

Why Is It Much Easier To Nucleate Gas Bubbles than Theory Predicts?

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Bubble nucleation from supersaturated gas solutions generally takes place at much lower supersaturations than are expected from the theory. Furthermore, the same theory predicts that the threshold concentration of gas needed to cause nucleation should be essentially independent of the gas species used, a finding contradicted by experiment. There are two general explanations: first, that the theory is wrong, or second, that there is a previously unidentified factor which is influencing the results of the experiments. Given the success of the fundamental theory in other areas, the second explanation is preferred. The previously unrecognized factor is identified here as being the surface activity of the gases which form the bubbles.

Introduction

Gas bubble nucleation from supersaturated solutions has not been extensively researched. The literature is fairly small, and it is thus possible to summarize the experimental data without great loss of accuracy. It appears to be true to say that in all cases of bubble evolution from supersaturated gas solutions so far examined, the experimental data are not in agreement with theoretical predictions. This disagreement is on two fronts: (1) first, quantitative, in that theory predicts much higher supersaturations are needed to cause bubble nucleation than are found necessary experimentally (characteristically, a factor of at least 2 orders of magnitude in the supersaturation); (2) second, qualitative, in that theory predicts that it is *only* the nature of the liquid which dictates the conditions required for gas bubble nucleation. Experimentally, the chemical nature of the gas is found to be important.

This dual disagreement holds for gas solutions, both aqueous and nonaqueous, but clearly is not universally true for bubble nucleation in general. For bubbles formed in single-component systems by boiling or cavitation, the theory rather accurately predicts the kinetic instability limits, although it does so better for boiling than for cavitation. The present paper addresses only the phenomena in binary (or *n*-ary) systems where the supersaturation is attributable to the presence of an excess of the second (volatile and usually gaseous) component.

The most common explanation for disagreements between nucleation theory and experiment is based on the catalytic effect of hetero surfaces. While the distinction between homogeneous and heterogeneous nucleation is fundamental and is certainly influential in many circumstances, it fails to account for the difference in nucleation kinetics between gas bubbles and boiling or cavitation. It is generally accepted that hetero nucleation (at a surface) will be substantially easier than homogeneous nucleation and so will take place at lower supersaturations, but there is nothing in the theory to suggest a preference in such a mechanism for *n*-ary as opposed to unary systems, or vice versa. With reasonable values for the contact angle, calculations predict reductions of an order of magnitude in the critical supersaturation necessary for nucleation, but without regard for whether the system is unary or binary. Even allowing for the more potent catalytic effect of rough, hydrophobic hetero

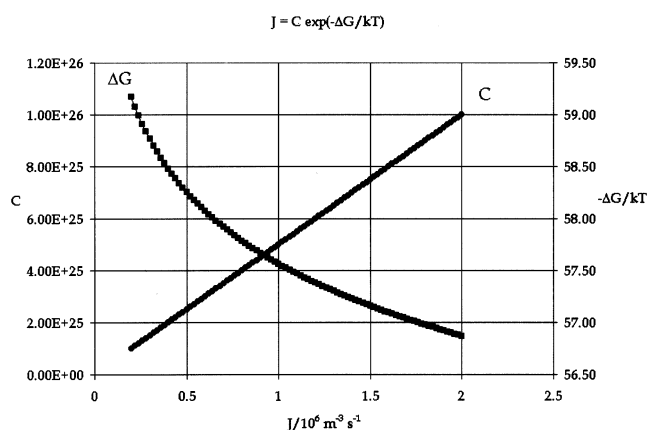


Figure 1. The scale on the left-hand axis is the pre-exponential, *C*, while the scale on the right-hand side is the exponential term. To produce an order of magnitude change in *J* (the horizontal axis) requires *C* to change by an order of magnitude but only involves a change of about 4% in ΔG .

surfaces, physically improbable combinations of values of contact angle and site geometry have to be assumed in order for the theory to reach acceptable agreement with the experimental gas bubble nucleation data. This is not so for boiling or cavitation, where the agreement is quite satisfactory under typical experimental conditions.

The theoretical expression for the rate of nucleation is made up of two parts, the pre-exponential (*C*) and the exponential (ΔG):

$$J = C \exp\left(\frac{-\Delta G}{kT}\right) \quad (1)$$

Changes in the pre-exponential result in relatively small changes overall in the nucleation rate compared to changes in the exponential: it is frequently stated in the nucleation literature that a change of an order of magnitude in the pre-exponential is equivalent to a change of about 1% in the exponential. A theoretical calculation of the rate of gas bubble nucleation in water, Figure 1, shows the change in either *C* or ΔG needed to effect an order of magnitude change in *J*. It will be seen that to produce this change, with constant *C*, ΔG must change by about 4%, while at constant ΔG , *C* must clearly change by 1000%. For systems with lower interfacial tension, the $\log(J)$ versus σ plot is steeper, and the conventional 1% to an order of magnitude

relationship is restored when the interfacial tension is about 30 mN m^{-1} . The general principle is however valid: changes in C are of minor importance in comparison to changes in ΔG .

For this reason, theoretical constructs and possible explanations of the poor agreement of experimental results and the classical theory have concentrated on the exponential term. This does not mean that the pre-exponential is negligible. At least in theory, there are cases where the pre-exponential is dominant (see discussion after Ward et al.¹).

Experiments are often designed to measure the supersaturation needed to cause appreciable nucleation. Commonly in the case of boiling, drops of the liquid are subjected to controlled temperature increases, and the onset of boiling appears as explosive vaporization of the droplet: the experimental result consists of recording accurately the temperature at which this occurs. Such experiments identify what is usually called a "critical supersaturation". This value has only a general theoretical significance and is a kinetic limit, not a thermodynamic one. This is the same entity that Ostwald referred to as the "metastable limit". Most data that appear in the literature are of this type, but there are also a few reports of studies of nucleation kinetics as a function of the applied supersaturation. Obviously, the latter type of data is richer.

Background

Most experimentalists in the area of gas bubble nucleation have felt it necessary to mention the large gap between theory and their experimental data, and a number of varied explanations for this discrepancy have already appeared in the literature. The experimentalists are not alone: A recent theoretical paper² notes that in some circumstances, the classical theory underestimates the bubble nucleation rate by a factor of 10^{20} . This is a staggeringly large discrepancy and is quite possibly the worst "agreement" between theory and experiment recorded in the scientific literature.

The literature offers a great variety of possible explanations for the poor agreement between theoretical predictions of the critical supersaturation and experiment. A selection of some of these follows.

1. A common criticism of the classical nucleation theory is that macroscopic values for the surface tension have to be assumed for the very small clusters representing subcritical and critical nuclei. This is sometimes referred to as the capillary approximation. A number of authors have mentioned this as a possible cause of disagreement between theory and experiment. Models to "correct" for this include that due to Tolman.

2. The interface between two phases is not sharp, and the transition from one phase to another occurs over a finite thickness. Thicker transition regions have been referred to as "diffuse". A statistical mechanical model of such diffuse interfaces was advanced by Kirkwood and Buff³ (see for example Shen and Debenedetti⁴) which involves a conceptual spreading out of the interfacial region, so that the transition from say the liquid to the vapor phase is gradual, at least spatially. Bowers et al.⁵

have postulated "blobs" which have a conceptual similarity to the diffuse interface. In their model, the region in the liquid described as a blob is characterized in that there is no sharp liquid/gas interface. Since there is no such sharp interface, the apparently reduced interfacial free energy (or equivalently, surface tension) appears to make the free energy of formation of the critical nucleus much smaller. Provided that far from the interface there are phases which could be described as "gas" and "liquid", the free energy of formation of a blob should be independent of the position of the Gibbs dividing surface. Arbitrarily increasing the thickness of the interfacial region does not ultimately change the work of formation of the critical nucleus.

3. Wilt⁶ describes the potential of certain types of geometrical imperfections to have the ability to reduce the free energy required for the formation of a critical bubble nucleus. The difficulty with this theory is that the new parameter introduced into the nucleation equation (the contact angle *in combination* with the conical pit half-angle) acts as an adjustable parameter needed to produce agreement with the theory. Physically, the requirements are rather stringent: For the case of CO_2 bubbles forming in water, contact angles of at least 94° with conical holes of maximum half-angle 4.7° combine to give a prediction of a measurable rate of nucleation at a supersaturation ratio of about 5, which is typical for carbonated drinks. The fact is that such contact angles are uncommon, particularly with hydrophilic surfaces such as glass, and the required cone half-angles do not appear likely to be common either. Fizziness in a glass of carbonated drink appears to be universal, however.

4. A more general approach, discussed by many authors,⁷ is that certain sites on a hetero surface are more catalytic for nucleation than others. Such "active sites" might be chemically inhomogeneous, structural, or geometrical, although such details are generally lacking in any specific case.

