Formation of Gas Bubbles in Supersaturated Solutions of Gases in Water

The objective of this study is to develop a model and correlate it with experimental measurements for predicting the tolerable degree of supersaturation of gas-water solutions. This model is also capable of predicting quite accurately the cavitation phenomenon in water.

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SCOPE

When the pressure of a gas over a saturated liquid solution is gradually reduced, the pressure can be significantly lowered before bubbles appear. This phenomenon occurs in many processes in nature and in engineering; however, its prediction is not possible and its mechanism is not yet clearly understood.

The present research deals with the above phenomenon in the following experimental method: A pressure cell contains a small glass beaker filled with water or an aqueous solution. Gas is compressed into the cell to a desired pressure, thus saturating the water with gas. After attaining equilibrium, the pressure is gradually released and its value is recorded when bubbles first appear. The difference between the initial saturation pressure and the pressure at bubble appearance, termed "pressure difference for bubble formation" and designated by ΔP_n, is the key parameter associated with the phenomenon of homogeneous bubble formation.

The objectives of the present study are:

1. To develop a reliable method for performing experiments associated with homogeneous bubble formation.
2. To advance scientific knowledge and to acquire a better understanding of homogeneous bubble nucleation by performing experiments with various gases over a wide range of pressures.
3. To isolate dominant parameters governing the phenomenon, to study minutely their roles, and to establish a physical model for explanation of the phenomenon and for prediction of the pressure difference for bubbles formation in terms of measurable and known quantities.

The gas-liquid systems, investigated over a pressure range of 120 MN/m^2, are solutions of inert and noble gases in water and aqueous salt solutions. The gases investigated are helium, neon, nitrogen, and argon in distilled water, as well as nitrogen in aqueous solutions of cesium chloride and uranyl nitrate.

CONCLUSIONS AND SIGNIFICANCE

The significant results obtained are as follows.

1. On release of pressure over a saturated solution of gas in water or aqueous solution, minute gas bubbles suddenly appear throughout the liquid volume. This takes place only after a certain pressure difference has been reached, typically characteristic of the gas used.
2. The pressure difference for bubble formation, ΔP_n, an expression for the degree of supersaturation which a solution can tolerate, has been observed to be constant. It is a distinguishing quality of the entire range of pressure, tested in experiments for each gas under investigation, with the exception of argon (which forms hydrates). The values of these pressure differences at approximately 303 K are:

Helium = 42.0 ± 1.4 MN/m^2
Neon = 32.4 ± 1.4 MN/m^2
Nitrogen = 13.8 ± 1.4 MN/m^2
Argon = 13.1 ± 1.4 MN/m^2
(in a low-pressure range,
up to 34.5 MN/m^2 where
hydrates are not formed).

The characteristic pressure difference for each gas is not influenced by solution density, surface tension, presence of the electrolyte, nuclear activity, or even by initial pressure from which the pressure release commences.

4. With the release of pressure, at values less than the pressure difference for bubbles formation there is no bubble formation even after a long lapse of time.
5. Experiments with organic liquids have not been successful because of the high volatility, under pressure, of the gas-liquid solutions formed.
6. A reliable engineering device for predicting ΔP_n, obtained for the first time, is the equation $\Delta P_n/P_c = 1.3(T/T_c)^{1.2}$.

From an analysis of the results, the following model can be established. In solutions of water saturated with gas, there are

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clusters of gas molecules acting as centers for bubble nucleation and whose specific number in the solution, at a given temperature, is constant and typically characteristic of such water, independent of gas solubility, the type of gas, and the total pressure. Each cluster is surrounded by a spherical space from which it is fed with gas molecules during the process of bubble eruption. It is assumed that when the pressure difference is smaller than a certain critical value, the process taking place in the solution is diffusion of gas molecules to the clusters which are, in fact, minute gas bubbles. At a pressure lower than the initial equilibrium pressure, these minute bubbles are formed and destroyed in a rapid dynamic process, where the process of diffusion is not rapid enough so as to cause bubble growth. At values above the pressure difference for bubbles formation, the nature of the process in the solution changes to "forced convection" induced by pressure difference between the gas molecules dissolved in the solution, equal the initial equilibrium pressure above the solution, and that within the minute bubbles, equal to the pressure above the solution when the bubbles form. At this point, phase separation occurs and gas bubbles are formed. By the application of thermodynamics of irreversible processes, appropriate equations were developed for the rates of entropy production in the diffusion as well as for convection processes. It is assumed that the point of bubble formation is precisely at the time when the entropy production of the diffusive process attains the value of convection dissipation. Thus, by equating the two dissipation functions, the radius *a* of the spherical space for bubble formation, a new concept defined in this work, was obtained denoted by $a = 64\, D\mu V_k / \Pi N \sigma^4 \Delta P_n$

By the substitution of the values of ΔP_n obtained from experiments for the different gases under investigation, a constant value of $a = (159 \pm 13) \times 10^{-10}$m was obtained for water at 303 K. Thus, an additional tool is provided for a binary mixture, consisting of water and a dissolved gas, to predict ΔP_n, using the above equation, a function of measurable quantities.

A noteworthy aspect of the results of this research is their relation to the behavior of pure water in cavitation, superheating, and supercooling. In calculating the pressure difference at 303 K to "tear" water (cavitation) according to the theoretical model developed here, a value very close to the experimental one was obtained. It was assumed that possible supersaturation phenomena—superheating and boiling, supercooling and crystallization—as well as gas-supersaturated solution and formation of bubbles, are all, in principle, similar and associated with homogeneous nucleation phenomena. This assumption made it possible to calculate the radius *a* of the spherical space for the formation of bubbles and crystals. The calculations also yielded the dependence of *a* on temperature. Generally, *a* increases with the increase of temperature except for the anomalous region of water (273–277 K) where there is a sharp increase in the value of the radius, with the decrease of temperature below 277 K.

INTRODUCTION AND OBJECTIVES

The phenomenon of bubble formation in gas-supersaturated liquid solutions, after a significant reduction of total pressure over the solution, is widely known in nature and in industry. However, according to Danckwerts (1970) "there seems to be no way of predicting the degree of supersaturation which can be tolerated without the formation of bubbles." And as stated by Harvey (1975), "the results are difficult to predict, in that bubble formation cannot be defined closely in a physical law." In the formation of bubbles, a distinction is made between homogeneous and heterogeneous formations. In the case of homogeneous formation of bubbles, it is assumed that this process is closely associated with the nucleation of a group of dissolved gas molecules so as to form together an "embryo" (La-Mer, 1952), which is the nucleus for bubble growth. It is also assumed (Hirth et al., 1970; Swanger et al., 1972; Nikiforov, 1973; Himmelblau, 1969; Tucker et al., 1975) that a stable "embryo" is formed only after reaching a critical size, at which its free energy is maximal. With regard to heterogeneous nucleation, the formation of bubbles, which is a result of the decrease of pressure above a supersaturated solution, is undoubtedly due to tiny bubbles existing on the solid surface of a container, or on solid particles that are present in the bulk of the liquid as impurities.

