Vaporization of Superheated Drops in Liquids

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The work reported in this paper is an outgrowth of an exploratory investigation of the feasibility of spray drying of materials in solution by using direct-contact heat transfer from a hot liquid rather than a gas to vaporize the solvent from the drops. Unexpectedly, it was found that drops suspended in a hot liquid had to be superheated to a very extreme degree in order to initiate vaporization. This effect was of such interest that the investigation was modified to a fundamental study of the vaporization of drops containing no dissolved solids. The results are closely related to problems of bubble formation in boiling, cavitation, and in the evolution of gases from supersaturated solutions. The experimental technique developed in this study is believed to be unique and capable of giving quite accurate data on homogeneous nucleation in superheated drops. After a discussion of the theory of homogeneous nucleation in pure liquids, the theory is extended to the formation of bubbles in superheated drops. The theoretical predictions were found to be in close agreement with the experimental results.

Bubble formation in a superheated liquid is of current interest in chemical engineering because it is a fundamental process in heat transfer by boiling (*1*), cavitation in high-speed liquid flow (*2*), and ultrasonic cavitation in liquids (*3*). The term *superheated liquid* refers to a liquid at a pressure lower than the equilibrium vapor pressure corresponding to its temperature. In ordinary boiling and flow cavitation, bubble formation usually occurs at a solid surface in contact with the liquid and is influenced by gas bubbles on the solid surface. However because the physical conditions at the liquid-solid interface are not completely understood, no theory has been developed which accurately predicts the conditions for bubble formation at solid surfaces. Attention has turned, therefore, to bubble formation in the body of a superheated liquid, uninfluenced by solid surfaces or gas bubbles, as a distinct limiting case more susceptible to theoretical treatment. The theory of bubble formation under these conditions is one aspect of the theory of homogeneous nucleation. This theory should be directly applicable to ultrasonic cavitation in gas-free liquids and is expected to be of value as a starting point for a more general theory of nucleation applicable in the presence of solid surfaces, suspended gas bubbles, and dissolved gases.

The theory of homogeneous nucleation predicts the rate of bubble formation in a superheated liquid. Since pressures well below the equilibrium vapor pressure are required to produce bubble formation through homogeneous nucleation, the production of even one bubble in an isolated mass of superheated liquid is usually sufficient to raise the pressure to the vapor pressure or to permit all the liquid to vaporize. For this reason measurements of the rate of bubble formation are made by observing the length of time required for a single bubble to form at fixed conditions of liquid temperature and pressure or by gradually changing these conditions at a steady rate until the liquid mass is disrupted by the formation of a single bubble. The set of conditions of temperature, pressure, and composition at which the rate of bubble production becomes large enough for a vapor bubble of detectable size to form within the time of observation is called the *superheating limit*. Attempts to measure the superheating limit (*4*, *5*, *6*, *7*, *8*) have shown that liquids can be subjected to pressures as much as 100 atm. below the vapor pressure without the formation of vapor bubbles. A thorough check of theory against experiment has not been possible because previous experimental results have been capricious and nonreproducible, leaving doubt as to whether vaporization occurred through homogeneous nucleation, through the action of tiny gas bubbles trapped on vessel walls, or through some other external influence.

This paper presents the results of a reexamination and modification of the theory of homogeneous nucleation in superheated liquids as developed by Döring (*9*), Volmer (*10*), Frenkel (*11*), and Takagi (*12*) and the extension of the theory to bubble formation in superheated drops freely suspended in another liquid, together with the results of new experiments which are in close agreement with the modified theory (*13*). In these experiments the superheated liquid was dispersed into drops in another liquid, which minimized the effects of external influences and thereby made possible reproducible measurement of the superheating limit.

THEORETICAL DEVELOPMENT FOR A SINGLE-PHASE SYSTEM

The chemical potential of a superheated liquid is higher than that of the same substance in the bulk vapor state at the same temperature and pressure. Consequently if such a bulk vapor phase were permitted to contact the superheated liquid, and the temperature and pressure were maintained constant, the liquid would vaporize into it completely. However, in the absence of contact with such a bulk vapor phase and in the absence of other external influences the liquid in order to vaporize must itself generate the vapor phase. To do this, very small regions of vapor in the liquid, called *embryos* or *nuclei*, must first be formed. The unbalance of intermolecular forces accompanying the formation of these vapor nuclei surrounded by liquid causes the free energy of the liquid and vapor to be greater than that of an equal mass of liquid. Thus the thermodynamic reason for the existence of the metastable superheated state is that the formation of the first elements of the new phase requires a temporary increase in the free energy of the system.

The effects of intermolecular forces appear thermodynamically in the excess free energy of the surface and in the free energy of the vapor molecules in the bubble. The vapor molecules have high free energy per molecule relative to the liquid because they are under pressure higher than the equilibrium vapor pressure corresponding to the liquid pressure and temperature. The higher pressure results from the curvature of the bubble surface and the surface tension of the liquid. An embryo that is not too small, containing perhaps a few dozen molecules, can be expected to assume a spherical shape under the influence of the intermolecular forces. If such a bubble formed in a moderately superheated liquid, it would tend to collapse, accompanied by a decrease in the free energy of the system (the bubble and the surrounding liquid). However if, instead, the bubble should continually increase in size by adding molecules to the vapor phase, the pressure in the bubble would fall and the free energy of the system would increase until the bubble reached a certain radius, called the *critical radius*. At this bubble size the free energy of the system reaches a maximum, and the chemical potential of the vapor is equal to that of the liquid. On further increase in the radius and in the number of molecules, the pressure in the bubble would continue to fall, but the chemical potential of a molecule in the vapor would now be less than in the liquid, whereupon the bubble would tend to grow until all the liquid vaporized or the pressure in the liquid rose to the vapor pressure.

According to nucleation theory, the nuclei come into existence and grow through spontaneous statistical fluctuations in the density of the liquid, which arise from the thermal motion of the liquid molecules. In theory nuclei also

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exist in nonsuperheated liquids, but the free energy of the system continually increases with bubble size because the molecular chemical potential in the vapor never becomes less than in the liquid. Consequently these bubbles do not grow to visible size. The following method of calculating the rate of production of visible bubbles through density fluctuations is based on the theory originally presented by Döring and later given a more extensive treatment by Volmer (*10*) in his book on the kinetics of phase transitions. The form of their presentation with certain modifications will be followed here.

BUBBLE FORMATION FREQUENCY

Döring and Volmer considered a vaporization process in a liquid at fixed temperature and pressure, with bubbles increasing and decreasing in size in a random fashion, due to local fluctuations in the energy of the molecules. In this process some bubbles vanish, others arise from homogeneous liquid, and some grow until they contain a number of molecules n_s, which is somewhat greater than the number n_k in a bubble of critical radius corresponding to the existing temperature and pressure in the liquid. The bubbles containing n_s molecules are considered removed from the liquid and an equivalent number of liquid molecules is added. The number of bubbles removed per unit time and volume is the nucleation frequency or bubble production rate. The bubbles which participate in these processes form a number distribution of bubbles of all sizes from those containing only a few molecules up to those containing n_s molecules. This distribution $Z(n)$ is the number of bubbles containing n molecules in unit volume of liquid.