5. Jones et al.⁸ are recent representatives of a significant school of thought which essentially postulates that under the circumstances prevailing for carbonated drinks (i.e., at low supersaturations) there is no nucleation step involved and thus that it is irrelevant what the nucleation theory predicts. This latter approach has been hinted at a number of times in the literature.⁹ The presence of any supercritical amount of any gas phase anywhere in the liquid phase of the system is theoretically enough to remove the need for nucleation.

6. There is quite an extensive literature on so-called "Harvey nuclei",¹⁰ and it seems likely that often such nuclei are indeed the centers for the production of bubbles. Furthermore, regardless of the source of the first bubble, detachment often will leave behind enough gas at the site to avoid the necessity for further nucleation.

7. Mesler¹¹ has invoked secondary nucleation to explain the lower than expected supersaturation needed to drive massive bubble nucleation and has postulated that gas/vapor nuclei (bubbles) can act as secondary nucleation

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centers, in a manner similar to the secondary (breeding) nucleation in crystallizers. Additional centers cause a proliferation of bubbles, thus increasing the rate of bubble production. The argument is that as bubbles burst, they produce many drops, each of which may entrain air or vapor. These entrained bubbles then act as centers for further bubble growth. Under conditions of low supersaturation, the presence of relatively few nucleation centers of the Harvey type could thus provide for the profusion of bubbles usually associated with bubble nucleation at high supersaturations or superheats. Depending as it does upon the presence of persistent bubbles of arbitrary size, this theory is open to the criticism that Ostwald ripening¹² would be expected to remove all such bubbles in due course of time. The rate of loss of bubbles will depend on various parameters including the size distribution of the bubbles present. These criteria are discussed more fully below.

8. The electrochemical literature has many examples of electrolytic gas bubble nucleation taking place at electrodes, where the active sites have at least tentatively been identified. Electrochemical experiments also have the significant advantage that the thermodynamic parameters can be followed with great accuracy in such systems; the voltage gives the (electro)chemical potential difference, and the current, the extent of reaction. Although there are some reports of somewhat higher supersaturations¹³ being attained in electrochemically generated bubble systems than for other types of gas supersaturation, typical results still give supersaturations far below the predictions of homogeneous¹⁴ nucleation theory. The poor agreement is made worse still by the apparent consensus between the electrochemists that in most cases examined, there is a zero (or very near zero) contact angle between the electrode and electrolyte. When the electrolyte has zero contact angle on the electrode, the surface is predicted not to be catalytic for the nucleation process, and thus the expectation would be that nucleation in such a system would be as difficult (i.e., occurring at similarly high supersaturations) as in the homogeneous case. Some rather careful electrolytic bubble nucleation experiments have been performed¹⁴ on very clean mercury surfaces, where the surface structure is not in dispute and where, in principle, no Harvey nuclei could be present. Even here, bubble nucleation was found to occur at supersaturations in the region of 9–16, 2 orders of magnitude lower than predictions for hetero nucleation on a flat surface and of the same order as found experimentally for other clean electrodes. It appears that the details of the surface topography may not be as critical as expected.

9. The Tolman¹⁵ prescription for the effect of curvature on the interfacial tension has been invoked by a number of authors in the case of condensed phase nucleation. However, what experimental evidence there is points to the Kelvin equation, with its reliance on the macroscopic description of the surface tension, being good to the curvatures typical of critical bubble radii for low to intermediate supersaturations in gas solutions, at least for liquids other than water.¹⁶ There appears to be little

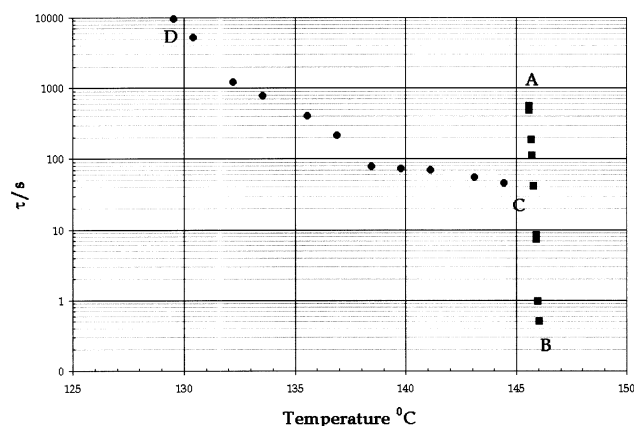


Figure 2. The data along the curve AB represent the result of homogeneous explosive vaporization of liquid drops and demonstrate that the waiting time (τ /s) before the drop boils decreases from about 550 to about 0.5 s as the temperature is raised a fraction of a degree (from 145.6 to 146 °C). In the presence of ionizing radiation along the curve DC, the nucleation of the phase change can take place at much lower superheats, as low as about 129.5 °C at point D, thus showing the catalytic effect of ionizing radiation on the boiling process. Graph replotted from ref 18.

if any experimental justification for using the Tolman description in the analysis of bubble nucleation rates.

10. Cosmic rays and high-energy subatomic particles can cause bubble nucleation in a bubble chamber.¹⁷ Experiments have successfully shown significant effects for boiling in unary liquids.¹⁸ It has been postulated that similar effects are at work with supersaturated gas solutions, but experiments designed to show such effects have not been successful.

11. Various "motes" have been mentioned¹⁹ as being the possible source of bubble nuclei, the ease of the nucleation process presumably being due to sites of the Harvey kind. Antibumping granules used in distillation are an example. In the "gushing" of beers where there is a sudden release of many gas bubbles when the beer is dispensed, various causes have been implicated,²⁰ including metal ions of various sorts, microorganisms, and "foreign bodies".

12. There have also been some suggestions that specific surface structures at the molecular level have the ability to facilitate nucleation. For liquid/crystal or vapor/crystal phase changes, the phenomenon is known as epitaxy,²¹ which depends for its effect on the excellence of the lattice match between the two crystalline solids (nucleating epitaxial crystal and substrate). Adsorbed surfactant layers have been implicated in making crystallization of emulsion droplets much easier.²² Recently, somewhat similar behavior has been seen for solids nucleating under two-dimensional adsorbed films at liquid/air interfaces,²³ but as far as the author is aware, there is no suggestion that any similar mechanism may act for gas bubbles, and none is to be expected on theoretical grounds. A possible exception is the somewhat ordered and at least partially hydrophobic environment of the interior of a suitable

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surfactant micelle. The hydrophobic tails may provide a preferred environment for the (hydrophobic) gas.

13. The effect of high electric field gradients has been invoked as a possible cause for the ease of electrolytic bubble nucleation,¹⁴ but the physical basis for the postulated effect is somewhat obscure. The more general suggestion has been made that high electric fields around motes in polar solvents are responsible for the anomalous results often found with water as the liquid in nucleation experiments. See for example Blander et al.²⁴

14. There are claims²⁵ in the literature of spontaneous bubble nucleation occurring at equilibrium (i.e., at zero supersaturation) as a possible cause of observed long-range hydrophobic attractions between hydrophobic surfaces, but no convincing explanation for how such bubbles might evolve has been advanced, and such experimental evidence as is available does not support this mechanism of bubble nucleation. It seems probable that such bubbles are either pre-existing or are actually generated by the force-distance measuring process. In a similar vein, Plesset²⁶ has suggested that hydrophobic surfaces might be covered with a gas layer and that such surfaces would then act as nucleation centers. This idea was analyzed by Yount and Kunkle²⁷ and shown to be unlikely to be correct.

15. Levine has suggested²⁸ chemisorption of oxygen ions as the reason for the ease of bubble nucleation in the cases of electrolytic oxygen evolution and the formation of CO bubbles in molten iron.

16. Pre-existing free bubbles (as opposed to trapped gas pockets in cracks, crevices, and pores of specified geometries, i.e., Harvey nuclei) have been postulated,²⁹ and their presence is pretty commonly assumed in the literature on the tensile strength of liquids and boiling incipience. Bubbles are more prone to Ostwald ripening than is the case for particulate suspensions or emulsions. Since all gases are appreciably soluble in water (and most other liquids too), a precondition for Ostwald ripening of bubbles is automatically fulfilled, which is not generally true for emulsions or particulate suspensions. Kinetic stability may be achievable in the short term for bubbles, but not in the long term. In common with all other macrosuspensions, they are thermodynamically unstable.

17. Ward et al.¹ have examined in detail the nonideality of the gas mixture inside the bubble and in the surrounding solution, and it has been convincingly shown that this effect is indeed important in certain cases.³⁰ As an explanation of the huge discrepancies commonly met with in gas bubble nucleation experiments, it does not serve, and indeed the authors did not claim that it would.

18. Volanschi and co-workers have done elegant experiments³¹ with cavities of well-defined geometry. As an example, an inverted square pyramidal cavity of accurately known size (depth and half-angle) was made by etching silicon. Electrochemical bubbles were generated in this

site and were observed with an optical system giving a magnification of about $\times 400$. Overpotential and capacitance measurements were made, and this allowed studies of individual bubble events. The results led the authors to postulate a phenomenon they call the "concentrator" effect: essentially, that the concentration of electrolytic gas-generating species is greater at the base of the cavity than elsewhere. Given that such sites are already favored for nucleation, this added effect could go a long way toward explaining the much lower than expected supersaturation needed to cause bubble nucleation.