The research on homogeneous bubble formation in gas-supersaturated solutions may be categorized into theoretical and experimental investigations. In the first category we may classify the investigations of Hirth et al. (1970), Swanger and Rhines (1972), Apfel (1972), Nikiforov (1973), and Yount and Kunkle (1975). This experimental work also is rather limited and an updated list contains the work of Buckles (1969), Mackay et al. (1971), Lever et al. (1971), Hills (1971), Walder and Evans (1974), and Harvey (1975), as well as that of Stroud (1975), Tucker and Ward (1975), Yount and Strauss (1976), Gerth and Hemmingsen (1976), Forest and Ward (1977), and Kunkle (1979). However, it seems that only the investigations of Himmelblau (1969) and Hemmingsen (1970, 1975, 1977–1979, 1982), have a direct relevance to the subject under review.

The major conclusions drawn from the foregoing are as follows.

1. The experimental results do not confirm the theoretical equations for tolerable difference in pressure for bubble formation, and are three times lower than the values calculated by Swanger (1972) or Hirth (1970).
2. The existence of homogeneous nucleation, which is crucial for understanding the process of bubble formation, is still to be proved experimentally.
3. The theoretical investigations attribute a major role in the process of bubble formation to surface tension. However, the experimental results do not support this argument (Hemmingsen, 1977, 1978).
4. No attempt has yet been made to investigate and isolate the factors which influence homogeneous nucleation. No engineering elaboration of experimental results has yet been made for the establishment of predictive tools, or for a quantitative mechanism which would describe the phenomenon in terms of measurable quantities.

As a result of final outcomes stipuated herein, the objectives of the present research are specifically (a), advancement of knowledge and understanding of homogeneous nucleation of bubbles by performance of experiments with various gases, over a wide range of pressures (gas solubility); and (b), isolation of dominant parameters, observing minutely their roles and linking them to form a quantitative model, in order to understand and predict the phenomenon on a transport level, using measurable thermodynamic quantities.

METHOD OF THE RESEARCH

Homogeneous bubble formation has been investigated as follows.

A pressure cell contains a small glass beaker filled with water or an aqueous solution. Gas is compressed into the cell up to a desired pressure, thus saturating the water with gas. After attaining equilibrium, the pressure is slowly released and, just at the moment of bubble formation, the pressure is observed and recorded. This process is continued until the pressure is reduced to that prevailing in the regime of bubble formation by heterogeneous nucleation. The difference between the initial saturation pressure and the pressure at which bubbles appear is called the pressure difference for bubble formation. It is designated by the symbol ΔP_n and is the central and most significant parameter in the present research.

Operating Conditions

Pressure. The major variable is obviously the total pressure. As reported in previous research work, bubble formation takes place in the heterogeneous regime where the total pressure is in the order of 25 MN/m^2. However, higher pressures are required in order to obtain homogeneous nucleation. This fact is also supported by Harvey et al. (1945), who reported that water compressed to about 100 MN/m^2 and brought back to atmospheric pressure exhibited a very peculiar behavior: it could be heated above 473 K without eruption of vapor. Moreover, it was possible to transmit acoustic waves at high frequency without cavitation or formation of bubbles. The reason is the removal of microcenters for nucleation under high pressure, due to their dissolution in water. Consequently, the present experimental system was designed with a view to operate at pressures reaching 120 MN/m^2.

Temperature. At high presures the compressed gas dissolves in water with a tendency to form solid hydrates (Marshall et al., 1964; Cook, 1961). Therefore, in order to avoid formation of hydrates the temperature should not be below 294 K (Marshall et al. 1964).

Purity. Bubble formation is sensitive to solid impurities such as dust, and even bacteria (size, 0.3–30 $\times$ 10^{-6}m), which might cause heterogeneous nucleation. As a result, filters of 0.15 $\times$ 10^{-6}m have been used to filter both gas and liquid.

Selection of Materials

Gases. Experiments at a high pressure require gases which have a low critical temperature and are also inert. This leads to selection of helium, neon, argon, and nitrogen. Krypton and xenon were rejected because they readily form hydrates at a low pressure (Marshall et al., 1964; Cook, 1961). Hydrogen and oxygen were rejected because of safety considerations.

Liquids. By fixing pressure and temperature ranges, two severe restrictions are imposed on the selection of a suitble liquid: a) it should maintain its molecular structure and transport properties in order to allow isolation of the dominant parameters; b) it should remain in the liquid state for over a wide range of pressures. The only liquid that completely satisfies these requirements is water, which is undoubtedly the most interesting liquid, and the most widespread solvent in nature.

Water. It is advantageous to review (Finkelstein, 1983) the following properties that are related to the molecular structure of water: 1) The wide range of the liquid state, between freezing and boiling points, despite the simple chemical structure of water, is due to hydrogen bonding. 2) The density of water changes by only 3.65% when the pressure is raised from atmospheric to 100 MN/m^2. For organic liquids, the density change is at least twice as great for the same pressure change. 3) Viscosity, heat capacity, and heat conductivity change less than 5% at 303 K in the above pressure range. By comparison, organic and other liquids exhibit a change of about 100 to 300%. 4) The diffusion coefficient of sparingly soluble gases in water does not significantly change with pressure, for the simple reason that $D\mu^{1.1}$ = constant, and due to the behavior of viscosity referred to in (3) above. 5) The index of refraction and the dielectric constant are related to molecular structure. The first property shows practically no change with pressure, while the second changes by less than 10% for a change in pressure of 150 MN/m^2. 6) Electrical conductivity is increased by less than 6% when the pressure is increased from atmospheric pressure to 100 MN/m^2.

As seen above, at room temperature and within a wide range of pressures, the change in the various properties of water is small. Hence it can be assumed that the molecular structure of water does not change significantly, and it is this factor that enables the isolation of dominant parameters of the process of bubble formation.

