# AGAINST THE VALIDITY OF THE CLOSED SYSTEM MODEL FOR CALCULATING OSMOTIC PRESSURE

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**Abstract**

This paper criticizes the model and the new definition for osmotic pressure given by Parsafar *et al.* [J. Sci. I. R. Iran, Vol. 10, No. 4, 233 (1999)]. The model is a closed system containing 1 kg of solvent plus $m$ mole of solute at constant temperature and under pressure $P_0 + \pi$ where $P_0$ is the standard pressure and $\pi$ is the osmotic pressure of the corresponding $m$ molal solution. While the total number of moles, temperature and pressure of the system are specified, the volume of the system has also been specified. The volume of the solution under pressure $P_0 + \pi$ is claimed to be the same as the volume of 1 kg of pure solvent under the standard pressure $P_0$. The present work shows that the two volumes can not be the same and their difference is not negligible. The use of an equation of state to calculate osmotic pressure and activity by Parsafar *et al.* has also been questioned.

**Keywords:** Osmotic pressure; Activity; Equation of state; Sodium chloride

## 1. Introduction

Osmosis is the phenomenon of solvent flow through a semi permeable membrane that blocks the transport of solute through it. When two aqueous solutions (or other solvent solutions) are separated by a semi permeable membrane, water will flow from the side of low solute concentration, to the side of high solute concentration. The flow may be stopped by applying external pressure on the side of higher concentration. If there exist solute molecules only in one side of the system, then the pressure that stops the flow of the solvent is called the *osmotic pressure,* $\pi$. At equilibrium, there will be no net

flow of solvent across the membrane, so the chemical potential of the pure solvent at pressure $P$ must be equal [1] to the chemical potential of the pure solvent at pressure $P + \pi$ as shown in Figure 1. In fact, the excess pressure on the solution compensates the decrease in chemical potential of pure solvent due to presence of solute.

Parsafar *et al.* [2] have used a closed system model to drive an analytical equation for the osmotic pressure and the activity of some electrolyte and non-electrolyte solutions. The aim of this work is to evaluate their model and the new approach for calculating osmotic pressure and activity.
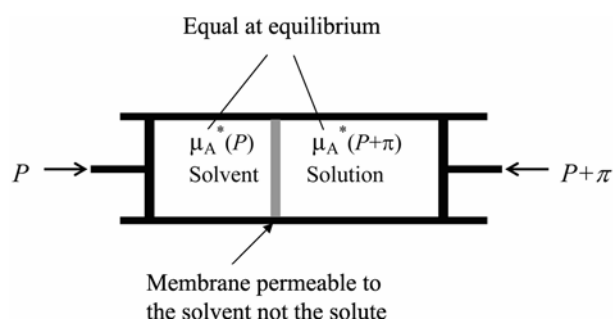
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**Figure 1**. The equilibrium is between pure solvent $A$ at a pressure $P$ on one side of the membrane and $A$ as a component of the solution on the other side of the membrane at pressure $P + \pi$.
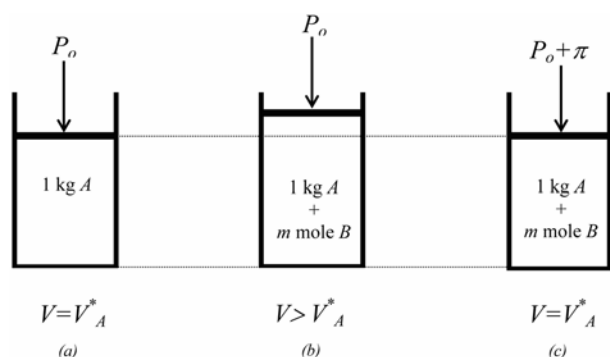


**Figure 2.** Definition of osmotic pressure in a closed system at constant $T$. (a) 1 kg of solvent under pressure $P_0$ and volume $V^*_A$ (b) Solving $m$ mole of solute with volume $V'$ under the previous pressure. (c) $m$ molal solution with volume $V=V^*_A$ under pressure $P_0+\pi$. (Taken from Ref. 2).