This list is not complete but gives a feeling for the variety of explanations for what has become a most puzzling set of discrepancies. Various modifications of the classical nucleation theory have been published,³² and generally speaking these have improved the agreement but have not resolved the discrepancy.

The key to understanding in this area is undoubtedly in experimental data. Unfortunately, at a fundamental level nucleation is a stochastic process and does not lend itself to generating large amounts of reliable, tightly bunched data. The biggest single source of reliable experimental bubble nucleation data is in the nucleate boiling area, where superheat limits and the effects of bubbles on the heat transfer are technologically critical. However, for reasons to be addressed below, the agreement between theory and experiment is rather good in these cases, in sharp contrast with the case of supersaturated gas solutions. For cavitation, the calculated theoretical strengths of liquids are generally an intermediate case: the agreement between theory and experiment is worse than for boiling, but still quite good, and certainly much better than for the formation of gas bubbles from solution. Any explanation for the poor agreement between experiment and theory for gas bubble formation needs to account for the rather good agreement of the very same theory with observations of boiling and cavitation. It is a common feature among the variety of explanations put forward above that they cannot distinguish between unary systems on one hand and binary gas solutions on the other, with the possible exception of the last two. Of those, the concentrator effect clearly could only influence electrolytic bubble nucleation.

Three Types of Bubble Nucleation

Spontaneous bubble formation (i.e., those cases where the overall free energy of the system is reduced by the appearance of the bubble) can be of three basic types. First, reducing the external pressure below the vapor pressure of the pure liquid can cause cavitation. Second, increasing the temperature to the point where the vapor is more stable than the pure liquid may cause boiling. Finally, if a gas or volatile vapor is dissolved in the liquid, then changing the conditions to create a supersaturated solution may cause gas bubbles to be formed. In the classical nucleation theory, all three types of bubble production mechanisms share a common mathematical description, with minor modifications to the pre-exponential. A consequence of this is that the theory describing gas bubble nucleation depends only on the properties of the liquid, but not on those of the gas.³³ Therefore, one would predict that in a series of experiments on bubble nucleation using a single gas but various different liquids, a wide variety of critical supersaturations would be observed. Conversely, during experiments conducted using a single liquid but various different gases, the expectation

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would be that a single critical supersaturation would be found. The experimental finding is that the gas matters.

Consider boiling nucleation. First, the experimental liquid is usually carefully purified before use, so the initial level of any dissolved gas is rather low. Gases are less soluble in hot liquids than in cold, and bubbles generated in the boiling process will carry with them a proportion of any dissolved gas to the free liquid surface, and thus out of the system. For this reason, boiling is an effective means of ridding a solution of dissolved gas. Thus boiling experiments show very little evidence of any effects of dissolved gases, and classical nucleation theory works well. For cavitation, a similarly careful purification of the experimental liquid is common. The cavitation experiment is not equally effective at self-cleaning as boiling experiments, particularly when the experiments concentrate on the observation of the first nucleation event rather than massive bubble nucleation. It is very common, though, for the experimental liquid to be distilled (boiled) before use. Overall, for these reasons, cavitation experiments may be expected to less closely adhere to the predictions of nucleation theory than will boiling. For gas bubble nucleation, on the other hand, it is clear that the precondition is satisfied for the full effects of the gas to be realized, and this is where theory and experiment diverge most strongly.

Gases as Surfactants

It is a known but somewhat obscure fact that gases can act as surfactants. A reasonably complete listing of literature relating to the effects of gases as surfactants is given in the reference list under Kundt³⁵ and the other references grouped with it. The surface tension of a gas solution is generally a function of the dissolved gas pressure, in accordance with an isotherm such as the Gibbs adsorption isotherm. The more soluble gases are more effective at reducing the surface tension than the less soluble. This may be related to the adsorbed amount, Γ , of the adsorbed species being determined by the concentration in the bulk liquid. The mechanism of action of gases as surfactants is not clear. The classical picture of a surfactant as a molecule with hydrophilic and hydrophobic parts is clearly inapplicable to the gases listed in Table 1 and completely inappropriate for gaseous elements, whether atomic or molecular. Nonetheless, the positive adsorption of these species is a well-established experimental fact, as is the resulting lowering of the interfacial tension, as reported for example by Massoudi et al.³⁶ Thus dissolved gases act to lower the surface

Table 1. Variation in Surface Tension of Water with Dissolved Gas Content, Expressed as $\gamma = \gamma_0 + bp + cp^2 + dp^3$, with p in Bar^a

gas	b	c	d
He	0.0000		
H ₂	-0.0250		
O ₂	-0.0779	+0.000104	
N ₂	-0.0835	+0.000194	
Ar	-0.0840	+0.000194	
CO	-0.1041	+0.000239	
CH ₄	-0.1547	+0.000456	
C ₂ H ₄	-0.6353	+0.00316	
C ₂ H ₆	-0.4376	-0.00157	
C ₃ H ₈	-0.9681	-0.0589	
N ₂ O	-0.6231	+0.00287	-0.000040
CO ₂	-0.7789	+0.00543	-0.000042
<i>n</i> -C ₄ H ₁₀	-2.335	-0.591	

^a Massoudi and King, ref 36.

tension, and the extent of lowering depends on the adsorbed amount, and hence on the pressure. The possible involvement of adsorption in gas bubble nucleation has been mentioned in the literature³⁷ but has not been quantitatively evaluated. The reduction in surface tension is highly significant for the rate of nucleation of bubbles, since the surface tension appears to the third power in the exponent in the expression for the nucleation rate, eq 2. With dilute gas solutions, this effect, though important, may not be dominant. However, as the gas concentration increases, so the importance of the surface tension term is increased.

A convenient measure of the surface activity of a gas is the rate of change of surface tension with applied pressure, $d\gamma/dp \equiv b$, values of which are given in Table 1. Since gases generally obey Henry's law at relatively low pressures, this is proportional to $d\gamma/dc$.

On the basis of these data, the size of the first coefficient, b , of the reduction in surface tension of aqueous solutions with pressure depends strongly on the nature of the gas, ranging from helium at one extreme to *n*-C₄H₁₀ at the other. The common atmospheric gases N₂ and O₂ have relatively modest coefficients, with the surface tension falling about 0.1 mN m⁻¹ bar⁻¹, whereas for *n*-C₄H₁₀, the corresponding reduction is about 2 mN m⁻¹ bar⁻¹. Similar data have been reported for ethene in cyclohexane by Lubetkin and Akhtar,³⁸ where the coefficient b was about 1 mN m⁻¹ bar⁻¹. Excluding the value for helium, the b coefficients for this restricted selection of gases dissolved in water cover the substantial range of about 2 orders of magnitude. There is a likelihood that when other gases are examined, this range will be extended (for example, based on its solubility, an estimate for Cl₂ is that it will have a somewhat greater b coefficient than *n*-C₄H₁₀).

At low pressures, the surface tension decreases in a roughly linear fashion with increasing pressure, so that to a fair approximation, the surface tension can be represented by the equation $\gamma = \gamma_0 + (d\gamma/dp)p$, and

(33) This is not exactly true. There is a factor $(1/m^{1/2})$ in the pre-exponential which accounts for the relative molecular mass (RMM) of the gas, but the relative unimportance of the pre-exponential and the fact that the gases of interest have a fairly restricted range of values for the RMM mean that the description is functionally accurate. For example, see: Swanger, L. A.; Rhines, W. C. *J. Cryst. Growth* **1972**, *12*, 323.