The elementary microscopic process of growth is considered to be the transfer of a single molecule from liquid to vapor in a bubble containing n molecules to produce a bubble containing $n + 1$ molecules and the reverse for the process of collapse. The total area per unit volume available for the vaporization process is $Z(n)S(n)$ and for the condensation process $Z(n + 1)\ S(n)$. It is considered that at the moment the condensation process takes place, the effective area for condensation is equal to the area of the bubble after condensation because the finite size of the condensing molecule makes the effective radius smaller. The net flux of molecules between the two bubble sizes in unit volume of liquid in time dt is

$$J(n, t)\,dt = [Z(n, t)S(n)W_L(n) - Z(n + 1, t)S(n)W_V(n + 1)]\,dt$$

It is now assumed that the average value of $Z(n)$ does not change with time, under which condition J is not a function of time and is also not a function of n. The net rate of formation of visible bubbles is then equal to the difference between the rates of the two opposing processes for any size bubble, since every time a bubble grows to contain n_s molecules and is removed, there has been a net flow of one bubble through each size to produce it. With this assumption the above equation reduces to

$$J = Z(n)S(n)W_L(n) - Z(n + 1)S(n)W_V(n + 1). \qquad (1)$$

One defines the quantity $\beta(n + 1) \equiv W_L(n)/W_V(n + 1)$ and introduces it into Equation (1) to obtain the first-order linear difference equation

$$\frac{Z_{n+1}}{\beta_{n+1}} - Z_n = -\frac{J}{W_{Ln}S_n} \qquad (2)$$

which has the solution

$$Z_{n_0} - \frac{Z_{n_s}}{\prod_{i=n_0+1}^{n_s} \beta_i} = J\left[\sum_{n=n_0}^{n_s-1} \frac{1}{W_{Ln}S_n \prod_{i=n_0+1}^{n} \beta_i}\right] \qquad (3)$$

The removal of bubbles containing n_s molecules makes

$$Z_{n_s} \Big/ \prod_{i=n_0+1}^{n_s} \beta_i$$

small compared to Z_{n_0}. Thus one obtains

$$J = Z_{n_0}\left[\sum_{n=n_0}^{n_s-1} \frac{1}{W_{Ln}S_n \prod_{i=n_0+1}^{n} \beta_i}\right]^{-1} \qquad (4)$$

The quantity β_i is the ratio of the probability of the transfer of a molecule in a bubble containing i molecules from the vapor phase to the liquid to that of its return from the liquid to the vapor. This ratio may be evaluated by use of the following arguments. In accordance with classical statistical mechanics, the proportion of time a particle spends in each of two accessible regions of phase space is equal to the ratio of the total partition functions for the particle in the two regions. Further the probability of transition of a particle from one region to the other is inversely proportional to the mean residence time in that region, that is, the longer a particle stays in one region on the average the less likely it is to leave within a given time interval. This is expressed by the relation

$$\frac{W_{\mathrm{II}}}{W_{\mathrm{I}}} = \frac{t_{\mathrm{I}m}}{t_{\mathrm{II}m}} = \frac{\text{total partition function per molecule for region I}}{\text{total partition function per molecule for region II}}$$

In addition, the chemical potential of a molecule in each region is given by

$$\frac{u_{\mathrm{I}}}{kT} = \ln\left(\begin{matrix}\text{total partition function per}\\ \text{molecule for region I}\end{matrix}\right)$$

Thus

$$\frac{W_{\mathrm{I}}}{W_{\mathrm{II}}} = \beta_{\mathrm{II}} = \exp\left(\frac{u_{\mathrm{I}} - u_{\mathrm{II}}}{kT}\right) \qquad (5)$$

and

$$\prod_{i=n_0+1}^{n} \beta_{\mathrm{II}i} = \exp\left[\sum_{i=n_0+1}^{n} \frac{u_{\mathrm{I}} - u_{\mathrm{II}i}}{kT}\right] \qquad (6)$$

FREE ENERGY OF BUBBLE FORMATION

As pointed out by Takagi (*12*), the magnitude of the Helmholz free energy required to form a bubble containing n molecules from a bubble containing n_0 can be calculated by summing the difference in chemical potential as each molecule is brought in turn from the liquid into the vapor. Thus at constant system temperature and liquid pressure

$$\Delta A_n - \Delta A_{n_0} = \sum_{i=n_0+1}^{n} (u_i - u_L) \qquad (7)$$

Now the thermodynamic development of the free energy of formation of the bubble containing n molecules from a bubble containing n_0 molecules actually need have no reference to bubbles as such but rather need refer only to the thermodynamic states of the molecules. Consequently the states need not be recognizable as bubbles for Equations (6) and (7) to apply; it is necessary only that the states be characterized by the number of molecules they contain and that there be some path available for transition between them. Therefore the liquid state can be thought of as being made up of bubbles containing one molecule and can serve as the reference state. For this state ΔA_{n_0} is zero, and Z_{n_0} equals the reciprocal of the volume per molecule in the liquid. Introducing Equations (6) and (7) into Equation (4) with these values for ΔA_{n_0} and Z_{n_0} one obtains

$$J = v_L^{-1}\left[\sum_{n=n_0}^{n_s-1} \frac{\exp\left(\dfrac{\Delta A_n}{kT}\right)}{W_{Ln}S_n}\right]^{-1} \qquad (8)$$

The above interpretation is a departure from the presentation of Volmer and Döring, who concluded that the proper reference state should be a bubble containing no molecules, that is a hole the size of a molecule in the liquid. The present interpretation is that the smallest embryo is simply a molecule in the liquid state. The exact mechanism by which the transition from liquid to vapor takes place to form bubbles containing only a few molecules will not affect the calculation of the bubble-formation frequency as long as the contribution of such transitions to the sum in Equation (8) is small compared with the contributions from transitions between larger bubbles. The author postulates that this is so.