Water-Gas Solutions. The solubility of noble gases, inert gases, and nonpolar gases in water is very small, as a result of which their dilute solutions differ very slightly from water. However, they reveal certain characteristic behaviors, governed by the structure of water; these are as follows:

- The solubility of inert gases in water, at a high or low pressure, is smaller than in other solvents, by an order of magnitude.
- The solubility of gases in water decreases with the increase of temperature, which is just the opposite of behavior in organic liquids.
- The dissolution of gases in water is closely associated with a relatively high negative heat and entropy of solution, compared with other solvents.
- The partial molar volume of gases dissolved in water is significantly lower than in organic solvents. The dependence on pressure is extremely weak.
- The diffusion coefficient of a gas in water is smaller than in an organic liquid, without hydrogen bonding, but with the same viscosity.
- Inert and noble gases form hydrates with water.

Electrolyte Aqueous Solutions. Electrolytes cause the break-up and build-up of the molecular structure of water, according to their ionic radius and charge. Ions which break the structure (for example, cesium ions), decrease the viscosity of water. On the other hand, small ions and the hydroxyl group build up a structure and thus increase the viscosity of the solution.

EXPERIMENTAL

The detailed structural design of the experimental system, which has to withstand approximately 138 MN/m^2, together with safety precautions, appears elsewhere (Finkelstein, 1983).

Experimental System

Figure 1 gives a general description of the system. The center of the system is the pressure cell in which a glass beaker of 0.02 m dia. and 0.012 m height is placed. The water height in the beaker is 0.007 m and its volume is approximately 2.10^{-6} m^3. The pressure cell is constructed of steel (SAE 4340), with 0.11 m O.D., 0.027 m I.D., and 0.255 m. It contains three sapphire observation windows sealed with O-rings.

Experimental Runs

An experimental run consists of the following steps: 1) Introduction of water (in the glass beaker) into the pressure cell. 2) Creation of a vacuum in the pressure cell and flushing it seven times up to 13.8 MN/m^2 with the tested gas. 3) Compression of the tested gas to about *110 to 124 MN/m^2 at* 303 K. 4) Maintenance of the system at pressure for 48 h until equilibrium is reached. 5) Slow manual release of pressure through a throttle valve within 10 to 30 s. 6) Continuous visual observation of the solution in the beaker during pressure release. Observation is made through the sapphire windows, by means of a periscope. The pressure release continues as long as the solution remains transparent and clear. The moment bubbles are formed,

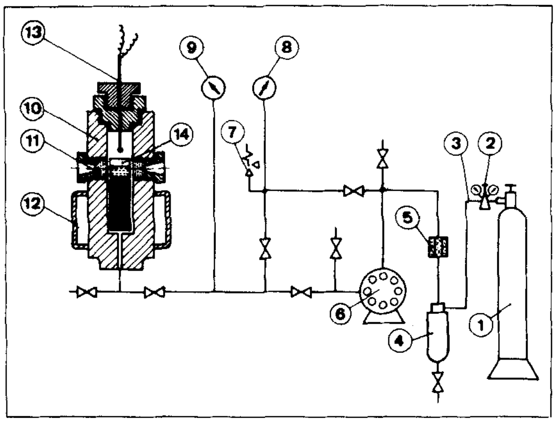

Figure 1. Experimental system.

1. Compressed gas cylinder
2. Pressure regulator (Matheson, Model 4)
3. Stainless steel pipe
4. Gas filter, 0.15 × 10^{-6}m
5. Additional filter, 5 × 10^{-6}m
6. Manual compressor for 138 MN/m^2 (AMINCO)
7. Pressure release valve
8. Pressure gauge, 34.5 MN/m^2
9. Pressure gauge, 207 MN/m^2
10. Pressure cell
11. Sapphire windows
12. Heating or cooling jacket
13. Thermocouple
14. Glass beaker

the solution loses its clearness at once and the release valve is closed. The pressure is recorded; subtracting it from the initial pressure yields ΔP_n. 7) After at least 24 h, the system is ready for another pressure-release run. 8) Pressure-release runs are continued until the pressure in the cell reaches about 27.6 MN/m^2. At that pressure, heterogeneous nucleation starts.

Taking into account the accuracy of the pressure gauge and the operator's response in closing the release valve, the accuracy of the pressure measurements is estimated to be ±1.4 MN/m^2.

Another technique, which employed a laser beam, was put into practice for the detection of bubbles. The beam was introduced through the solution and was not discernible when the solution was clear. At the time of bubble formation, a significant scatter of the beam occurred and the beaker grew bright. No advantage was gained by this method over direct visual observation, and it was therefore abandoned.

Seventeen runs were conducted, each consisting of five to ten pressure-release experiments. In these experiments, the following systems were tested:

1. Nitrogen (99.99%, Maxima) dissolved in double-distilled, 0.12 × 10^{-6} m filtered waters, as well as in completely unfiltered water.
2. Nitrogen (99.99%) dissolved in cesium chloride aqueous solution (1.072 kg cesium per 0.001 m^3 solution).
3. Nitrogen (99.99%) dissolved in uranyl nitrate aqueous solution (178.5 kg uranium per m^3). Solution activity was seven spontaneous fissions per h, 9,000 alpha decompositions per s.
4. Nitrogen (99.99%) dissolved in carbon tetrachloride.
5. Nitrogen (99.99%) dissolved in normal decane.
6. Nitrogen (99.99%) dissolved in 96.4% heavy water in water.
7. Neon (99.99%, Messer-Griescheim; 99.999%, Matheson) dissolved in distilled water.
8. Helium (99.999%, Messer-Griescheim) dissolved in distilled water.
9. Argon (99.99%, Maxima; 99.999%, Matheson) dissolved in distilled and filtered water.

Presure and temperature ranges varied from 20 to 138 MN/m^2 and from 298 to 303 K, respectively. A typical example of pressure-release experiments, belong to the nitrogen-distilled water system, is illustrated in Table 1. The interval between each run was somewhere between 24 and 72 hours.

TABLE 1. PRESSURE RELEASE EXPERIMENTS FOR NITROGEN-WATER

Run	Init. Pres. MN/m^2	Final Pres. MN/m^2	ΔP_n MN/m^2	Temp. K
1	135.1	121.3	13.8	300
2	120.6	106.2	14.4	300
3	104.8	89.6	15.2	298
4	89.6	75.8	13.8	298
5	75.8	62.1	13.8	298
6	110.3	96.5	13.8	303
7	96.5	82.7	13.8	303
8	82.7	68.9	13.8	303
9	68.9	55.2	13.8	303
10	55.2	41.4	13.8	303