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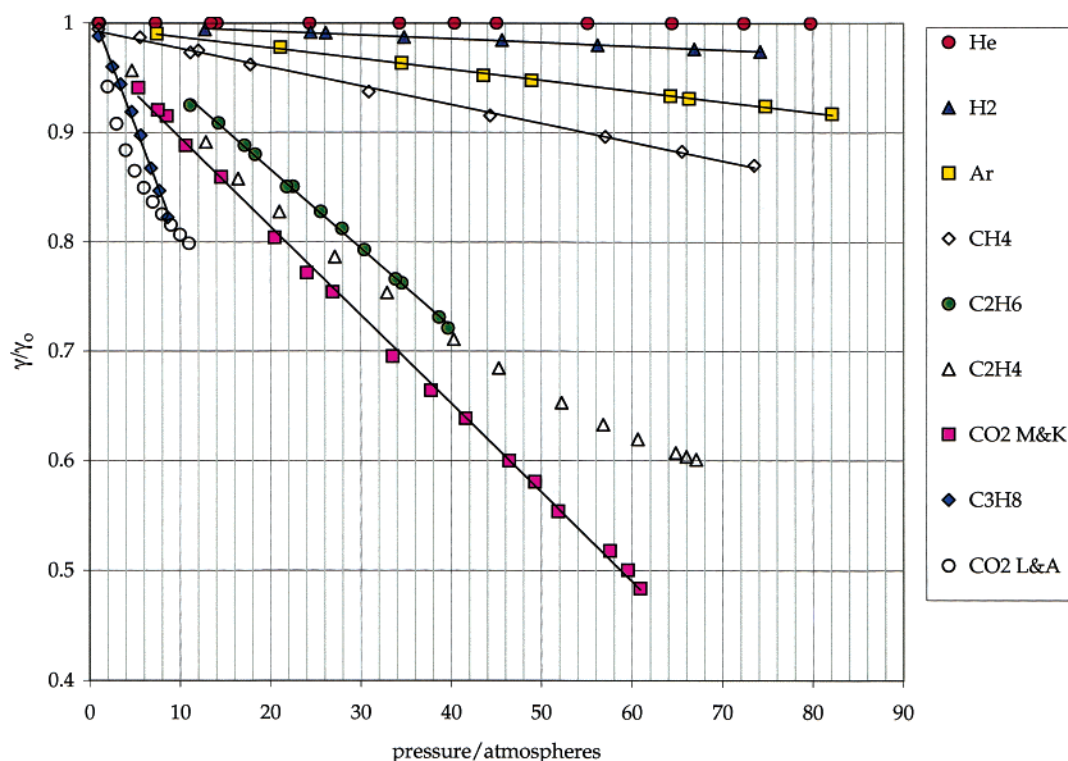


Figure 3. The sensitivity of the interfacial tension for various gases in contact with water, as a function of pressure.

$d\gamma/dp \equiv b$, where b is the first coefficient shown in Table 1, and γ_0 is the surface tension against air at atmospheric pressure.

For helium, the available data suggest that b is close to zero, as can be seen in Figure 3. For all other gases so far examined, b is a negative quantity, showing that the gases are positively adsorbed and thus reduce the surface tension. This reduction in surface tension will result in a significant reduction in the size of the critical nucleus.

At the critical size, the bubble is in (unstable) equilibrium. The pressure in the critical bubble is given by p^* . Since the pressure is inversely proportional to the radius of the bubble, below the critical size, the pressure in the incipient bubble is p' , which is greater than p^* . Thus, below the critical size, the adsorption of the gas and the corresponding reduction in surface tension could be even greater than for the case of the critical nucleus. The extent of the reduction in surface tension depends on the kinetics of adsorption as balanced by the rate of collapse or growth of the subcritical bubbles. These kinetic details are not known at present.

The b coefficient for helium gas is close to zero. If helium were to be used in a bubble nucleation experiment, is it anticipated that the predictions of classical nucleation theory would be verified? Perfect agreement is not expected, even in the absence of the gas acting as a surfactant: it is not only the adsorption of the gas reducing the surface tension which matters. The pressure of gas in the critical bubble will reduce its size and will also affect the vapor pressure of the liquid, and corrections for this can be applied. These aspects are discussed in more detail below. Nonidealities in the gas phase or in solution may also be influential. Nonetheless, given that the size of the surface tension reduction effect is minimized or absent with helium, it is not surprising to see helium at the top of the list of supersaturations measured experimentally (see Table 6), with a ratio $R_{\text{theory/experimental}}$ (see below), close to that measured for water cavitation, Table 3, and noticeably smaller than for all other gases. In other words,

helium is not acting as a surfactant, so that the nucleation process is somewhat similar to that found in unary bubble nucleation systems, with the reductions noted above. It is probably also relevant that helium has the lowest solubility in water of any common gas. The theoretical calculation of Ward et al.¹ for the case of a dilute, nonideal gas should apply to this case, and the scale of correction to the nucleation rate calculated therein is expected to be appropriate here.

While the surfactant property of simple gases for aqueous solutions is a well-established fact, reports of organic gas adsorption causing reduction of surface tension for organic solvents seem to be restricted to Lubetkin and Akhtar.³⁸ For inorganic gases dissolved in organic liquids, data are available for N_2 gas in various organic solvents, reported by Kwak and Kim³⁹ and Rubin and Noyes.⁴⁰ The effects of dissolved CO_2 on bubble nucleation thresholds in three organic liquids were reported by Mori et al.⁴¹ The conclusion remains the same: gases are generally surface active in liquids. The mechanism of this action is not clear. For aqueous systems, there is a correlation between the water solubility of the gas and the degree to which it lowers the surface tension. Figure 4 has the summary. In the figure, k_H is defined by $x = k_H p$, where x is the gas mole fraction in the aqueous phase, and p is the partial pressure of the gas in atmospheres. Larger values of k_H thus denote gases that are more soluble. The correlation between solubility and the b coefficient is convincing, though by no means perfect. Thus, the largest lowering of the surface tension occurs for the most soluble gases: as an approximation, Γ (the surface excess of the gas surfactant) is roughly proportional to the concentration of gas molecules in solution.

Turning to Figure 5, there is also a correlation between the b coefficient and the measured critical supersaturation

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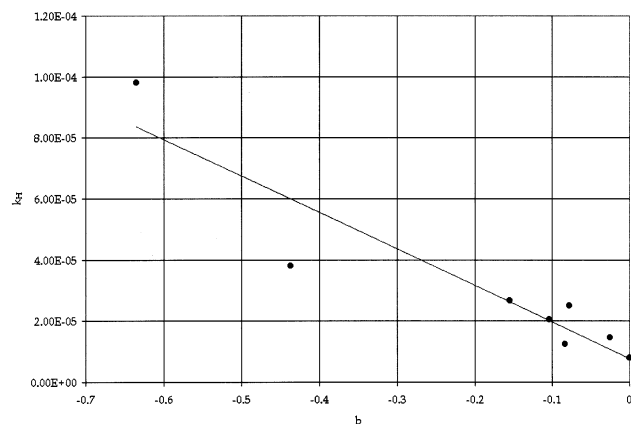


Figure 4. The plot of the Henry's law constant, k_H , against the first coefficient of the pressure dependence of the surface tension, b . The more soluble the gas (the larger k_H), the greater the magnitude of the coefficient.

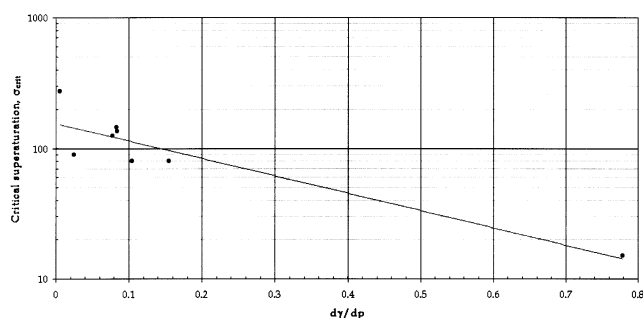


Figure 5. The experimentally determined critical supersaturation needed to cause appreciable bubble nucleation correlates with the b coefficient (plotted here as dy/dp). The smaller the coefficient, the greater the critical supersaturation needed to cause nucleation. This clearly fits with the notion that the gases which cause the least reduction in surface tension will nucleate at the highest supersaturation (closest to the predictions of the theory), thus emphasizing the importance of this gas property for bubble nucleation.

needed to cause bubble nucleation. This is a further indication that the reduction in surface tension caused by gas adsorption governs the bubble nucleation rate.

Data

We now examine the data from the literature for the three types of bubble nucleation mentioned earlier: boiling, cavitation, and gas bubble formation. In each case, the attempt is to make an objective judgment of how well classical nucleation theory accounts for the data. To have an objective criterion for judgment, the ratio, $R_{\text{theory/experimental}}$, of the appropriate parameter (superheating, supersaturation) is used. This ratio is then used to evaluate how well classical nucleation theory accounts for the experimental results. Obviously, ratios near 1 indicate agreement with the theory, while the standard deviation (SD) of the ratios indicates the spread. The sample size for some of the data is rather small, and no particular level of statistical significance is claimed for this analysis: the data are suggestive rather than definitive.

Boiling. The behavior of unary bubble nucleation systems is the foundation from which to make a judgment. In Table 2 are shown data for boiling nucleation, mostly derived from drop explosion experiments, which are generally regarded as the most reliable data available. The last column lists the values of the ratio $R_{\text{theory/experimental}}$,

while the last row gives a statistical summary of the mean and standard deviation for all the $R_{\text{theory/experimental}}$ values.

Both the early, relatively unsophisticated experiments reported in Table 2A and the later, more accurate methods in Table 2B give values for the mean of the parameter $R_{\text{theory/experimental}}$ close to 1, with small values of the standard deviation. Clearly, the classical nucleation theory very accurately accounts for the boiling kinetics of a wide range of liquids.

Cavitation. Turning next to the case of cavitation, in Table 3 are summarized the results for a variety of liquids, including mercury. The mean and standard deviation are based on the data excluding mercury, which appears to be anomalous. The agreement of the classical theory with these data is good, but clearly not as good as for the formation of bubbles by boiling. The spread of the data is also wider here than for the boiling data, and this may be due to the effects of heterogeneous nucleation. It may also be relevant that the two cases where the deviation appears to be greatest are for the liquids with the highest surface tensions, water and mercury.