## 2. The Closed System Model [2]

The system consists of $n_A$ mole (1 kg) of solvent $A$ and $n_B$ mole of solute $B$ at constant temperature. It is assumed that the volume of solution, $V'$, (Fig. 2b) is larger than that of the pure solvent, $V^*_A$ (Fig. 2a). Then the osmotic pressure has been defined [2] so that it satisfies two constraints:

1. The osmotic pressure equals that pressure which equalizes the chemical potential of solvent, $\mu_A$, in solution with that of pure solvent, $\mu^*_A$, at the same temperature:

$$\mu_A (T, P_0+\pi, X_A) = \mu_A(T, P_0) \qquad (1)$$

2. Due to the fact that the increasing pressure causes the reduction of volume, Parsafar *et al.* defined the osmotic pressure such that it will equalize the volume of

the solution, $V$, at the temperature $T$ and pressure $P_0 + \pi$ with the volume of 1kg of pure solvent, $V^*_A$, at $P_0$ and $T$:

$$V (T, P_0 + \pi, X_A) = V^*_A (T, P_0) \qquad (2)$$

According to these two assumptions, the osmotic pressure can be viewed as the pressure needed to insert the solute molecules among solvent molecules without any change in volume (Fig. 2c) [2].

## 3. Evaluation of the Model

The first constraint is in fact the standard definition of osmotic pressure. At extra pressure on the solution, which is called osmotic pressure, the net flow of solvent is zero. This happens only when the chemical potential of the solvent on both sides of the membrane becomes the same (Fig. 1). Since one side is pure solvent, the chemical potential of $A$ in the solution side must be equal to that of pure solvent. However, the second constraint, which is claimed to be a new definition for osmotic pressure, can not be true. This will be discussed in three ways:

**3.a)** This constraint seriously fails when a solute with negative partial molar volume such as $MgSO_4$ is used. The limiting partial molar volume of $MgSO_4$ is $-1.4$ $cm^3\,mol^{-1}$. This means that the addition of small amount of $MgSO_4$ to large volume of water results in a decrease in volume [1]. In order to restore the volume, a negative pressure must be applied to the solution and the osmotic pressure, based on the second constraint, becomes negative. Negative osmotic pressure requires spontaneous migration of solvent from the side of solution to the side of solvent which is against the diffusion law. For the case of positive partial molar volume, there is also no guarantee that when the excess pressure $\pi$ is applied, the volume of the solution becomes the same as the volume of the pure solvent.

**3.b)** The state of a thermodynamic system is defined by specifying the values of its thermodynamic properties [3]. However, it is not necessary to specify all the properties to define the state. For a single-phase system containing specified fixed amounts of nonreacting substances, specification of two additional thermodynamic properties, such as pressure $P$ and temperature $T$, is generally sufficient to determine the thermodynamic state [3]. Once the thermodynamic state is specified, other thermodynamic properties such as the volume $V$, of the system is specified too. If the restriction of fixed composition is dropped, the state of the system will depend on its composition as well as on $P$ and $T$. We then have the *equation of state* [3]:

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$$V = f(n_A, n_B, T, P) \tag{3}$$

where $n_A$ and $n_B$ are the number of moles for solvent and solute respectively and $f$ is some function that depends on the nature of the system. Given values of $P$, $T$, $n_A$ and $n_B$ of this system, the value of $V$ of the system is determined. In the closed system model described by Parsafar *et al.*, the variables $n_A$ and $T$ are fixed. For a given $n_B$ mole of solute, in the presence of given $n_A$ mole of solvent, the osmotic pressure $\pi$ is also known, because osmotic pressure is a function of temperature and composition. Therefore, the total pressure of the system, $P = P_0 + \pi$, is specified too. On the other hand, the volume of the system has been fixed to $V^*_A$ (the volume of 1kg of pure solvent). Since all variables $V$, $n_A$, $n_B$, $T$ and $P$ in Equation 3 are fixed, no degrees of freedom left for the system. This violates the basic principles in physical chemistry. In principle, it is not possible to dictate the volume when other variables of the system are specified. In other words, once the values of $n_A$, $n_B$, $T$ and $P$ of the system are specified, the volume of the system is determined by the equation of state. Therefore, the volume of the system in Figure 2c has not to be necessarily the same as $V^*_A$ and Equation 2 is wrong.

