrane against the counterflow $J_{B \to A}$ (see Fig. 2).

Equating the function J_D by both expressions (94) and (96) and allowing for Eq. (97), we have

$$b_A X_A \langle C_A \rangle = D_A h^{-1} \psi \tag{98}$$

If both sides of Eq. (98) are multiplied by the Avogadro number N and the thickness h and divided by the mobility b_A, we obtain

$$N h X_A \langle C_A \rangle = N D_A b_A^{-1} \psi \tag{99}$$

Now consider an arbitrary volume $V_M = Ah$ of the membrane M, A being some area on the surface of M. Clearly $N \langle C_A \rangle V_M$ is the number of the particles of the current $J_D = \langle C_A \rangle v_A$ in the volume V_M at any given moment t. Accordingly, $F = N \langle C_A \rangle V_M X_A \equiv N \langle C_A \rangle A h X_A$ is the resultant of all the elementary driving forces X_A in V_M directed from compartment A to compartment B. To stop the flux J_D one must apply the same force F in the opposite direction, from B to A. Dividing this force by the area A, we obtain a stress $F/A = NhX_A \langle C_A \rangle$ which, by definition, is equal to the osmotic pressure π. In other words, $\pi = NhX_A \langle C_A \rangle$. Given this expression, Eq. (99) becomes

$$\pi = N D_A b_A^{-1} \psi \tag{100}$$

Equation (100) can be manipulated further by means of the Einstein relation[123] $D_A = kTb_A$, where $k = R/N$ is the Boltzmann constant. In view of this relation, Eq. (100) takes the form

$$\pi = RT\psi \tag{101}$$

Equation (101) is the solution to the osmotic pressure problem we have sought for in this paper.

V. PARTICULAR CASES OF THE THEORY

The solution (101) includes the function ψ to be written *in extenso*. Substituting ψ from Eq. (95) into (101), we have

$$\pi = RT\left[C_{1,A}C_{2,B}\lambda_B\sigma_{2,B} - C_{1,B}C_{2,A}\lambda_A\sigma_{2,A} + C_{2,A}C_{2,B}\lambda_A\lambda_B(\sigma_{2,B} - \sigma_{2,A})\right]/(C_{1,B} + C_{2,B}\lambda_B) \tag{102}$$

In this relation, the reflection coefficients $\sigma_{2,A}$, $\sigma_{2,B}$ have supplanted the permeation coefficients $\tau_{2,A}$, $\tau_{2,B}$ in conformity with Eqs. (86)-(87).

Equation (102) involves the parameters λ_A and λ_B to be replaced with the volumes $V_{A(1,1)}$, $V_{B(1,1)}$, $V_{A(1,2)}$, $V_{B(1,2)}$ according to Eqs. (66)-(67). Note that these volumes, by definition in Sec. IV, are measured in *liters* of solution per *liter* of solvent. It is therefore convenient to drop the dimension "*liter* per *liter*" and treat all the volumes $V_{A(1,1)}$, $V_{B(1,1)}$, $V_{A(1,2)}$, $V_{B(1,2)}$ as dimensionless quantities, as will be done further.

In view of this remark, Eqs. (62)-(63) yield the following dimensionless relations

$$1/V_{A(1,1)} = m_1'/(m_1' + m_{2,A}') \equiv x_{1,A} \tag{103}$$

$$1/V_{B(1,1)} = m_1'/(m_1' + m_{2,B}') \equiv x_{1,B} \tag{104}$$

where $x_{1,A}$ and $x_{1,B}$ are the mole fractions of solvent 1 in solutions A and B, respectively. Given relations (103)-(104), Eqs. (66)-(67) become

$$\lambda_A = V_{A(1,2)}\,x_{1,A} \tag{105}$$

$$\lambda_B = V_{B(1,2)}\,x_{1,B} \tag{106}$$

The identities

$$x_{1,A} \equiv C_{1,A}/(C_{1,A} + C_{2,A}) \tag{107}$$

$$x_{1,B} \equiv C_{1,B}/(C_{1,B} + C_{2,B}) \tag{108}$$

$$x_{2,A} \equiv C_{2,A}/(C_{1,A} + C_{2,A}) = m_{2,A}'/(m_1' + m_{2,A}') \tag{109}$$

$$x_{2,B} \equiv C_{2,B}/(C_{1,B} + C_{2,B}) = m_{2,B}'/(m_1' + m_{2,B}') \tag{110}$$

permit the following manipulations:

$$C_{2,A}x_{1,A} = C_{2,A}C_{1,A}/(C_{1,A} + C_{2,A}) = C_{1,A}x_{2,A} \tag{111}$$

$$C_{2,B}x_{1,B} = C_{2,B}C_{1,B}/(C_{1,B} + C_{2,B}) = C_{1,B}x_{2,B} \tag{112}$$

$$m_{2,A}'x_{1,A} = m_{2,A}'m_1'/(m_1' + m_{2,A}) = m_1'x_{2,A} \tag{113}$$

$$m_{2,B}'x_{1,B} = m_{2,B}'m_1'/(m_1' + m_{2,B}) = m_1'x_{2,B} \tag{114}$$

Also, Eqs. (72), (74) bring about a new formula

$$C_{1,A}/C_{1,B} = V_{B(1,2)}/V_{A(1,2)} \tag{115}$$

Now we insert the parameters λ_A, λ_B by (105)-(106) into Eq. (102) and make use of Eqs. (111)-(112) and (115). As a result, Eq. (102) will take the desired form

$$\pi = RTV_BV_A^{-1}(1 + x_{2,B}V_B)^{-1}[\sigma_BC_{2,B}x_{1,B}V_B(1 + x_{2,A}V_A) - V_AV_B^{-1}\sigma_AC_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)] \tag{116}$$

where for simplicity we have denoted $V_A \equiv V_{A(1,2)}$, $V_B \equiv V_{B(1,2)}$, $\sigma_A \equiv \sigma_{2,A}$, $\sigma_B \equiv \sigma_{2,B}$.

Equation (116) is written in terms of molarities. It can easily be transformed into the molal scale by taking account of Eqs. (73) and (75):

$$\pi = RTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[\sigma_Bm_{2,B}'x_{1,B}V_B(1 + x_{2,A}V_A) - \sigma_Am_{2,A}'x_{1,A}V_A(1 + x_{2,B}V_B)] \tag{117}$$

If the reflection coefficient $\sigma_B \neq 0$, Eqs. (116)-(117) may be rewritten as

$$\pi = \sigma_BRTV_BV_A^{-1}(1 + x_{2,B}V_B)^{-1}[C_{2,B}x_{1,B}V_B(1 + x_{2,A}V_A) - V_AV_B^{-1}\alpha_{A/B}C_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)] \tag{118}$$

and respectively

$$\pi = \sigma_BRTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[m_{2,B}'x_{1,B}V_B(1 + x_{2,A}V_A) - \alpha_{A/B}m_{2,A}'x_{1,A}V_A(1 + x_{2,B}V_B)] \tag{119}$$

where $\alpha_{A/B} \equiv \sigma_A/\sigma_B \neq \infty$ is a measure of comparative reflection of solute molecules of different mixtures A and B from the same membrane M (see Fig. 2). If the solute molecules of both the mixtures are equally reflected from or permeated through this partition, the ratio $\alpha_{A/B} = 1$. Otherwise $\alpha_{A/B} \neq 1$. Hence $\alpha_{A/B}$ characterizes the leakage 'asymmetry' of the membrane: it is 'symmetric' at $\alpha_{A/B} = 1$ and 'asymmetric' at $\alpha_{A/B} \neq 1$.

The basic equations (116)-(119) of our theory have some advantageous features to be emphasized here:

1. They hold for both semipermeable and leaky membranes.
2. They include no adjustable parameters.
3. They are derived without resorting to the concepts of ideal and non-ideal solutions.
4. They impose no restrictions on the concentrations of the liquid mixtures involved.

It follows that Eqs. (116)-(119) apply in principle to any real liquid solutions, no matter whether they are ideal or non-ideal, dilute or concentrated.

Now we can specify particular cases of the basic equations (116)-(119). For convenience we split up the liquid solutions under discussion into two groups, *concentrated* and *infinitely dilute*.

1. Concentrated solutions (no restrictions on the solute concentrations $C_{2,A}$, $C_{2,B}$, $m_{2,A}'$, $m_{2,B}'$).

1.1. Binary solution A—Binary solution B.

1.1.1. Completely leaky membrane ($\sigma_A = \sigma_B = 0$). The solute molecules of both mixtures A and B can freely pass through the membrane. According to Eqs. (116)-(117), osmotic pressure is absent: $\pi = 0$ as could be expected.

1.1.2. Partially leaky symmetric membrane ($\sigma_A = \sigma_B = \sigma < 1$, $\alpha_{A/B} = 1$). The membrane is equally permeable to the solute molecules of mixtures A and B. The molar equation (118) and the molal equation (119) take respectively the form

$$\begin{aligned}&\pi = \sigma RTV_B V_A^{-1}(1 + x_{2,B}V_B)^{-1}[C_{2,B}x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - V_A V_B^{-1} C_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{120}$$

$$\begin{aligned}&\pi = \sigma RTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[m_{2,B}' x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - m_{2,A}' x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{121}$$

1.1.3. Semipermeable symmetric membrane ($\sigma_A = \sigma_B = 1$, $\alpha_{A/B} = 1$). The membrane is impermeable to the solute molecules of both mixtures A and B. Equations (116), (118) change to

$$\begin{aligned}&\pi = RTV_B V_A^{-1}(1 + x_{2,B}V_B)^{-1}[C_{2,B}x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - V_A V_B^{-1} C_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{122}$$

and Eqs. (117), (119) to

$$\begin{aligned}&\pi = RTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[m_{2,B}' x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - m_{2,A}' x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{123}$$

1.1.4. Semipermeable asymmetric membrane-1 ($\sigma_B = 1$, $\sigma_A < \sigma_B$, $\alpha_{A/B} < 1$). The membrane is impermeable to the solute molecules of mixture B. Equations (118)-(119) become

$$\begin{aligned}&\pi = RTV_B V_A^{-1}(1 + x_{2,B}V_B)^{-1}[C_{2,B}x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - V_A V_B^{-1} \alpha_{A/B}C_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{124}$$

$$\begin{aligned}&\pi = RTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[m_{2,B}' x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - \alpha_{A/B}m_{2,A}' x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{125}$$