To evaluate the sum in Equation (8) one uses the spherical bubble model. Volmer and Döring considered the vaporization probability per unit area W_L to be independent of bubble size. This follows from their assumption that the molecules in the liquid surface are in thermodynamic equilibrium with those in the main body of liquid, and so the chemical potential of the molecules at the surface is determined by the temperature and liquid pressure alone. This is probably not true for bubbles containing only a few molecules, but it is necessary only that it be approximately true for transitions which make large contributions to the sum in Equation (8). Since the vapor in the critical bubble is in equilibrium with the liquid, u_L is equal to the chemical potential of the vapor molecules in the critical bubble; thus from Equation (5) W_L equals W_{Vk}. W_{Vk} was calculated by Volmer and Döring as the mean collision frequency of vapor molecules on unit area of transfer surface, derived from the kinetic theory of gases to be

$$W_{Vk} = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \cdot v_k^{-1} \qquad (9)$$

Volmer and Döring used the ideal-gas law throughout their development. This introduces some uncertainty in the results, and, since for many systems measurements at pressures above atmospheric can be made only at reduced temperatures above about nine tenths, it is desirable to examine the effects of vapor nonideality. First the following assumptions in the derivation of Equation (9) and in its application to the present problem may be examined:

1. The translational contributions to the partition functions are separable from all other contributions.
2. All contributions other than translational are the same in the transfer region as in the main body of vapor.
3. The particles are weakly interacting and have zero volume (ideal gas).
4. No potential-energy difference exists between the transfer region and main body of vapor at any time or in any region of the transfer surface.

The first two of these are good approximations for simple molecules with the same structure in the vapor as in the liquid. It is impossible to assess the effects of vapor nonideality on the partition functions without knowledge of the cause of any difference in potential in the transition region over that in the main vapor phase. If there is no such difference other than the existence of a uniform potential field that does not affect the intermolecular potential, the ratio of the number of particles in the transfer region to those in the main body of vapor reduces to that for an ideal gas, and so Equation (9) is valid for nonideal gases also. Ideal gas law deviations can then be handled by the use of

$$pV = znkT \qquad (10)$$

The restriction of no potential barriers means that there can be no steric hindrance repulsion effects or delays in transfer of excess translational energy to the liquid as the molecule passes from liquid to vapor and that the potential energy of a vapor molecule is always decreased on approaching the force field of the liquid surface. Potential barrier effects should be assessed for each individual vapor-liquid system, but the restriction should be satisfied for most nonpolar substances of simple structure. From these considerations

$$W_L = \frac{p_k}{z_k\sqrt{2\pi mkT}} \qquad (11)$$

is obtained.

The quantity ΔA_n has been evaluated in accordance with the spherical bubble model in terms of the radius of the bubble r_n and the pressure p_n within it for a vapor following the ideal gas law [Takagi (*12*)]

$$\Delta A_n = nkT \ln\frac{p_n}{p_k} + \frac{4}{3}\pi r_n^2\sigma \qquad (12)$$

For a vapor following the gas law, Equation (10), the equation for ΔA_n is different only in that the vapor pressures are replaced by fugacities. This equation is only valid for r_n and n sufficiently large for the spherical bubble model to be a reasonably close approximation to the actual state of the embyro. It is then independent of vapor nonideality for r equal to r_k, except insofar as nonideality affects r_k because the first term on the right-hand side vanishes and the second term depends only on the bubble radius and the surface tension. In adopting Equation (12) and later Equation (15) one must assume that the Gibbs theory of capillarity is adequate for this model and that in making numerical calculations one can use the macroscopic value of the surface tension without excessive error.

Now an examination of the terms of the sum in Equation (8) according to the model reveals that they reach a sharp maximum at $n = n_k$, and, for $n_k \gtrsim 50$, only terms for which $0.8 < r_n/r_k < 1.2$ are significant to the value of the sum. Consequently the failure of the model at small values of n is immaterial as long as n_k is reasonably large. Further, in these significant terms the ratio f_n/f_k will be nearly one, and, since the first term on the right hand side of Equation (12) is smaller than the second in this range, f_n/f_k can be replaced by p_n/p_k without noticeable error. For this reason nonideality of the vapor does not have a large effect on the work of formation even close to the critical point.

Since the terms of the sum reach a sharp maximum at n equal to n_k, one may expand the logarithm about this point in powers of $x \equiv 1 - (r_n/r_k)$ and neglect powers of x higher than 2 to obtain

$$\frac{\Delta A_n}{kT} = \frac{\Delta A_k}{kT}[1 - (3 - b)x^2] \qquad (13)$$

in which $b \equiv 1 - (p_L/p_k)$. For $n_k \gtrsim 100$, there are at least one hundred terms for which $0.8 < r_n/r_k < 1.2$ in the sum of Equation (8). Consequently the sum may be replaced by an integral, and because of the sharp maximum the limits may be extended from $-\infty$ to $+\infty$:

$$\sum_{n=n_0}^{n_s-1}\frac{\exp\left(\frac{\Delta A_n}{kT}\right)}{S_n} = \frac{1}{S_k} \cdot\int_{-\infty}^{\infty}\frac{\exp\frac{\Delta A_k}{kT}[1-(3-b)x^2]}{r^{*2}} \cdot\left(\frac{dn}{dr^*}\right)dr^* \qquad (14)$$

in which $r^* \equiv r_n/r_k$. Again using the gas law, Equation (10), and the condition of mechanical equilibrium

$$p_n - p_L = \frac{2\sigma}{r_n} \qquad (15)$$

one may evaluate the derivative

$$\frac{dn}{dr^*} = \frac{n_k}{z^*}\left[3(1-b)r^{*2} + br^*\left\{2 + \left(\frac{\partial \ln z_n}{\partial \ln p_n}\right)_T\right\}\right] \qquad (16)$$

in which $z^* = z_n/z_k$. On introducing Equation (16) into Equation (14) and noting that $dr^* = -dx$ one obtains

$$\sum_{n=n_0}^{n_s-1}\frac{\exp\left(\frac{\Delta A_n}{kT}\right)}{S_n} \doteq \frac{n_k}{S_k}\exp\left(\frac{\Delta A_k}{kT}\right)\int_{-\infty}^{\infty}\frac{3(1-b)+\frac{b}{r^*}\left\{2+\left(\frac{\partial \ln z_n}{\partial \ln p_n}\right)_T\right\}}{z^*} \cdot\exp\left(-\frac{\Delta A_k}{kT}(3-b)x^2\right)\cdot dx \qquad (17)$$

As previously noted, the entire significant contribution to the integral in Equation (17) occurs in the region of x close to zero. This is the justification for extending the limits of integration to infinity in both directions and will further justify the substitutions $r^* = 1$ and $z^* = 1$, and the evaluation of $(\partial \ln z_n/\partial \ln p_n)_T$ at $p_n = p_k$ in the coefficient before the exponential. The asymptotic value of the integral for large n_k obtained by integrating with these approximations may be introduced into Equation (17) to give

$$\sum_{n=n_0}^{n_s-1} \frac{\exp\left(\frac{\Delta A_n}{kT}\right)}{S_n} \doteq \frac{\left[3 - b\left\{1 - \left(\frac{\partial \ln z}{\partial \ln p}\right)_T\Big|_{p_k}\right\}\right]}{S_k} \cdot\sqrt{\frac{2\pi n_k}{b(3-b)}}\cdot\exp\left(\frac{\Delta A_k}{kT}\right) \qquad (18)$$

The quantity $(\partial \ln z/\partial \ln p)_T$ approaches large negative values as the temperature approaches the critical temperatures; however it is only -0.6 at $T_r = 0.9$. The effect of this term is to make dn/dr^* smaller and thus to make the frequency of bubble formation given by Equation (18) smaller at a given value of P_L or b than would be obtained by omitting it. Equation (18) with this term omitted will then predict the nucleation pressure to be at a higher pressure than when it is included. However, because of the small value of b near the critical point, the inclusion of the derivative actually makes little difference in the nucleation frequency and far less in the nucleation pressure.