**3.c)** When $\pi$ is equal to zero, the volume of the system under given pressure $P_0$ would be $V^*_A$. Consider $n_B$ mole of solute $B$ is added to the system and at the same time an excess pressure of $\pi$ is applied to the system. Suppose the excess pressure satisfies the first constraint, *i.e.*, compensates the chemical potential of the solvent which has been reduced by the addition of the solute. The question now is; how much would be the new volume of the system under the new conditions? One may think that, although we can not fix the volume of the system under the new circumstances, the system itself would choose its volume to be the same value (or nearly) as $V^*_A$. In other words, the excess pressure $\pi$ causes both the volume of the system and the chemical potential of the solvent to be constant as a solute is added to the system. The possibility of such behavior for a system will be investigated here.

Let, first evaluate the change in chemical potential of the solvent when $dn_B$ mole of $B$ is added to the system and the external pressure changes by $dP$. If the chemical potential of the solvent $\mu_A$ is regarded as a function of temperature, the total pressure $P$, and the mole fraction of the solvent $X_A$, *i.e.*,

$$\mu_A = f(T, P, X_A) \tag{4}$$

then a change in chemical potential at constant temperature can be expressed as:

$$d\mu_A = \left(\frac{\partial \mu_A}{\partial P}\right)_{T,X_A} dP + \left(\frac{\partial \mu_A}{\partial X_A}\right)_{T,P} dX_A \tag{5}$$

Since $(\partial G/\partial P)_T = V$, the derivative $(\partial \mu_A/\partial P)_{T,X}$ can be substituted by the partial molar volume of the solvent, $\overline{V}_A$. The second term in Equation 5 may be easily calculated using the fundamental relation; $\mu_A = \mu^*_A + RT \ln(a_A)$ where $a_A$ is the activity of the solvent and related to the mole fraction by $a_A = \gamma X_A$, ($\gamma$ is the activity coefficient). Substitution of the derivatives in Equation 5 gives:

$$d\mu_A = \overline{V}_A dP + RT \left[\frac{1}{X_A} + \left(\frac{\partial \ln \gamma_A}{\partial X_A}\right)_{T,P}\right] dX_A \tag{6}$$

The differential $dX_A$ may also be calculated from $X_A = n_A/(n_A+n_B)$. At constant $n_A$, $dX_A = -X_A \cdot dn_B/n$ where $n = n_A + n_B$. In order to satisfy the first constraint, the change in chemical potential of the solvent, $d\mu_A$, must be zero *i.e.*

$$\overline{V}_A dP = \frac{RT}{n}\left[1 + X_A\left(\frac{\partial \ln \gamma_A}{\partial X_A}\right)_{T,P}\right] dn_B \tag{7}$$

Here, $dP$ is the required pressure change to keep the chemical potential of the solvent constant as $dn_B$ mole of solute is dissolved into the system. The osmotic pressure $\pi$ may be obtained by integration of Equation 7.

$$\int_{P_o}^{P_o+\pi} \overline{V}_A dP = \int_o^{n_B} \frac{RT}{n}\left[1 + X_A\left(\frac{\partial \ln \gamma_A}{\partial X_A}\right)_{T,P}\right] dn_B \tag{8}$$

Let see how much the volume of the system changes by addition of $dn_B$ mole of $B$ and changing the pressure by $dP$. The volume of the system is a function of $n_A$, $n_B$, temperature and total pressure (Eq. 3):

$$dV = \left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A} dn_B + \left(\frac{\partial V}{\partial P}\right)_{T,n_A,n_B} dP \tag{9}$$

or

$$dV = \overline{V}_B dn_B - \kappa_T V dP \tag{10}$$

where $\overline{V}_B$ is the partial molar volume of the solute and $\kappa_T$ is the isothermal compressibility of the solution. The

