

# The Stability of Bubbles Formed from Supersaturated Solutions, and Homogeneous Nucleation of Gas Bubbles from Solution, Both Revisited

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The solution of the problem of the relative stability of all possible equilibrium bubble states that can form from a closed, finite, supersaturated gas–liquid solution, maintained at a fixed temperature and a fixed external pressure is given. The supersaturated solution may contain any number of dissolved volatile solutes. The full solution to this problem has remained elusive for decades, because of the complication of pressure inequalities between the bubbles and the constant external (or reservoir) pressure. The method of solution is one that had been used previously to solve the related problem of the stability of a liquid droplet in a supersaturated vapor, where the same complication occurred. The derived equations were found to reduce correctly when simplified; they were consistent with experiment, and the system Gibbs free energy appropriately obeyed the Law of Corresponding States. The expressions were used in the context of transition state theory to provide semiempirical predictions of the rate of homogeneous bubble formation from a supersaturated solution, and the “critical pressure for homogeneous nucleation ( $P_{\text{crit}}$ )”. The nucleation Gibbs free energy expression derived here had a lower barrier height and resulted in a reduction of  $P_{\text{crit}}$  values, relative to what was obtained from the basis of a pre-existing approximate expression taken from the literature. Applications to chemical engineering and human decompression modeling are briefly described.

## 1. Introduction

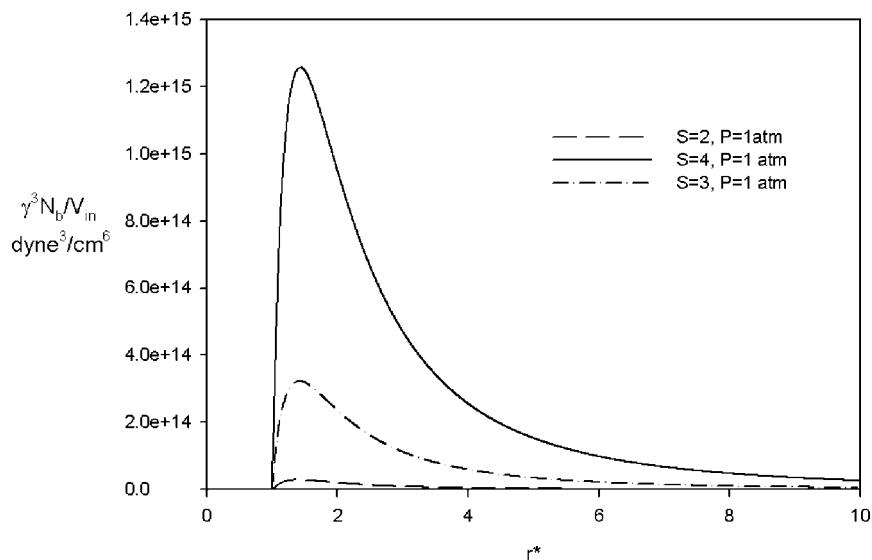
We seek a thermodynamic function that will provide an exact measure of relative stability of all possible equilibrium bubble states that can form when a finite supersaturated gas–liquid solution (e.g., water supersaturated with dissolved nitrogen) releases its excess solute as bubbles. This is needed both in its own right and in order to derive an expression for the relative stability per bubble. The latter is required for the calculation of the rate of bubble formation. Both the system relative stability<sup>1</sup> and the rate of bubble formation<sup>2</sup> arise in work related to human decompression from supersaturated dissolved gas states and in the related problem of prevention of decompression sickness (“the bends”).<sup>1–4</sup> The need for an accurate barrier height to gas bubble nucleation in liquids also arises in chemical engineering. The interest here is that the barrier height is needed to predict the degree of superheating required in order for a liquid (neat or a solution) to boil.<sup>5,6</sup>

Each equilibrium bubble state is characterized by a specific bubble radius and bubble number density. These are “equilibrium” states in the sense that the temperature is uniform throughout, the bubbles are mechanically stable (because they each satisfy the Laplace equation (eq 4, below)), and there is no net flux of matter between the bubbles and the surrounding solution. The zero-flux condition is ensured by equating the chemical potential of each component in the bubble to its corresponding value in the surrounding solution (eq 3, below).

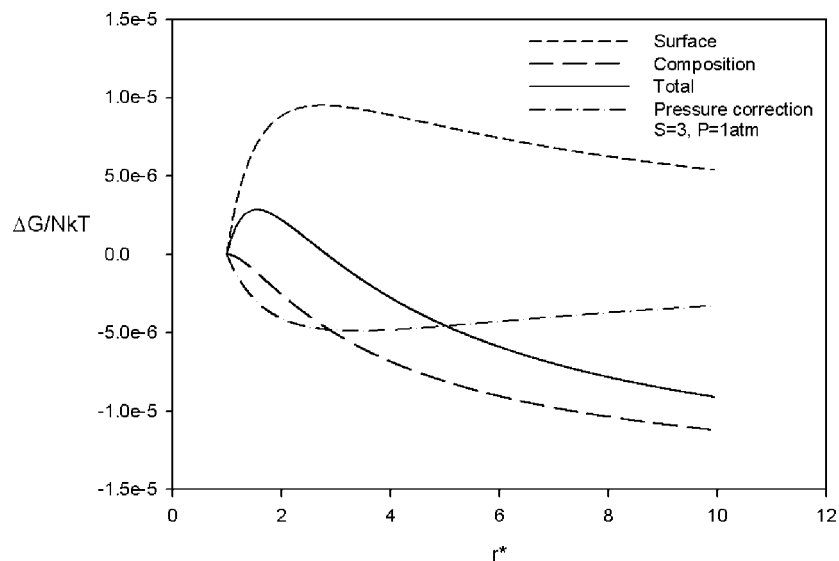
Although the problem has been around since Gibbs’ time,<sup>7</sup> because of a complication it has never been fully solved. The complication is that the pressure is not uniform throughout the composite system of bubbles plus solution. Specifically, while the pressure in the solution will equal that of the external “reservoir”, the pressure inside the bubbles will exceed the pressure of the reservoir by  $2\gamma/r$ , where  $r$  and  $\gamma$  are the

equilibrium bubble radius and the surface tension of the solution, respectively. As conventionally formulated, the Gibbs free energy function provides an exact measure of relative stability for a finite system, only if the system is closed, and if all of its component subsystems are at the same temperature and pressure as the corresponding external reservoir temperature and pressure.<sup>8</sup> Hirth et al.,<sup>9</sup> and later Ward et al.,<sup>10</sup> pointed out this fundamental impediment to using the conventionally formulated Gibbs free energy function for this problem. Further, Ward et al. asserted (correctly from the basis of conventionally formulated thermodynamics) that because of the pressure inequality, no existing thermodynamic function correctly provided the desired measure of relative stability for finite systems.<sup>10</sup> Interestingly, the solution to the problem, at least in principle, has been known for decades by some scientists. For example, Frenkel used it in his book some 70 years ago, where he applied it both to a 1-component vapor bubble surrounded by a liquid and to the converse problem of a 1-component liquid droplet surrounded by a supersaturated vapor.<sup>11</sup> The solution was first given in a detailed systematic way by Abraham some 35 years ago, who used it in his work on the thermodynamics and kinetics of nucleation of liquid droplets formed from supersaturated vapor.<sup>12</sup>

