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Note on the Calculation of the Second Osmotic Virial Coefficient in Stable and Metastable Liquid States

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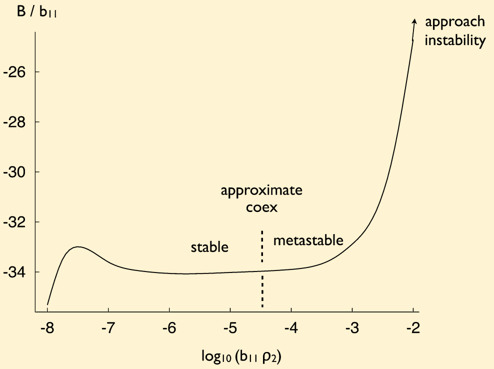
ABSTRACT: The second osmotic virial coefficient is calculated from analytical equations of state as illustrated with the van der Waals two-component equation. It is shown that when the fixed solvent chemical potential or pressure at which the virial coefficient is calculated is taken to be that of the pure solvent in coexistence with its vapor, as in a recent report, the liquid solution is in a metastable state. When, by contrast, that fixed chemical potential or pressure is that of the pure solvent in its one-phase liquid state, the solution, with increasing solute concentration, is initially in a stable state; then, on crossing the liquid–vapor equilibrium line, it becomes metastable and ultimately approaches a spinodal and incipient instability. Nevertheless, in practice, as seen in a numerical illustration for a hydrocarbon dissolved in water, there is scarcely any difference in the virial coefficient calculated with the fixed solvent chemical potential or pressure of the pure solvent at its vapor pressure (metastable states of the solution) or at 1 bar (initially stable states). It is also seen in that example that the virial coefficient may be reliably calculated only for solute concentrations that are neither too small nor too large; typically only for mole fractions roughly from 10^{-7} to $10^{-3.5}$.



This is an extension of work reported in a recent paper,[1] in which there was illustrated the calculation of the second osmotic virial coefficient from an analytical equation of state in which the pressure p is given as a function $p(\rho_1,\rho_2,T)$ of the number densities ρ_1 and ρ_2 of solvent and solute, respectively, and the temperature T. That virial coefficient B occurs in the coefficient of the second-order term in an expansion of the activity z_2 of the solute in powers of ρ_2 at fixed T and fixed activity z_1 of the solvent:[2]

$$z_2 = \frac{1}{\Sigma}\rho_2(1 + 2B\rho_2 + \cdots) \quad (T,\, z_1 \text{ fixed}) \tag{1}$$

The dimensionless Σ is a measure of the solubility of the solute, closely related to the Henry's-law constant and the Ostwald absorption coefficient.

The activities z_1 and z_2 are exponential measures of the respective chemical potentials μ_1 and μ_2 at the densities ρ_1 and ρ_2; thus,

$$z_i = \rho_i e^{[\mu_i - \mu_i(\text{i.g.})]/kT} \tag{2}$$

where k is Boltzmann's constant and μ_i(i.g.) is what would be the chemical potential of component i if it were at density ρ_i in an ideal gas at temperature T.

By known thermodynamics, the activities z_1 and z_2 may be obtained from $p(\rho_1,\rho_2,T)$ as functions of those same independent variables ρ_1, ρ_2, T. When z_1 is then inverted as a function of ρ_1 and the resulting $\rho_1(z_1,\rho_2,T)$ is inserted for ρ_1 in the expression for z_2, the result is z_2 as a function of z_1, ρ_2, T. This, by eq 1, may then be expanded in powers of ρ_2 at fixed z_1 and T, thus yielding the required osmotic virial coefficient B.

The commonly used equations of state $p = p(\rho_1,\rho_2,T)$ are analytic functions, not reconstructed by the common-tangent-plane construction, so the ρ_1 that results from the inversion of z_1 in the foregoing is generally multi-valued. One must choose the root ρ_1 that corresponds to the density of the solvent in the liquid solution. As this is usually much the largest root, it is easily identified. The inversion and the subsequent calculation of B must, in practice, be done numerically.

In Figure 1, four curves are shown schematically in the z_2, ρ_2 plane at a fixed temperature. Those marked Lcoex and Vcoex are the liquid and vapor branches of the coexistence curve at that temperature. Those marked fixed z_1 and fixed p are for the liquid solutions in which z_1 and p are fixed at their values in the pure solvent at liquid–vapor coexistence. The three liquid curves, Lcoex and those at fixed z_1 and fixed p, share the same initial slope $1/\Sigma$, which, for low solubility solutes, is much greater than 1, while the slope of the vapor curve Vcoex, if the vapor is a dilute gas, is close to 1. There are also vapor branches of the fixed z_1 and fixed p curves that share with Vcoex the same initial slope near 1.[1] These are not relevant here and are not shown in the figure.