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second constraint implies that the volume of the system remains unchanged, *i.e. dV* in Equation 10 must be zero. Thus

$$\kappa_T V dP = \overline{V}_B dn_B \tag{11}$$

where, *dP* is the required pressure change to keep the volume of the system constant when $dn_B$ mole of solute is added to the system. If the partial molar volume of *B* is negative, as in the case of $MgSO_4$ in dilute solutions, then the required pressure change would be negative. However, *dP* in Equation 7 would be positive since at infinitely dilute solution, $\ln\gamma = 0$ and $\overline{V}_A$ is positive. This clearly shows that a certain excess pressure can not always fix both the volume and the chemical potential of the solvent at the same time when solute is added to the solvent. The applied pressure fixes either the volume of the system or the chemical potential of the solvent.

When $n_B$ mole of solute is dissolved, the total excess pressure, $\phi$, to keep the volume of the system the same as that of pure solvent may be calculated by integrating Equation 11.

$$\int_{P_o}^{P_o + \phi} \kappa_T V dP = \int_o^{n_B} \overline{V}_B dn_B \tag{12}$$

For the closed system model claimed by Parsafar *et al.*, [2] $\phi = \pi$ and Equations 8 and 12 are satisfied simultaneously. The relations must be true for any value of $n_B$ and the corresponding value of $\pi$. This can only happen if Equations 7 and 11 are simultaneously satisfied. Dividing the two equations gives a general condition to satisfy both constraints.

$$\frac{n\overline{V}_A}{\kappa_T V} = \frac{RT}{\overline{V}_B}\left[1 + X_A\left(\frac{\partial \ln \gamma_A}{\partial X_A}\right)_{T,P}\right] \tag{13a}$$

or

$$\overline{V}_B = \frac{\kappa_T V R T}{n\overline{V}_A}\left[1 + \left(\frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)_{T,P}\right] \tag{13b}$$

Here, $\overline{V}_A$ and $\overline{V}_B$ are the partial molar volumes of the solvent and solute, respectively, and *V* and *n* are the total volume and the total number of moles of the system, respectively. It is possible to show that such a relation is only true for a mixture containing two perfect gases. In such a system, $\gamma$ is always unity, thus the

derivative in Equation 13 vanishes. The partial molar volumes are also equal to the molar volume $\overline{V}$ so that $V = n\,\overline{V}_A$, thus Equation 13 reduces to:

$$V_B = n_B \kappa_T RT \tag{14}$$

The isothermal compressibility, $\kappa_T$, of perfect gas is *1/P*. Substitution of $\kappa_T$ in Equation 14 gives the perfect gas equation; $PV_B = n_B RT$ which is valid for any component in a mixture of ideal gases. Therefore, a system composed of two ideal gases satisfies both constrains expressed in Equations 1 and 2. This means that the addition of a perfect gas *B* to another perfect gas *A* at constant temperature and volume will not change the chemical potential of the gas *A*. The reason is that for a perfect gas the chemical potential is [1]

$$\mu_A = \mu_A^\theta + RT \ln \frac{P_A}{P^\theta} \tag{15}$$

where, $\mu_A^\theta$ is the standard chemical potential at the standard pressure $P^\theta$ and $P_A$ is the partial pressure of the gas *A*. The addition of a second perfect gas to the system at constant volume and temperature will not affect the partial pressure, $P_A$, thus $\mu_A$ remains unchanged. The change in the total pressure of the system may be attributed to osmotic pressure if the system is placed in contact with the pure gas *A* at standard pressure $P^\theta$ via a membrane permeable to gas *A* but not to gas *B*.