Gas Bubble Nucleation. (1) *Chemically Generated in Aqueous Media.* Most of these data (Table 4) are from experiments performed by Noyes and co-workers. All the reactions involved have ionic materials either as reagents or as products, or both. The data therefore relate to high (and necessarily variable) ionic strength media. The ionic strength is known⁴⁰ to have a significant effect on bubble nucleation. Furthermore, ionic species are negatively adsorbed at the solution/gas interface and are known to raise the interfacial tension. This may counteract to some extent the effect of the gas in lowering the surface tension, particularly for gases with small values of b , like H_2 .

(2) *Electrochemically Generated in Aqueous Media.* Many of the same remarks as made above need to be repeated for this data set (Table 5): electrochemical bubble generation always involves high ionic strength media. There is an additional factor which may be relevant. The supersaturation required to cause growth of a bubble is strongly dependent on the bubble size (because of the Laplace pressure), so the use of growth rates of bubbles to measure supersaturations has to take the bubble size into account.

(3) *Generated by Pressure Release in Aqueous Media.* Some of these data (Table 6) are at high ionic strength: Gerth and Hemmingsen⁵¹ used solutions of various salts (KNO_3 , KCl , succinic acid in the range 2–6 M). They found strong effects for the presence of salts and for crystals produced from the supersaturated salt solutions. The results quoted for Ar and N_2 were influenced by the presence of salts in this way. The other data are for pressure release with distilled water as the solvent. The last entry in the table is for repetitive bubble release from

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Table 2. Calculated and Measured Values of the Superheat Required for Boiling^a

(A) Calculated and Early Experimentally Measured Values of the Superheat Required for Boiling

liquid	expt boiling temp (K)	calculated	$R_{\text{theory/experimental}}$	liquid	expt boiling temp (K)	calculated	$R_{\text{theory/experimental}}$
water	543	539	0.99	<i>n</i> -heptane	484	485.8	1.01
methanol	453	435	0.90	<i>i</i> -pentane	411	410.1	0.99
ethanol	474	444	0.85	cyclopentane	453	451	0.99
diethyl ether	416	400	0.89	methylcyclopentane	473	470	0.99
benzene	480	476	0.98	cyclohexane	489	492.3	1.02
chlorobenzene	523	534	1.04	diethyl ether	420	417	0.98
<i>n</i> -pentane	419	419.5	1.00	mean \pm SD			0.97 \pm 0.05
<i>n</i> -hexane	455	453.3	0.99				

(B) Calculated and More Recently Measured Values of the Superheat Required for Boiling

substance	boiling point (1 bar)	measured superheat limit	calculated superheat limit	$R_{\text{theory/experimental}}$	substance	boiling point (1 bar)	measured superheat limit	calculated superheat limit	$R_{\text{theory/experimental}}$
methane	-161.5		-107.5		chloroform	61.7	173.		
ethane	-88.6	-4	-3.5	0.88	2,3-dimethylbutane	58.0	173.2	175.9	1.02
fluorethene	-72.2	16.9			acetone	56.2	174.		
sulfur dioxide	-10.	50.			cyclopentene	44.2	173.2		
propene	-47.7	52.4	50.3	0.96	perfluorooctane	94.8	183.8	185.2	1.01
propane	-42.1	53.0	55.3	1.04	cyclopentane	49.3	183.8	173.2	0.94
1,1-difluoroethane	-24.7	70.4			hexane	68.7	184.	184.3	1.00
propadiene	-34.5	73.			methanol	65.0	186.0	186.5	1.00
cyclopropane	-32.9	77.5			ethanol	78.5	189.5	191.8	1.01
propyne	-23.2	83.6	88.2	1.06	1-hexyne	71.3	192.		
2-methylpropane	-11.8	87.8	87.7	1.00	hexafluorobenzene	74.5	194.7	195.4	1.00
chloromethane	-24.2	93.0			methylcyclopentane	71.8	202.9		
2-methylpropene	-6.9	96.4	99.3	1.03	perfluorononane	114.5	205.3	205.7	1.00
1-butene	-6.3	97.8	100.2	1.02	heptane	98.0	214.	214.5	1.00
chloroethene	13.9	100.9			2,2,4-trimethylpentane	99.2	215.3	214.9	1.00
1,3-butadiene	-4.4	104.1			cyclohexane	80.7	219.6	216.3	0.98
butane	-0.5	105.	105.2	1.00	perfluorodecane	133.0	223.9	223.1	1.00
trans 2-butene	0.9	106.5			benzene	80.1	225.3		
perfluoropentane	27.0	108.3	108.9	1.01	1,3-dimethylbenzene	139.1	235.		
<i>cis</i> -2-butene	3.7	112.2			1-octene	121.3	237.1		
2,2-dimethylpropane	9.5	113.4			methylcyclohexane	100.9	237.2	232.0	0.98
ethyl chloride	12.3	126.			octane	125.7	239.8	242.7	1.01
perfluorohexane	50.9	136.6	137.4	1.01	chlorobenzene	132	250.		
2-methylbutane	27.9	139			bromobenzene	156.	261.		
1-pentene	30.0	144.	141.9	0.99	aniline	184.1	262.		
diethyl ether	34.5	147.	145.	0.99	nonane	150.8	265.3	262.0	0.99
pentane	36.0	147.8	148.3	1.00	decane	174.1	285.1	282.8	0.99
perfluoroheptane	70.9	161.6	161.2	1.00	cyclooctane	148.5	287.5		
carbon disulfide	46.3	168.			mean \pm SD				0.997 \pm 0.03

^a Table adapted from M. Blander (ref 42) and Blander and Katz (ref 43); results calculated using a variant of eq 9.**Table 3. Calculated and Theoretical Fracture Tensions for Various Liquids at 20 °C^a**

liquid	theoretical fracture tension/bar	measured fracture tension/bar	$R_{\text{theory/experimental}}$
water	1380	270	5.11
chloroform	318	290	1.10
benzene	352	150	2.35
acetic acid	325	288	1.13
aniline	625	280	2.23
carbon tetrachloride	315	275	1.15
mercury	23100	425	54.35
mean \pm SD			2.18 \pm 1.55

^a Data from Briggs (ref 44).

a site where no nucleation was occurring: the bubbles were growing and detaching without a nucleation step. This last point has not been included in the statistical summary.

(4) *Nonaqueous Liquids*. The first set of data (Kwak and Kim) in Table 7 was measured using a pressure release method. The authors claim that the bubble nucleation was homogeneous, but the evidence is not cited in the paper. The second data set is based on chemical release

Table 4. Supersaturations Needed to Cause Bubble Nucleation in Aqueous Solutions^a

gas	measured	references	$R_{\text{theory/experimental}}^b$
N ₂	100–140	5, 51	14–10
N ₂	50	40	28
O ₂	100–150	5	14–9
O ₂	95–127	45	15–11
H ₂	80–90	46	17–14
CO	80–90	5	18
CH ₄	80	5	18
N ₂	19–30	46	70–47
O ₂	50	45	87–28
NO	16	46	88
CO ₂	10–20	5	140–70
CO ₂	4.62	47	303
mean \pm SD			51 \pm 73

^a Supersaturations generated by chemical means. Variable but generally high ionic strength. ^b Calculation for a gas dissolved in water gives a value for σ_{crit} of about 1450.

of the gas concerned in the solvent listed; the effect of the added ionic species is likely to be significant here. The third set of data is for a combined pressure/temperature experiment, with data for a few concentrations of gas in each case. The ratios have been estimated by extrapolation.