The fixed z_1 and fixed p curves in Figure 1 lie within the region of liquid–vapor coexistence, so the homogeneous liquid

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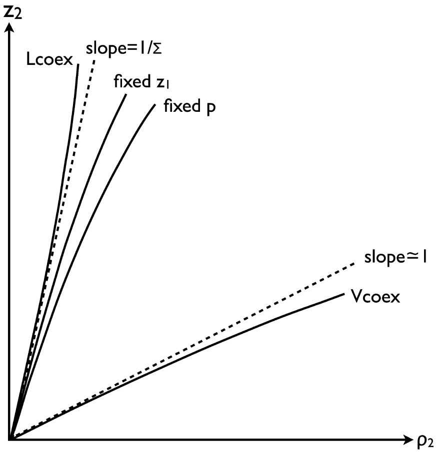


Figure 1. The ρ_2, z_2 plane at fixed temperature; schematic. The curves marked Lcoex and Vcoex are the liquid and vapor branches of the liquid–vapor coexistence curve. The curves marked fixed z_1 and fixed p are metastable liquid solution states in which z_1 and p are fixed at their values in the pure solvent ($\rho_2 = 0$) at liquid–vapor coexistence. The three liquid solution curves, Lcoex and those at fixed z_1 and fixed p, share a common initial slope $1/\Sigma$, which for low solubility solutes is much greater than 1, while the initial slope of the Vcoex curve, if the vapor is a dilute gas, is close to 1. Not shown in the figure are metastable vapor states at the same fixed z_1 and p as in the liquid states. These would share with Vcoex the same initial slope near 1.

solution in those thermodynamic states is metastable and would ultimately separate into stable, coexisting liquid and vapor. Nevertheless, the second osmotic virial coefficient in those metastable liquid solution states is readily calculated by the methods outlined above. That is what was done before, using, for illustration, the van der Waals two-component equation of state.[1]

In this note we do the analogous calculations for z_1 or p fixed at values such that, at high dilutions, the liquid solutions are in stable rather than metastable states, and compare the resulting values of the osmotic virial coefficient B with those found earlier. It will be seen that, in practical cases, there is little difference between them.

The reason for considering fixed-p representations of the thermodynamic states of the solution as well as those of fixed z_1 is because the coefficient B' in the expansion of z_2 in powers of ρ_2 at fixed T and p,

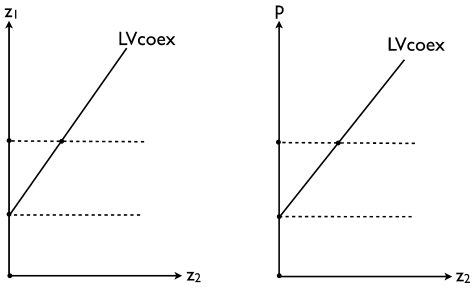
$$z_2 = \frac{1}{\Sigma}\rho_2(1 + 2B'\rho_2 + \cdots) \quad (T,\, p \text{ fixed}) \tag{3}$$

is closely related to B in eq 1, and B may be obtained from it:[1,3]

$$B = B' + \frac{1}{2}(v_2 - kT\chi) \tag{4}$$

where v_2 is the partial molecular volume of the solute at infinite dilution in the liquid solvent, and χ is the compressibility of the pure liquid solvent. Both v_2 and χ are readily calculable from an assumed $p(\rho_1,\rho_2,T)$. The calculation of B' proceeds as outlined above for B except that now one inverts $p(\rho_1,\rho_2,T)$ to obtain ρ_1 as a function of p, ρ_2, T instead of inverting $z_1(\rho_1,\rho_2,T)$. One then substitutes the resulting $\rho_1(p,\rho_2,T)$ for the ρ_1 in $z_2(\rho_1,\rho_2,T)$, which now becomes the function of p, ρ_2, T required for the expansion in eq 3.

In Figure 2a,b are shown, again schematically, the liquid–vapor equilibrium line, now in the z_2, z_1 and z_2, p planes at fixed temperature. The stable states in the region above the coexistence line, lying at higher z_1 and higher p for any given z_2, are liquid; those below are vapor. The dashed horizontal lines are states of fixed z_1 in Figure 2a and of fixed p in Figure 2b. As one follows the upper of the two dashed lines in each figure, starting from the pure solvent at $z_2 = 0$, the liquid is the stable phase and remains the stable phase until the coexistence line is crossed, when it becomes metastable. With further increase of z_2 (increasing concentration of solute), with the analytical equations of state, this metastable liquid ultimately reaches its spinodal and becomes unstable. On the lower of the two dashed lines in each figure, starting from the base of the coexistence line at $z_2 = 0$, the liquid phase is immediately metastable and ultimately reaches its spinodal and becomes unstable. These horizontal dashed lines that start at the base of the coexistence line in Figure 2 (a) and (b) are, in a different representation, the constant-z_1 and constant-p curves in Figure 1. As remarked above, it is in these metastable states that B and B' were calculated in the earlier work.[1]