It can be easily proved that Equation 13 will not be satisfied for liquid solutions. If the total volume of the system, *V* is approximated to $n \times \overline{V}_A$, Equation 3 reduces to

$$\overline{V}_B \approx \kappa_T RT \left[1 + \left(\frac{\partial \ln \gamma_A}{\partial \ln X_A}\right)_{T,P}\right] \tag{16}$$

The term $\kappa_T RT$ for gases is of the same order of partial molar volume. However, for condensed fluids $\kappa_T$ is much smaller than that of gasses. For example, $\kappa_T$ for water [1] is $4.96 \times 10^{-5}$ atm$^{-1}$ and the term $\kappa_T RT$ at 298 K becomes 1.21 mL/mol while the molar volume of NaCl as a solute is 27 mL/mol, *i.e.* 22.3 times larger than the value of $\kappa_T RT$. If Equation 16 is true then the term $(\partial \ln\gamma / \partial \ln X_A)$ should be as big as 21.3. This requires a very steep slope for the plot of $\gamma_A$ against $X_A$. Starting from pure solvent ($\gamma_A = 1$), the activity coefficient of the solvent must drop quickly to zero to give such a steep

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slope. This is obviously against the experimental observations. In order to examine this in more detail, the term $\kappa_T\, VRT/n\ \overline{V}_A$ in Equation 13b was calculated (using experimental data presented in Table 1) and compared with the experimental values for $\overline{V}_B$. Clearly the experimental and calculated values differ very much.

The corresponding values for $\partial\ln\gamma/\partial\ln X_A$ to justify Equation 13 are given in the last column of Table 1. The derivative varies with $X_A$ as:

$$\frac{\partial\ln\gamma}{\partial\ln X_A} = -336.44 + 782.67 X_A - 432.5 X_A^2 \qquad (17)$$

Integration of Equation 17 yields;

$$\ln\gamma = -336.44 X_A + 782.67 X_A - 216.25 X_A^2 - 566.42 \qquad (18)$$

The calculated (using Eq. 18) and the experimental [2] activities for water in sodium chloride solutions have been plotted in Figure 3. As it can be observed the experimental activity does not decrease as fast as the predicted values by Equation 13.

## 4. Calculation of the Osmotic Pressure Using an Equation of State

A question may be asked here. Why the experimental data fits very well ($R^2 > 0.99999$) in the model proposed by Parsafar *et al.* [2]? In Reference 2, osmotic pressures were calculated by using the Dense System Equation of State [4] (DSEOS) which is as follows:

$$P = A_0\rho^2 + A_1\rho^3 + A_2\rho^4 \qquad (19)$$

where $P$ and $\rho$ are pressure and molar density, respectively. The $A_i$ coefficients depend on the kind of solution, temperature, and solvent mole fraction. For the closed system the pressure and density have been defined by Parsafar *et al.* [2] as follows:

$$P = P_0 + \pi \qquad (20)$$

$$\rho = (n+m)/V \qquad (21)$$

where $n$ and $V$ are the number of moles and the volume of 1 kg of pure solvent and $m$ is molality. The pressure and the density for different solutions have been calculated (using Eqs. 20 and 21) and then $P/\rho^2$ has been fitted to a function of $A_0 + A_1\rho + A_2\rho^2$ to find the

coefficients $A_0$, $A_1$ and $A_2$. The $A_i$ coefficients and the correlation coefficient of the curves were reported. The method seems to be just fitting the data in a complicated way. The credibility of this method will be evaluated here.

**4.a)** The actual density of solution is:

$$\rho = \frac{n+m}{V+\Delta V} = \frac{n(1+m/n)}{V(1+\Delta V/V)} \qquad (22)$$

where $V$ is the volume of $n$ mole of pure solvent and $\Delta V$ is the change in the volume when $m$ mole of solute is added to the solvent. In the original paper [2] $\Delta V$ has been neglected. From the experimental data, given in Table 1, it can be concluded that for 1kg of pure water ($n = 55.508$ mol and $V = 1002.92$ cm$^3$) the ratio $m/n$ is smaller than the ratio of $\Delta V/V$ for all molalities. In principle, if $m$ is not neglected, $\Delta V$ must not be neglected either. Even at high osmotic pressures, $\Delta V/V$ is still smaller than $m/n$ because the compressibility factor of water is very small ($\kappa_T = 4.96\times10^{-5}$ atm$^{-1}$). Therefore, $\Delta V$ should not have been ignored.