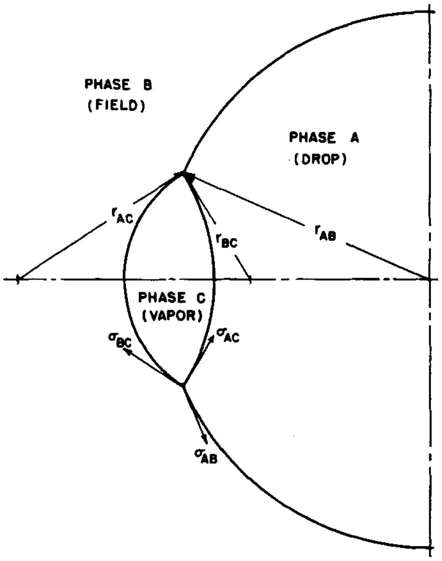

Fig. 1. Vapor lens at the surface of a drop.

When Equations (10), (11), (15), (18), and $S_k = 4\pi r_k^2$ are substituted into Equation (8), one finds that

$$J = \frac{\sqrt{\frac{6\sigma(3-b)}{\pi m z_k}}\cdot\frac{1}{v_L}\cdot\exp\left(-\frac{\Delta A_k}{kT}\right)}{\left[3 - b\left\{1 - \frac{\partial \ln z}{\partial \ln p}\Big|_{p_k}\right\}\right]} \qquad (19)$$

If z_k is set equal to one and $(\partial \ln z/\partial \ln p)$ is set equal to zero, this result reduces to that given by Volmer except that it contains no term involving the latent heat of vaporization of the liquid:

$$J = \sqrt{\frac{6\sigma}{\pi m(3-b)}}\cdot\frac{\exp\left(-\frac{\Delta A_k}{kT}\right)}{v_L} \qquad (20)$$

The quantity ΔA_k is obtained by evaluating Equation (12) for the critical bubble:

$$\Delta A_k = \frac{4}{3}\pi r_k^2 \sigma \qquad (21)$$

The critical radius is in turn evaluated by expressing the chemical potentials of vapor and liquid as functions of pressure and equating when the equilibrium difference in pressure is reached. The results, valid for n_k not too small, is

$$r_k = 2\sigma\left[\frac{\nu_\infty p_\infty}{\nu_k} \cdot\exp\left(\frac{v_{Lm}}{kT}(p_L - p_\infty)\right) - p_L\right]^{-1} \qquad (22)$$

Equations (19), (21), and (22) permit any one of the quantities J, T, or P_L to be calculated from the other two for a pure substance, with the limitation that b must be somewhat less than 3. The mathematical approximations used to derive Equation (19) are not valid for b close to or greater than 3, and the upper limit $n_s - 1$ on the sum in Equation (3) must be evaluated somewhat differently (*12*).

It should be emphasized that the foregoing equations and development apply only to one-component systems. In order to establish the modifications required for comparison with the experimental results, the extension of the theory to the particular type of two-component system used is presented in the following paragraphs.

NUCLEATION OF BUBBLES IN DROPS

The application of the foregoing analysis to bubble formation in superheated drops is complicated by the presence of two components and of the liquid-liquid interface. It is possible for a vapor bubble to form either at the interface or in the interior of the drop, depending on the mechanical stability of a vapor mass at the interface. A bubble at the interface would be lens shaped (Figure 1), with spherical vapor-liquid surfaces which intersect at the surface of the drop. The stability of the lens is determined by the surface tensions at the lens edge, σ_{AB}, σ_{AC}, and σ_{BC}. The subscripts refer to the spherical surfaces between the phases; phase A is the drop, phase B is the surrounding liquid (field liquid), and phase C is the vapor lens. Now if $\sigma_{AC} > \sigma_{AB} + \sigma_{BC}$, the force related to σ_{AC} is able to overbalance both of the forces related to σ_{AB} and σ_{BC}, and the bubble would enter into the drop. If $\sigma_{BC} > \sigma_{AC} + \sigma_{AB}$, the bubble would be expelled into the surrounding liquid. If both $\sigma_{AC} \leq \sigma_{AB} + \sigma_{BC}$ and $\sigma_{BC} \leq \sigma_{AB} + \sigma_{AC}$, the lens would remain at the interface. The following analysis applies to the first-mentioned case, that is $\sigma_{AC} > \sigma_{AB} + \sigma_{BC}$. In this case the vaporization process should occur by formation of spherical bubbles in the interior of the drop.

The presence of two components will be treated by assuming the two liquids to be almost totally immiscible; that is, there is very little of the suspending liquid in the superheated drop but enough to make the total vapor pressure of the drop equal to the sum of the vapor pressures of the individual components. Further, the vapor solution will be assumed to be ideal, as expressed by the relations

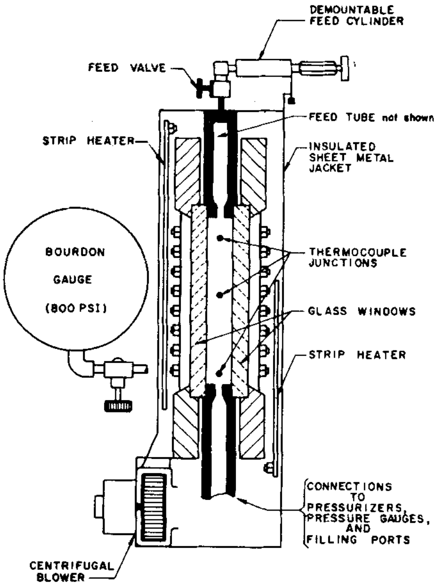

Fig. 2. Schematic sectional view of pressure cell.

$$f_a = y_a f_a^0 \qquad f_b = y_b f_b^0 \qquad (23)$$

Since

$$f_{an}^0 = \nu_{an}^0 p_n \quad \text{and} \quad f_{bn}^0 = \nu_{bn}^0 p_n \qquad (24)$$

the free-energy increase as each molecule vaporizes is given by the difference in chemical potential of its initial and final states in the form

$$\frac{u_n - u_L}{kT} = \ln\frac{f_n}{f_k} = \ln\frac{y_n \nu_n^0 p_n}{y_k \nu_k^0 p_k}. \qquad (25)$$

for each component. From thermodynamic reasoning one may expect that the steps in the vaporization process will occur in the order of smallest free-energy increases; that is molecules of component