1.1.5. Semipermeable asymmetric membrane-2 ($\sigma_A = 1$, $\sigma_B < \sigma_A$, $\alpha_{A/B} > 1$ and $\alpha_{B/A} \equiv \sigma_B/\sigma_A = 1/\alpha_{A/B} < 1$). The membrane is impermeable to the solute molecules of mixture A. Relations (116)-(117) take the form

$$\begin{aligned}&\pi = RTV_B V_A^{-1}(1 + x_{2,B}V_B)^{-1}[\alpha_{B/A}C_{2,B}x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - V_A V_B^{-1} C_{2,A}x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{126}$$

$$\begin{aligned}&\pi = RTV_A^{-1}(1 + x_{2,B}V_B)^{-1}[\alpha_{B/A}m_{2,B}' x_{1,B}V_B(1 + \\ &x_{2,A}V_A) - m_{2,A}' x_{1,A}V_A(1 + x_{2,B}V_B)]\end{aligned} \tag{127}$$

1.2. Pure solvent A—Binary solution B ($C_{2,A} = m_{2,A}' = 0$, $V_A = 1$, $\sigma_B \equiv \sigma$, $C_{2,B} \equiv C_2$, $m_{2,B}' \equiv m_2'$, $V_B \equiv V$, $x_{1,B} \equiv x_1$, $x_{2,B} \equiv x_2$).

1.2.1. Partially leaky membrane ($0 < \sigma < 1$). The basic equations (116)-(117) change to

$$\pi = \sigma RTC_2V^2 x_1/(1 + x_2V) \tag{128}$$

$$\pi = \sigma RTm_2'Vx_1/(1 + x_2V) \tag{129}$$

or, in view of identities (108) and (110), to

$$\pi = \sigma RTC_2V^2/[1 + (1 + V)C_2/C_1] \tag{130}$$

$$\pi = \sigma RTm_2'V/[1 + (1 + V)m_2'/m_1'] \tag{131}$$

1.2.2. Semipermeable membrane ($\sigma = 1$). Equations (128)-(131) are simplified:

$$\pi = RTC_2V^2 x_1/(1 + x_2V) \tag{132}$$

$$\pi = RTm_2'Vx_1/(1 + x_2V) \tag{133}$$

$$\pi = RTC_2V^2/[1 + (1 + V)C_2/C_1] \tag{134}$$

$$\pi = RTm_2'V/[1 + (1 + V)m_2'/m_1'] \tag{135}$$

2. Infinitely dilute solutions ($C_{2,A} \to 0$, $C_{2,B} \to 0$, $m_{2,A}' \to 0$, $m_{2,B}' \to 0$, $x_{2,A} \to 0$, $x_{2,B} \to 0$, $x_{1,A} \to 1$, $x_{1,B} \to 1$, $V_A \to 1$, $V_B \to 1$).

2.1. Binary solution A—Binary solution B. The basic equations (116)-(119) become

$$\pi \to RT(\sigma_B C_{2,B} - \sigma_A C_{2,A}) \tag{136}$$

$$\pi \to RT(\sigma_B m_{2,B}' - \sigma_A m_{2,A}') \tag{137}$$

$$\pi \to \sigma_B RT(C_{2,B} - \alpha_{A/B}C_{2,A}) \tag{138}$$

$$\pi \to \sigma_B RT(m_{2,B}' - \alpha_{A/B}m_{2,A}') \tag{139}$$

2.1.1. Partially leaky symmetric membrane ($\sigma_A = \sigma_B = \sigma < 1$, $\alpha_{A/B} = 1$). Equations (136)-(139) assume the form

$$\pi \to \sigma RT\Delta C_2 \tag{140}$$

$$\pi \to \sigma RT\Delta m_2' \tag{141}$$

where $\Delta C_2 = C_{2,\mathrm{B}} - C_{2,\mathrm{A}}$, $\Delta m_2' = m_{2,\mathrm{B}}' - m_{2,\mathrm{A}}'$.

2.1.2. Semipermeable symmetric membrane ($\sigma_\mathrm{A} = \sigma_\mathrm{B} = 1$, $\alpha_{\mathrm{A/B}} = 1$). Equations (140)-(141) reduce to

$$\pi \to RT\Delta C_2 \tag{142}$$

$$\pi \to RT\Delta m_2' \tag{143}$$

2.1.3. Semipermeable asymmetric membrane-1 ($\sigma_\mathrm{B} = 1$, $\sigma_\mathrm{A} < \sigma_\mathrm{B}$, $\alpha_{\mathrm{A/B}} < 1$). Equations (136)-(139) become

$$\pi \to RT(C_{2,\mathrm{B}} - \sigma_\mathrm{A} C_{2,\mathrm{A}}) \tag{144}$$

$$\pi \to RT(m_{2,\mathrm{B}}' - \sigma_\mathrm{A} m_{2,\mathrm{A}}') \tag{145}$$

$$\pi \to RT(C_{2,\mathrm{B}} - \alpha_{\mathrm{A/B}} C_{2,\mathrm{A}}) \tag{146}$$

$$\pi \to RT\,(m_{2,\mathrm{B}}' - \alpha_{\mathrm{A/B}} m_{2,\mathrm{A}}') \tag{147}$$

2.1.4. Semipermeable asymmetric membrane-2 ($\sigma_\mathrm{A} = 1$, $\sigma_\mathrm{B} < \sigma_\mathrm{A}$, $\alpha_{\mathrm{B/A}} < 1$). Equations (136)-(139) take the form

$$\pi \to RT(\sigma_\mathrm{B} C_{2,\mathrm{B}} - C_{2,\mathrm{A}}) \tag{148}$$

$$\pi \to RT(\sigma_\mathrm{B} m_{2,\mathrm{B}}' - m_{2,\mathrm{A}}') \tag{149}$$

$$\pi \to RT(\alpha_{\mathrm{B/A}} C_{2,\mathrm{B}} - C_{2,\mathrm{A}}) \tag{150}$$

$$\pi \to RT(\alpha_{\mathrm{B/A}} m_{2,\mathrm{B}}' - m_{2,\mathrm{A}}') \tag{151}$$

2.2. Pure solvent A—Binary solution B ($C_{2,\mathrm{A}} = m_{2,\mathrm{A}}' = 0$, $\sigma_\mathrm{B} \equiv \sigma$, $C_{2,\mathrm{B}} \equiv C_2$, $m_{2,\mathrm{B}}' \equiv m_2'$).

2.2.1. Partially leaky membrane ($0 < \sigma < 1$). Equations (136)-(139) change to

$$\pi \to \sigma RTC_2 \tag{152}$$

$$\pi \to \sigma RTm_2' \tag{153}$$

2.2.2. Semipermeable membrane ($\sigma = 1$). Equations (152)-(153) are simplified to the extreme

$$\pi \to RTC_2 \tag{154}$$

$$\pi \to RTm_2' \tag{155}$$

The right-hand sides of Eqs. (154) and (155) coincide with those of van't Hoff's law (1) and Morse's formula (2), respectively. Hence in the simplest particular case **"Pure solvent A—Infinitely dilute binary solution B and Semipermeable membrane"** the just established basic equations (116)-(117) reduce to the celebrated laws (1) and (2).

VI. COMPARISON WITH THE CLASSICAL LAWS. EXPERIMENTAL VERIFICATION OF THE THEORY

The sheer bulk of experiments on osmotic pressure refers to the case of a semipermeable membrane separating a pure solvent from a binary solution. This case is represented here by the classical laws of van't Hoff (1) and Morse (2) for infinitely dilute solutions and by our equations (134)-(135) for concentrated mixtures. It is therefore reasonable, before turning to experimental data, to compare Eqs. (1) and (2) with relations (134) and (135). Such a comparison will enable us to evaluate the upper limits m_2^* and C_2^* of applicability of the laws (1) and (2) (see Sec. I).

For this purpose we introduce the following ratios:

$$\beta_1 \equiv \pi_{(134)}/\pi_{(1)} = V^2/[1 + (1 + V)C_2/C_1] \tag{156}$$

$$\beta_2 \equiv \pi_{(135)}/\pi_{(2)} = V/[1 + (1 + V)m_2'/m_1'] \tag{157}$$

where $\pi_{(1)}$, $\pi_{(2)}$ $\pi_{(134)}$ and $\pi_{(135)}$ denote the osmotic pressures by Eqs. (1), (2), (134) and (135), respectively. The ratio β_1 characterizes a deviation of the osmotic pressure $\pi_{(134)}$ from the van't Hoff one $\pi_{(1)}$; the ratio β_2 does the same with respect to the osmotic pressure $\pi_{(135)}$ and the Morse one $\pi_{(2)}$.

Both β_1 and β_2 in Eqs. (156) and (157) depend critically on the volume V which in turn is a function of the concentrations C_1 and C_2 or m_1' and m_2'. Remind that V is a dimensionless quantity, viz., the specific volume of a solution in liters per liter of solvent. We may thus take V "in liters" and drop the words in the quotes.

According to Eqs. (3) and (72)-(75), $C_2/C_1 = m_2'/m_1' = m_2/m_1$. Therefore the couple of relations (156)-(157) can be transformed into either the molar scale

$$\beta_1 = V^2/[1 + (1 + V)C_2/C_1] \tag{156}$$

$$\beta_2 = V/[1 + (1 + V)C_2/C_1] \tag{158}$$

or the molal scale

$$\beta_1 = V^2/[1 + (1 + V)m_2'/m_1'] =$$

$$V^2/[1 + (1 + V)m_2/m_1] \tag{159}$$

$$\beta_2 = V/[1 + (1 + V)m_2'/m_1'] =$$

$$V/[1 + (1 + V)m_2/m_1] \tag{160}$$

To compute β_1 and β_2 by Eqs. (156)-(160), we should first know the specific volume V. For aqueous solutions, the values of V can be derived in terms of the total water concentration C_w in kg of water per liter of solution:

$$V = \rho_\mathrm{w}/C_\mathrm{w} \tag{161}$$

Here ρ_w is the density of pure water under the specified temperature T and pressure P. For instance, $\rho_w = 0.99823$ kg/l at $T = 20$ °C and $P = 1$ atm.[124] The values of C_w can also be borrowed from the handbook[124] where they are tabulated against the molar concentrations of solute C_2, i.e., $C_w = C_w(C_2)$.