Table 5. Experimental and Theoretical Values for Electrochemically Induced Supersaturation^a

Section A			
author(s)	σ (c_e/q_b) or ($c_e - q_b$)	reference	
Sides	~ 100	48	
Westerheide & Westwater	8–24	49	
Dapkus & Sides	9–16	14	
Shibata	7–70	13	
Glas & Westwater	see section B below	50	
mean \pm SD		93.8 \pm 79.3	
Section B			
H ₂	O ₂	CO ₂	Cl ₂
1.54	1.36	1.08	1.018
19.9	15.4	1.64	1.324
mean \pm SD			856 \pm 516
overall mean \pm SD			100 \pm 69

^a Aqueous solutions of high ionic strength.**Table 6. Supersaturations Needed to Cause Bubble Nucleation (Mostly Heterogeneous) in Water or Aqueous Solutions^a**

gas	measured	references	$R_{\text{theory/experimental}}^b$
He	230–320	52, 37	6–4
Ar	110–160	37, 5, 51	13–9
N ₂	100–190	37, 52	14–8
O ₂	100–150	37, 5	14–9
O ₂	95–127	45	15–11
H ₂	80–100	46	17–14
CO	80	53	18
CH ₄	80	5	18
N ₂	20–30	46	70–47
O ₂	16–50	45	87–28
NO	16	46	88
CO ₂	10–20	5	140–70
CO ₂	5.4–7.6	9	260–184
Cl ₂	5	54	280
CO ₂	1.3–2.1	8	1077–667
mean \pm SD			74 \pm 96

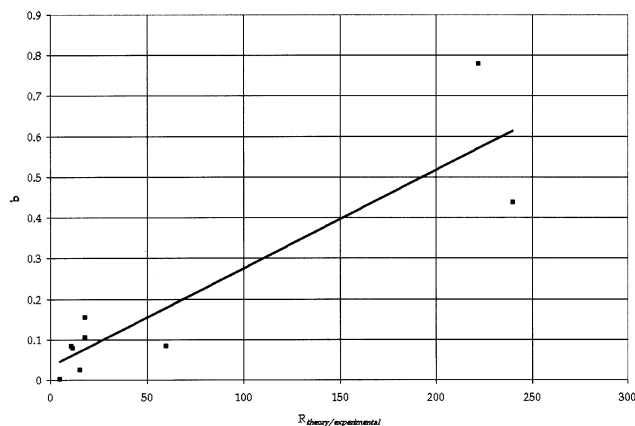
^a Supersaturations generated by pressure release. ^b Calculation for a gas dissolved in water gives a value for σ_{crit} of about 1450.**Table 7. Homogeneous N₂ & CO₂ Bubble Nucleation in Nonaqueous Liquids**

liquid	theory	measured	$R_{\text{theory/experimental}}$
methanol ^a	250	90	3
ethanol ^a	252	80	3
chloroform ^a	330	70	5
carbon tetrachloride ^a	326	53	6
benzene ^a	361	35	10
<i>n</i> -hexane ^a	184	56	3
ethanol ^b	252	31	8
acetonitrile ^b	282	47	6
dioxane ^b	316	37	9
acetic acid ^b	392 [#]	33	12
DMSO ^b	365	95	4
Freon 22 ^c		[289.35 K]	
propane ^c		[287.05 K]	6
i-butane ^c		[347.45 K]	
mean \pm SD			6 \pm 3

^a Data from ref 39. ^b Data from ref 40. ^c Data from ref 41.

The case that the nature of the gas is important to bubble nucleation in binary systems thus rests on good experimental data. The nearly 2 orders of magnitude variation in the $R_{\text{theory/experimental}}$ ratio shown in Table 6 is related to the 2 orders of magnitude variation in the b coefficient seen in Table 1. This relation is plotted in Figure 6. The correlation is far from perfect but clearly shows the trend.

Quantitatively, the magnitude of the mean value of $R_{\text{theory/experimental}}$ is close to 1 for boiling and close to 2 for cavitation, both with rather small ranges of values. For

**Figure 6.** The effectiveness of the gas in reducing the surface tension (the b coefficient) correlates reasonably with the parameter $R_{\text{theory/experimental}}$. The greater the effect of the gas on the surface tension, the greater the disparity between experiment and theory. This is clear evidence of the importance of this gas property in the nucleation kinetics.

gas bubble nucleation, it has an order of magnitude of ~ 100 and, as seen in Table 6, has a range of values from $R_{\text{theory/experimental}} = 4$ to 280. This emphasizes that the gas species used obviously matters. Ascribing this important role to the dissolved gas does not reduce the importance of the other factors which have been listed earlier, for example, the distinction between homo and hetero nucleation, the importance of contact angle, or the importance of the presence of pre-existing Harvey nuclei.

Theory

The classical nucleation theory for the rate of heterogeneous nucleation of bubbles from a supersaturated solution, on a surface, is embodied in the equation of for example Ward et al. as modified by Lubetkin and Blackwell.⁵⁵

$$J = C \exp\left(\frac{-16\pi\gamma^3\Phi(\theta)}{3kT(\sigma P)^2}\right) \quad (2)$$

The quantity C is not truly a constant and is slowly varying with σ , but to a good approximation can be treated as constant. The chief experimental variable, σ , is the supersaturation of the gas in the liquid. The surface tension γ , of the liquid against the gas, is usually taken as being the surface tension of the liquid against air at 1 bar, or atmospheric pressure. Φ is a function of the contact angle, θ , and is given by

$$\Phi(\theta) = \frac{1}{4}(1 + \cos \theta)^2(2 - \cos \theta) \quad (3)$$

P is the applied pressure at which nucleation takes place (often atmospheric pressure), and σ is the supersaturation:

$$\sigma = \alpha - 1 = \frac{P_{\text{high}}}{P_{\text{eqm}}} - 1 \quad (4)$$

P_{high} is the pressure used to dissolve the amount of gas into the liquid, or the concentration achieved by the

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(54) Hillman, A. R. Personal communication.

(55) Lubetkin, S. D.; Blackwell, M. R. *J. Colloid Interface Sci.* **1988**, *26*, 610.

chemical or electrolytic reaction generating the gas, while p_{eqm} is the amount of gas soluble in the liquid at equilibrium under the conditions used, for a flat interface. This latter quantity is the measured solubility of the given gas in the liquid under the stated conditions. For a more accurate treatment under conditions where Henry's law does not apply (particularly at large p_{high}), the pressures should be replaced by fugacities, or they could be replaced with concentrations obtained experimentally:

$$\sigma = \frac{c_{\text{high}}}{c_{\text{eqm}}} - 1 \quad \text{or} \quad \sigma = \frac{f_{\text{high}}}{f_{\text{eqm}}} - 1 \quad (5)$$

The solubilities of all gases increase with increasing pressure. Thus, dissolving (or generating in situ) a gas at the high pressure (or high concentration) p_{high} and then releasing the pressure to the target pressure P in eq 2 will result in the imposition of a supersaturation. The nonideality of the solution phase (and the gas phase in the bubble) can be accounted for, as described by Ward et al.¹

$$\eta = \exp \left[\frac{\Omega(P - p_{\infty})}{kT} - \frac{c'_2}{c'_1} \right]$$

This gives an expression for the radius of the critical nucleus, r^* , in terms of the concentration of the dissolved gas, c_{high} , and the equilibrium concentration, c_{eqm} :

$$r^* = \frac{2\gamma}{\left(\eta p_{\infty} + \frac{c_{\text{high}}P}{c_{\text{eqm}}} - P \right)} \quad (6)$$

The definitions of the saturation ratio, $\alpha = c_{\text{high}}/c_{\text{eqm}}$, of $k_{\text{HP}} = c$, and of the supersaturation, $\sigma = \alpha - 1$ allow for some simplification:

$$r^* = \frac{2\gamma}{(\eta p_{\infty} + \sigma P)} \quad (7)$$

The factor

$$\eta p_{\infty} = p_{\infty} \exp \left[\frac{\Omega(P - p_{\infty})}{kT} - \frac{c'_2}{c'_1} \right]$$

increases the size of the denominator; thus it is immediately apparent that r^* is smaller than before and that nucleation will therefore be easier. Allowance can be made for the nonideality of the gas solution and of the gas mixture by using the activity coefficients, ν_{S} and ν_{V} :

$$r^* = \frac{2\gamma}{\left(\frac{\eta p_{\infty}}{\nu_{\text{V}}} + \frac{c_{\text{high}}P}{c_{\text{eqm}}\nu_{\text{S}}} - P \right)} \quad (8)$$

The full expression for the classical homogeneous nucleation rate is given by

$$J = \beta Z n \left(\frac{6\gamma}{m(3 - B)} \right)^{1/2} \exp \left(- \frac{H_{\text{V}}}{kT} \right) \exp \left(- \frac{4\pi r^{*2}\gamma}{3kT} \right) \quad (9)$$

where

$$C = \beta Z n \left(\frac{6\gamma}{m(3 - B)} \right)^{1/2} \exp \left(- \frac{H_{\text{V}}}{kT} \right)$$

The variables in C are the condensation coefficient (β), the Zeldovich nonequilibrium factor, Z , and the number of molecular sites per unit volume, n . B is a constant (approximately 1 here), m is the molecular mass of the gas, and H_{V} is the latent heat of vaporization. Generally, for the cases we are considering in this paper, the dissolved gas is present at relatively high concentrations, meaning that the vapor pressure of the liquid is small in comparison with the partial pressure of the dissolved gas. Simplification can be achieved since the assumption that the gas concentration is large is equivalent to the statement that the denominator in the nucleation equation, while retaining the same form as before, now represents the dominance of the dissolved gas in the critical nucleus. Neglecting the term in ηp_{∞} in comparison with σP becomes a better approximation as the proportion of gas increases, and the use of the eq 10 is a satisfactory approximation:

$$r^* = \frac{2\gamma_0}{p^* - P} \approx \frac{2\gamma}{\sigma P} \quad (10)$$

This approximation leads directly to the simplified expression for the rate of bubble nucleation, eq 2.