**4.b)** The use of an equation of state seems not to be in its appropriate way here, since $n + m$ belongs to the solution but $V$ is taken from pure solvent. An equation of state is a relation among the thermodynamic properties of a system with a fixed composition. For example, Equation 19 gives the pressure of the system for a given density of a specific solution at constant temperature. For that specific composition, if the pressure is changed, the density will also be changed to satisfy Equation 19. The composition of the system must be fixed otherwise we face a new system with its own equation of state. Since the molality of the closed system model changes, the composition is not fixed and it is not possible to use an equation of state, with unique temperature dependent parameters, to describe the system.

**4.c)** In the closed system model, $n$ and $V$ are assumed to be constant, thus the molar density becomes;

$$\rho = \rho_0 + m/V \qquad (23)$$

where $\rho_0$ is the molar density of pure solvent. If the pressure and the density from Equations 20 and 23 are substituted in Equation 19, we will have:

$$P_0 + \pi = A_0(\rho_0 + m/V)^2$$
$$+ A_1(\rho_0 + m/V)^3 + A_2(\rho_0 + m/V)^4 \qquad (24)$$

Expanding this expression gives:

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**Table 1.** Experimental data for solutions of NaCl in 1 kg pure water at 298 K [5]. The last column represents values of $\partial\ln\gamma/\partial\ln X_A$ to satisfy Equation 13

| % NaCl | Molality | Total number of moles $N$ | Volume of solution (cm³) | Density of solution (g cm⁻³) | $\overline{V}_A$ (H₂O) (cm³mol⁻¹) | $\overline{V}_B$ (NaCl) (cm³ mol⁻¹) | $\dfrac{\kappa_T\, VRT}{n\, \overline{V}_A}$ | $\dfrac{\partial\ln\gamma}{\partial\ln X_A}$ from Eq. 13b |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.00000 | 55.5080 | 1002.92 | 0.99709 | 18.0680 | 17.8213 | 1.2120 | 13.7037 |
| 1 | 0.17284 | 55.6808 | 1005.99 | 1.00409 | 18.0675 | 18.1192 | 1.2120 | 13.9499 |
| 2 | 0.34920 | 55.8572 | 1009.19 | 1.01112 | 18.0662 | 18.4144 | 1.2121 | 14.1921 |
| 4 | 0.71295 | 56.2210 | 1015.96 | 1.02530 | 18.0606 | 18.9954 | 1.2127 | 14.6636 |
| 6 | 1.09218 | 56.6002 | 1023.28 | 1.03963 | 18.0514 | 19.5612 | 1.2139 | 15.1145 |
| 8 | 1.48789 | 56.9959 | 1031.15 | 1.05412 | 18.0388 | 20.1082 | 1.2156 | 15.5421 |
| 10 | 1.90119 | 57.4092 | 1039.60 | 1.06879 | 18.0228 | 20.6322 | 1.2178 | 15.9423 |
| 12 | 2.33328 | 57.8413 | 1048.64 | 1.08365 | 18.0039 | 21.1282 | 1.2205 | 16.3113 |
| 14 | 2.78547 | 58.2935 | 1058.31 | 1.09872 | 17.9826 | 21.5906 | 1.2236 | 16.6446 |
| 16 | 3.25919 | 58.7672 | 1068.64 | 1.11401 | 17.9597 | 22.0129 | 1.2272 | 16.9378 |
| 18 | 3.75602 | 59.2640 | 1079.65 | 1.12954 | 17.9361 | 22.3874 | 1.2310 | 17.1856 |
| 20 | 4.27769 | 59.7857 | 1091.39 | 1.14533 | 17.9131 | 22.7055 | 1.2352 | 17.3826 |
| 22 | 4.82611 | 60.3341 | 1103.88 | 1.16140 | 17.8926 | 22.9567 | 1.2394 | 17.5230 |
| 24 | 5.40339 | 60.9114 | 1117.20 | 1.17776 | 17.8768 | 23.1290 | 1.2435 | 17.5995 |
| 26 | 6.01188 | 61.5199 | 1131.38 | 1.19443 | 17.8687 | 23.2085 | 1.2474 | 17.6052 |