(a) (b)

Figure 2. The liquid–vapor coexistence curve LVcoex (shown here schematically as a line) in the z_2, z_1 plane in (a) and in the z_2, p plane in (b), both at fixed temperature. Stable liquid states are those above the respective coexistence curves, and stable vapor states are those below. On the upper horizontal dashed line, at fixed z_1 in (a) and at fixed p in (b), are liquid states that start in the pure liquid solvent at $z_2 = 0$, are stable liquid solutions up to the coexistence curve, and are then metastable liquid solutions beyond. The liquid states on the lower horizontal dashed line in each figure are those of mixtures that are immediately metastable, starting at infinite dilution ($z_2 = 0$).

Osmotic virial coefficients of low-solubility gases in water are conventionally calculated at 1 bar,[4,5] which is higher than the vapor pressure of water at any temperature below 373 K. Such calculations are then for states represented by the upper of the two dashed horizontal lines in Figure 2a,b. These states may also be represented in the constant-temperature ρ_2, z_2 plane of Figure 1, now in Figure 3, again schematically. The common initial slope $1/\Sigma$ of the fixed z_1 and fixed p curves in Figure 3 is no longer exactly the same as that of the Lcoex curve. It is shown here as greater; in practical cases it is only very slightly greater.

If one contemplates a fixed-p expansion as in eq 3 (cf. Figure 2b), one specifies the fixed value of p (e.g., 1 bar) and the temperature T, and then calculates the density ρ_1 of the pure solvent ($\rho_2 = 0$) at that p and T from the assumed equation of state $p = p(\rho_1,0,T)$. In the meantime, z_2 had been obtained as a function of ρ_1, ρ_2, T, so with the solvent ρ_1 now known at $\rho_2 = 0$, one may then identify the infinite dilution limit of z_2/ρ_2, which is $1/\Sigma$. Then B' is obtained (usually numerically) from eq 3. Alternatively, if one contemplates a fixed z_1 expansion as in eq 1 (cf. Figure 2a), but starting at infinite dilution at a specified pressure (e.g., 1 bar), one calculates $1/\Sigma$ as above and in addition, from the known z_1 as a function of ρ_1, ρ_2, T, obtains

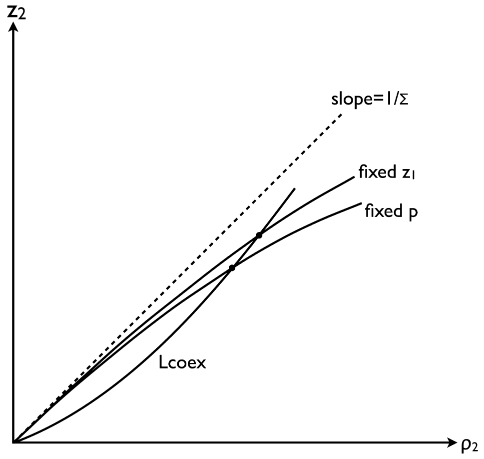


Figure 3. As in Figure 1, but now with the fixed z_1 and p both greater than they are at liquid−vapor coexistence at the fixed temperature of the figure; the common initial slope $1/\Sigma$ of those two curves is greater than that of the Lcoex curve. The fixed z_1 and fixed p states are those of stable liquid solutions for small z_2 and ρ_2, up to the intersections of their curves with the Lcoex curve, and of metastable liquid solutions beyond.

the infinite dilution limit of z_1, now to be the fixed z_1 in question. One then obtains B (usually numerically) from eq 1.

To compare such values of B and B' with those calculated earlier in metastable states, we shall again use for illustration the van der Waals two-component equation of state with the same values of its parameters as before. This is a six-parameter equation of state of the same form as its one-component version, $p = \rho kT/(1 - b\rho) - a\rho^2$, but now with[6]

$$\rho = \rho_1 + \rho_2 \tag{5}$$

$$a = (\rho_1^2 a_{11} + 2\rho_1\rho_2 a_{12} + \rho_2^2 a_{22})/(\rho_1 + \rho_2)^2 \tag{6}$$

$$b = (\rho_1^2 b_{11} + 2\rho_1\rho_2 b_{12} + \rho_2^2 b_{22})/(\rho_1 + \rho_2)^2 \tag{7}$$