The Surface Tension, γ . The surface tension of a solution of a gas in a liquid will generally be different from that of the pure liquid, and the more gas that is dissolved, the greater the reduction from the surface tension of the pure liquid. With the possible exception of helium, all gases so far examined decrease the surface tension of water. The general increase in gas solubility with pressure implies that the decrease in surface tension gets larger with increasing pressure.⁵⁶ In short, gases act as surfactants and obey the Gibbs adsorption equation (Massoudi and King,⁵⁷ Lubetkin and Akhtar³⁸). Here, $\Gamma_{2,1}$ is the adsorbed amount of component 2 (the gas) as a result of the partial pressure, p_2 .

$$\Gamma_{2,1} = - \frac{p_2}{RT} \frac{d\gamma}{dp_2} \quad (11)$$

Consider the situation in a solution supersaturated to a degree σ . There is a quasi-equilibrium distribution of subcritical size bubbles of all sizes up to and including the critical size nucleus. The critical size nucleus is in mechanical (hydrostatic) equilibrium with the surrounding solution, but this is not the case for the other sizes of clusters. The frequency of capture of a monomer unit by critical size clusters is the frequency of nucleation, J .

The pressure in the critical cluster depends on its size, r^* , and the relationship between the quantities is expressed in the Laplace equation, which applies only at equilibrium:

$$\Delta p = \frac{2\gamma_0}{r^*} \quad (12)$$

Here, Δp is the excess pressure (above the applied hydrostatic stress) inside the critical nucleus as a result of its curvature. The surface tension γ_0 has generally been taken in the past as that of the water/air interface at 1

(56) Note that the thermodynamic effect of pressure on the surface tension should be separated from the effect of increased dissolution of the gas applying the pressure. Because of the very low compressibility of most liquids (and water in particular), the effect of pressure per se is negligible at normal pressures.

(57) Massoudi, R.; King, A. D., Jr. *J. Phys. Chem.* **1974**, *78*, 2262. Massoudi, R.; King, A. D., Jr. *J. Phys. Chem.* **1975**, *79*, 1670. Massoudi, R.; King, A. D., Jr. *Colloid and Interface Science*, Vol. III; Kerker, M., Ed.; Academic Press: New York, 1976; p 331.

bar. However, given the surfactant property of the gas, account should be taken of the reduction anticipated because of adsorption. The surface tension of the gas/liquid interface is approximately given by the expression

$$\gamma(p) = \gamma_0 + bp \quad (13)$$

or more accurately the equation would include the other terms in the expansion:

$$\gamma(p) = \gamma_0 + bp + cp^2 + dp^3$$

Substituting in eq 10,

$$r^* = \frac{2(\gamma_0 + bp^*)}{p^* - P} \approx \frac{2\gamma_0}{\sigma P} + 2b + \frac{1}{\sigma} \quad (14)$$

The coefficient b is negative; thus the second term represents a reduction in the size of the classical critical nucleus (which is given by the first term). The third term decreases in importance as σ grows. By contrast, the second term is invariant with σ and becomes increasingly important as the supersaturation increases. This formulation of the problem is neither complete nor correct since as it stands, r^* can become negative at large σ , when $|bp^*| > \gamma_0$. Nonetheless, it is a useful approximation for small σ .

Note that since the dissolved gas is the main contributor to the pressure in both subcritical and critical size bubbles, the necessary precondition for the lowering of the surface tension (the presence of a substantial pressure of surface active gas) is fulfilled. Here the assumption underlying this calculation is that the pressure is that given by the classical evaluation of the critical size, inserted in eq 10, using the value of γ_0 for the surface tension. The pressure having been evaluated, the reduction in surface tension appropriate to that pressure is calculated, and then that reduced surface tension is used to calculate J . This is the conceptual basis for eq 15:

$$J = C \exp\left(\frac{-16\pi(\gamma_0 + \sigma b)^3 \Phi(\theta)}{3kT(\sigma P)^2}\right) \quad (15)$$

This equation is incorrect since as σ increases, eventually $|\sigma b| > \gamma_0$, and then the exponent becomes positive and ceases to produce physically meaningful results. For $|\sigma b| < \gamma_0$, it is a useful approximation.

Another Approach. Clearly, eq 15 will give an upper bound on the value of σ_{crit} . Another approach would be to allow for adsorption to occur simultaneously with the formation of the subcritical bubble, rather than after it. Such a mechanism would result in a more substantial reduction in σ_{crit} , but there are difficulties in formulating the analytical solution to the complex kinetics. It is possible to give a qualitative description, however.

Let a bubble be created instantaneously of radius r . The pressure p' inside the bubble will be near the equilibrium value given by

$$p'' = p' + 2\gamma/r$$

Since in general, the value of r is not equal to the critical radius,⁵⁸ r^* , the system is not at equilibrium, but the closer the value of r is to the critical radius, the nearer

the system is to equilibrium. Immediately after its creation, the bubble will begin the various relaxation processes toward equilibrium. The expected changes include both the size of the bubble and adsorption at the gas/liquid interface. Three cases can be envisaged:

Case 1: $r > r^$.* If the radius exceeds the critical radius, the system will descend the free energy curve to larger bubble sizes: the phase transition has effectively been initiated.

Case 2: $r = r^$.* Let the bubble be at the critical size. What will happen to it? Classically, the answer is that this is a position of unstable equilibrium and that at the maximum in the free energy curve, any perturbation will cause the system to move to a state of lower free energy. Three subcases are possible. (1) First, consider the situation where there is no gain or loss of monomer units. Now, if factors other than the temperature and pressure are examined and, in particular, the possibility of adsorption is taken into account, it becomes an obvious question to ask, what happens to the surface tension? The new liquid/vapor interface created by the instantaneous appearance of the bubble is not at adsorption equilibrium with respect to the dissolved gas. Since the dissolved gas is positively adsorbed, the surface tension will fall as the adsorption proceeds. Clearly, in the process, the compression due to the surface tension is lessened, and the pressure inside the bubble may now be sufficient to resist (or exceed) this reduced compression; in other words, a new, smaller r^* is established, and the (now supercritical) bubble will become free growing.

If the possibility of addition or loss of a monomer is taken into account, as well as the adsorption, then other two other cases can be considered. (2) Addition of a monomer: the addition of a monomer unit to the critical bubble will certainly result in the system becoming supercritical, and it will descend the free energy curve; the system will undergo a phase change, as before. (3) Loss of a monomer: given a fluctuation which results in the loss of a monomer unit, the result depends on the relative magnitudes of the rate of the collapse of the incipient bubble and the rate of adsorption of the gas. The adsorption reduces the surface tension, and this in turn reduces the Laplace pressure causing the collapse. Provided that the rates are comparable, a new equilibrium position may be traversed, with a smaller critical size than that calculated by the "classical" procedure. Note the use of the word "traversed". Since the equilibrium is unstable, there is no reason for the system to come to rest at this new critical size: if the system can get to that point, it will probably traverse the new "critical" size and become free growing.

Case 3: $r < r^$.* This case is an extension of that considered in case 2 (subcase 3) above. If the size is more than one monomer unit below the classical critical radius, adsorption will take place, reducing the necessary radius. There will be some characteristic size of subcritical bubble where even at full adsorption, the surface tension will be sufficiently great to cause collapse of the incipient bubble. The net effect is that at this size, the system does not surmount the nucleation barrier. The key question is, how far below the classical critical size does this bubble have to be in order to be too small, or in other words, what is the new critical radius?

Discussion. Overall, the effect of the positive adsorption of a gas is to lower the surface tension in the incipient bubble. This results in shifting the critical size to smaller values. A bubble germ whose size would be subcritical when assessed by the classical theory may become supercritical when adsorption is taken into account. The

(58) The quantity r^* , referred to here as the critical radius, is actually the critical radius calculated according to the "classical" nucleation theory, for the supersaturation and other conditions prevailing, but taking no account of any possible reduction in the surface tension as a result of gas adsorption.

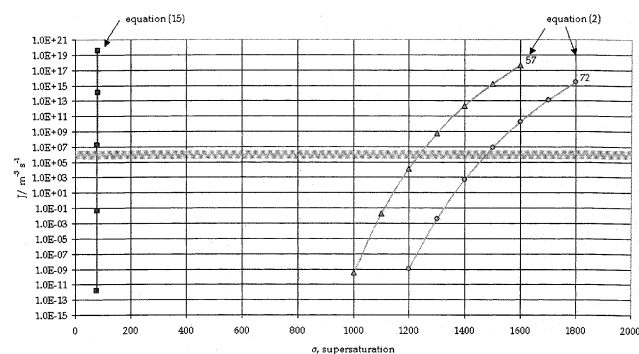


Figure 7. The rightmost curve represents the classical calculation of the bubble nucleation rate according to eq 2 for CO₂ in water of surface tension 72 mN m⁻¹. The curve next to it is the result of using the same theory but inserting the measured (ref 38) surface tension of a solution of CO₂ in water under 11 bar of pressure. The third curve is the result of using the present theory as embodied in eq 15. To give this result using the classical theory, a surface tension of 9 mN m⁻¹ would be required. It is expected that the curves become steeper as the interfacial tension becomes smaller.

threshold for nucleation has thus been lowered. The extent of this lowering will depend on several factors. Dominant among these will be the pressure in the bubble, which decides the extent of adsorption, the efficiency of the relevant gas as a surfactant (crudely, the b coefficient), and the relative speed of adsorption and bubble collapse. Most often, the relaxation time for nucleus formation will be greater than that for adsorption.⁵⁹ The gas pressure in the subcritical nucleus seems to be an inaccessible quantity. Not only is the system far from equilibrium, which makes estimation of the pressure rather uncertain, but also the distribution of subcritical bubble sizes makes the kinetics of the adsorption process difficult to calculate. These kinetics would be expected to be a function of the surface area to volume ratio for each bubble and thus be a function of the incipient bubble size distribution.