$$P_0 + \pi =$$

$$A_0\rho_0^2 + A_1\rho_0^3 + A_2\rho_0^4$$

$$+ A_1'm + A_2'm^2 + A_3'm^3 + A_4'm^4 \qquad (25)$$

where the $A_i'$ coefficients are the combination of $A_i$ coefficients, $\rho_0$ and $V$. The first three terms in the right hand side cancel out $P_0$ from left hand side since for $m = 0$ the osmotic pressure $\pi$ must be zero. Thus the osmotic pressure would be:

$$\pi = A_1'\, m\,(1+A_2''m+A_3''m^2+A_4''m^3) \qquad (26)$$

This is not something new. It is just a virial-like expansion of osmotic pressure. Almost every function fits very well to a forth order polynomial. Therefore, the results presented in Tables 1 and 2 and Figures 3 to 5 of Reference 2 do not prove the validity of the model. At $m = 0$ Equation 24 reduces to $P_0 = A_0\rho_0^2 + A_1\rho_0^3 + A_2\rho_0^4$. Mathematically, the $A_i$ coefficients must be the same for all solutes because $P_0$ and $\rho_0$ are constant. However, Inspection of Tables 1 and 2 of Reference 2 shows that the $A_i$ coefficients for sodium chloride and sucrose

solutions at the same temperature differ considerably. This puts a question to the validity of such fitting. Instead of such long and indirect way, it would be easier and better to fit the experimental data, $\pi$ directly into a polynomial function of $m$. If the data are fitted to a forth order polynomial, the quality of fit will be much better, ($R^2 > 0.9999999$) and one can more easily and more accurately calculate the osmotic pressure at any concentration.

**4.d)** Osmotic pressure is a colligative property, depending on the number of particles in the solution regardless of their nature. Although this is true for extremely dilute solutions it can be approximately applied to real solutions. Therefore, a solution of let say 0.05 molal NaCl should produce an osmotic pressure almost as much as that of a 0.1 molal sucrose solution. An appropriate approach should lead to a general equation that regardless of the nature of the solute, predicts the osmotic pressure as a function of the effective molality (molality times the Van't Hoff coefficient). Comparison of Tables 1 and 2 in Reference 2 shows that the proposed equations for calculating osmotic pressure are solute dependent.

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## 5. Calculation of the Activity

The solvent activity has also been calculated in Ref. 2, using the fundamental formula $RT \ln a_A = -V_A dp$. However, the molar volume of the solution, $1/\rho$, has been taken as the partial molar volume of the solvent (Eq. 14 of Ref. 2). The two quantities $\bar{V}_A$ and $1/\rho$, are equal only for pure solvent. Figure 4 compares the two quantities for aqueous solutions of NaCl using the data presented in Table 1. As illustrated, the partial molar volume of water decreases by adding the solute while the molar volume of the solution increases up.

It seems that the problem is in deriving Equation 10 of Reference 2 *i.e.* $dP = (2A_0\rho + 3A_1\rho^2 + 4A_2\rho^3)d\rho$ which is the differential of Equation 19 at constant $m$ and $T$. In driving this expression the $A_i$ coefficients were assumed to be constant. However, this is not true since the composition of the system would be changed. Obviously, the $A_i$ coefficients depend on the mole fraction of the solvent. Therefore, Equation 14 of Reference 2 is in fact an approximation ($\bar{V}_A \approx 1/\rho$) which can be used only for dilute solutions. In fact, what has been used to calculate the activities is neither $\bar{V}_A$ nor the real molar density ($1/\rho$), but it is the molar density defined by Equation 21. This quantity differs

very much from the actual molar density. The difference is demonstrated in Figure 4. Clearly among different molar volumes presented in Figure 4, the best approximation is to take $V_A^*$ as $\bar{V}_A$, but the authors preferred to use the worth case, *i.e.* $1/\rho$ (Eq. 21).