RESULTS AND CONCLUSIONS

Summary of Results

1. Compression of argon and nitrogen in normal decane and carbon tetrachloride resulted in what could be termed "disappearance" of the liquid phase due to the formation of a solution, with high vapor presure (Poynting effect). Pressure release was performed later on, hence there was a decrease in temperature, causing homogeneous nucleation of liquid and the appearance of drops in the pressure cell space.
2. In contrast to the phenomenon of liquid evaporation with organic liquids, water did not evaporate. The height of the water in the glass beaker remained constant for months at the entire pressure range.
3. Experiments were conducted over a temperature range of 291 to 303 K, but the majority were at 303 K. In the course of the pressure release, there is a temperature drop in the pressure cell-vapor space of about 7 to 10 K for all gases tested. The temperature of the liquid in the beaker also dropped by 3 to 3.5K. The reason for this phenomenon is the almost adiabatic expansion of the gases.
4. Argon solution in water is completely different from solutions of helium, nitrogen, and neon in water. At temperatures of 291 to 293 K a compressed solution of argon in water formed a solid jelly. At 303 K a solid jelly is not formed, but the solution is very viscous. The viscosity of the solution decreases with reducing pressure, and at a low pressure (from 20 to 35 MN/m^2) its behavior is qualitatively similar to the other gas-water solutions.
5. By releasing the pressure above a saturated gas-water solution, small bubbles could be made to appear suddently throughout the liquid volume. This phenomenon occurred above a certain difference in pressure, which is typical for a given gas. This key pressure factor is called the pressure difference for bubble formation and is designated by ΔP_n.
6. The pressure difference for bubble formation in water is constant over the entire pressure range for all tested gases except argon. The mean values of ΔP_n are:

Helium = 42.0 ± 1.4 MN/m^2
Neon = 32.4 ± 1.4 MN/m^2
Nitrogen = 13.8 ± 1.4 MN/m^2
Argon = 13.1 to 5.5 ± 1.4 MN/m^2

7. ΔP_n is completely independent of temperature in the range of 293 to 303 K.

8. ΔP_n is the same after waiting for 24 hours to reach equilibrium, and after waiting for a month.

9. ΔP_n is repeatable for clean and unclean water, either filtered or unfiltered.

10. ΔP_n is not affected by the presence of a "break-up-structure" electrolyte dissolved in water.

11. ΔP_n is not affected by the solution density in the range of 1,000 to 1,800 kg/m^3.

12. ΔP_n is unaffected by the nuclear activity of the solution.

13. In a pressure release from an equilibrium pressure of about 34 MN/m^2 downward, heterogeneous nucleation of bubbles appears on the walls of the vessel and on its bottom.

14. In pressure-release experiments, at pressure changes smaller than ΔP_n no bubbles occur even after hours.

Summary of Conclusions

The conclusions drawn from the above results are:

a) Argon is a typical hydrate-forming gas in water, and as such causes a drastic change in the solution properties. In the following analysis we shall consider the behavior of helium, neon, and nitrogen at the entire pressure range. Argon will be considered only at a low-pressure range.

b) The concentration of dissolved gas shows an almost linear variation with pressure. Since ΔP_n is virtually a constant value which characterizes a certain type of gas, it can be assumed that at each outburst of bubbles a constant amount of gas is also liberated. This amount is a characteristic value of each gas in a gas-water system.

c) ΔP_n is independent of the solubility of gas. This follows from the constant value of ΔP_n, as well as from the fact that although helium and nitrogen have a similar solubility in the high-pressure range, their ΔP_n values are completely different.

d) Since ΔP_n is reproducible for each gas in many experiments, and for a clean and an unclean liquid, it follows that this phenomenon is dependent on the nature of the gas and the water in which it is dissolved, and that the nucleation is a homogeneous nucleation.

e) The aqueous gas solution surface tension is almost constant for all gases. Thus, the significant difference in the values of ΔP_n for vanious gases indicates that surface tension is not at all an influencing factor.

f) The diffusion coefficient of gas in water is not a dominant influencing parameter, For example, neon and nitrogen have similar diffusivities in water; nevertheless, their ΔP_n values are significantly different.

ANALYSIS OF THE RESULTS

Reduced Critical Properties Approach—Preliminary Analysis

Considering the significantly different values of the pressure difference for bubble formation in water for various gases, and its constant value for a certain type of gas over a wide range of pressures, led to the conclusion, as stated by Marcus (1977), that the interacting forces between gas molecules and water are small, and that the intermolecular forces between gas molecules in the liquid play a major role in the phenomenon of bubble formation. The fact that gas maintains its "independence" even when dissolved in a liquid, and that the dominating factor is the intermolecular forces between the gas molecules, led us to apply the corresponding states principle in order to correlate ΔP_n data with the critical properties of gas. This is presented in Figure 2, where a plot of $\Delta P_n/P_c$ vs. T/T_c for the various gases yields a straight line on a log-to-log scale. The line in Figure 2, and the data in Table 2, are correlated within experimental accuracy by the following equation:

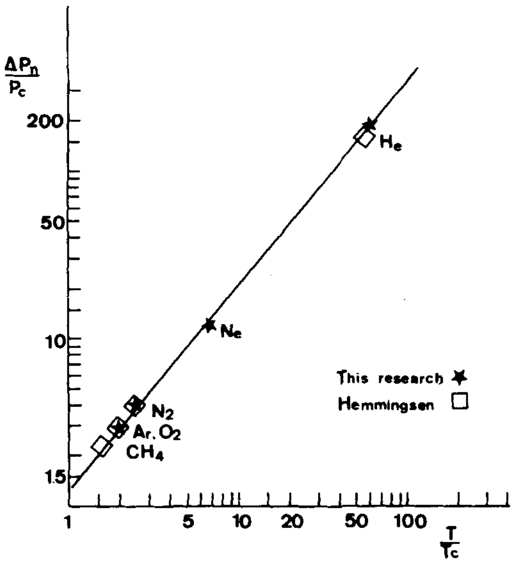

Figure 2. Reduced pressure difference for bubble formation as a function of reduced temperature.

$$\frac{\Delta P_n}{P_c} = 1.3\left(\frac{T}{T_c}\right)^{1.2} \tag{1}$$

Equation 1 is a very simple equation and, for the first time, an engineering tool is provided in terms of basic quantities for predicting the phenomenon of inert gas bubble formation in water.