The solution consists of two parts. First, one uses the postulatory approach of Callen<sup>13</sup> to reformulate thermodynamics in terms of state functions which are to be taken as fundamental constructs rather than processes. This has the practical advantage of obviating the need to construct a reversible path between the initial and final states along which the pressure of all parts of the system and the reservoir are equal (an impossibility here). The free energies of the final and initial states alone are used in this reformulation. Second, one uses Abraham’s extensions of Callen’s postulates (specifically Abraham’s Postulate 3’) to correct the Gibbs free energy in the composite system to what it would be if the bubbles were at the reservoir pressure, rather



**Figure 1.** Variation of the scaled bubble density with the reduced bubble radius  $r^*(= r/r_{crit})$ , from eqs 8, 10, and 12.  $r_{crit} = 0.02007 \mu$ ,  $0.01006 \mu$ , and  $0.00671 \mu$  for the supersaturation ratios  $S = 2, 3$  and  $4$ , respectively, and reservoir pressure  $P = 1$  atm.  $S = P_{in}/P$ , where  $P_{in}$  is the total vapor pressure of the initial supersaturated solution across a planar interface.  $T = 298.15$  K,  $K_2 = 85\,381$  atm,  $VP_1 = 0.031258$  atm, here and in Figures 2–5, where  $T$ ,  $K_2$ , and  $VP_1$  are the absolute temperature, the Henry’s law constant of  $N_2$  in water, and the vapor pressure of pure water, each at 1 atm and 298.15 K (see text).



**Figure 2.** Variation of the reduced relative system Gibbs free energy and its components with  $r^*$ , from eqs 6, 8, 10, and 12.  $r_{crit} = 0.01006 \mu$ , here and in Figures 3 and 4. The asymptotic planar limit for the curves labeled “Total” and “Composition” is  $-1.537 \times 10^{-5}$ . The curves labeled “Surface” and “Pressure correction” converge to zero in this limit.

than at their actual pressure.<sup>12</sup> The key point is that when this is done, the Gibbs free energy of the composite system becomes additive over its component subsystems (bubbles, surface, and solution), and the relative Gibbs free energy is simply the difference between its values in the composite and initial states, both of which are now properly calculable.

## 2. Thermodynamics of Homogeneous Bubble Formation from Solution

The solutions to be considered (both in the initial and composite states) are of macroscopic dimensions, and the number of molecules in each bubble will turn out to be in the range of  $\approx 5 \times 10^3$  to  $\approx 10^{14}$ . Consequently, macroscopic thermodynamics should be applicable as a good approximation, with the possible exception of the smallest bubbles in the range. Approximating  $\gamma(r)$  by  $\gamma(\infty)$  for the smallest bubbles is potentially problematic, therefore we examine this approximation below.

For any multicomponent system, the smallest possible bubble radius is given by the critical radius  $r_{crit}$  for that system (eq 12, below). The smallest bubbles to be considered here will have a radius of  $\approx 0.005 \mu$  (see Captions for Figures). Nothing is known about the  $r$ -dependence of  $\gamma(r)$  at small  $r$  for the specific application to be studied ( $N_2$  in  $H_2O$ ). However, some sense of the quality of the approximation  $\gamma(r) \cong \gamma(\infty)$  can be had from earlier studies on simpler systems, the most relevant of which is probably one by Rao and Berne.<sup>14</sup> These authors used Monte Carlo simulations on an argon-like vapor–liquid interface to determine the relative position of the surface of tension and the Gibbs equimolar dividing surface.<sup>12,14</sup> From this they derived the approximation:  $\gamma(r)/\gamma(\infty) \cong 1 - (2\delta_\infty/r)$  and determined that  $\delta_\infty = (0.96 \pm 0.12)\sigma$ , where  $\sigma (= 3 \times 10^{-4} \mu)$  is a measure of the Argon-like particle’s diameter. Thus, for an argon-like droplet,  $\gamma(0.005 \mu)/\gamma(\infty) \cong 0.90$ . Consequently, as far as can be determined from the limited information that exists, the maximum expected error entailed in approximating  $\gamma(r)$  by  $\gamma(\infty)$

will be on the order of 10%. An error of this magnitude should not upset our conclusions. Of course, the problem would have been more severe if it were not for the critical point that acts as a lower bound on the smallest possible bubble that can form.

Using Abraham's Postulate 3',<sup>12</sup> the free energy of the composite system, relative to the supersaturated solution from which it is formed, is given by eq 1. Because the temperature is constant, it is omitted in order to simplify the notation.

$$\Delta G(r, P) = G_{\text{fin}}(r, P) - G_{\text{in}}(\{x(\text{in})\}, P) \quad (1)$$

Here:

$$\begin{aligned} G_{\text{in}}(\{x(\text{in})\}, P) &= \sum_j N_j \mu_{j,l}(x_j(\text{in}), P) \\ G_{\text{fin}}(r, P) &= G_{\text{surf}}(r, P) + G_l(r, P) + G_g(r, P) \\ G_{\text{surf}}(r, P) &= 4\pi r^2 \gamma N_b(r, P) \\ G_l(r, P) &= \sum_j N_{j,l}(r, P) \mu_{j,l}(x_{j,l}(r, P), P) \\ G_g(r, P) &= \sum_j N_{j,g}(r, P) \mu_{j,g}(P_j(r, P)) \end{aligned}$$

In the above,  $G_{\text{in}}(\{x(\text{in})\}, P)$  and  $G_{\text{fin}}(r, P)$  are the Gibbs free energies in the initial and final states, respectively,  $\gamma$  is the surface tension of the solvent,<sup>15,16</sup>  $r$  is the equilibrium bubble radius,  $P$  is the reservoir pressure, and  $N_j$  is the total (or initial) number of molecules of type  $j$  in the system. Also,  $G_{\text{surf}}(r, P)$ ,  $G_l(r, P)$ , and  $G_g(r, P)$  are the surface, liquid, and gas phase free energies of the composite system, respectively; and  $N_{j,l}(r, P)$ ,  $N_{j,g}(r, P)$ , and  $N_b(r, P)$  are the total number of molecules of type  $j$  in the liquid and gas phases of the composite system and the total number of bubbles, respectively, all at  $(r, P)$ .  $\mu_{j,l}(\cdot)$  and  $\mu_{j,g}(\cdot)$  are the chemical potentials of  $j$  in the liquid and gas phases, respectively;  $x_j(\text{in})$  and  $x_{j,l}(r, P)$  are the mole fractions of  $j$  in the initial supersaturated solution and the composite system solution, respectively; and  $P_j(r, P)$  is the partial pressure of  $j$  in the gas phase of the composite system, corrected or scaled to the (total) pressure  $P$ . Combining the components of eq 1 gives eq 2.