We will further consider aqueous solutions of ethanol CH_3CH_2OH and sucrose $C_{12}H_{22}O_{11}$. For both these solutions, the above values of $C_w(C_2)$ along with the density $\rho_w = 0.99823$ kg/l are substituted in Eq. (161) and so the specific volumes $V(C_2)$ are found. In view of the identity $m_2 \equiv C_2V/\rho_w$, the functions $V(C_2)$ are converted to $V(m_2)$. On inserting $V(m_2)$ in relations (159)-(160), the osmotic pressure ratios β_1 and β_2 are obtained as functions of the variable molality m_2, the water molality m_1 being taken equal to 55.51 mol/kg.

The plots β_1 and β_2 versus m_2 for the aqueous solutions of ethanol and sucrose are shown in Fig. 3 and Fig. 4, respectively. From these figures, one can see the following features of β_1 and β_2.

With increase in the molal concentrations m_2, the van't Hoff ratio β_1 rises sharply and builds up by 10%, i.e., becomes equal to 1.10, at moderately low $m_2 = 1.41$ mol/kg (Fig. 3) and $m_2 = 0.256$ mol/kg (Fig. 4).

The behavior of Morse's ratio β_2 is dissimilar. Unlike β_1, the curves β_2 are flat in both the cases (Fig. 3 and 4). They keep close to unity and do not fall outside the limits $0.90 \le \alpha_2 \le 1.10$ over different ranges of concentrations. These ranges are wide in Fig. 3 ($0 \le m_2 \le 29.2$ mol/kg) and narrow in Fig. 4 ($0 \le m_2 \le 0.591$ mol/kg).

The above data make it possible to evaluate the upper limits m_2^* and C_2^* of applicability of the classical laws (1) and (2). Provided Eqs. (134) and (135) are practically exact (which will be shown later), the limits m_2^* and C_2^* can be approximated to an accuracy of ± 10% as follows.

For the van't Hoff equation (1):
$m_2^* \approx 1.4$ mol/kg and $C_2^* \approx 1.3$ mol/l (ethanol),
$m_2^* \approx 0.26$ mol/kg and $C_2^* \approx 0.24$ mol/l (sucrose).

For the Morse equation (2):
$m_2^* \approx 29$ mol/kg and $C_2^* \approx 11$ mol/l (ethanol),
$m_2^* \approx 0.59$ mol/kg and $C_2^* \approx 0.52$ mol/l (sucrose).

These results confirm (see Sec. I) that van't Hoff's law (1) is extremely limited. It fails when a solution is moderately dilute ($m_2 \sim 1$ mol/kg), no matter whether it involves molecules of ethanol (the molecular weight $M_2 = 46.07$) or larger molecules of sucrose ($M_2 = 342.3$).

The Morse formula (2) has a wider range of applicability which depends, however, on the kind of solute molecules. Being unfit for moderately dilute solutions of sucrose, it is nonetheless appropriate for very concentrated solutions of ethanol ($m_2 \sim 30$ mol/kg).

Figures 3 and 4 also display some other salient features of the classical laws (1) and (2).

For the solutions of both ethanol and sucrose, the van't Hoff ratio $\beta_1 \equiv \pi_{(134)}/\pi_{(1)} > 1$ and hence $\pi_{(1)} < \pi_{(134)}$ at all the concentrations $m_2 > 0$. In addition, the higher m_2, the more β_1. It follows that van't Hoff's law (1) *always underestimates* osmotic pressures, the error growing as the concentrations m_2 increase.

The same drawback is also inherent in the Morse formula (2) as applied to the aqueous solutions of sucrose (Fig. 4). Indeed, here the ratio $\beta_2 \equiv \pi_{(135)}/\pi_{(2)} > 1$ and thus $\pi_{(1)} < \pi_{(135)}$ over all the feasible range of concentrations m_2 up to the molality $m_{2,\mathrm{sat}}$ on the verge of saturation. Note that at $T = 20$ to 30 °C, $m_{2,\mathrm{sat}} \sim 6$ mol/kg.[29] As to the solutions of ethanol, Morse's ratio $\beta_2 \ge 1$ only at $0 < m_2 \le 18.67$ mol/kg (Fig. 3). Hence for such solutions, the Morse law (2) *either underestimates* osmotic pressures (at $m_2 \le 18.67$ mol/kg) *or overestimates* them (at $m_2 > 18.67$ mol/kg).

We conclude the discussion of Eqs. (1) and (2) with a brief remark. Considering aqueous solutions of ethanol and sucrose, we have tacitly assumed that in both of these mixtures osmotic pressures are physical realities which can be determined experimentally. In the meantime, there are experimental data on osmotic pressures of solutions of sucrose, but no such data are available, to our knowledge, on solutions of ethanol. It does not mean, however, that ethanol solutions cannot generate osmotic pressures. The detection and measurement of these pressures may only be hindered by difficulties in preparation of appropriate membranes.[16,125] This obstacle is not insurmountable in principle. Therefore the above analysis of osmotic pressures is justifiable not only for solutions of sucrose, but also for those of ethanol. We may add to the point that as early as 1908, G. N. Lewis in his classical work[21] made a similar analysis considering solutions of (i) ethylene chloride in benzene and (ii) propylene bromide in ethylene bromide despite the absence of direct experimental data on osmotic pressures of those mixtures.

Let us now return to the aqueous solutions of sucrose and compare two kinds of osmotic pressures of these solutions at $T = 20$ °C: experimental data π_{exp} and theoretical values π_{theor}.

The experimental data π_{exp} are shown in Fig. 5 as the following five series.

Series 1 (hollow circles) represents π_{exp} from two sources: $\pi_{\mathrm{exp}} = \pi_{\mathrm{morse}}$ by Morse et al.[126] at the molalities $m_2 \le 1$ mol/kg, and $\pi_{\mathrm{exp}} = \pi_{\mathrm{lotz}}$ by Lotz and Frazer[127] at $m_2 > 1$ mol/kg.

It should be noted that the pressures π_{lotz} were measured at the temperature 30 °C ≡ 303.15 K, whereas π_{theor} have been computed at 20 °C ≡ 293.15 K. To make these pressures comparable, π_{theor} should have been recalculated to 303.15 K or, the same, multiplied by a correction factor $\zeta_1 = 303.15/293.15$. Meanwhile, an opposite operation is equally permissible: instead of multiplying π_{theor} by ζ_1, we have divided π_{lotz} by ζ_1 and thus transformed π_{lotz} to the designed temperature $T = 20$ °C. In both the cases the ratio $\pi_{\mathrm{theor}}/\pi_{\mathrm{exp}} = \pi_{\mathrm{theor}}/\pi_{\mathrm{lotz}}$ remains the same which complies with the needs of our comparative analysis.

Series 2 (hollow boxes) shows experimental osmotic pressures $\pi_{\mathrm{exp}} = \pi_{\mathrm{frazer}}$ by Frazer and Myrick.[128] The original data π_{frazer} were obtained at 30 °C. Therefore, as in Series 1, we have divided π_{frazer} by the same correction factor ζ_1 and thus reduced them to the given temperature $T = 20$ °C.

Series 3 (hollow diamonds) depicts osmotic pressures $\pi_{\mathrm{exp}} = \pi_{\mathrm{berkeley}}$ according to the experiments of the Earl of Berkeley and Hartley.[129] Since the original pressures π_{berkeley} were measured at 0 °C ≡ 273.15 K, we have divided these data by the corresponding correction factor $\zeta_2 = 273.15/293.15$ to transform them to the designed temperature $T = 20$ °C.

Series 4 (dots) and **Series 5** (filled circles) represent osmotic pressures $\pi_{\mathrm{exp}} = \pi_{\mathrm{tab}}$ and $\pi_{\mathrm{exp}} = \pi_{\mathrm{kremann}}$, respectively. Here both the pressures π_{exp} have been obtained as follows.

We adopted an expression for the solvent activity a_1 (notation is partially changed)[29]

$$\ln a_1 = 1.9462\,(T_f^*/T_f - 1) - 4.5920\,\ln\,(T_f^*/T_f) \qquad (162)$$

where $T_f^* = 273.15$ K is the normal freezing point of pure water, T_f is the freezing point of an aqueous solution. The freezing-point depression ΔT_f is defined as

$$\Delta T_f \equiv T_f^* - T_f \qquad (163)$$

Having then inserted $\ln a_1$ by Eq. (162) into Eq. (7) and included identity (163), we obtained osmotic pressure, denoted here by π_{exp}, as function of the relative freezing-point depression $\Theta_f \equiv \Delta T_f/T_f^*$:

$$\pi_{\mathrm{exp}} = -\,(RT/V_1^\circ)\;[1.9462\;\Theta_f/(1 - \Theta_f) + 4.5920\,\ln\,(1 - \Theta_f)] \qquad (164)$$

Since ΔT_f depends on the concentration m_2 of the solution, the osmotic pressure π_{exp} by Eq. (164) is also a function of m_2, as should be expected.

Equation (164) has been used for determining π_{exp} via experimental data on the freezing-point depression ΔT_f at variable molalities m_2 and constant $T_f^* = 273.15$ K, $T = 20$ °C ≡ 293.15 K, $R = 0.082057$ liter × atm × mol^{-1} × K^{-1} and $V_1^\circ = 0.01802$ liter × mol^{-1}. For the osmotic pressures $\pi_{\mathrm{exp}} = \pi_{\mathrm{tab}}$ (Series 4) the data on ΔT_f have been taken from Table 88 of the handbook,[124] and for $\pi_{\mathrm{exp}} = \pi_{\mathrm{kremann}}$ (Series 5) from the experiments by Kremann and Eitel.[130]

Series 6 (a solid line) plots theoretical osmotic pressures π_{theor} versus variable molalities $m_2 = m_2'/\rho_w$ at $\rho_w = 0.99823$ kg/l. The pressures π_{theor} have been computed by Eq. (135). The specific volumes V involved in this relation have being calculated in terms of Eq. (161) just as described above, while analyzing the osmotic pressure ratios β_1 and β_2. The values of R and V_1° have been taken as in Series 4 and 5.