The Physical Model

On the basis of experimental results and the conclusions drawn therefrom, the following physical model is suggested to explain the phenomenon of bubble formation in gas-supersaturated liquids: A solution of gas in water, at a certain temperature but within the pressure range under investigation, contains clusters of gas molecules which act as centers for bubble nucleation, whose specific number is constant and characteristic of the system. It does not depend on solubility, type of gas, or pressure. It can be assumed that for each cluster there is a symmetrical spherical space from which it is fed with gas molecules when the process of bubble outburst occurs. Some support to this assumption is given by observing the photographs taken by Hemmingsen (1982), where it is seen that the bubbles formed are uniform in size. It is further assumed that if the pressure difference is smaller than the pressure difference for bubble formation, ΔP_n, the process which takes place in the solution is the diffusion of gas molecules to clusters, which are in fact minute gas bubbles. These very small bubbles are formed and destroyed in a rapid dynamic process, and the process of diffusion in the solution is not sufficiently rapid so as to cause bubble growth. A steady-state condition is maintained by dissipative effects and no separation of phases occurs. Above the critical pressure difference ΔP_n, the nature of the process in the solution

TABLE 2. VALUES OF REDUCED PRESSURE FOR BUBBLE FORMATION AND REDUCED TEMPERATURES

Gas	$\Delta P_n/P_c$	T/T_c
Helium	184.1	57.7
Neon	11.9	6.8
Nitrogen	4.1	2.4
Argon	2.7	2.0

changes and mass transport is conducted by forced convection. This process is affected by the driving force, ΔP_n, namely the pressure difference between the pressure of gas molecules dissolved in water—which is equivalent to the initial equilibrium pressure (before the pressure release was started)—and the pressured inside the minute bubbles—which is equal to the total pressure above the solution at the point where bubbles appear. This is also the point where separation of phases takes place.

The model described herein is also supported by theoretical models of the structure of liquid water, where it is assumed that was contains structures of molecular clusters or "molecular cages" (Hildebrand et al., 1970). The latter form spaces in the bulk of the liquid, where dissolved gas molecules are concentrated. The number of such structures is constant but dynamic in behavior, and it is independent of the type of dissolved gas. As a matter of fact, it depends on the nature of the solvent, namely, water. The fact that ΔP_n for a certain gas is independent of pressure is explained by the constant structure of water over the pressure range investigated in the present research.

Quantitative Treatment of the Physical Model

The approach adopted here is based on themodynamics of irreversible processes. As shown later, appropriate equations have been developed for the rates of entropy production, or the dissipation function in the diffusion and convection processes. The key value, i.e., the critical pressure difference for bubble formation in terms of measurable quantities, is then obtained by comparing the two dissipation functions. The following assumptions are made in establishing the model:

a) The process and the system are isothermal.
b) Prior to the outburst of bubbles there is no net motion in the liquid.
c) Surface tension effects are negligible.
d) Viscosity of water and the diffusion coefficient of gas in water remain constant.
e) Pressure drop for bubble formation is a constant value for a certain gas, but this varies from gas to gas.
f) The number of centers for bubble formation and the spherical symmetrical spaces around them is a constant value and a characteristic number for water. Thus the radius of the spherical space is also a characteristic value for water.
g) The system boundaries, namely, the walls of the beaker, are much larger in comparison to the spherical radius.
h) As long as the pressure difference is smaller than the pressure difference for bubble formation, the gas molecules move in the liquid in a diffusion motion.
i) When a pressure gradient larger than ΔP_n is established, a stream of gas molecules appears in a spherically symmetrical motion toward the minute bubbles acting as centers for bubble formation.
j) The system may be considered as stable if the pressure difference is smaller than ΔP_n. The transition from a stable to an unstable state occurs at ΔP_n, and this is associated with a mass transport phenomenon.
k) The system and the phenomenon are designated "the transport phenomenon in a continuous hydrodynamic system." This definition is important for the proper selection of the manner in which the quantitative analysis of the results are to be treated.

Dissipation Function for Diffusion in Liquids, (Haase, 1969)

The dissipation function Ψ is generally defined by:

$$\Psi = T\frac{d_i s}{dt} \tag{2}$$

For a diffusive binary system in the absence of chemical reaction, external forces, viscous flow, pressure gradients on the liquid body, and where k designates the dissolved gas, Eq. 2 reads as follows:

$$\Psi = J_k \mathrm{grad}(-\mu_k^c) \tag{3}$$

μ_k^c is the chemical potential of the dissolved gas, solely dependent on concentration, and J_k is the diffusive flux.

In the present experiments

$$C_k = HP \tag{4}$$

where H is a constant.
Noting that

$$\mathrm{grad}\ \mu_k^c = \frac{\partial \mu_k^c}{\partial C_k}\ \mathrm{grad}\ C_k$$

and that

$$\overline{V}_k = \left(\frac{\partial \mu_k^c}{\partial p}\right)_T \tag{6}$$

where $\overline{V}_k$ is the partial molar volume of the dissolved gas, and that Fick's Law is given by

$$J_k = -D \cdot \mathrm{grad}\ C_k \tag{7}$$

finally yields

$$\Psi = HD\,\overline{V}_k\,(\mathrm{grad}\ P)^2 \tag{8}$$

The spherical radius around a center for bubble formation is designated by a. In a spherical geometry, and for a uniform gradient,

$$\mathrm{grad}\ P = \frac{\partial P}{\partial r} = \frac{\Delta P}{a} \tag{9}$$

The isothermal rate of entropy production in a hydrodynamic system in the absence of external forces, liquid flow, electrical or magnetic effects and chemical reaction, is given by

$$\frac{\partial s}{\partial t} = \frac{1}{T} J_k\ \mathrm{grad}\ (-\mu_k) \tag{10}$$

Thus the entropy production in a single spherical space, which follows from Eqs. 3, 8, 9, and 10, is given by

$$\frac{\partial s}{\partial t} = \frac{4}{3}\Pi a^3 \cdot \frac{1}{T} \cdot D \cdot H\overline{V}_k \left(\frac{\Delta P}{a}\right)^2 \tag{11}$$

In a solution, which contains n_B spherical spaces for bubble formation, the total entropy production will be:

$$\left(\frac{\partial s}{\partial t}\right)_{\text{total}} = \frac{4\Pi a n_B \overline{V}_k\,DH}{3T}(\Delta P)^2 \tag{12}$$

From the definition of the dissipation function in Eq. 2, the ultimate form of the dissipation function is:

$$\Psi = \frac{4\Pi}{3} a n_B\,DH\,\overline{V}_k(\Delta P)^2 \tag{13}$$

Dissipation Function for Convective Flow in Liquids

We have to calculate here the dissipation function for a convective flow of gas molecules in a liquid toward centers in which a new phase is created, namely, gas bubbles. We adopt here the approach which assumes that molecules are rigid spheres with a given diameter. The flow mechanism can be descried in two ways: The first is the mass transfer of gas molecules through a liquid medium, similar to the "molecular flow" through a membrane, namely Knudsen flow. The second mechanism is the flow of a fluid in a viscous medium, thus an application of the Hagen-Poiseuille equation, obtained from the Navier-Stokes equation, for the case of a one-directional slow flow, without velocity gradients in the fluid and without gravity forces.