$$\begin{aligned} \Delta G(r, P) &= 4\pi r^2 \gamma N_b(r, P) + \sum_j \{N_{j,g}(r, P) \Delta \varphi_j(r, P) + \\ &\quad N_{j,l}(r, P) kT \ln[x_{j,l}(r, P)/x_j(\text{in})]\} \\ \Delta \varphi_j(r, P) &= \Delta \mu_j(r, P) + kT \ln[x_{j,l}(r, P)/x_j(\text{in})] \\ \Delta \mu_j(r, P) &= \mu_{j,g}(P_j(r, P)) - \mu_{j,l}(x_{j,l}(r, P), P) \end{aligned} \quad (2)$$

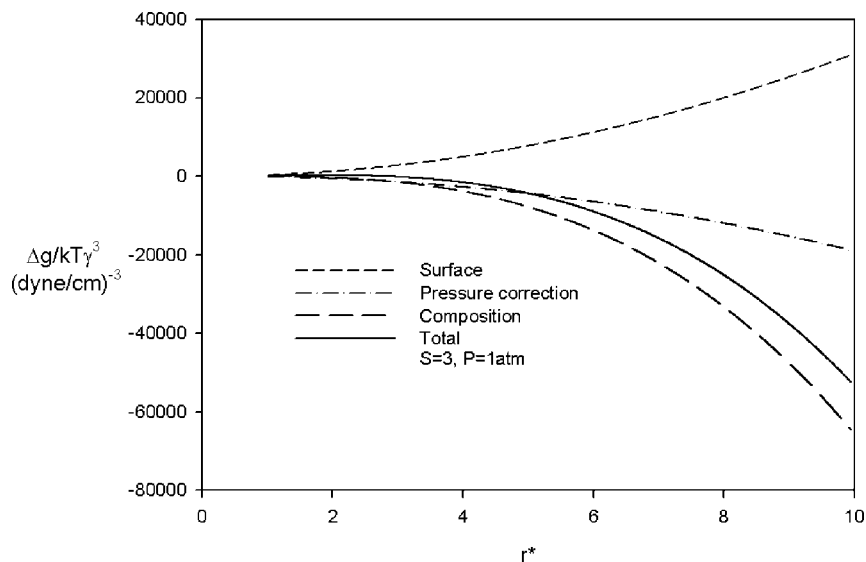
In the above,  $k$  and  $T$  are Boltzmann's constant and absolute temperature, respectively, and  $\Delta \mu_j(r, P)$  represents the relative chemical potential of  $j$  in the composite system (gas relative to liquid) when both phases are at the reservoir pressure  $P$  and at their respective equilibrium compositions.  $\Delta \mu_j(r, P)$  is readily determined from the equality of chemical potentials of  $j$ , when  $j$  is at its equilibrium composition in both phases and at total pressures  $P$  and  $P_b$  in the solution and gas phases, respectively.  $P_b$  represents the total equilibrium gas phase pressure inside the bubble. From the condition of equality of chemical potentials:

$$\begin{aligned} \mu_{j,l}(x_{j,l}(r, P), P) &= \mu_{j,g}(P_j(r, P_b)) \\ &= \mu_{j,g}(P_j(r, P)) + kT \ln(P_b/P) \\ \Delta \mu_j(r, P) &= -kT \ln(P_b/P) = -kT \ln[1 + (2\gamma/rP)] \end{aligned} \quad (3)$$

In the top two lines of eq 3 the chemical potential of  $j$  in an ideal gas mixture at a total gas phase pressure  $P_b$ , is related to the value it would have if the total gas phase pressure were  $P$ , at the same gas phase composition and temperature. Each partial pressure  $P_j$  is reduced by a factor  $P/P_b$ , and consequently each  $\mu_{j,g}$  is reduced by  $kT \ln(P_b/P)$ . In the second line, the Laplace equation (eq 4) was used to relate  $P$  to  $P_b$ .<sup>17</sup>

$$P_b = P + 2\gamma/r \quad (4)$$

Substituting the above expressions for  $\Delta \varphi_j(r, P)$  and  $\Delta \mu_j(r, P)$  into the summation in eq 2 gives eq 5.



**Figure 3.** Variation of the scaled relative Gibbs free energy per bubble, and its components, with  $r^*$ , from eqs 7, 8, 10, and 12, for intermediate  $r^*$  values, and the  $S$  and  $P$  values in Figure 2.

$$\Delta G(r, P) = 4\pi r^2 \gamma N_b(r, P) + kT[-N_g(r, P) \ln(P_b/P) + \sum_j N_j \ln[(x_{j,i}(r, P)/x_j(\text{in}))]] \quad (5)$$

Using the ideal gas law in the form:  $N_g(r, P)kT = (4/3)\pi r^3 N_b(r, P)P$  in eq 5 gives eqs 6 and 7 as the working forms of eq 1.

$$\Delta G(r, P)/NkT = N_b(r, P)[4\pi r^2 \gamma - (4/3)\pi r^3 P \ln(P_b/P)]/NkT + \sum_j x_j(\text{in}) \ln[x_{j,i}(r, P)/x_j(\text{in})] \quad (6)$$

$$\Delta g(r, P)/kT = [4\pi r^2 \gamma - (4/3)\pi r^3 P \ln(P_b/P)]/kT + (N/N_b(r, P)) \sum_j x_j(\text{in}) \ln[x_{j,i}(r, P)/x_j(\text{in})] \quad (7)$$

$$\Delta g(r, P) \equiv \Delta G(r, P)/N_b(r, P)$$

In the above,  $\Delta G(r, P)$  is the relative Gibbs free energy for the entire compound system of  $N$  molecules and  $N_b(r, P)$  bubbles, for bubbles of equilibrium radius  $r$  and for reservoir pressure  $P$ . It is a measure of relative stability of the compound system at any equilibrium radius  $r$ , and corresponding equilibrium bubble density  $N_b(r, P)/V_{\text{in}}$ .  $\Delta g(r, P)$  is the relative Gibbs free energy of the compound system per bubble. Its maximum with respect to  $r$  provides the barrier height needed to predict rates of bubble formation.

These expressions contain three contributions: a positive surface free energy term (the first term), a negative term that corrects the gas phase free energy so that it corresponds to the reservoir pressure (the second term), and the last term, also negative, which is in the form of the mixing free energy of an ideal solution.<sup>18</sup> It arises from dilution of the supersaturated solution upon bubble formation. This term provides the driving force for the off-gassing process. It makes the only nonzero contribution to  $\Delta G(r, P)$  in the limit  $r \rightarrow \infty$ . All three terms contribute significantly to  $\Delta G(r, P)$  and  $\Delta g(r, P)$  at small values of  $r$  (Figures 2–4). It remains to provide working expressions for the solution mole fractions and the number of bubbles, at each equilibrium bubble radius. This is readily done from the conditions of mass balance and equilibrium for each component, and the Laplace equation. For more than two components these equations have to be solved simultaneously and numerically. We will restrict our applications to two-component systems (a solvent and a single volatile solute) for which the mole fractions are obtained separately from the Laplace equation, and the results can be expressed in closed form.