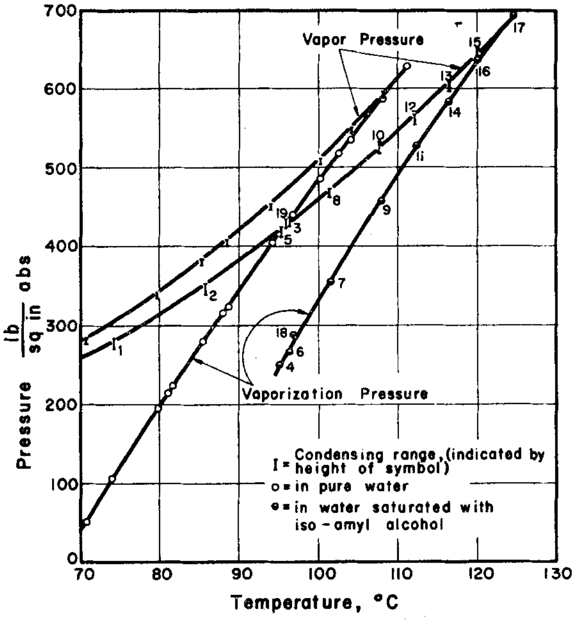

Fig. 3. Vaporization pressures for commercial-grade Freon-12 drops.

a will vaporize into a bubble until the free-energy increase resulting from the vaporization of a *b* molecule is less than that for another *a* molecule in the absence of the *b* molecule. The free-energy increase of the next *a* molecule to vaporize will be less than that for the same molecule if the *b* molecule had not vaporized because of the entropy increase accompanying the change in composition. Consequently it is reasonable to assume that for any size bubble the chemical potential differences for vaporization are the same for the two kinds of molecules and further that the composition of the vapor is the same as in the critical bubble. With these assumptions the work of formation of a bubble is given by Equation (12) as before. Further, although the individual transfer probabilities in an embryo are different for the two kinds of molecules, the ratio of transfer probabilities is the same for both kinds:

$$\beta_n = \exp{(u_n - u_L)_a} = \exp{(u_n - u_L)_b}$$

It may be noted that although the vapor was assumed to be an ideal solution and the mole fractions in the vapor to be constant in the redevelopment of Equation (12) for the two-component system, ΔA_k is given by Equation (21) irrespective of nonideality in the system, except insofar as nonideality affects r_k. This is due to the fact that once the critical radius of the bubble is fixed, mechanical considerations govern the bubble shape and the pressure within it and that the chemical potentials of the vapor molecules are the same as in their reference state, the liquid phase.

The critical radius may be obtained as before, with the assumption that the vapor pressures are additive. Thus

$$\begin{aligned} r_k = 2\sigma_{AC}\Bigg\{&\frac{\nu_{a\infty}p_{a\infty}}{\nu^{0}_{ak}} \\ &\cdot\exp\left[\frac{v_{am}}{kT}\left(p_B + \frac{2\sigma_{AB}}{r_{AB}} - p_{a\infty}\right]\right. \\ &+ \frac{\nu_{b\infty}p_{b\infty}}{\nu^{0}_{bk}}\exp\left[\frac{v_{bm}}{kT}(p_B - p_{b\infty})\right] \\ &- p_B - \frac{2\sigma_{AB}}{r_{AB}}\Bigg\}^{-1} \end{aligned} \tag{26}$$

The rate equations for the net flow of bubbles may now be constructed as before, but the solution separates into two terms, one for each type of molecule:

$$J\Bigg[\underset{\substack{\text{(only values of } n\\ \text{where an } a \text{ molecule}\\ \text{transfers)}}}{\sum_{n=n_0}^{n_s-1}}\left[(W_IS_n)_a\prod_{i=n_0+1}^{n}\beta_i\right]^{-1} + \underset{\substack{\text{(only values of } n\\ \text{where a } b \text{ molecule}\\ \text{transfers)}}}{\sum_{n=n_0}^{n_s-1}}\left[(W_IS_n)_b\prod_{i=n_0+1}^{n}\beta_i\right]^{-1}\Bigg] = Z_0 - \frac{Z_s}{\prod_{i=n_0+1}^{n_s}\beta_i} \tag{27}$$

Under circumstances such that very few molecules of *b* vaporize along with the numerous *a* molecules in the formation of a bubble with n_s molecules, the quantity $(W_IS_n)_b$ can be assumed to equal $(W_IS_n)_a$ with small error, so that Equation (27) reduces to Equation (4) and the evaluation may be performed as before to produce Equation (19). Under these circumstances the net effect of introducing drops in another liquid has been to change the effective vapor pressure and thereby to change the critical radius, which is now given by Equation (26).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The superheating limit was measured experimentally by spraying drops of purified Freon-12 (dichlorodifluoromethane) into degassed distilled water in a pressure cell and, with temperature held constant, slowly releasing the pressure until several drops of a predetermined size vaporized simultaneously. The apparatus and techniques for the measurement of vaporization pressure and of physical properties necessary for comparison with the pressures predicted by theory are briefly described here.

The pressure cell (Figure 2) was a liquid-level gauge made of type-316 stainless steel, with Teflon-impregnated Fibreglas gaskets. Steel blocks were silver soldered to the ends of the chamber section and covers to increase the thermal capacity and minimize temperature gradients in the chamber section. Electrical strip heaters were attached to the edges of the chamber and covers. One-half-inch type-316 stainless steel pipe nipples passed through the end blocks and connected the chamber to fittings for the unheated parts. The cell was mounted in a U frame having sleeve bearings to permit inverting the cell for measurements with drops rising or falling.

Drops were produced by compressing liquid Freon-12 in feed cylinders with screw operated pistons, then releasing the pressure through a midget needle valve connected to a stainless steel feed capillary which entered the pressure cell through a Teflon-packed gland and delivered the Freon to a glass capillary. At the outlet of the glass capillary there was a small stage on which drops could be caught and observed microscopically for determination of vaporization and condensation pressures. Before the feed cylinders were filled, the Freon-12 was transferred from the supply cylinder through an evacuated manifold to a stainless steel reservoir and degassed by repetitive freezing in liquid air, evacuation, and boiling, until no pressure rise in the evacuated transfer manifold was observed on opening the reservoir valve over the frozen liquid. The degassed Freon-12 was heated and transferred under pressure to the evacuated feed cylinders, which were then removed from the manifold and attached to the feed capillary on the cell. The pressure cell was evacuated to 50μ, then filled by permitting distilled water degassed by boiling to flow into it.