We have tried to calculate the spherical radius a for bubble formation by the Knudsen equation; however, this yielded unreasonable results, namely, a smaller than 1.10^{-10} m. The reason for such results is that the Knudsen equation was developed for molecular flow in a solid capillary; hence it is not plausible that the liquid medium in the present case obeys the Knudsen equation. The second mechanism is based on the Hagen-Poiseuille equation; its justification would be agreement between the theoretical model and the experimental results.

In the following derivations we assume that dissolved gas molecules move in cylindrical ducts, the walls of which are the liquid, in a spherical symmetry toward the centers for bubble formation. The flow is slow, one-directional, with no velocity gradients in the liquid, hence viscous effects are negligible. In the absence of gravity forces, the following equation holds:

$$\frac{\partial V}{\partial t} = \frac{\mu}{\rho}\nabla^2 V - \frac{1}{\rho}\frac{\Delta P}{a} \tag{14}$$

where a is the spherical radius and $\Delta P/a$ is the pressure gradient due to the concentration gradient in the spherical space.

The denotation of

$$-\frac{\Delta P}{a} = G \tag{15}$$

yields at steady state and in cylindrical coordinates the following:

$$\frac{G}{\rho} + \frac{\mu}{\rho}\left(\frac{\partial^2 V}{\partial r^2} + \frac{1}{r}\frac{\partial V}{\partial r}\right) = 0 \tag{16}$$

The solution of the above equation for a cylinder with radius R, is (Batchelor, 1967):

$$V = \frac{G}{4\mu}(R^2 - r^2) \tag{17}$$

where

$$V_{\max} = V_{r=0} = \frac{GR^2}{4\mu} \tag{18}$$

The tangential stress along the walls of the cylindrical duct, at the critical gradient of phase separation, is obtained from Eq. 17, as follows

$$-\mu\frac{dV}{dr} = -\tfrac{1}{2}GR \tag{19}$$

Thus the friction force along the walls of a cylinder with length a is

$$2\Pi Ra\frac{1}{2}GR = \Pi R^2 Ga \tag{20}$$

The rate of the dissipation work in a pipe having the diameter of a gas molecule, R, dissolved in a liquid, is:

$$\frac{dW_{\text{diss}}}{dt} = \Pi R^2 GaV_{\max} = \frac{\Pi}{4}\frac{aG^2R^4}{\mu} \tag{21}$$

At the moment of the outburst of bubbles, the dissolved gas molecules move from a spherical space to the new molecular arrangement, in a concentration less by ΔC, from the initial equilibrium concentration. In order to calculate the dissipation function, it is assumed that each molecule belonging to the same ΔC covers a distance a, and hence the dissipation function per unit volume reads

$$\Psi = \frac{dW_{\text{diss}}}{dt} = \frac{N\Delta C\Pi aG^2R^4}{4\mu} \tag{22}$$

where N is the Avogadro number. The substitution of Eqs. 4 and 15 in the above equation yields the dissipation function for a convective flow of the dissolved molecules in a liquid, which states:

$$\Psi = \frac{NH\Pi R^4(\Delta P)^3}{4a\mu} \tag{23}$$

Equation and Values for Radius *a*

In order to isolate radius a of the spherical space for bubble nucleation, we apply the idea that the transition from a diffusive steady state to phase separation occurs when the level of dissipation of the first process becomes equal to the dissipation of the second process, namely Eq. 13 is equal to Eq. 23. Assuming that a unit volume contains n_B spherical spaces, that is to say,

$$n_B = 1\Big/\left(\frac{4}{3}\Pi a^3\right) \tag{24}$$

and by equating Eq. 13 with Eq. 23, we get

$$a = \frac{4D\mu\bar{V}_k}{\Pi NR^4\Delta P_n} \tag{25}$$

The last equation is the most important result of the present research, since it provides a simple experimental way for calculating the radius of the spherical space of the center of bubble formation, on the basis of known quantities and measurements of ΔP_n. Moreover, these results indirectly shed some light on the structure of water and of aqueous solutions. In order to calcualte a we use, in the above equation, values of the effective molecular diameter σ of the dissolved gas, instead of the radius R of the molecule. Thus Eq. 25 reads:

$$a = \frac{64D\mu\bar{V}k}{\Pi N\sigma^4\Delta P_n} \tag{26}$$

A difficult problem, however, has to be faced in the calculation of a, which seems to be simple: while values of the diffusivities and partial volumes which appear in various references are similar, and possible deviations among them do not affect the value of a, the situation is quite different with regard to the effetive molecular diameter, σ. The values of σ which appear in literature are in a large scatter and the fourth power of σ in Eq. 26 increases even more the scatter in calculated values of the radius a for bubble nucleation.

TABLE 3. DATA AT 303 K FOR CALCULATING THE RADIUS OF THE SPHERICAL SPACE, *a*

	$\sigma \times 10^{10}$ (m)						
Gas	Virial Coefficient	Viscosity	Rigid Sphere	Crit. Data	$D \times 10^9$ m²/s	$V_k \times 10^6$ m³/gmol	ΔP_n MN/m²
Helium	2.60	2.35	2.20	2.66	8.0	15.5	42.0
Neon	2.71	2.69	2.38	2.38	3.2	20.4	32.4
Nitrogen	3.65	3.47	3.30	3.60	3.50	37.0	13.8
Argon	3.39	3.45	3.14	3.20	2.68	31.7	13.1

Table 4. Summary of Values of the Radius of the Spherical Space for Bubble Formation —$a \times 10^{10}$ (m)

Gas	Second Virial Coeff.	Viscosity	Rigid Sphere	Critical Data	Mean
Helium	174	260	339	159	233 ± 83
Neon	101	104	170	170	136 ± 39
Nitrogen	143	175	214	141	168 ± 34
Argon	133	124	180	167	151 ± 27
Mean	138 ± 30*	166 ± 69	226 ± 78	159 ± 13	172 ± 43

* Sample standard deviation.

The values of the effective molecular diameter were collected from many references, and are reported elsewhere (Finkelstein, 1983). In order to calculate a, mean values for σ were calculated. These values are summarized in Table 3. The substitution of data appearing in Table 3 into Equation 26 yields the values of a summarized in Table 4.

As seen, the value of a with a minimal standard deviation is obtained from σ based on critical data. In addition, in the preliminary analysis of experimental results a good correlation was obtained on the basis of critical data (Eq. 1). Hence, we select the following value of a, the radius of the spherical space for bubble formation in solutions of inert gases dissolved in water:

$$a = (159 \pm 13) \times 10^{-10} m \qquad (27)$$

The constancy of a within the experimental error, and the accuracy of the input data, in particular σ, give support to our physical model for the formation of gas bubbles in gas-supersaturated-liquid, which assumes that a is a characteristic property of water and is independent of the dissolved gas.