As indicated, for two components the equilibrium compositions come directly from the Laplace equation, as shown below.

$$\begin{aligned} P_1(r, P) + P_2(r, P) &= P + 2\gamma/r \\ VP_1(P)[1 - x_{2,i}(r, P)] + K_2(P)x_{2,i}(r, P) &= P + 2\gamma/r \\ x_{2,i}(r, P) &= [P - VP_1 + 2\gamma/r]/[K_2(P) - VP_1(P)] \\ x_{1,i}(r, P) &= 1 - x_{2,i}(r, P) \end{aligned} \quad (8)$$

In the above equations,  $VP_1(P)$  and  $K_2(P)$  are the vapor pressure of the pure solvent and the Henry's law constant of the solute, respectively, each at pressure of the liquid phase (which equals the reservoir pressure  $P$ ).

To get  $N_b(r, P)$ , one combines the expressions for mass balance for the two components with the ideal gas law for each, as shown in eq 9.

$$\begin{aligned} N_{j,i}(r, P) &= x_{j,i}(r, P)N_i(r, P) \\ &= N_j - [P_j(r, P)(4/3)\pi r^3 N_b(r, P)/kT] \end{aligned} \quad (9)$$

Eliminating  $N_i(r, P)$  between eqs 9 written for  $j = 1, 2$  gives eq 10,

$$N_b(r, P) = kT([N_2/x_{2,i}(r, P)] - [N_1/x_{1,i}(r, P)]) / ((4/3)\pi r^3 [K_2(P) - VP_1(P)]) \quad (10)$$

for the total number of bubbles in the composite system at equilibrium. The expressions for  $x_{j,i}(r, P)$  given in eq 8 are used in eq 10.

The working equations were checked in three independent ways. (1) Equations 3, 6, and 7 each reduce correctly when simplified. Specifically: (1a) Frenkel<sup>11</sup> derived a first-order approximation for  $\Delta\mu(r, P)$  for both a 1-component liquid containing a bubble of its vapor and a 1-component droplet surrounded by its vapor, with the liquid and vapor in equilibrium. The expressions are isomorphic when expressed in terms of  $v_B$ , the molecular volume of the inner phase. For a bubble behaving as an ideal gas, Frenkel's expression, in our notation, becomes:  $\Delta\mu(r, P) = -2\gamma v_B/r = -2\gamma kT/rP$ . Expanding the right-hand side of  $\Delta\mu_j(r, P)$  in eq 3 to first-order gives this result. (1b) In the limit  $r \rightarrow \infty$ , eq 6 reduces to its third term (the summation term). This term is readily shown to be the correct expression for the Gibbs free energy change associated with a supersaturated ideal solution releasing its excess solute to form a second phase in equilibrium with a saturated ideal solution, in the absence of both surface effects and pressure inequalities between the phases. (1c) For a 1-component system, the third term in eqs 6–7 does not arise and eq 7 reduces to eq 11.

$$\Delta g(r, P) = 4\pi r^2 \gamma - (4/3)\pi r^3 P \ln(1 + (2\gamma/rP)) \quad (11)$$

Equation 11 gives the reversible work at constant temperature and pressure required to form a gas bubble of radius  $r$  in equilibrium with its surrounding liquid maintained at pressure  $P$ , for a 1-component closed system. Under these conditions, the Laplace equation can be satisfied only in the limit  $r \rightarrow \infty$ .<sup>11</sup> In this limit, from eq 11,  $\Delta g(r, P) \rightarrow 4\pi r^2 \gamma/3$ , which is the correct expression for the Gibbs free energy of formation of a bubble (or droplet) in equilibrium with its surrounding fluid in a 1-component system.<sup>11,12</sup>

(2) This is a problem that involves a critical point. Inverting eq 8 gives eq 12 for the critical bubble radius—the radius of the smallest possible equilibrium bubble that can form.

$$r_{\text{crit}} = 2\gamma/[x_2(\text{in})[K_2(P) - VP_1(P)] - [P - VP_1(P)]] \quad (12)$$

$r_{\text{crit}}$  sets the physically based unit of distance for the compound system. Replacing the absolute radius  $r$  in eq 6 by  $r^* r_{\text{crit}}$ , where  $r^*$  is the reduced radius ( $r^* \equiv r/r_{\text{crit}}$ ), and using  $r_{\text{crit}}$  given by eq 12 shows that  $\Delta G(r^*)$  is not a function of surface tension. Consequently, all supersaturated solutions, when compared at the same values of temperature, supersaturation ( $S$ ) and pressure ( $P$ ), fall on the same  $\Delta G(r^*)$  curve (e.g., Figure 2, solid curve).

In other words, the Gibbs free energy of the compound system obeys the Law of Corresponding States, which is expected of thermodynamic functions that describe the equilibrium states for systems with a critical point.<sup>18,19</sup>

(3) Equation 6 will be shown to be consistent with experiment (Results and Discussion, Figure 5).

### 3. Kinetics of Homogeneous Bubble Formation from Solution

The foregoing expressions are needed to predict homogeneous nucleation rates for closed supersaturated dissolved gas solutions maintained at a fixed temperature  $T$  and reservoir pressure  $P$ . In particular, the saturation pressure at which the onset of homogeneous nucleation first occurs is of considerable interest and practical importance. Because the onset occurs suddenly, this saturation pressure is called the “critical pressure for homogeneous nucleation” ( $P_{\text{crit}}$ ).<sup>20</sup>

The rate of bubble formation is estimated from a putative rate law together with an expression for the rate constant for the nucleation process. A form of transition state theory (TST)<sup>21</sup> is used for the latter. The expression for the rate of homogeneous nucleation, in units such as (No. of bubbles/cm<sup>3</sup> sec) takes the form shown in eq 13.

$$\text{rate} = Cf(P_{\text{in}}) \exp(-\Delta g^*/kT) \quad (13)$$

In eq 13,  $f(P_{\text{in}})$ , the frequency factor, is proportional to the rate at which embryonic bubble precursors form, and  $C$  is a product of constants,<sup>12</sup> including the transmission coefficient,  $\kappa$ .<sup>22</sup> This is the fraction of precursors that, having made it to the barrier top, continue on to form the product (a bubble). The term  $\Delta g^*/kT$  represents the maximum of  $\Delta g(r,P)/kT$  with respect to  $r$ . It is not possible to determine the rate of nucleation and/or  $P_{\text{crit}}$  solely from first principles, because although  $\Delta g^*$  is an equilibrium function that is known, the pre-exponential factor in eq 13 is known only very approximately. This is both because the exact form of  $f(P_{\text{in}})$  is in general not known, and because  $\kappa$  is a dynamical (i.e., nonequilibrium) variable that can be determined exactly only by specialized (rare-event) molecular dynamics simulations. Its determination for much simpler systems is an active field of current research.<sup>22</sup>

Therefore, in order to predict how homogeneous nucleation rates and  $P_{\text{crit}}$  vary in general, and with surface tension in particular, we use a semiempirical approach. Specifically, we will use a simple analytical approximation for  $f(P_{\text{in}})$  provided by Blander et al.,<sup>6</sup> but will determine  $C$  by calibration to an experimental estimate of  $P_{\text{crit}}$  for pure water.