An estimate of the minimum size of this effect can be made by assuming that the pressure in the bubble will be that given by the Laplace equation at the (classical) critical size and that then adsorption equilibrium is achieved as a consequence of that gas pressure. This places an upper bound on the radius of the bubble, and thus a prediction of the minimum adsorption effect, and a maximum supersaturation necessary to cause nucleation. Equation 15 is based on this assumption and thus gives a minimum estimate of the reduction in the critical nucleus size. The plot in Figure 7 shows the extent of this reduction. The classical prediction, that is, eq 2, is shown for CO₂ bubble nucleation in water with the surface tension appropriate to pure water (72 mN m⁻¹). This is the line represented by circles labeled 72. The corrected classical theory allowing for the effect of applied pressure of dissolved gas, for water equilibrated with CO₂ at about 11 atm pressure (57 mN m⁻¹), is shown as the line labeled 57, with triangles for the points. The third line (squares) is a plot of eq 15 and corresponds to the classical result with a surface tension of 9 mN m⁻¹.

For the case of bubble nucleation in water at room temperature, with the surface tension of the water/air interface at 72 mN m⁻¹, eq 2 predicts that a bubble threshold rate of 10⁶ m⁻³ s⁻¹ for homogeneous nucleation will be achieved when the supersaturation is about 1450. On the same figure, the curve for an interfacial tension

Table 8

quantity	unit	value
C	m ⁻³ s ⁻¹	1×10^{35}
γ_0	N m ⁻¹	72×10^{-3}
b	N m ⁻¹ Pa ⁻¹	-7.79×10^{-9}
$\Phi(\theta)$	dimensionless	1
k	J K ⁻¹ molecule ⁻¹	1.38×10^{-23}
T	K	2.93×10^2
P	Pa	101322
σ	dimensionless	[79] – derived
J	m ⁻³ s ⁻¹	1×10^6

of 57 mN m⁻¹ is shown: this corresponds to the measured value for CO₂/water at 11 bar pressure. This level of dissolved CO₂ was seen experimentally to be enough to cause very rapid bubble nucleation. This corresponds to a supersaturation of $\sigma \sim 10$. The plot on the left in the figure (marked with squares) was obtained by inserting the values given in Table 8) into eq 15, thus calculating the critical condition, $\sigma_{\text{crit}} \sim 79$.

The surface tension ($\gamma_0 + \sigma b$) at the critical supersaturation was about 9 mN m⁻¹. To produce an agreement with the experimental result that bubble nucleation is rapid at $\sigma \sim 4$, one needs a value for $\gamma = 4$ mN m⁻¹. A relatively modest change in the value of b would produce a numerical agreement with experiment. The value of b used here is the published value from Massoudi and King.³⁶ Lubetkin and Akhtar have measured this coefficient, but only for low pressures (0–11 bar), and obtained a somewhat larger value ($b \sim 1.2 \times 10^{-8}$). Using this value gives much closer agreement with the experimental result, but this is deceptive, since the plot of surface tension versus pressure is very nonlinear in this low-pressure range,³⁸ and the extrapolation to the pressures in the critical nucleus would give a significant overestimate of the reduction in surface tension.

This failure to predict exactly the experimental result is in line with the expectation that eq 15 will give a minimum reduction in σ_{crit} . To see why this is so, note that in deriving eq 15, conceptually it was assumed that the critical size was established (which is at mechanical equilibrium, by definition) and only then was adsorption allowed to occur, and the surface tension was calculated, appropriate to the “equilibrium” set of conditions. Of course this procedure is a conceptual one only, since if adsorption equilibrium is proceeding, mechanical equilibrium is by definition unattainable. The purpose in deriving eq 15 was to set a minimum for the size of the effect. Allowing adsorption equilibration to take place concurrently with the other adjustments (for example, size) gives the possibility of a greater reduction and thus would predict a lower σ_{crit} . Making allowance for nonideality in the bubble and in solution would bring such agreement much closer. The use of the simplified denominator in eq 15, with its assumption of ideality, and its reduced values of the pressure in the critical bubble, significantly increases the predicted σ_{crit} . In other words, beyond eq 15, no attempt has been made to bring the theoretical prediction more in line with experiment; this would simply obscure the underlying processes.

Finally, note that no account has been taken in this analysis of the possible reductions in σ_{crit} due to heterogeneous nucleation. Clearly, values of $\Phi(\theta)$ could be chosen to bring the experiment and the theory into register, but this is equally true for the classical theory and would add no fresh insight.

The Nature of the Gas. The answer to the question posed by the title of this paper is that dissolved gas reduces the surface tension, and reduced surface tension causes

(59) See the discussion by J. P. Hirth following: Ward, C. A.; Balakrishnan, A.; Hooper, F. C. *J. Basic Eng.* **1970**, *92*, 695.

a dramatic lowering of the threshold for nucleation. Generally speaking, the biggest discrepancy between theory and experiment is found for gas bubbles nucleating in water, with more soluble gases giving bigger effects than less soluble ones. The disagreement is reduced when looking at lower surface tension liquids with a single gas, or essentially eliminated when one looks at cavitation or boiling in a single-component system. The explanation advanced here is that gases act as surfactants, and at the pressures in subcritical nuclei, the adsorption of the surfactant gas is sufficient to reduce the size of the critical nucleus to the point where nucleation occurs readily at low supersaturations. Water as the carrier liquid for the gas bubble nucleation shows the strongest effects, since it has a unique combination of high surface free energy, coupled with good solvency for a wide variety of gases. Lower surface free energy liquids are generally much closer to their critical points than is water, and they are correspondingly less affected by gas adsorption. Examples include N_2 in diethyl ether where the theoretical calculation was performed by Ward.³⁰ Experimental data for this system are given in Forest and Ward.⁶⁰ Results for N_2 bubble nucleation in other relatively low surface tension, organic liquids are given in Table 7.

Finally, the nucleation is almost certainly purely homogeneous in the case of drop explosion experiments, may be a mixture of homo and hetero nucleation for the cavitation experiments, and will be largely hetero nucleation in the case of gas bubble nucleation. The relevance of this is that for homo nucleation, all conditions are the same for each nucleation event, but for hetero nucleation, the specific circumstances of the active site are expected to vary. The phenomenon of nucleation rate dispersion³⁴ is an expression of this underlying fact. Thus, one would expect the spread of the measured critical supersaturations to be in the order hetero/homo mixed nucleation > pure hetero > pure homo, which is consistent with the summary in Table 9.

(60) Forest, T. W.; Ward, C. A. *J. Chem. Phys.* **1977**, *66*, 2322; **1978**, *69*, 2221.

Table 9. Summary Comparison of Theoretical Predictions and Measured Drives Required for Bubble Nucleation

system	average $R_{\text{theory/experimental}}$ \pm SD	comment
boiling (single-component system)	0.997 ± 0.03	homogeneous
cavitation (single-component system)	2.18 ± 1.55	homogeneous (?)
single gas (N_2 , from various organic liquids)	6 ± 3	homogeneous (?)
various gases (from water)	70 ± 84	homo/heterogeneous

A quantitative theory accounting for at least a part of the effect is presented, based on the idea that in a critical nucleus, adsorption will take place, reducing the work of formation of the critical size bubble. This theory has several shortcomings, not the least of which is that it does not produce quantitative agreement with the experimental data, despite going a long way toward doing so. Qualitatively, an extension of this treatment is expected to improve the agreement further. This extension is based on the principle that adsorption will occur in subcritical nuclei, and depending on the rate at which the surface tension is reduced compared to the rate of collapse of the subcritical bubble, a new and smaller critical size may be established. It should of course be emphasized that the effects of nonideality, the effect of pressure on the vapor pressure, and the catalytic effects of hetero surfaces, and nucleation site geometry have deliberately been ignored. Any or all of these could be taken into account and together with the reduction predicted by eq 15 could bring the data and predictions into accord. This has not been done here in order to clearly separate the effects of gas adsorption from any other possible reasons for reduction in the critical supersaturation needed for gas bubble nucleation. These other corrections are established and well-known in the literature.

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