Pressures up to 500 lb./sq. in. were applied with a lever-operated piston pressurizer and up to 1,500 lb./sq. in. with a screw-operated piston pressurizer similar to the feed cylinders, both Teflon-packed. Pressures were measured with a Bourdon gauge with a range up to 800 lb./sq. in. The gauge was calibrated and used in a vertical position. A very sensitive pressure balance was used to calibrate the gauge to the accuracy at which it could be read, namely 1 lb./sq. in. A 1,500 lb./sq. in.

TABLE 1. PURIFIED FREON-12 WATER SYSTEM

Vapor pressure		Vaporization pressure	
Temperature, °C.	Condensation range, lb./sq. in. abs.	Temperature, °C.	Vaporization pressure, lb./sq. in. abs.
65.0	248–250	69.3	32
68.3	266–267	71.1	62
69.0	269–270	71.5	67
71.2	283–285	73.4	95
73.3	295–296	73.5	97
73.5	297–299	75.6	130
75.6	311–313	75.8	135
78.6	331–333	78.5	178
81.2	349–351	81.2	216
85.5	381–383	85.6	278
90.5	419–421	90.5	348
95.8	464–466	95.8	422
100.1	502–504	99.8	477
103.4	536–538	100.2	482
106.7	570–572	103.0	520
111.0	616–618	103.3	522
111.3	619–621	103.7	527
		106.7	566

Bourdon gauge was used for pressures above 800 lb./sq. in.

The temperature of the field liquid was measured at three places in the cell chamber by means of bare copper-constantan thermocouples which entered the cell through Teflon glands. One thermocouple was positioned near the observation stage, the second near the center of the cell chamber, and the third near the bottom, as shown in Figure 2. The thermocouples were calibrated to 0.1°C.

To achieve temperature uniformity, the cell and U frame were enclosed in a sheet-metal jacket, and air inside the jacket was circulated with a small blower. The jacket had a layer of asbestos paper on the outside to prevent burns and had plate-glass windows opposite the windows in the cell. The heaters on the cell were disconnected after heating to the desired temperature level, and four strip heaters inside the jacket connected to two variable-voltage circuits were used to regulate the cell temperature. Thermocouple traverses of the cell chamber showed that no hot spots were present when the thermocouple temperatures were within a few degrees of each other. For the experimental measurements the heater controls were adjusted until a variation of 0.1°C. or less between the center and end thermocouples was obtained.

To obtain vaporization pressures at temperatures where the drop density was greater or only a little less than the density of the field liquid (up to 100°C. for Freon-12 in water), the following technique was used. With the cell and feed cylinders at the same pressure above the vapor pressure at the cell temperature, a cloud of drops was produced by turning the handwheel on one of the cylinders about one-half turn with the feed valve shut, opening the valve quickly, and displacing the drops formed in the valve body and feed tube into the cell by a few turns of the handwheel. The excess Freon-12 was then drawn back through the valve by a few turns of the handwheel, and the valve closed. The cloud of drops so produced displayed a distribution of drop diameters from about 1 mm. down to those barely visible. The size distribution and total number of the drops could be controlled by the pressure applied to the liquid before the valve was opened and by the amount displaced into the cell. The largest drops moved relatively quickly, depending on the density difference at the existing temperature, and generally traveled down to the bottom of the cell. The intermediate sizes moved relatively slowly and the smallest hardly at all. Many of the smallest would disappear by dissolving as they were being observed. The valve to the lever pressure generator was opened and regulated so that the pressure in the system fell quickly at first and then slowly, at about 1 lb./sq. in./5 sec., as the pressure limit was approached. During the time the pressure was falling, the largest drops struck the metal at the bottom of the cell and vaporized. The resulting bubbles produced a moderate mixing action as they rose through the chamber. These large drops were all permitted to vaporize and leave the chamber before the pressure dropped the last few pounds to the vaporization limit. When the slowly moving drops, in the range 0.1 to 0.3 mm. in diameter, were observed to vaporize, as detected by the change in velocity and usually by a change in direction of motion, the valve to the pressure gauge was quickly closed the final one-half turn to hold the pressure reading on the gauge, and then the valve to the lever pressure generator was closed. Thermocouple voltages from the couples closest to the drops when they vaporized were measured, the Bourdon gauge was gently tapped to shake the movement to its equilibrium position, and the reading recorded. The cell was repressurized, and the measurements were repeated several times. The observed vaporization pressure generally varied at most by ±2 lb./sq. in. because of different rates of pressure fall, temperature variations of 0.1 to 0.2°, or differences in the drop sizes observed. Usually five to ten repetitions were made, depending on the size distribution and position of the cloud of drops produced. When a slow temperature drift was occurring, more repetitions were made.

The following observations give an indication of the sensitivity of this method. A temperature change of 0.1° made a noticeable change in the pressure readings obtained by this procedure. On occasion, while a temperature gradient to lower temperatures at the bottom of the cell existed, the drops were observed to vaporize progressively down the cell as the pressure was allowed to fall through a range of 5 lb./sq. in. Also when the drops were rising and higher temperatures existed at the top of the cell, it was possible to adjust the pressure to a constant value and observe the drops vaporize as they rose into the region alongside the upper thermocouple.

At temperatures where the drops were considerably less dense than the field liquid, the density change on vaporization was small enough to make the changes in velocity during vaporization difficult to observe. A single drop or a few drops were then captured on the face of the feed capillary alongside the outlet and observed with a 10-power microscope as the pressure was lowered with the screw pressurizer. The change in size on vaporization was easily observed. In fact, the variation of limiting pressure with drop size could be observed in a roughly quantitative way if a few drops of different sizes were observed at the same time. In regions where they could both be used conveniently, from 90 to 100°C. for Freon-12 in water, the methods of observing free-moving and captured drops gave the same results to within 1 lb./sq. in. The captured drops could be recondensed by pressurizing the cell and vaporization could be observed repeatedly and reproducibly; by permitting a temperature drift an essentially continuous curve could be obtained. The critical point for the system was observed by permitting a slowly-increasing-temperature drift and observing the interface as it progressed through the drop in both directions alternately. The temperature at which meniscus disappearance occurred could be detected to within 0.2°C. by this method.

At all temperatures the vapor pressure was measured by slowly increasing the pressure to cause condensation of a vapor bubble captured on the capillary face. The upper thermocouple was located about 5 mm. from this face.

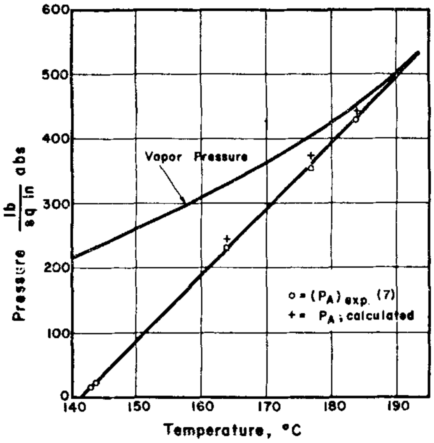

Fig. 4. Vaporization pressures for ethyl ether.