The approximation of Blander et al. for the frequency factor for homogeneous bubble nucleation from a supersaturated solution is of the form shown in eq 14.

$$f(P_{\text{in}}) \cong (P_{\text{in}} - P)/\gamma^{1/2} \quad (14)$$

Here (as elsewhere)  $P_{\text{in}}$  and  $P$  are the initial saturation pressure and the pressure at which the solution is decompressed, respectively. Also, in eq 14 the temperature  $T$  has been taken to be constant. With this approximation, eq 13 becomes eq 15.

$$\text{rate} = C[(P_{\text{in}} - P)/\gamma^{1/2}] \exp(-\Delta g^*/kT) \quad (15)$$

$C$  will be determined by fitting to experiment. To do this  $P_{\text{crit}}$

is defined as the lowest value of  $P_{\text{in}}$  at which the bubbling rate first becomes “significant”. Somewhat arbitrarily, as done elsewhere,<sup>2,23</sup> we choose a rate of 1 (bubble/cm<sup>3</sup> sec) as significant. From Hemmingsen,<sup>24</sup> we take the estimate  $P_{\text{crit}} = 200$  atm for  $N_2$  in water at  $P = 1$  atm and  $T = 310$  K. Using these values and  $\gamma = 70$  dyne/cm in eq 15 gives eq 16,

$$C = (70^{1/2}/199) \exp(\Delta g^*[(200, 1, 70)/310k]) \quad (16)$$

so that the working expression for the rate of homogeneous nucleation becomes:

$$\text{rate} = [(P_{\text{in}} - P)/199](70/\gamma)^{1/2} \exp\{-\Delta g^*(P_{\text{in}}, P, \gamma) + \Delta g^*(200, 1, 70)/310k\} \quad (17)$$

Equation 7 will be used to determine the  $\Delta g^*$ s in the exponent of eq 17.

The only other expression for  $\Delta g(r,P)$  for a 2-component system that exists (of which the author is aware) is an approximation for it derived by Weathersby et al.<sup>2</sup> These workers based their derivation on physical arguments and on a 1-component approximation of the system. Using the present notation, their expression is given by eq 18.

$$\Delta g_w(r, P) = 4\pi r^2 \gamma + (4/3)\pi r^3 P_b \ln(P_b/P_{\text{in}}) \quad (18)$$

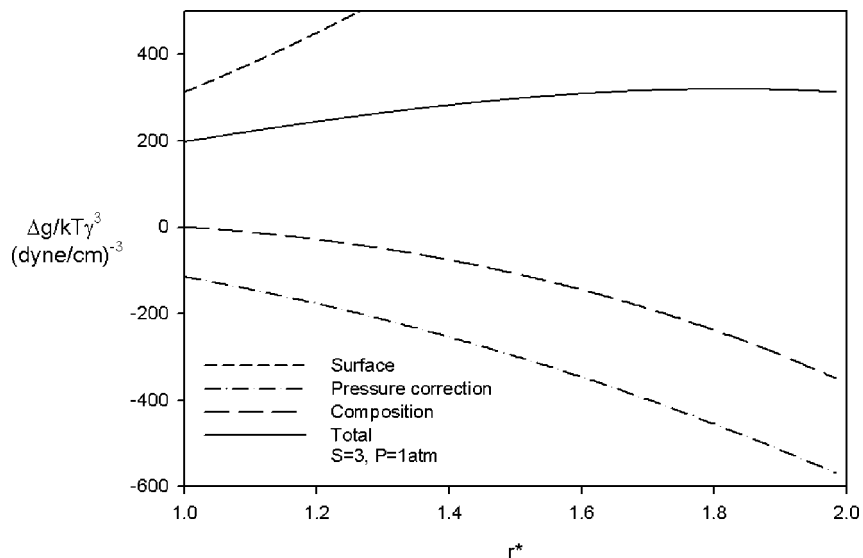
Like here,  $P_b$  is the pressure inside the bubble given by eq 4. We will compare the functions  $\Delta g(r,P)$ , based on eq 7, with  $\Delta g_w(r,P)$ , based on eq 18, and  $P_{\text{crit}}(\gamma)$  calculated from the basis of both functions (Figures 6 and 7, below).

### 4. Results and Discussion

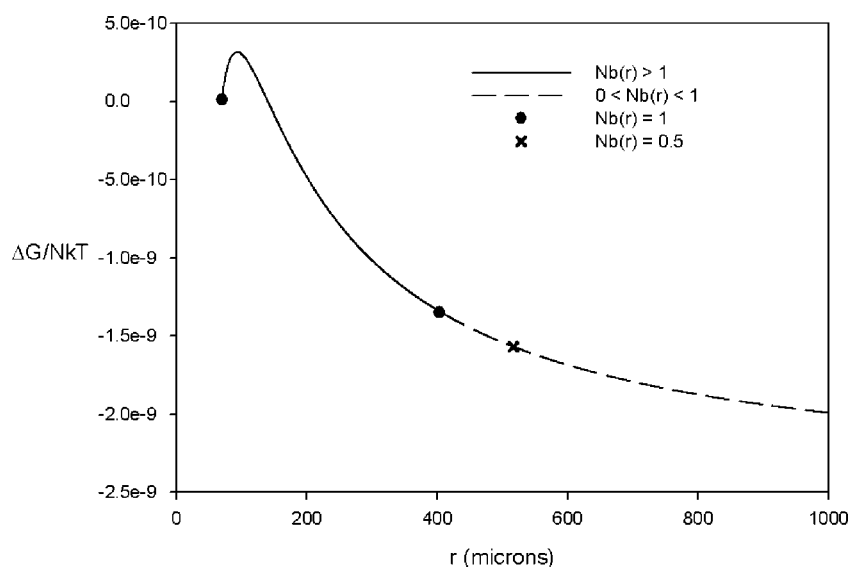
The results are given graphically in Figures 1–7. In Figures 1–4 the bubble number density and relative Gibbs free energies (total and per bubble) are shown as functions of the reduced bubble radius  $r^*$ . As indicated earlier, because of the existence of a critical point,  $\Delta G(r^*,P)$  has no explicit surface tension-dependence. The surface tension is subsumed in  $r^*$ . For similar reasons, the bubble number density  $N_b(r^*)/V_{\text{in}}$  and  $\Delta g(r^*)$  follow simple scaling relations with respect to the surface tension. From eqs 7, 10, and 12, one finds, respectively,  $\Delta g(r^*) \propto \gamma^3$  and  $N_b(r^*)/V_{\text{in}} \propto \gamma^{-3}$ . This makes it possible to display these functions compactly, because their explicit surface tension-dependences needn't be shown. In Figures 5–7, where comparisons are made with other work, it is more convenient to return to absolute units.