Figure 5 shows that all the experimental data π_{exp} on osmotic pressures are very close to the values π_{theor} by our theory [Eq. (135)]. There are only minor deviations D of π_{exp} from π_{theor} depicted in Fig. 6 where the experimental Series 1 to 5 coincide with those in Fig. 5. For each couple $\{\pi_{\mathrm{exp}}, \pi_{\mathrm{theor}}\}$, the deviation D have been calculated in percent as

$$D = 100 \times (\pi_{\mathrm{exp}}/\pi_{\mathrm{theor}} - 1) \qquad (165)$$

A majority of these deviations D (37 out of 43, or 86%) range approximately from – 8% to + 7%. The other six values of D (14%) are within the limits – 11% and + 12%.

It is also seen from Fig. 6 that all the experimental data π_{exp} are split up into two different sets G_1 and G_2.

The set G_1 includes the values of π_{exp} obtained indirectly, through the measurements of the freezing-point depression ΔT_f (Series 4 and 5). These data π_{exp} are represented in Fig. 6 by dots and filled circles that are almost equally scattered above and below the zero dispersion level $D_\mathrm{o} = 0$. In other words, with about equal probability any value of $\pi_{\mathrm{exp}} \in G_1$ may be either more or less than its theoretical counterpart π_{theor}. This implies that the dispersions D of the set G_1 are caused mainly by random errors of the ΔT_f measurements.

Unlike G_1, the set G_2 covers the data π_{exp} measured directly by osmometers (Series 1 to 3). The hollow circles, boxes and diamonds depicting this set in Fig. 6 are spread mostly below the level $D_\mathrm{o} = 0$, i.e., the experimental data $\pi_{\mathrm{exp}} \in G_2$ are less than their theoretical counterparts π_{theor}. It follows that the dispersions D of the set G_2 originate not so much from random errors of measurements as from some systematic deviations.

These deviations occur because in reality the semipermeable membranes tend to be leaky through mechanical faults or by not being quite impermeable to the solute molecules. In general, the more concentrated the solution, the higher the osmotic pressure and consequently the more intense the solute leakage[127,128] As a result, the experimental data $\pi_{\mathrm{exp}} \in G_2$ become less as compared with their would-be theoretical values π_{theor}. Such pressure drop can be corrected by the reflection coefficient $\sigma < 1$ that enters into our Eqs. (116)-(121), (128)-(131), etc. Yet we have avoided this because the relation (135) tested is valid at $\sigma = 1$ and if $\sigma < 1$ were included, it would be transformed into its 'leaky' counterpart (131).

In addition to the membrane imperfections, there are some other factors responsible for the decline in the measured values of π_{exp}.[7,8,16,95,125] We do not, however, discuss these factors as well as the values of the reflection coefficient σ as being outside the scope of the present paper.

Now return to the deviations D by Eq. (165) which give us a point estimation of how each π_{exp} departs from the corresponding π_{theor}. A similar global estimation for a set of $n > 1$ experimental data π_{exp} can be represented by the standard deviation S defined in percent by the formula[131]

$$S = 100 \times [n^{-1} \sum_{k=1}^{n} (\pi_{\mathrm{exp}(k)}/\pi_{\mathrm{theor}(k)} - 1)^2]^{1/2} \qquad (166)$$

Equation (166) has been applied to computing the values of S for the series of experimental data shown in Figures 5 and 6. The results are given in Table I.

TABLE I. Standard deviations S of experimental osmotic pressures π_{exp} from their theoretical counterparts π_{theor}.

Series included	Characteristics of experimental data	Standard deviation S, %
1	Direct experiments[126,127]	5.9
2	Direct experiments[128]	8.6
3	Direct experiments[129]	6.8
4	Indirect experiments[124]	4.3
5	Indirect experiments[130]	4.5
1 to 3	All the direct experiments	7.0
4 and 5	All the indirect experiments	4.4
1 to 5	All the experiments	5.8

We see that all the values of S are small enough and do not exceed 8.6%. The most representative of these standard deviations is the last one which covers all the set of 43 experimental data over the entire range of the sucrose concentrations, from $m_2 = 0$ to 6 mol/kg. Since this deviation is about 5-6%, the theoretical equation (135) tested is able to predict osmotic pressures of concentrated solutions of sucrose with possible errors of the order of 5-6%. Such errors are admissible in most applications. This fact bears witness to the validity of the molal formula (135) and its molar variant (134).

Consider now Figures 7 and 8 extending our comparative analysis to the classical laws (1) and (2). These figures, instead of two sets of the above experimental data π_{berkeley} and π_{lab} in Fig. 5, include two new theoretical curves: Series 3 (a dashed line) by Morse's equation (2) for $\pi_{(2)}$, and Series 4 (a dotted line) by van't Hoff's law (1) for $\pi_{(1)} = \pi_{(2)}/V$. Series 1, 2, 5 and 6 remain as in Fig. 5.

Figures 7 and 8 display an additional drawback of the classical laws (1) and (2). These laws fail to reproduce osmotic pressures of concentrated solutions not only quantitatively, as shown earlier in this Section, but also qualitatively. Indeed the plot 4 by van't Hoff's law (1) is a curve concave downward and the plot 3 by Morse's equation (2) is a straight line. Both the plots are at variance with the experimental data π_{exp} (Series 1, 2 and 5) clustered round the curve 6 by our Eq. (135) which is concave upward at $0 < m_2 \leq m_2^\circ$ ($m_2^\circ \approx 6$ mol/kg) and concave downward at $m_2 > m_2^\circ$.

VII. DISCUSSION

A. Lower and upper limits of osmotic pressure

If the membrane is semipermeable and the solution infinitely dilute, then the concentration $m_2' \to 0$, the molar fraction $x_2 \to 0$ and consequently the volume $V \to 1$. As shown in Sec. V, in this case the osmotic pressure π by Eq. (135) tends to the lower limit $\pi_{(-)}$ given by the Morse law (2):

$$\pi \to \pi_{(-)} \equiv RTm_2' \quad \text{as} \quad x_2 \to 0 \tag{167}$$

When both components of the solution, solvent and solute, are completely miscible with each other, the solute concentration m_2' may range from zero to infinity and hence the solution can be infinitely concentrated. In this case, which is opposite to the previous one, $m_2' \to \infty$, $x_2 \to 1$ and $V \to \infty$. Then, as may easily be proven, the osmotic pressure π by Eq. (135) tends to an upper limit $\pi_{(+)}$:

$$\pi \to \pi_{(+)} \equiv RTm_1' \quad \text{as} \quad x_2 \to 1 \tag{168}$$

Given the identity $m_1' \equiv 1/V_1^\circ$, Eq. (168) can be written as

$$\pi \to \pi_{(+)} \equiv RT/V_1^\circ \quad \text{as} \quad x_2 \to 1 \tag{169}$$

It is noteworthy that the limit $\pi_{(+)}$ depends only on the molar volume V_1° of a pure solvent. If it is water at $T = 20$ °C, the volume $V_1^\circ = 0.018047$ liter/mol, so that by Eq. (169) $\pi_{(+)} = 1333$ atm.

Equations (167)-(169) bring to light a startling feature of a completely miscible solution: at any given concentration m_2' of the solute, from zero to infinity, **osmotic pressure of the solution is always restricted**—it cannot fall below the lower limit $\pi_{(-)}$ and go over the upper limit $\pi_{(+)}$:

$$RTm_2' \equiv \pi_{(-)} \leq \pi \leq \pi_{(+)} \equiv RTm_1' \equiv RT/V_1^\circ \tag{170}$$

While the restriction (167) is well known, the limitations (168)-(169) are new and should therefore be validated.

Before doing this, let us remind that there is no direct experimental information on osmotic pressures of infinitely concentrated solutions. We can, however, dispense with it by using Eq. (164) to obtain the necessary data indirectly, just as in Sec. VI. Toward this end we may consider any kind of completely miscible binary mixtures, e.g., an aqueous solution of ethanol. If this solution is infinitely concentrated, it only consists of pure ethanol, its freezing point T_f ranging from −110.5 to −117.3 °C.[132-135]

In view of these data, Eqs. (163)-(164) give us the following maximum values of osmotic pressures at 20 °C: $\pi_{\max} = 1413$ atm at $T_f = -110.5$ °C,[132] and $\pi_{\max} = 1484$ atm at $T_f = -117.3$ °C[134]. The above upper limit $\pi_{(+)} = 1333$ atm by Eqs. (168)-(169) is less than these values by 5.7 and 10.2%, respectively. Such departures are, however, insignificant since Eq. (162) and its corollary Eq. (164) are not completely accurate as the freezing point T_f falls considerably below 0 °C.[29] We thus may conclude that the relations (168)-(169) tested are validated by the indirect experimental data.

Apart from possible chemical applications, Eqs. (168)-(169) may be of importance to such a seemingly remote field as marine biology. We will only touch upon one facet of this subject from a mechanical point of view on Eqs. (168)-(169), without any intention of going into the subtleties of underlying biological processes.

A biological cell is known[5,10,95,107,136] to contain a material of considerable concentration—macromolecules of proteins, mostly in a colloid state, and a solution of sugar, various salts and other substances. This material is retained by a semipermeable membrane supported by the cell wall. As the cell is healthy, the membrane is *turgid*, i.e., kept expanded against the cell wall by osmotic pressure developed by diffusion flux of water through the membrane into the cell.

Most animal cells are weak. Therefore in order to cope with the osmotic pressure, if it is too high, they have evolved two major mechanisms.[107] First, the entering water is simply pumped out of the cell by a contractile vacuole. Second, the cell can also drive out a diffusible component (solute) and thus diminish both the concentration gradient and the osmotic pressure. So, the two mechanisms are aimed at reducing osmotic pressure π_i inside the cell. Yet there might be quite an opposite situation when the cell will be in need to increase the osmotic pressure.