For the six parameters a_{ij}, b_{ij}, we take the same values to represent solutions of propane in water at 25 °C as taken before for illustration;[1] thus,

$$a_{11} = 1.5038 \times 10^{-35}\,\text{erg cm}^3, \quad b_{11} = 2.7538 \times 10^{-23}\ \text{cm}^3 \tag{8}$$

$$a_{12}/a_{11} = 1.6093, \qquad b_{12}/b_{11} = 2.2887 \tag{9}$$

$$a_{22}/a_{11} = 2.2015, \qquad b_{22}/b_{11} = 4.096. \tag{10}$$

These values of the parameters are to be treated as though they are of infinite precision. One then specifies small values of ρ_2, calculates (numerically) the associated z_2 by the procedure outlined earlier, and then, with $p = 1$ bar at infinite dilution and with the known Σ, obtains B or B' as $(z_2\Sigma/\rho_2 - 1)/(2\rho_2)$ (cf. eqs 1 and 3), as outlined above. There is a range of values of ρ_2, neither too large nor too small, over which the resulting B or B' is independent of ρ_2. Outside that range, the calculated B and B' are spurious. The reason the chosen ρ_2 must not be too small is that, within the precision of the calculation (e.g., carrying 10 digits), if ρ_2 is too small, one cannot reliably distinguish $z_2\Sigma/\rho_2$ from 1. The reason ρ_2 must not be chosen too large is, first, higher order terms in the expansions (1) and (3) may affect the results, and, second, one may have entered too deeply into the metastable region and be approaching the spinodal.

This is illustrated for the calculation of B in Figure 4, where B/b_{11} is plotted against $\log_{10}(b_{11}\rho_2)$. The plateau, where the calculated B is independent of ρ_2, extends roughly from $b_{11}\rho_2 = 10^{-7}$ to $10^{-3.5}$. The coexistence line is crossed at around $b_{11}\rho_2 = 10^{-4.5}$; at smaller ρ_2, the liquid solution is in stable states, and at larger ρ_2 it is metastable. In this calculation, 10 digits were carried. (With 20 digits, say, the plateau would have extended to smaller ρ_2 but not to larger.) Outside the range $10^{-7} < b_{11}\rho_2 < 10^{-3.5}$, the calculated values are increasingly unreliable, and by 10^{-8} at the low end and 10^{-2} at the high end they have become essentially meaningless.

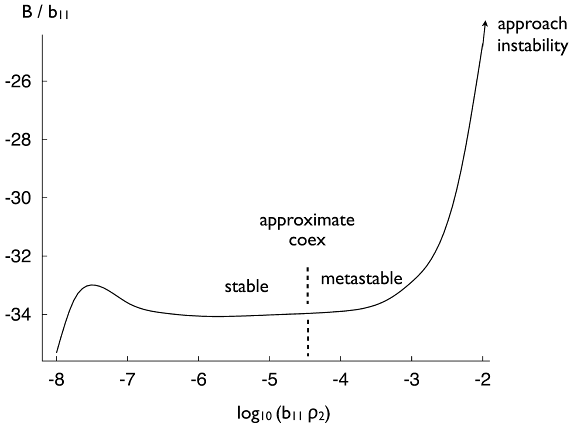


Figure 4. Calculated B/b_{11} as a function of $\log_{10}(b_{11}\rho_2)$ for propane in water at 25 °C. The liquid−vapor coexistence point lies somewhere between $b_{11}\rho_2 = 10^{-5}$ and 10^{-4}. At lower ρ_2 the liquid phase is stable, at higher ρ_2 it is metastable. The spinodal lies somewhere between $b_{11}\rho_2 = 10^{-2}$ and 10^{-1}.

The $b_{11}\rho_2$ in Figure 4 may be thought of as roughly the mole fraction x_2 of the solute. That is because the solutions are very dilute, so $x_2 = \rho_2/(\rho_1 + \rho_2) \simeq \rho_2/\rho_1 = b_{11}\rho_2/b_{11}\rho_1$; while the solvent is a dense liquid, so $b_{11}\rho_1$ is not far from 1.

The plateau value of B/b_{11} in Figure 4 is −34 (so, from eq 8, B for propane in water at 25 °C is estimated to be −570 cm^3/mol). To these two significant figures, it is the same as found before,[1] when the fixed z_1 was that of water coexisting with its vapor at 25 °C so that the solution with any $\rho_2 > 0$ was metastable. The reason it has made so little difference is that the dense liquid solvent is so nearly incompressible that it hardly matters whether the fixed z_1 is that of the pure solvent at 1 bar or at its much lower vapor pressure.

Likewise, one calculates $B'/b_{11} = -36$, again the same to two significant figures as in the earlier calculation.[1] It may be verified from the equation of state that, to this precision, the resulting $B - B' = 2b_{11}$ satisfies the identity in eq 4.

We have thus confirmed that in practical cases, for the calculation of the second osmotic virial coefficient, it matters little whether it is calculated in fully stable or in metastable states of the solution.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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