In Figures 1–4 the  $r^*$ -dependences of the above functions are shown for initial supersaturation ratios ( $S$ ) of 2–4 and for decompression at  $P = 1$  atm. It is seen from Figure 1 that (except for at the maximum) there are two values of  $r$  (for real  $r$ ) for each value of  $N_b(r,P)$ . Using eq 8 for  $x_{j,i}(r,P)$ ,  $j = 1, 2$  in eq 10, gives a quartic equation in  $r$ , for a given value of  $N_b(r,P)$ . Ward et al.<sup>10,25,26</sup> solved this quartic equation numerically for its two real  $r$  roots at specific values of  $N_b(r,P)$ . Here we reverse what is taken as known, and what is calculated from it. We calculate  $N_b(r^*,P)$  values for all  $r^* \geq 1$ , using eqs 8, 10, and 12. We do this because here the  $N_b(r^*,P)$  values are needed for the calculation of both  $\Delta G(r^*,P)$  and  $\Delta g(r^*,P)$  via eqs 6 and 7 at all possible equilibrium values of  $r^*$ .

The  $r^*$ -dependence of  $N_b(r^*)$  shown in Figure 1 has a simple physical basis.  $N_b(r^*)$  rises rapidly from  $r^* = 1$  because of the relatively rapid initial rate of off-gassing with respect to  $r^*$ .



**Figure 4.** Variation of the scaled relative Gibbs free energy per bubble and its components with  $r^*$ , from eqs 7, 8, 10, and 12, in the region of the peak maximum and the  $S$  and  $P$  values in Figure 2. The peak maximum (for the curve labeled “Total”)  $\cong 320$  (dyne/cm) $^{-3}$ , at  $r^* \cong 1.83$ .



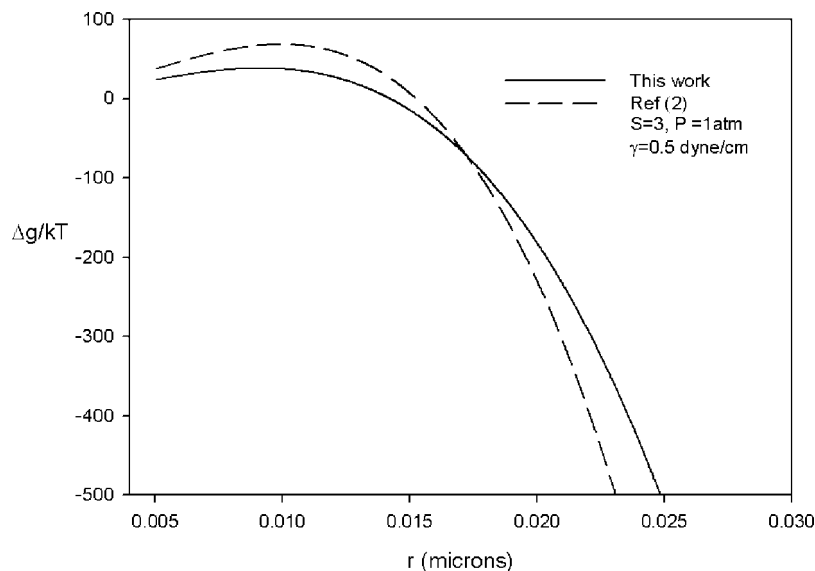
**Figure 5.** Variation of the reduced relative system Gibbs free energy with absolute bubble radius for a supersaturation ratio  $S = 1.02041$ ,  $P = 1$  atm,  $\gamma = 71.01$  dyn/cm,  $T = 298.15$  K and initial solution volume  $V_{in} = 1$  cm $^3$ . Peak maximum  $\cong 3.16 \times 10^{-10}$ , at  $r \cong 93.2$   $\mu$ . The asymptotic planar limit of the curve  $\cong -2.49 \times 10^{-9}$ .  $N_b(r)$  is the total number of bubbles with radius  $r$  in the system.

(Using eq 8, it is readily shown that  $d(N_{2g}(r^*))/dr^* \propto r^{*-2}$ .) The need to put a large amount of gas into small bubbles, initially, forces the rapid initial rise in  $N_b(r^*)$ . Subsequently,  $N_b(r^*)$  goes through a maximum since, at large  $r^*$ ,  $N_b(r^*)$  falls asymptotically as  $r^{*-3}$  (see eq 10). This cubic falloff in  $N_b(r^*)$  also causes the surface tension and pressure correction terms in  $\Delta G(r^*, P)/NkT$  each to vanish in the limit  $r^* \rightarrow \infty$ .

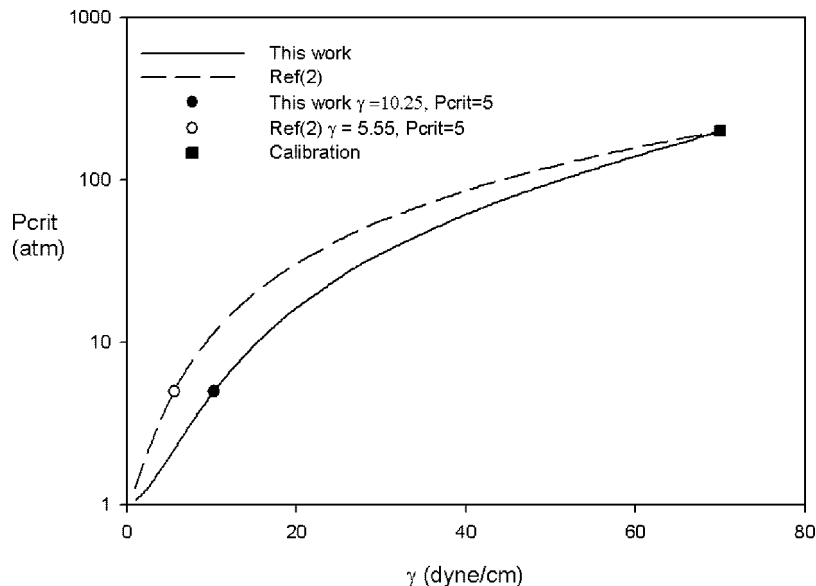
Figure 2 shows the  $r^*$ -dependence of  $\Delta G(r^*, P)/NkT$  and its components. At positive and negative values of  $\Delta G(r^*, P)/NkT$  the composite system is unstable and stable, respectively, relative to the initial supersaturated solution. For boundless systems  $r^* \rightarrow \infty$ , but for finite systems, the curves terminate at the finite large  $r^*$ -solution of  $N_b(r^*) = 1$ . Since at large  $r^*$ ,  $\Delta G(r^*, P)/NkT$  decays monotonically with  $r^*$ , this termination point corresponds to the most stable state that a finite system can achieve (see Figure 5). Also, since both the surface tension and pressure correction terms approach zero as  $r^* \rightarrow \infty$ , the total  $\Delta G(r^*, P)/NkT$  and its composition component converge in this limit.