If the cell is placed in a medium of high external hydrostatic pressure P_e, it will be able to survive if P_e is equal to the internal osmotic pressure π_i. Otherwise the cell may burst if $P_e < \pi_i$ or it may be crushed if $P_e > \pi_i$. As mentioned above, the cell can come through the first situation. The second situation is, however, more serious and may even become deadly at sufficiently high external pressures P_e. Let us show this.

Consider the sea environment where the external hydrostatic pressure P_e is independent of the cell. Consequently, in the case of $P_e > \pi_i$, the cell is unable to lower the dangerous pressure P_e. The only way for the cell to succeed now is to increase the internal osmotic pressure π_i. There are certain mechanisms to make it really possible—numerous deep-sea animals bear witness to this. Nevertheless, there remains one essential question to be cleared up: Can those mechanisms work at *any* high external pressures P_e or not?

In search for an answer, we resort to Eqs. (168)-(169) by which the limiting osmotic pressures of aqueous solutions vary from $\pi_{(+)} = 1244$ to 1333 atm at 0 to 20 °C. These values of $\pi_{(+)}$ correspond approximately to the depths of 12.85-13.8 km of pure water or, disregarding 2-3.5% salinity,[137] to the same depths of sea-water. The above upper limits of osmotic pressure $\pi_{(+)}$ are fixed and remain the same for any animal cell at any depth of sea-water unlike the hydrostatic pressure P_e that increases with depth. If the depth falls below the range of 12.85-13.8 km, the pressure P_e will exceed the highest possible values of osmotic pressure $\pi_{(+)} = 1244\text{-}1333$ atm and crash the animal cell.

It follows an important conclusion. If not protected by an additional mechanism of high-pressure pumping, as it is in the ordinary way, any animal cell will not be able to survive in the ocean below the critical depths of 12.85-13.8 km. Note that so far the maximum ocean depth, namely 11.515 km, has been recorded in the Mindanao Trench of the Pacific Ocean.[138]

The foregoing conclusion is in accord with marine ecology.[139,140] Indeed, the ocean biomass is found to decline impetuously with depth: below 9 km it only amounts to 0.5% and 0.005% of the biomass at the depths from 4 to 5 km and from 0 to 0.2 km, respectively (see Table 7.1[140]).

A number of factors are considered to govern such a remarkably inhomogeneous distribution of the biomass in depth: extreme *external* pressure and temperature, darkness, scanty food sources, etc.[139] Now it is possible to add one more factor, the restriction $\pi_i \le \pi_{(+)} \sim 1300$ atm imposed on the *internal* osmotic pressure π_i. Because of this limitation, the life of marine animals in deep-sea zones is not only aggravated but also might be wiped out below the critical depths of about 13 km, should they exist.

B. The activity and the chemical potential of solvent

Let us return to Eq. (7) that has already been touched upon in Sec. I. Recall that within the framework of the NMTs, Eq. (7) is regarded as an exact law of osmotic pressures of concentrated non-electrolyte solutions. As shown above, this is also true for Eq. (135) and hence for all its equivalent variants from (132) to (134). Now, since Eq. (132)-(135) are mechanistic counterparts of the thermodynamic law (7), we may equate (7) and (133) to get a new relation for the solvent activity a_1

$$\ln a_1 = -\,\bar{V}_1 V m_2' x_1 (1 + V x_2)^{-1} \tag{171}$$

Here we have used more rigorous variant of Eq. (7) with the partial molar volume $\bar{V}_1$ instead of the molar volume V_1°.

Given that $V_1^\circ m_1' \equiv 1$, $x_2 = 1 - x_1$ and $m_1' x_2 = m_2' x_1$, Eq. (171) becomes

$$\ln a_1 = -\,\eta V x_2 (1 + V x_2)^{-1} \tag{172}$$

or

$$a_1 = \exp\left[-\,\eta V x_2 (1 + V x_2)^{-1}\right] \tag{173}$$

where $\eta \equiv \bar{V}_1 / V_1^\circ$. If the solution is infinitely dilute, the solute mole fraction $x_2 \to 0$, the specific volume $V \to 1$ and, by Eq. (173), $a_1 \to 1$. On the other hand, if the solution is infinitely concentrated, then $x_2 \to 1$, $V \to \infty$ and $a_1 \to e^{-\eta}$. We thus have

$$a_1 \to 1 \quad \text{as} \quad x_2 \to 0. \tag{174}$$

$$a_1 \to e^{-\eta} \quad \text{as} \quad x_2 \to 1. \tag{175}$$

As a result, the solvent activity a_1 by our theory falls within the limits

$$e^{-\eta} \le a_1 \le 1 \quad \text{and} \quad -\,\eta \le \ln a_1 \le 0 \tag{176}$$

On substitution a_1 from Eq. (173) into (11), we obtain a new expression for the chemical potential μ_1 of the solvent

$$\mu_1 = \mu_1^\circ - RT\eta V x_2 (1 + V x_2)^{-1} \tag{177}$$

In the above limiting cases, Eq. (177) results in

$$\mu_1 = \mu_1^{\circ} \qquad \text{as } x_2 \to 0 \text{ and } V \to 1 \tag{178}$$

$$\mu_1 = \mu_1^{\circ} - RT\eta \qquad \text{as } x_2 \to 1 \text{ and } V \to \infty \tag{179}$$

In the second case the solution consists of solute molecules only. It is therefore quite natural to take the chemical potential μ_1 of the solvent in such a solution equal to zero and thus obtain its value μ_1° in the standard state (when $x_1 = 1$, $x_2 = 0$ and $P = 1$ atm):

$$\mu_1^{\circ} = RT\eta \tag{180}$$

In view of this expression, Eq. (177) takes a simple final form

$$\mu_1 = RT\eta(1 + Vx_2)^{-1} \tag{181}$$

C. Ideality and non-ideality of solutions

Relations (171)-(181) may have several applications. Consider one of these concerning the concept of ideal and non-ideal solutions. The borderline between these kinds of solutions is governed by the solvent activity coefficient γ_1 which is, in general, an empirical factor.[141] Now it may also be found theoretically on the basis of Eq. (173) and identity (10). Indeed, taking $\gamma_1 \equiv a_1/x_1 = a_1/(1 - x_2)$ by (10) and substituting here a_1 by (173), we get

$$\gamma_1 = (1 - x_2)^{-1} \exp\,[- \eta V x_2 (1 + Vx_2)^{-1}] \tag{182}$$

If the activity coefficient $\gamma_1 = 1$, the solution under discussion is ideal by definition. In this case the chemical potential μ_1 of the solvent is determined by Eq. (12) that brings about the corresponding osmotic pressure[26]

$$\pi_{\text{ideal}} = -\,(RT/\,\bar{V}_1)\ln(1 - x_2) \tag{183}$$

Now suppose that the activity coefficient $\gamma_1 \neq 1$ and hence the solution is non-ideal. As such, it may display two types of deviation from ideality: *positive* when $\gamma_1 > 1$, and *negative* when $\gamma_1 < 1$. Is it possible to tell *apriori* which one of these deviations will occur in reality?

To answer this question, we take $\gamma_1 = 1$. Equation (182) then gives us

$$V^{*} = -\ln(1 - x_2)\,[x_2(\eta + \ln x_2)]^{-1} \tag{184}$$

The volume V^{*} marks a border between the positive and the negative deviations from ideality:

1. If the real volume $V = V^{*}$, then $\gamma_1 = 1$ and there is no deviation. In this case the osmotic pressure π_{ideal} by Eq. (183) is equal to the corresponding osmotic pressure π by our theory [either of Eqs. (132) to (135)], i.e., $\pi_{\text{ideal}} = \pi$.

2. If $V < V^{*}$, then $\gamma_1 > 1$ and the deviation is positive. As a result, $\pi_{\text{ideal}} > \pi$.

3. If $V > V^{*}$, then $\gamma_1 < 1$ and the deviation is negative. Consequently, $\pi_{\text{ideal}} < \pi$.

Equation (184) is illustrated by Fig. 9 where the volume borderlines V^{*} are plotted versus the mole fraction x_2 of solute at $\eta = 1$ (Series 1, a solid line), $\eta = 0.8$ (Series 2, a dashed line) and $\eta = 1.2$ (Series 3, a dotted line). The domains of positive and negative deviations of ideality lie respectively below and above the corresponding borderline V^{*}. All the values of V^{*} are seen to grow as the concentration x_2 increases, save Series 3 in the vicinity of $x_2 = 0$. Also, the growth of V^{*} is intensified as $\eta \equiv \bar{V}_1/V_1^{\circ}$ declines from 1.2 to 0.8.

The real values of V in comparison with V^{*} are shown in Fig. 10. Here the theoretical curves of V^{*} (Series 1-3) are the same as in Fig. 9 whereas Series 4 and 5 (dots and hollow circles) refer to the experimental volumes V of aqueous solutions of sucrose and ethanol, respectively, V being determined by Eq. (161) as described in Sec. VI.

As is clear from Fig. 10, the sucrose solutions are markedly non-ideal. Their deviation from ideality is negative everywhere, at all the feasible concentrations $x_2 < 0.13$ regardless of the parameter η, except a small region $0 < x_2 < 0.025$ at $\eta = 0.8$. The ethanol solutions also exhibit non-ideal behavior. It is, however, not so pronounced as that of the sucrose mixtures. Moreover, the ethanol solutions may have either positive or negative deviation depending on η and x_2:

1. If $\eta = 1$ (Series 1), the deviation is negative at $0 < x_2 \leq 0.47$ and positive at $x_2 > 0.47$.

2. If $\eta = 0.8$ (Series 2), the deviation is positive everywhere, at any mole fraction $x_2 > 0$.

3. If $\eta = 1.2$ (Series 3), the deviation is negative over the whole range of concentrations $0 < x_2 < 0.48$ shown in Fig. 10.