TABLE 2. VAPORIZATION PRESSURE VS. DROP DIAMETER

Drop diameter, μ	Vaporization pressure, lb./sq. in.
52	62
65	64
130	66
195	67
910	73

Interfacial tension between the drop and field liquids was measured by the drop-volume technique. The glass feed tube in the pressure cell was replaced with a stalagmometer, and the feed cylinders were used to draw in and displace water from it.

RESULTS

The experimental vapor pressure and vaporization pressures for drops of purified Freon-12 in distilled water are presented in Table 1. The purified Freon-12 used was a 1-lb. sample described by the suppliers as having been taken from the stock used for measurement of accurate P-V-T properties, which was the center 50% of a careful distillation, dried over phosphorus pentoxide and deaerated. They found that the stock analyzed 0.01% of air by volume in the vapor phase and detected no impurities other than water by infrared absorption. In the present experimental work this material was found to have a 2 lb./sq. in. condensation range after it had been degassed. When the vapor pressure of the Freon-12–water system was calculated by adjusting the published vapor-pressure data (*14*) to the pressure in the cell and adding the vapor pressure of water, the result was within 1 lb./sq. in. of the limits of the experimental condensation range for the five points checked.

For an examination of the effects of a surface-active agent, vapor and vaporization pressures for degassed commercial-grade Freon-12 in distilled water and in water saturated with iso-amyl alcohol at about 85°C. were obtained. The results are shown in Figure 3. This sample of Freon had a 5 lb./sq. in. condensation range in distilled water. The effect of the iso-amyl alcohol was to decrease the vapor pressure and broaden the condensing range of the drops considerably and to decrease the vaporization pressure at a given temperature. It is not certain whether the pressure difference between the vaporization and vapor-pressure curves was decreased at a given reduced temperature as a result of the alcohol addition, because the critical point was difficult to observe and the composition of the system changed as more and more alcohol-free Freon was sprayed into the chamber. The data are numbered in the order in which they were taken so that the extent of the effects of the composition change can be seen.

Similar experiments with small amounts of Dreft and of the supernatant liquid from the Teflon suspensoid used in making up the pipe joints added to the water gave results no different from those obtained when the contaminants were not present. Subjecting the drops to mechanical shock by striking the cell with a metal hammer made no noticeable difference in the vaporization pressure. Vibration from the air-circulation blower had no effect, as checked by turning it off during a few measurements.

Motion pictures of droplet vaporization were made, and the details may be found in reference *13*.

The effect of drop diameter may be seen in the following results. At 71.4°C. the pressure was observed at which purified Freon-12 drops of various sizes vaporized on the glass stage as pressure was reduced fairly slowly. These data are given in Table 2. Diameters were estimated to the nearest one-tenth division of the ocular micrometer and thus are relatively inaccurate in the small sizes. As rate of pressure fall was not closely regulated, these data are not highly precise. However, as expected, larger drops clearly vaporized at higher pressures than smaller drops.

Some interesting phenomena were observed at temperatures between 100°C. and the critical point. With a drop of Freon-12 captured on the glass stage, the pressure was reduced rapidly with the screw pressurizer, while the drop was observed by transmitted light. At a definite pressure the drop momentarily became opaque because of the formation of hundreds of tiny bubbles in it; then it cleared as it became completely vaporized. With Freon-12 of condensing range 589 to 592 lb./sq. in. abs. at 108.2°C., when the pressure was held between 588 and 589 lb./sq. in. abs. dozens of bubbles were seen forming and rising through the drop to the vapor-liquid meniscus as it passed through the drop. Several seconds were required for the meniscus to pass through the drop. At 589 lb./sq. in. abs. the bubbles stopped forming, although the meniscus continued to move as vaporization from the surface took place. At 588 lb./sq. in. abs. the bubble-formation rate and the meniscus velocity were much greater and increased further at still lower pressures. Opalescence, believed to be of the type described by Maass, Mason, and coworkers (*15*), was observed in the neighborhood of the meniscus disappearance temperature, especially when sudden changes of about 5 lb./sq. in. or more in the pressure in the cell were made. The opalescence occurred in moving horizontal bands about one fifth as high as the bubble diameter. At 114.7°C. it was most pronounced at about 616 lb./sq. in., at 115.2°C. at 630 to 641 lb./sq. in., although present over the range 605 to 665 lb./sq. in. It was observed at temperatures from 110° to 116°C., with no indication that limits had been reached.

DISCUSSION

An estimate of n_k by use of Equation (10), the relation $V_n = (4/3)\pi r_n^3$, and the experimental vapor-pressure data indicated that there were from two-hundred to several thousand molecules in the critical bubble, the former figure for temperatures around 70°C. The mole fraction of water in the vapor is given approximately by the ratio of the vapor pressure of pure water to the vapor pressure of the mixture. At 70°C. the ratio is about 0.02, which indicates that about four molecules of water were present in the critical bubble. These numbers are small enough to permit neglecting the second sum of Equation (27) in analyzing the results of the experiments. The contribution of the second sum may be greater at higher temperatures, but it should be realized that an error of even a factor of two in the sum of the two terms represents only a change of at most 1 lb./sq. in. in the calculated vaporization pressure. Thus Equation (19) may be used for the calculation of the vaporization pressure. In this calculation, as a convenience to avoid repetitive trial and error, the experimental value of the vaporization pressure was used as a first approximation to determine the coefficient of the exponential in Equation (19), and the experimental conditions were used to determine the value of the bubble formation frequency. Equation (19) was then solved for $\Delta A_k/kT$. The value of r_k was obtained from Equation (21), and Equation (26) was solved for P_B, which was equal to P_A for the drop sizes observed. The resulting calculated value of P_A was always so close to the experimental that recalculation of the pre-exponential term was unnecessary. Since the interfacial tension was found in the experimental work to be about 25 dynes/cm., the term $2\sigma_{AB}/r_{AB}$ in Equation (26) is less than 0.1 lb./sq. in. for drops larger than 8 μ in diameter and thus can be neglected for such drops. For these larger drops the effect of drop size on nucleation pressure is limited to the change in bubble-formation frequency per drop resulting from the change in volume of the drop.