Figures 3 and 4 illustrate the  $r^*$ -dependence of  $\Delta g(r^*, P)$  and its components for intermediate and small  $r^*$  values, for the same conditions of the initial supersaturation ratio, temperature, and reservoir pressure as in Figure 2. As indicated previously,  $\Delta g(r^*, P)$  is needed to predict of the rate of bubble formation. Its maximum with respect to  $r^*$  is the barrier height that occurs in the rate expressions (eqs 13–17). Because the rate depends exponentially on the maximum value of  $\Delta g(r^*, P)$  with respect to  $r^*$ , getting an exact expression for  $\Delta g(r^*, P)$  is essential if the rates are to be calculated accurately. Also, because of the factor  $N_b(r, P)$  that distinguishes them, the position of the peak maximum is shifted outward in  $\Delta g$  relative to  $\Delta G$  ( $r^*(\max) \cong 1.82$  vs  $r^*(\max) \cong 1.54$  for  $\Delta g$  and  $\Delta G$ , respectively). For boundless systems these curves would go to  $+\infty$  (surface term) and  $-\infty$  (the others) as  $r^* \rightarrow \infty$ , but for finite systems they terminate with finite magnitudes at the large- $r^*$  solution of  $N_b(r^*, P) = 1$ .

Figure 5 illustrates the behavior of  $\Delta G(r, P)/NkT$  at a very low value of the initial supersaturation ratio ( $S = 1.02041$ ,  $T =$



**Figure 6.** A comparison of the relative Gibbs free energy per bubble as a function of absolute bubble radius obtained from eqs 7, 8, and 10 of this work, and from ref 2 (see eq 18).  $T = 310$  K. Peaks: 38.5 at 0.00915  $\mu$  (this work) vs 68.5 at 0.00994  $\mu$  (ref 2).  $r_{\text{crit}} \cong 0.00503 \mu$ ;  $K_2$  and  $VP_1$  as in caption for Figure 1.



**Figure 7.** A comparison of the variation of  $P_{\text{crit}}$  with surface tension as predicted using the  $\Delta g(r,P)$  expression from this work (i.e., eqs 7, 8, and 10) with the corresponding expression from ref 2 (i.e., eq 18).  $T$ ,  $K_2$ , and  $VP_1$  are as in the caption for Figure 6.

298.15 K,  $P = 1$  atm). This state point was studied previously by Ward et al.,<sup>10</sup> so that by using it here, a direct connection can be made with their work. Also, for purposes of this comparison, the values chosen for the Henry's law constant of nitrogen and the vapor pressure of pure water were the same as those used in ref 10. These are given in the caption to Figure 1.

The curves and points shown in Figure 5 were all generated from eqs 6, 8, and 10. The abscissas of the solid points ( $r \cong 69.999 \mu$ ;  $r \cong 403.4 \mu$ ) are the two real roots of eq 10 for  $N_b(r,P) = 1$  (i.e., for a bubble density of 1 bubble/cm<sup>3</sup>). They agree perfectly with the small- and large-bubble radii reported for these conditions by Ward et al.<sup>10</sup> The solid curve shows the  $\Delta G(r,P)/NkT$  values in the range  $69.999 \mu \leq r \leq 403.4 \mu$ . In this range, from eq 10,  $N_b(r,P) \geq 1$ . The dashed curve shows the  $\Delta G(r,P)/NkT$  values for bubble densities less than 1 bubble/cm<sup>3</sup>, and the abscissa of the point, shown as an  $\times$  (at  $r \cong 516 \mu$ ), was determined from eq 10 for  $N_b(r,P) = 0.5$ .

The results in this figure are consistent both with the theoretical predictions and the experimental observations of

Ward et al.<sup>10</sup> These workers addressed the more limited question of the relative stability of a pair of bubbles of different equilibrium radii that corresponded to the same bubble density. They found (as in Figure 1) that for a given bubble density two equilibrium radii were possible and referred to these as small- $r$  and large- $r$  equilibrium states. On the basis of a perturbation analysis that involved a mix of Gibbs and Helmholtz free energy functions, they concluded that their small- $r$  and large- $r$  states represented the unstable and stable equilibrium states of their composite system, respectively, consistent with the specified  $N_b(r,P)$ . They also experimentally measured the radius of a stable bubble of N<sub>2</sub> that had been injected into a saturated water–nitrogen solution and found that it was consistent with the large- $r$  radius.<sup>10,25</sup> (For the conditions used in Figure 5, this would be  $r \cong 403.4 \mu$ ).

$\Delta G(r,P)/NkT$ , on the other hand, provides the relative stability of all possible equilibrium bubble states, at all possible values of the equilibrium bubble radius, regardless of bubble density. The latter is given by eqs 8 and 10 for any specific equilibrium

radius. In a multicomponent system the equilibrium bubble radius can assume an infinite number of possible values ranging continuously from the critical radius to either a finite value for a finite system or to infinity for a boundless system.

It is seen from Figure 5 that for  $N_b(r,P) = 1$ , the 403.4  $\mu$  point corresponds to  $\Delta G/NkT \approx -1.34 \times 10^{-9}$ , whereas the 69.999  $\mu$  point corresponds to  $\Delta G/NkT \approx +1.09 \times 10^{-11}$ , so that the large- $r$  solution is stable, relative to the small- $r$  solution. Also, because the small- $r$  solution corresponds to a positive relative Gibbs free energy, it will be unstable, relative to the initial supersaturated solution. Moreover, because there cannot be less than one bubble in a composite system, the large- $r$  point, which is the physical termination point of the graph, will always correspond to the most stable state possible in a finite system. This is consistent with the observation of Ward et al. that the large- $r$  single-bubble state was indefinitely stable.<sup>10,25</sup> Although not a stationary minimum, and therefore not a “stable minimum” in the usual thermodynamic sense,<sup>8</sup> it is manifestly the most stable state that a finite system can have. The dashed curve and the  $\times$  represent  $\Delta G/NkT$  values that would arise for bubble densities less than 1 bubble/cm<sup>3</sup> (achievable, for example, by using the  $S$ ,  $P$ , and  $T$  in Figure 5 but an initial solution volume greater than 1 cm<sup>3</sup>).