One should mention that the question of whether a solution at hand is ideal or non-ideal is not of great importance *per se*. It is clarified as soon as we know the underlying activity coefficient γ_1. The usual way of obtaining the values of γ_1 is based on the relation[1]

$$\gamma_1 = p_1/(p_1^{\circ} x_1) \tag{185}$$

where the solvent vapor pressures p_1° and p_1 are directly measured at the solvent concentrations $x_1 = 1$ and $x_1 < 1$, respectively. At the same time, the present theory of osmotic pressure offers another method of determining the activity coefficient γ_1 by employing Eq. (182). This equation may rival formula (185) not only in accuracy, but also in simplicity because of including the parameter V—the volume of solution per liter of pure solvent—which is measurable much more easily than the above vapor pressures p_1° and p_1.

D. Comparison of the activity equations

The deviations of solutions from ideality and limitations of the corresponding logarithmic law (12) were revealed at the early stages of physical chemistry. Just at that time G. N. Lewis revised the relation (12) in his celebrated works[142,143]. Lewis' approach was straightforward: intending to preserve the logarithmic *form* of (12), he simply replaced the mole fraction x_1 by a new *unknown* function a_1 termed "activity" and thus transformed Eq. (12) into Eq. (11). Since then the logarithmic relation (11) has been generally accepted as the law for non-ideal solutions.

In essence, however, Lewis' *formal* procedure only exchanged one difficulty for another. It has neither advanced the understanding of non-ideality nor enabled a theoretical determination of the chemical potentials. As wrote one of Lewis' contemporaries about the functions of activity and fugacity, "their introduction adds nothing new to the content of thermodynamic theory, and they are not so important as the more fundamental functions such as entropy and energy."[144] Even sixty years later, the modern authors[33] echo that opinion and call the activity "a very tricky concept in thermodynamics." We may now add that the logarithmic law (12) based on the "tricky concept" of activity leads in some instances to quite erroneous results. Let us show this.

Within the framework of classical thermodynamics, the solvent activity a_1 is a "*fudge factor*"[141] that can only be determined through experimental data. Several methods have been devised to make it possible.[1,11,26,29,49,141] One of these is based on Eq. (162) which permits calculations of the solvent activity a_1 proceeding from experimental data on freezing points of aqueous solutions.

Another method stems from Eqs. (185). Combining it with Eq. (10) results in

$$a_1 = p_1/p_1^{\circ} \tag{186}$$

Relation (186) enables computing the solvent activity a_1 in terms of experimental vapor pressures p_1° and p_1. This is good news. The bad news is that Eq. (186) leads to a mathematical singularity which is hardly consistent with physical reality. The point is that the vapor pressure p_1 declines as the solvent concentration x_1 decreases and hence the solute concentration $x_2 = 1 - x_1$ grows, so that $p_1 \to 0$ as $x_1 \to 0$ and $x_2 \to 1$. Since p_1° = constant, the activity a_1 by Eq. (186) tends to zero:

$$a_1 \to 0 \quad \text{as} \quad x_2 \to 1 \tag{187}$$

Consequently, the function ($-\ln a_1$) and the osmotic pressure π, by the logarithmic theory (7), tend to infinity:

$$-\ln a_1 \to \infty \quad \text{as} \quad x_2 \to 1. \tag{188}$$

$$\pi \to \infty \quad \text{as} \quad x_2 \to 1 \tag{189}$$

On substituting ln a_1 from (188) into (11), we have

$$\mu_1^{\circ} - \mu_1 \to \infty \quad \text{as} \quad x_2 \to 1 \tag{190}$$

Expressions (187)-(188) and (189) are at variance with the corresponding limiting equations (175) and (168)-(169). They also contradict the results furnished by other thermodynamic methods including Eq. (162). For instance, in the cases of aqueous solutions of ethanol and those of methanol, whose freezing points at $x_2 \to 1$ are respectively -114.5 and -97.9 °C,[134] equation (162) brings about the following values of the solvent activities:

$$a_1 = 0.336 \quad \text{as} \quad x_2 \to 1 \quad \text{(ethanol)} \tag{191}$$

$$a_1 = 0.386 \quad \text{as} \quad x_2 \to 1 \quad \text{(methanol)} \tag{192}$$

which are far from $a_1 \to 0$ by Eq. (187) and very close to the theoretical limit $a_1 \to e^{-1} \approx 0.368$ by Eq. (175) at $\eta = 1$.

Also, Eq. (190) means that following the logarithmic law (11), the difference in magnitude between the standard μ_1° and the actual μ_1 chemical potentials of the solvent tends to infinity as the concentration $x_2 \to 1$. This runs counter to Eqs. (180) and (181) which at the same $x_2 \to 1$ and hence $V \to \infty$ give us a finite difference: $\mu_1^{\circ} - \mu_1 \to RT\eta$.

Needless to say that in real *finite* systems, *infinite* values of pressures and chemical potentials are impossible. As they sprung up in theoretical calculations, it is an indication that something is wrong with the mathematical description of the system, just as happened in the case of the logarithmic law (11) and its corollary (7) when applied to the extremely concentrated solutions at $x_2 \to 1$.

VIII. CONCLUSION

1. In this work a new theory of osmotic pressures of incompressible binary solutions of non-electrolytes is developed. Unlike the previous theories that are either empirical or stem from thermodynamic considerations, the present theory is based on the diffusion mechanism of osmosis.

2. The proposed mechanistic theory is validated by direct and indirect experimental data on osmotic pressures of aqueous solutions of sucrose and those of ethanol at all their feasible concentrations.

3. In comparison with the earlier (empirical and thermodynamic) models of osmotic pressure, the mechanistic theory has at least one of the following advantages:

- It holds for both ideal and non-ideal solutions.
- It imposes no restrictions on the concentrations of the mixtures involved.
- It includes no adjustable parameters.

It is also equally applicable to semipermeable and leaky membranes.

4. Due to the mechanistic theory, the existence of an upper limit of osmotic pressures is revealed. This limitation is

borne out by indirect experimental data and is shown to be able to have considerable influence on the life of marine animals in deep sea-water.

5. The present theory also brings about new expressions for the activity, the activity coefficient, and the chemical potential of solvent. In contrast with the similar classical laws, these expressions are in better agreement with physical reality and experimental data.

6. The mechanistic approach, which has resulted in the proposed theory for binary solutions, may be naturally extended to many-component mixtures. It also admits of including such phenomena as, for instance, the solution compressibility, the solute dissociation on dilution,[7] the interruption of hydrogen bonds.[145-147] These problems will be dealt with in the forthcoming publications.

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A new theory of osmotic pressures of binary solutions of non-electrolytes

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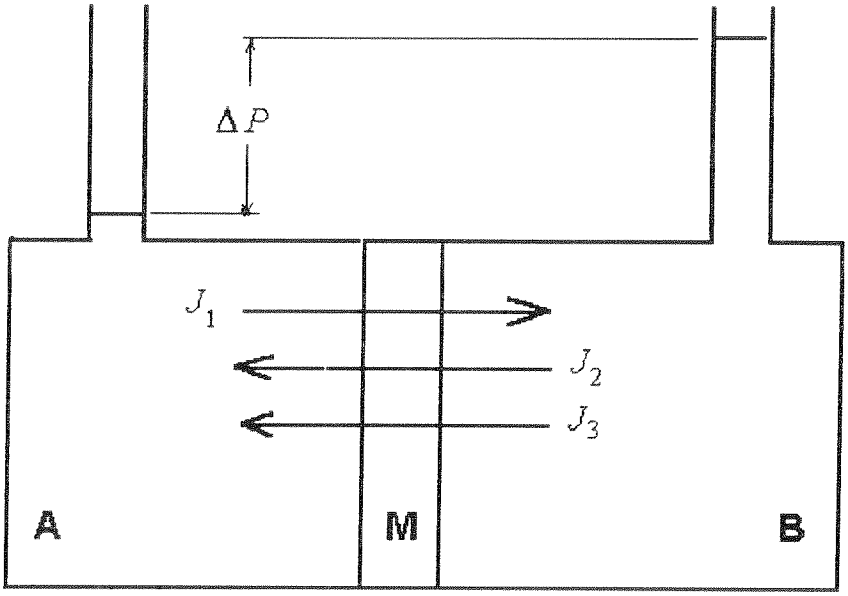

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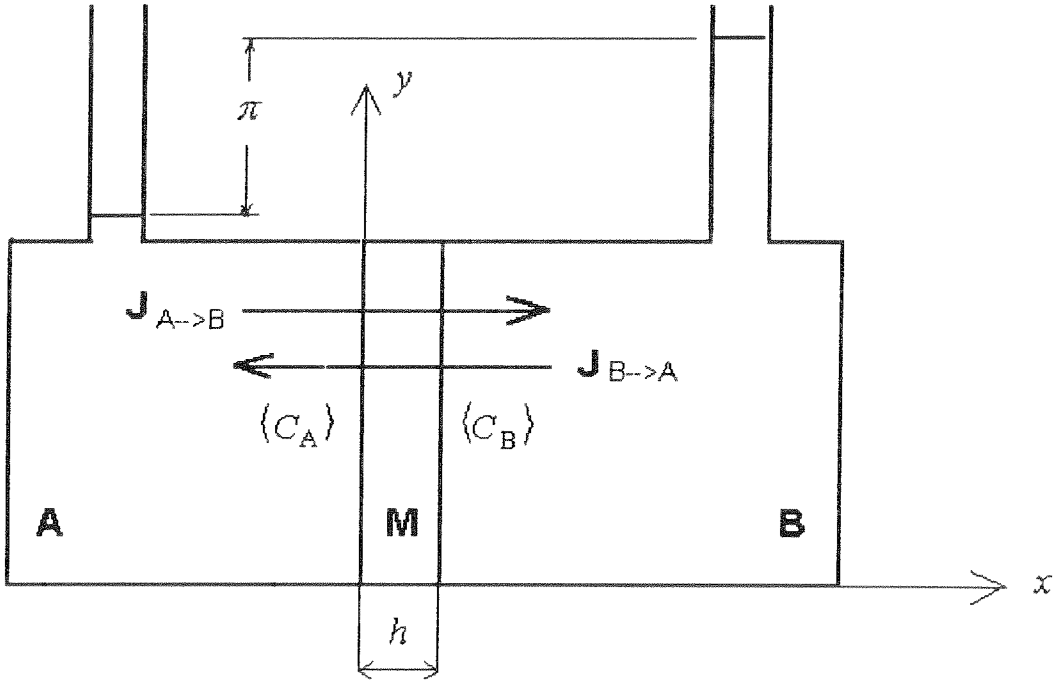