Relation Between a and Critical Data of Dissolved Gas

In a preliminary analysis of data based on reduced critical data of dissolved gas, a relation was obtained between the reduced pressure difference for bubble formation and reduced temperature. The relation is expressed by Eq. 1. Equations 25 and 26, derived on the basis of a physical model, give the pressure difference for bubble formation, as a fuction of measurable quantities with a, given by Eq. 27. It is reasonable to assume also that, from this starting point, it would be possible to express the reduced pressure difference for bubble formation as a function of reduced temperature. Indeed, substitution of the Wilke-Chang equation (Geankoplis, 1972) for estimating the diffusion coefficient of gases in water, and the relation between P_c and T_c based on van der Waal's equation of state, for Eq. 26, gives:

$$\frac{\Delta P_n}{P_c} = \text{constant} \cdot \frac{\bar{V}_k \bar{V}_b^{-0.6} b}{\sigma^4} \left(\frac{T}{T_c}\right) \qquad (28)$$

Table 5. Data for Predicting ΔP_n

Gas	T/T_c at 303 K	$D \times 10^9$ m^2/s	$\bar{V}_k \times 10^6$ $m^3/gmol$	$\sigma \times 10^{10}$ m
Hydrogen	9.11	7.0	20	2.92*
Oxygen	1.96	2.8	30	3.42**
Methane	1.59	3.0	37	3.81**

*Not available from critical data; a mean value based on the second virial coefficient was employed.
** From critical data.

Molecular Size of Centers for Bubble Formation

The theoretical model previously developed assumes the existence of permanent centers for bubble formation. The molecular size of such centers is interesting and, from our knowledge about the formation of hydrates of gases in water, this size can be estimated as follows (King, 1969): Hydrates are formed from molecules with a diameter less or equal to 6.5×10^{-10} m. For example, 1.1-dichloroethane, methane, ethane, propane, and i-butane form hydrates in water, whereas 1.2-dichloroethane and n-butane do not form hydrates, nor do hydrocarbons with more than four carbon atoms. This behavior is explained by the structure of molecular clusters or "cages" (Hildebrand et al., 1970) in water, in which few gas molecules can accumulate to form centers for bubble formation. As regards gas hydrates, each such cluster contains four to ten atoms.

Prediction of ΔP_n for Various Gases in Water and Comparison with Other Investigations

Gases which might be of interest are hydrogen, oxygen, and methane. The prediction of ΔP_n will be made by applying two methods, namely, by reduced variables (Eq. 1 or Figure 2), and by Eq. 26. The value of a was taken from Eq. 27. Table 5 summarizes the required data, the reference for which appears elsewhere (Finkelstein, 1983). The results calculated for ΔP_n by Eqs. 1 and 26, based on data in Table 5, as well as on the viscosity of water at 303 K from Table 7, appear in Table 6 and will be discussed later. For comparison, the only investigations which can be considered are those of Hemmingsen (1970, 1975, 1977, 1978) who performed bubble-formation experiments with water and aqueous solutions in glass capillaries. In spite of the effect of walls, his resutls are very similar to the present ones. A comparison between the results is presented in Table 6. A graphic presentation for the values of ΔP_n obtained in this research, as well as those of Hemmingsen,

Table 6. Predicted Values and Comparison of Present Results for ΔP_n (MN/m^2) with the Work of Hemmingsen

Gas	Present Exper.	Predicted Eq. 1 or Fig. 2	Predicted Eq. 26	Hemmingsen's Exp.
Helium	42.0	—	—	35.3
Neon	32.4	—	—	—
Argon	13.8	—	—	13.2
Nitrogen	13.1	—	—	14.7
Hydrogen	—	23.8	32.4	—
Oxygen	—	14.7	10.4	14.7
Methane	—	12.5	8.9	11.8

*It should be noted that by a selective choice of σ, it is possible to obtain identical values for ΔP_n as predicted by Eq. 1.

TABLE 7. DATA FOR CALCULATING THE VARIATION OF *a* VS. TEMPERATURE FOR WATER*

Temp. K	Molar Volume $(m^3/gmol) \times 10^6$		Viscosity $(Ns/m^2) \times 10^3$		Self-Diffusion $(m^2/s) \times 10^9$		Pressure Difference Bar (=0.1 MPa)	
	Value	Reference	Value	Reference	Value	Reference	Value	Reference
473	20.8	Steam Tables	0.14	Eisenberg (1969)	20	Extrap.	90	Briggs (1950,1955)
423	19.7	Steam Tables	0.19	Eisenberg (1969)	14	Extrap.	110	Briggs, (1950,1955)
393	19.7	Steam Tables	0.24	Eisenberg (1969)	9.4	Extrap.	120	Briggs (1950,1955)
373	18.8	Steam Tables	0.28	Eisenberg (1969)	7.4	Hayduck (1974)	130	Briggs (1950,1955)
328	18.3	Steam Tables	0.51	Eisenberg (1969)	5.45	Wang (1953)	210	Briggs (1950,1955)
318	18.2	Steam Tables	0.59	Eisenberg (1969)	4.38	Wang (1953)	220	Briggs (1950,1955)
303	18.08	Steam Tables	0.79	Eisenberg (1969)	3.08	Wang (1953)	250	Briggs (1950,1955)
293	18.06	Steam Tables	1.00	Eisenberg (1969)	2.44	Wang (1953)	270	Briggs (1950,1955)
283	18.02	Steam Tables	1.30	Eisenberg (1969)	1.90	Wang (1953)	275	Briggs (1950,1955)
278	18.01	Steam Tables	1.52	Eisenberg (1969)	1.58	Wang (1953)	260	Briggs (1950,1955)
277	18.01	Steam Tables	1.59	Horne (1966)	1.53	Interp.	200	Briggs (1950,1955)
275	18.01	Steam Tables	1.68	Horne (1966)	1.44	Interp.	150	Briggs (1950,1955)
274	18.01	Steam Tables	1.75	Horne (1966)	1.40	Wang (1953)	30	Briggs (1950,1955)
273	18.02	Steam Tables	1.787	Eisenberg (1969)	1.33	Wang (1953)	—	—
272	18.02	Eisenberg (1969)	—	—	—	—	120	Bridgman (1964)
270	—	—	—	—	1.00	Franks (1979)	—	—
269.5	—	—	2.0	Hayduck (1974)	0.85	Hayduck (1974)	—	—
268	18.03	Eisenberg (1969)	—	—	—	—	598	Bridgman (1964)
264.5	—	—	2.5	Hayduck (1974)	0.7	Hayduck (1974)	—	—
263	18.04	Eisenberg (1969)	—	—	—	—	1,108	Bridgman (1964)
258	—	—	—	—	—	—	1,559	Bridgman (1964)
253	19	Extrap.	—	—	—	—	1,931	Bridgman (1964)

* In the calculation of *a* the effective molecular diameter, σ, of water was equal to 2.6×10^{-10}m. It was assumed that water molecule has a rigid spacial geometry, which is maintained both in its liquid and solid states (Ben-Naim, 1974).