Again the fact that the experimental activities fit very well in Equation 17 of Reference 2 ($\ln a = B_0 + B_1\rho + B_2\rho^2 + B_3\rho^3$) does not prove the validity of the approach. If $\rho$ is substituted from Equation 23, then we have:

$\ln a =$

$$B_0 + B_1\rho_0 + B_2\rho_0^2$$
$$+ B_3\rho_0^3 + B_1'm + B_2'm^2 + B_3'm^3 \qquad (28)$$

where $B_i'$ coefficients are combination of $B_i$ coefficients, $\rho_0$ and $V$. The first four terms vanish since for pure solvent ($m = 0$) the activity is defined to be unity. The remaining terms are just a third order polynomial, which is a very appropriate way to express the activity of the solvent as a function of the molality. Therefore, it is not surprising that the experimental activities fit quite well in the proposed equation.
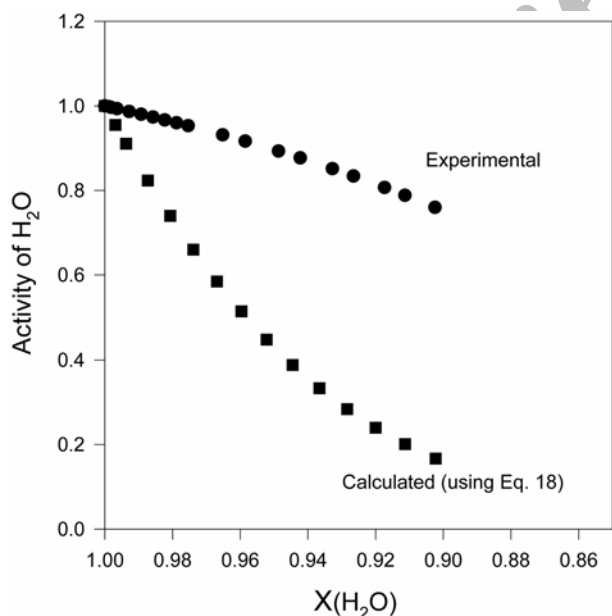


**Figure 3.** The experimental and the calculated (using Eq. 18) activities for water in sodium chloride solutions as a function of mole fraction of water.
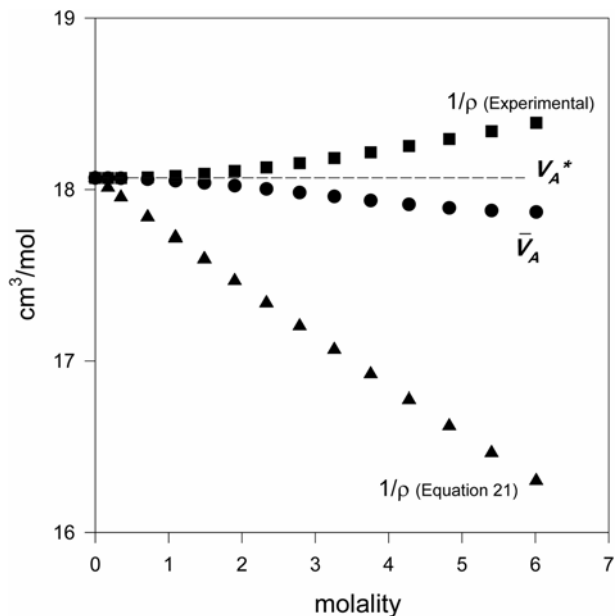


**Figure 4.** Different molar volumes for sodium chloride solutions.

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## Conclusion

Osmotic pressure is usually defined for a solution when it is in contact with its solvent via a semipermeable membrane. In fact the osmotic pressure is a property that can not be related to only one solution. Since the closed system is not placed in contact with the solvent the osmotic pressure has no meaning here and the definition proposed by Parsafar *et al.* [2] is obscure and imprecisely expressed form of the standard definition of osmotic pressure. In addition, the second constraint, expressed in Equation 2, is not true. Such an expression has not been observed in any common literature on physical chemistry describing the osmosis phenomenon. The defining formula for osmotic pressure is true for any volume of solvent or solution so that Equation 2 is irrelevant.

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