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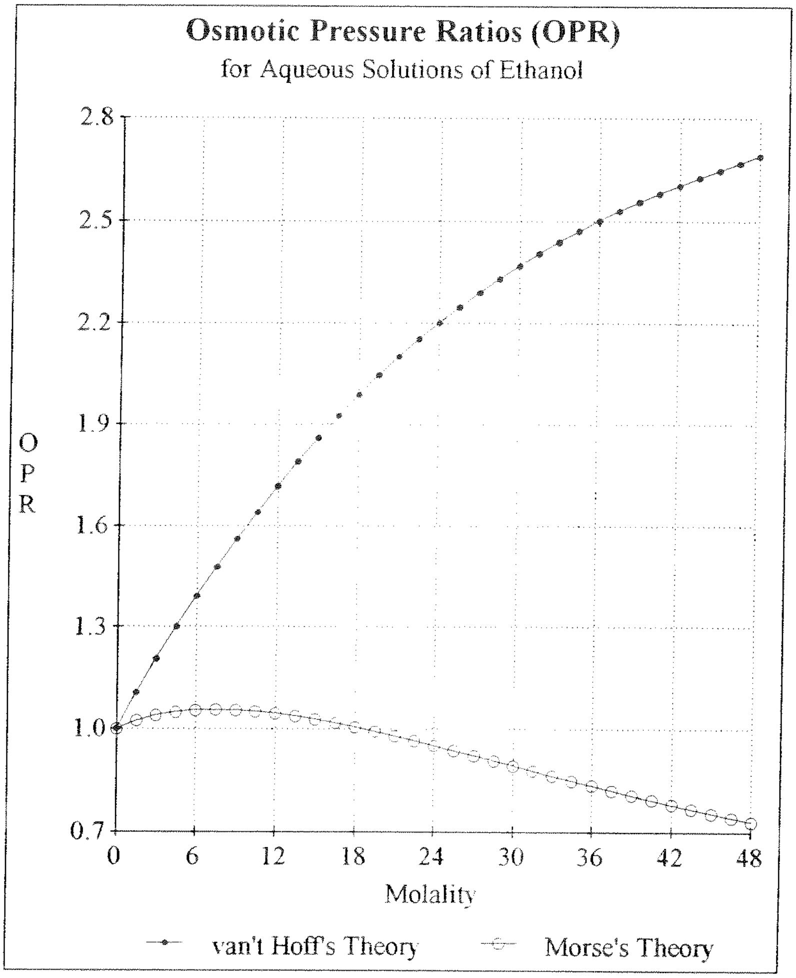

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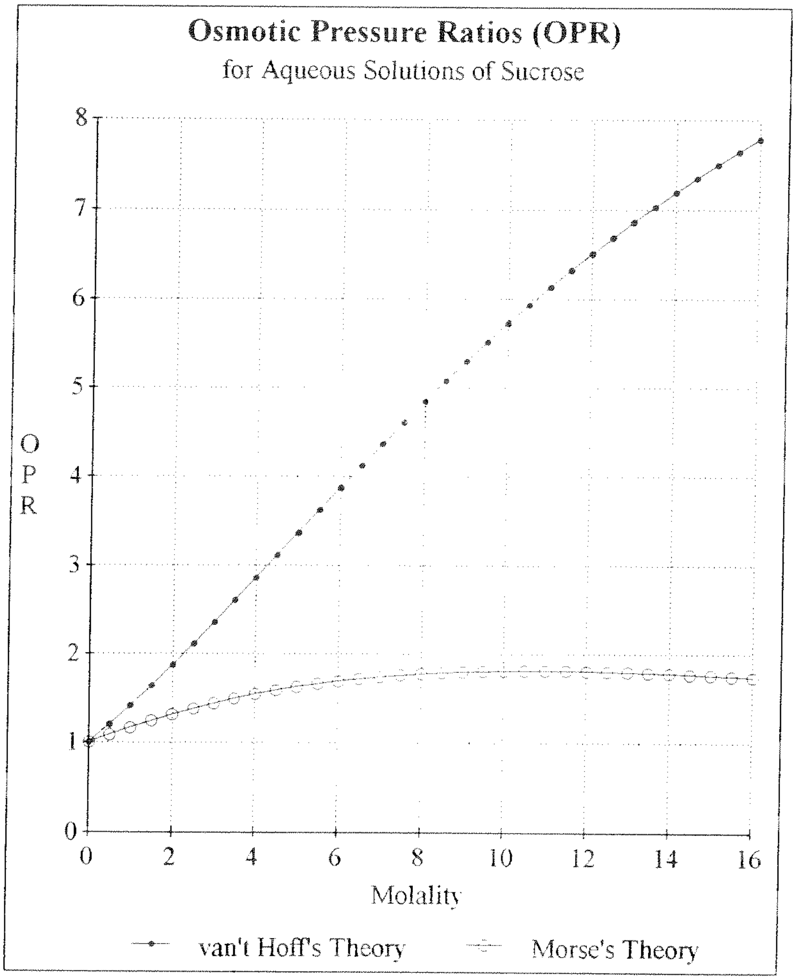

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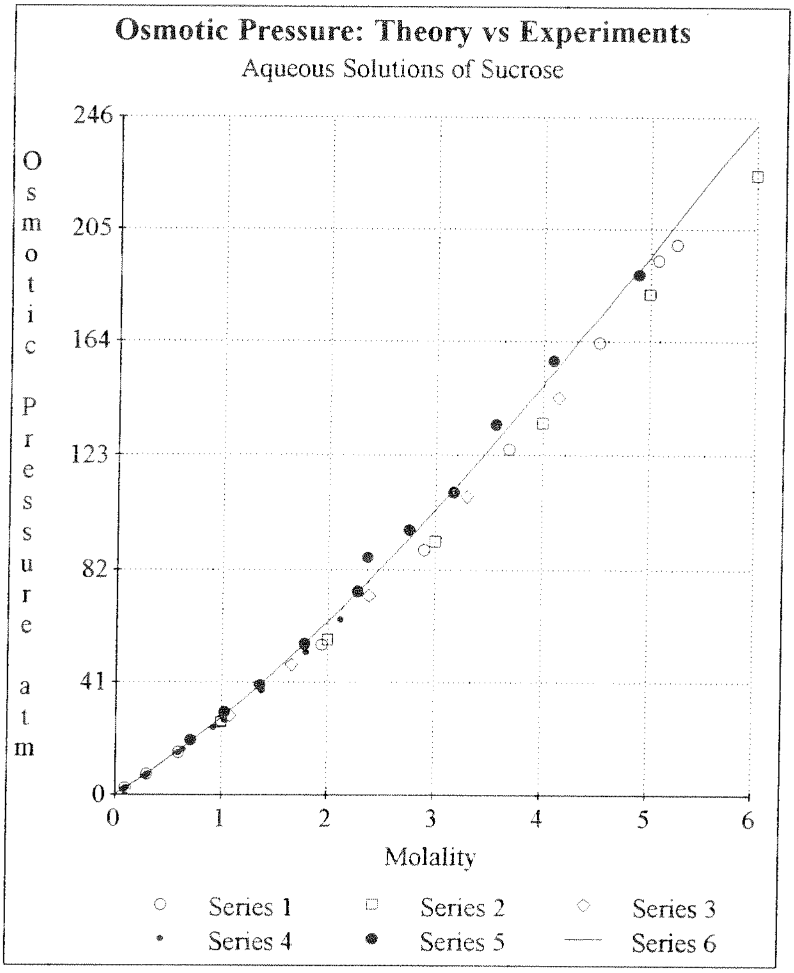

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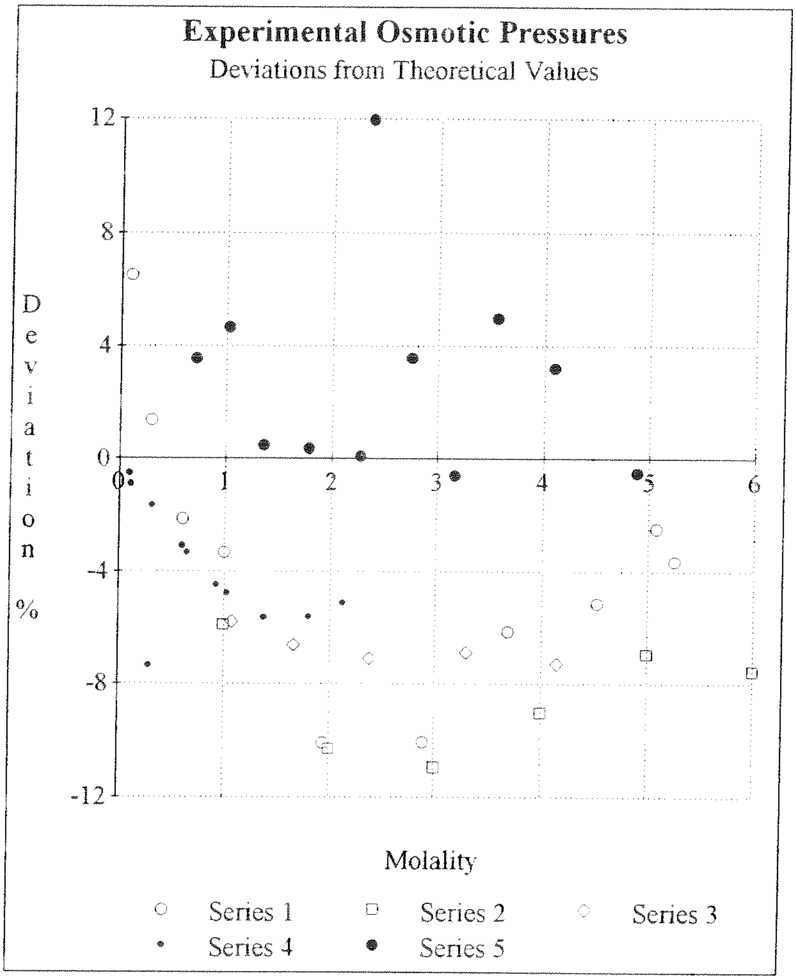