The rate-related results are shown in Figures 6 and 7, where comparisons are made with the previous work of Weathersby et al.<sup>2</sup> As indicated in Section 3, these workers used physical arguments and a 1-component approximation of the system to derive their working equation for  $\Delta g(r,P)/kT$  (eq 18). The pre-exponential factor used by Weathersby et al.<sup>2</sup> differed from the one derived by Blander et al.<sup>6</sup> The latter was used here in eq 17 to determine the effect of the expression used for  $\Delta g(r,P)/kT$  on the calculated value of  $P_{\text{crit}}$ . It is well-known that  $P_{\text{crit}}$  is very insensitive to the form assumed for the pre-exponential factor.<sup>2,23</sup> This was confirmed in trial calculations. Specifically, a change of the pre-exponential factor from the one used by Blander et al. to the one used by Weathersby et al., while keeping the exponential unchanged, and using the same point for the calibration, had no discernible effect on the  $P_{\text{crit}}$  values shown in Figure 7. In other words, the thickness of the curves in Figure 7 bounded the variation found when the pre-exponential factor alone was changed from the one used here to the one used by Weathersby et al.

A comparison of our expression for the Gibbs free energy per bubble (eqs 7, 8, and 10), with that given by eq 18 is shown in Figure 6, for the state conditions used by Weathersby et al.<sup>2</sup> Although the curves shown in Figure 6 are qualitatively similar, there are significant quantitative differences between them. The solid curve, which represents the present work, peaks at a smaller value of the bubble radius ( $\approx 0.00915 \mu$  vs  $\approx 0.00994 \mu$ ). More importantly, its maximum is considerably lower than that obtained using eq 18 ( $\approx 38.5$  vs  $\approx 68.5$ ). The significantly lower barrier height will have important implications for the predicted critical pressure for homogeneous bubble nucleation  $P_{\text{crit}}$ , as discussed below.

Figure 7 shows the calculated values of  $P_{\text{crit}}$  based on the two  $\Delta g(r,P)/kT$  expressions. These values were obtained by solving eq 17 numerically for  $P_{\text{in}}$ , using rate = 1 bubble/cm<sup>3</sup> sec, and  $P = 1$  atm. This was done for a range of values of the solution surface tension  $\gamma$  and for each of the two  $\Delta g(r,P)/kT$  functions. A “Golden Search” procedure<sup>27</sup> was used to determine the peak maximum with respect to  $r(\Delta g^*/kT)$ , and “Bisection”<sup>27</sup> was used to solve eq 17 numerically for  $P_{\text{crit}}$ .

The results in Figure 7 show that (for  $\gamma < 70$  dyne/cm), when the exact expression for  $\Delta g(r,P)/kT$  is used to determine  $\Delta g^*/$

$kT$ , homogeneous nucleation is predicted to occur (at a given degree of supersaturation) at higher values of the solution surface tension than when the earlier approximate expression based on eq 18 is used.

These results are immediately applicable to improving the accuracy of the nucleation barrier heights needed for superheating calculations of interest in chemical engineering (Introduction). The rate expressions both for neat liquids and mixtures used previously in these applications did not include the required pressure correction term (the second term in eq 7). Also, for mixtures, the proper free energy of mixing contribution (the third term in eq 7), was not used.<sup>5,6</sup>

However, a further approximation is needed before this work can be applied to human decompression studies. The Gibbs free energy expressions are strictly applicable only to closed systems. Tissues in the body are not closed. They are perfused by blood, and thus open with respect to diffusion-driven dissolved gas exchange with the circulatory system. However, for those tissues wherein the rate of dissolved gas exchange with the circulatory system is much slower than the rate of bubble nucleation, the tissue can, as a good approximation, be taken to be closed over the course of the nucleation process. This kind of approximation—requiring a separation of time scales for its validity—is ubiquitous both in the physical and biological sciences. The Born–Oppenheimer approximation<sup>18</sup> is perhaps the best-known example in chemistry and physics, and “perfusion-limited” exchange kinetics (wherein intratissue diffusion of a dissolved solute is much faster than tissue perfusion) is widely used in physiology, in general, and in decompression modeling, in particular.<sup>1–4</sup>

For systems in which this approximation holds, the results in Figure 7 indicate that homogeneous gas bubble nucleation in tissues, if it occurs at all, is likely to be a minor contributor to bubble formation on decompression. Only tissues that mimic very low surface tension solutions ( $\gamma \leq 10$  dyn/cm) can be considered as possible sites for homogeneous nucleation in typical human decompression situations ( $P_{\text{crit}} < 5$  atm). Moreover, supersaturation pressures considerably lower than 5 atm are known to elicit Doppler-detectable bubbles resulting from decompression.<sup>28</sup> Therefore other mechanisms for bubble formation and growth, that involve lower barriers and faster rates, are almost certainly more significant than homogeneous nucleation. These include heterogeneous and tribonucleation<sup>3</sup> and the growth of pre-existing bubbles stabilized in hydrophobic crevices<sup>30,31</sup> and on hydrophobic surfaces.<sup>32</sup>

## 5. Summary and Conclusions

A thermodynamic procedure first systematically developed by Abraham in his study of liquid droplets surrounded by their vapor<sup>12</sup> was used to derive expressions for the Gibbs free energy of gaseous bubble formation from finite multicomponent supersaturated gas–liquid solutions. The systems are closed, and the temperature and external pressure are maintained constant. The expressions correctly reduce to known limits when simplified and are consistent with experiment, and the system Gibbs free energy appropriately obeys the Law of Corresponding States. These expressions provide a significantly lower barrier height for the Gibbs free energy of bubble formation from a supersaturated solution than is obtained from previously published work.

The derived expressions can be applied directly to improve the accuracy in barrier height predictions needed in chemical engineering. A further requirement based on a separation of time scales must be met in order to render the expressions applicable



to studies on human decompression from supersaturated dissolved gas states.

In future work the accuracy of the predictions in the small bubble regime can be improved by incorporating an  $r$ -dependent surface tension in the expressions, with the latter estimated either from theory or simulations. It would also be interesting (and challenging) to extend this work by carrying out a thermodynamic analysis of the kind used here (involving Callen's and Abraham's postulates) on heterogeneous nucleation, tribonucleation, and on bubbles stabilized in hydrophobic crevices and on hydrophobic surfaces.

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- (16) We assume that the surface tension of the solution equals that of the pure solvent, i.e., it is unaffected by the presence of dissolved solute. This is an excellent approximation for the low solute concentrations used here (see ref 23).
- (17) An alternate, longer, less intuitive, but fully equivalent method can be used to derive:  $\Delta\mu_j(r,P) = kT \ln(P/P_b)$ . It is to express each of  $\mu_{i,g}(P_j(r,P))$  and  $\mu_{j,l}(x_{j,l}(r,P),P)$  in terms of their respective standard state chemical potentials<sup>18</sup>,  $P_j$ ,  $P$ ,  $P_b$ , and  $x_{j,l}(r,P)$ . Then, using the relations between standard state chemical potential differences and equilibrium partition coefficients (here the Henry's law constant(s) and the solvent vapor pressure), and the relations between these partition coefficients and  $P$ , gives:  $\Delta\mu_j(r,P) = kT \ln(P/P_b)$ .
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