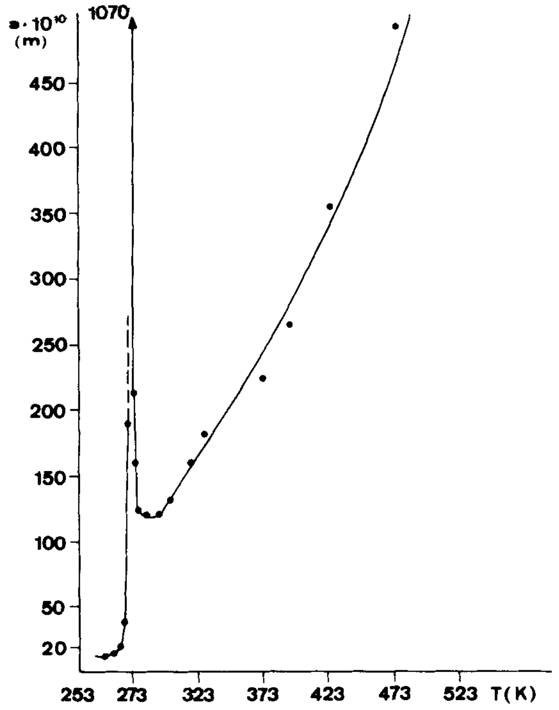

Figure 3. Spherical space radius *a* as a function of temperature.

is given in Figure 2, wherein no experimental results are available for hydrogen. It should be noted that the difference in results of ΔP_n for helium are, in all probability, due to the effect of walls in Hemmingsen's work, mainly because of the use of capillaries.

Application of the Model to Nucleation Phenomena in Pure Water

The classical theory for predicting bubble formation in a superheated pure liquid, reviewed by Blander (1979), emphasizes the dominant role of surface tension on the phenomena. Indeed, for hydrocarbons there is a good agreement between experimental values of the degree of superheating and those predicted by an equation based on classical theory with fitted parameters. However, this sort of agreement failed completely in the case of water. Attempts to apply the classical theory to the phenomenon of homogeneous bubble formation in solutions of a gas in water, made by Hirth et al. (1970) and by Swanger and Rhines (1972) were not successful. In our attempts (Finkelstein, 1983), we made use of the basic classical equation for calculating the rate of bubble formation (Blander, 1979) for the soluble gas-water system. We have obtained for ΔP_n an almost constant value for all gases, which was about 1,420 bar (142 MPa). The constant value of ΔP_n for all gases on the one hand, and its significant deviation from the experimental values, as reported in Table 6, indicates unequivocally that the classical theory for bubble formation cannot be applied to the gas-water system. However, the application of the new model developed in the present work for gas-water solutions was also successful in predicting the cavitation phenomenon in pure water, which originates from a homogeneous nucleation of bubbles. Indeed, on the basis of data reported in Table 7, using Eq. 26, with $\sigma = 2.6 \times 10^{-10}$ m (Eisenberg and Kauzman, 1969) and $a = (159 \pm 13) \times 10^{-10}$ m (Eq. 27), we have calcualted that for water at 303 K the "limiting negative pressure" (identical to ΔP_n) is equal to 210 ± 20 bar (21 ± 2MPa). This value is in very close agreement with the value of 250 bar (25 MPa) measured by Briggs (1950, 1955).

On the basis of the above result, and by assuming that for water the phenomena of cavitation, supercooling and crystallization, superheating and boiling, as well as the formation of gas bubbles in supersaturated solutions, are in principle quite similar and closely associated with homogeneous nucleation, it is feasible to apply the model developed here for calculating the radius of the spherical space for bubble nucleation, a, over a wide temperature range. The data for water, reported in Table 7, needed for such calculations are: ΔP_n, namely, the limiting negative pressure needed for cavitation (Briggs, 1950), the degree of superheating (Briggs, 1955), and the degree of supercooling (Bridgman, 1964). The latter quantity is expressed as the equilibrium pressure between ice and supercooled water. In addition, viscosity, molar volume, and self-diffusing data (Hayduck, 1974) for water were used. The final values for the variation of a vs. temperature, calculated from Eq. 26, are shown in Figure 3.

In general, a increases with the increase of temperature, exclusive of the range 273–277 K. In this range a increases with the decrease of temperature, which is identical with the behavior of the molar volume of water. This peculiar behavior is undoubtedly due to change in the structure of water within this range. The fact that a shows the anomalous behavior, which characterizes the general behavior of water, gives additional confidence in the validity of the model developed in the present research.

ACKNOWLEDGMENT

The authors greatly appreciate the splendid cooperation of Elisha Elijah, for his rigid scrutiny in editing this paper.

NOTATION

a = radius of the spherical space for bubble nucleation
b = volume constant in van der Waal's equation, $m^3/gmol$
C = concentration
C_k = concentration of the dissolved gas in a binary mixture
ΔC = concentration difference
D = binary diffusivity of dissolved gas in the liquid, or self-diffusivity in the case of pure compounds
G = gradient equal to $-\Delta P/a$.
H = constant in Eq. 4
J_k = flux of the dissolved gas.
n_B = number of centers for bubble formation per unit volume
N = Avogadro number
P = total pressure
P_c = critical pressure
ΔP = pressure difference
ΔP_n = pressure difference for bubbles formation
r,R = radius
s = entropy per unit volume
S = entropy
T = absolute temperature
T_c = critical temperature in absolute units
t = time
V_b = molar volume of dissolved gas at the normal boiling point, $m^3/gmol$
V_k = partial molar volume of dissolved gas in the liquid, $m^3/gmol$
V = velocity
W_{diss} = dissipation work

Greek Letters

μ = viscosity of the solvent
μ_k^c = chemical potential of dissolved gas, solely dependent on concentration
ρ = specific gravity of the solvent
σ = effective molecular diameter
ψ = dissipation function

Subscripts or Superscripts

k = the dissolved gas
c = dependence on concentration only

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Manuscript received May 29, 1984; revision received Oct. 29 and accepted Oct. 29.