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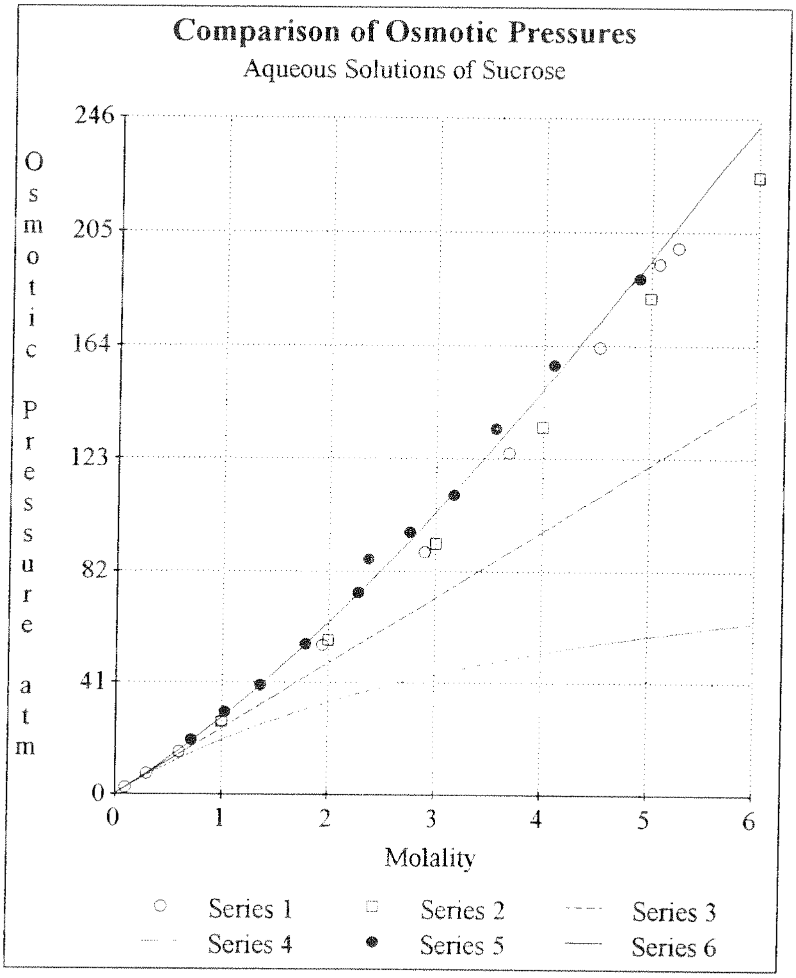

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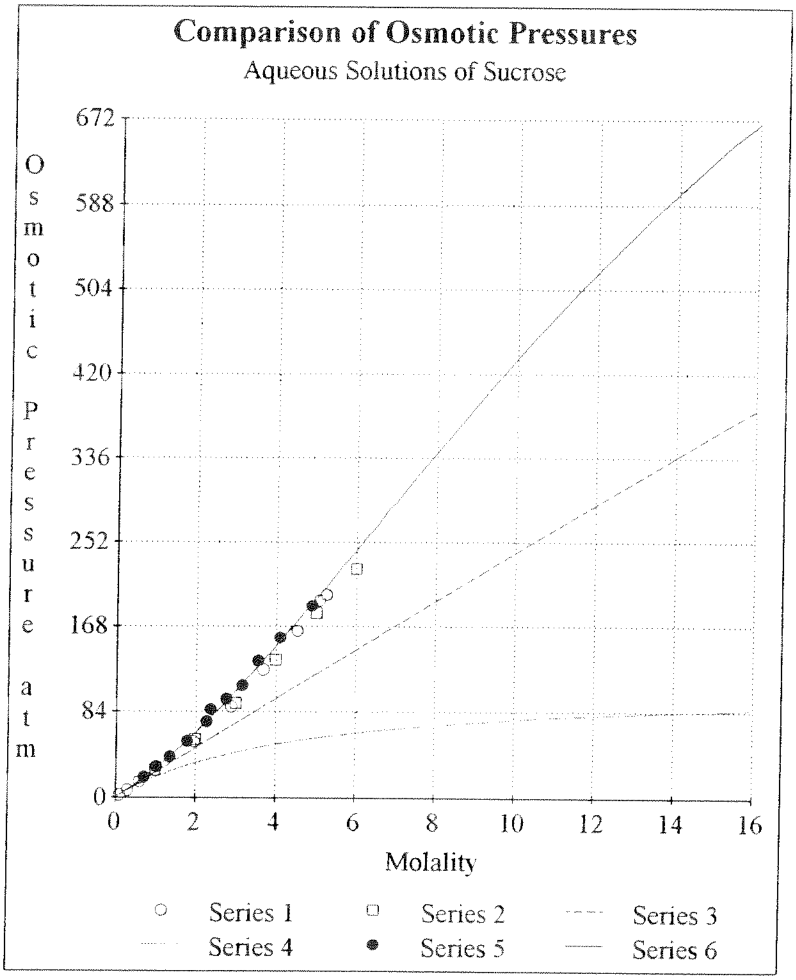

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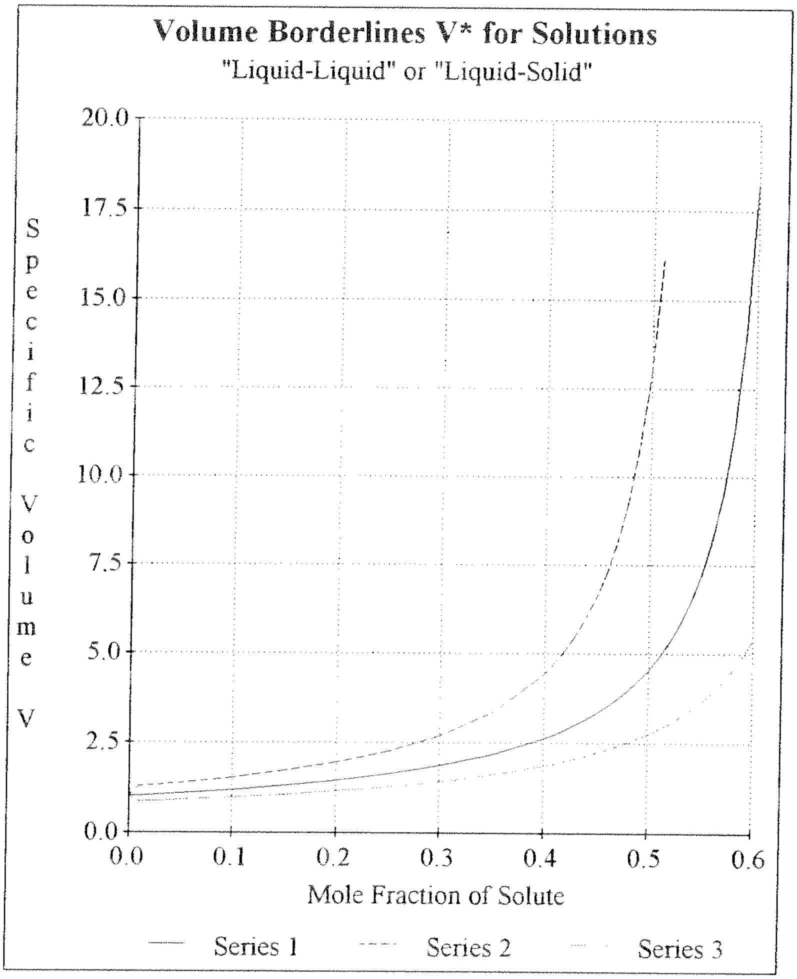

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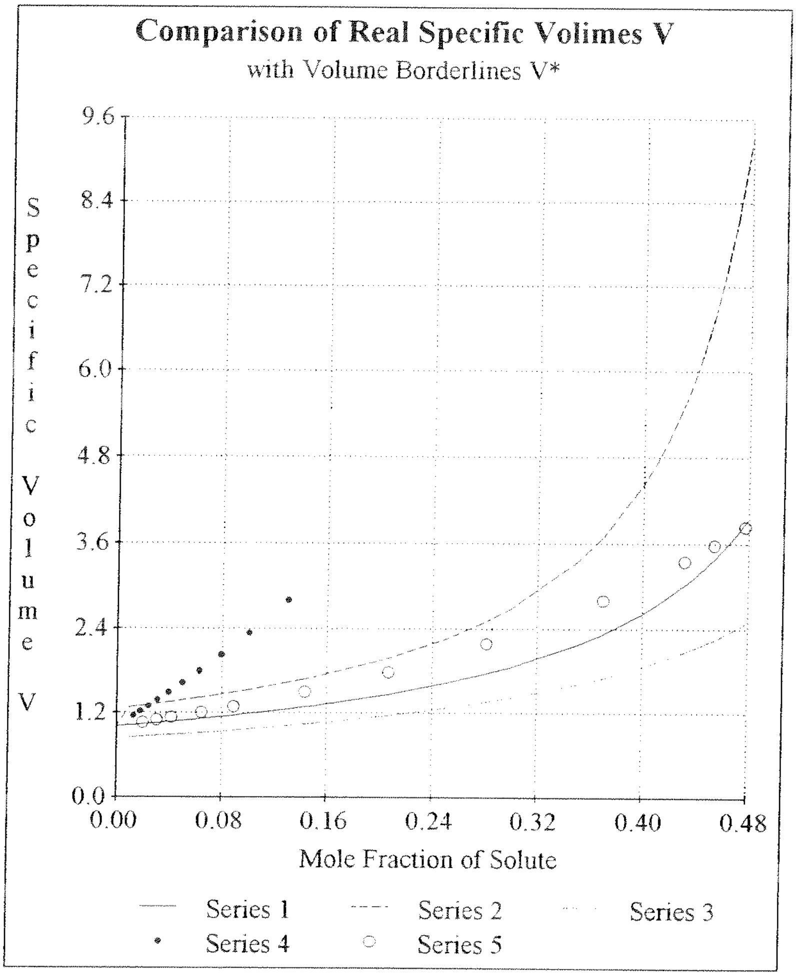

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