With regard to the surface tension of Freon-12 in the calculation, there was a small quantity of water dissolved in the Freon, which could be expected to raise its surface tension over that of pure Freon-12, the usual result for the solution of a nonsurface-active component in a liquid of lower surface tension. In the present case the effect should be slight because the solubility is very low. Consequently the recent data on the surface tension of dichlorodifluoromethane reported by Plank (*16*), at 0°C. 11.7

TABLE 3. COMPARISON OF CALCULATED VAPORIZATION PRESSURES FOR FREON-12 DROPS IN WATER WITH EXPERIMENTAL VALUES

T, °C.	69.3	71.2	81.2	95.8	106.7
$(p_\infty)_{exp.}$, lb./sq. in. abs.	271–273	283–285	349–351	464–466	570–572
σ_{AC}, dynes/cm.	3.59	3.38	2.38	1.06	0.240
p_k, lb./sq. in. abs.	258	269	338	460	571
n_k,	206	237	531	3000	47,200
r_k, 10^{-7} cm.	4.52	4.67	5.64	8.58	18.2
$\frac{J_{P_{A-1}}}{J_{PA}}$	1.75	1.84	2.86	35.4	4×10^{14}
$P_A(+)_{calc.}$*, lb./sq. in. abs.	17	49	210	422	567
$(P_A)_{calc.}$*, lb./sq. in. abs.	28	59	216	424	567
$P_A(-)_{calc.}$*, lb./sq. in. abs.	38	68	221	426	567
$(P_A)_{exp.}$, lb./sq. in. abs.	32	63	216	422	566

*$(P_A)_{calc.}$, calculated for $J = 1$ bubble/(drop) (5 sec.).

dynes/cm., at 30°C. 8.1 dynes/cm., were used. These values were extrapolated into the region of interest by use of the relationship

$$\sigma = g(T_c - T)^j \tag{28}$$

The exponent j was set equal to 11/9, the value found for a great number of organic compounds. The mean value $g = 0.0372$ derived from the two experimental values was used in the calculations.

Table 3 gives the summarized results of the calculations. In Table 3 P_A is the pressure at which a drop 0.2 mm. in diameter should vaporize within 5 sec. on the average, calculated from the theory by using values of surface tension from Equation (28). $P_A(-)$ and $P_A(+)$ are the pressures calculated when the surface tension from Equation (28) is decreased and increased by 3%. $J_{P_{A-1}}/J_{P_A}$ is the approximate factor by which the bubble formation frequency increases with 1 lb./sq. in. decrease in P_A, as determined from the change in the work of formation. Table 3 also gives the number of molecules and radius of the critical bubble. Comparison of the theoretical vaporization pressures P_A with the experimental values $(P_A)_{exp}$ leads to the conclusion that within the experimental errors of ±0.1°C., ±1 lb./sq. in., drop diameters from 0.1 to 0.3 mm., and observation times from 1 to 5 sec. the theoretical curve is in agreement with the experimental data when reasonable latitude is allowed the value of the surface tension.

It is considered that the number and small size of the drops observed in this work precluded the possibility that the drops were caused to vaporize by the influence of cosmic rays or other background radiation or by the presence of solid particles and that the degassing of the liquids by boiling eliminated small gas bubbles so that they were not the cause of bubble formation. These certainly were not the origin of the copious bubble evolution seen in captured drops near the critical point. The decay rate of even recently formed organic matter resulting from the take-up of radioactive carbon-14 from the atmosphere is only about 12 disintegrations/min./g. of carbon. The particle produced is a weakly penetrating electron. Radiation from carbon-14 is not sufficient to influence the measurements because of the small quantity of carbon in a drop, the short time of exposure to low pressure, and the large number of drops observed. Since striking the cell with a hammer did not influence the results, the possible influence of vibrations in the building or from the air-circulation blower is improbable because the sharp shocks should have intensified any such effects and made them noticeable. There was never any indication that the motion of the drops had any effect on the nucleation pressure. Large free-falling drops vaporized at about the same pressure as drops trapped in the glass cage. In any event the small drops for which the comparison with theory was made moved slowly, and no effects of motion are to be expected.

The experimental vaporization pressures of Wismer (*7*) for ethyl ether were also compared with values predicted by the theory. The nucleation pressure for ethyl ether was calculated according to Equation (19) at a few temperatures, with vapor pressures and densities obtained from the data of Schnaible and Smith (*17*) and surface tensions from the data of Jeffries, Derrick, and Musgrave (*18*) extrapolated graphically by passing a line of slope 1.22 through a log-log plot of the data. The calculation technique followed was similar to the calculations for Freon-12 in water. J was assumed to be 1 bubble/cc./sec., which implies that the product of the experimental quantity of liquid and the observation time was 1 cc. sec. This product was not specifically stated in Wismer's work but should be of the correct order of magnitude. The summarized results of the calculations are given in Table 4. The agreement with Wismer's data, also given in Table 4, is satisfactory only at atmospheric pressure, since there only can the discrepancies observed be explained in terms of reasonable variations in the quantity of material and time of exposure to low pressure in the experiments. Curvature in the line through the experimental data (Figure 4), which should be evident over so large a temperature range regardless of the purity of the ether, is absent. It is to be especially noted that the experimental values not in agreement are lower than the theoretical, which indicates they could not be caused by external influences. The satisfactory agreement found for Freon-12 makes it unlikely that the discrepancies result from defects in the theory or from the assumptions made in the numerical calculations, except possibly that the surface tension of ether may not follow Equation (28) above 145°C., although there is no reason to suspect that it does not. It appears much more probable that a difference in the experimental conditions caused the high-pressure data to be erroneous, whereas the data at atmospheric pressure are valid. The most likely explanation appears to be that the Bourdon pressure gauge in the high-pressure apparatus of Wismer had an inaccurate calibration in addition to the large zero error mentioned in his description of the apparatus (*7*).

One should note that the exponential factor involving the latent heat of vaporization, which appeared in Döring's equation for the bubble formation rate and which has been rejected on theoretical grounds, would decrease the calculated vaporization pressure for Freon-12 in water by about 7 lb./sq. in. at 70°C. and about 4 lb./sq. in. at 80°C. The resulting values would still be reasonably close to the experimental values, considering the possible errors in surface tension among others, but the values calculated omitting the factor are in noticeably closer agreement. The same holds for the agreement with Wismer's data at atmospheric pressure.

TABLE 4. VAPORIZATION PRESSURES FOR ETHYL ETHER

T, °C.	143.0	143.8	163.8	176.8	183.8
$(p_\infty)_{exp}$, lb./sq. in. abs.	227	231	327	405	456
σ, dynes/cm.	3.70	3.63	1.94	0.97	0.51
p_k, lb./sq. in. abs.	214	218	319	401	455
P_A, lb./sq. in. abs.	12	22	244	375	445
$(P_A)^*_{exp}$, lb./sq. in. abs.	15	22	230	350	430

*Data of Wismer (7).

SUMMARY AND CONCLUSIONS

This paper has presented the equations to be used for predicting the conditions required for homogeneous nucleation in liquids at atmospheric pressure and above; it has described the measurement of these conditions with an apparatus in which the effects of external influences are minimized or avoided, and it has shown the experimental and theoretical work to be in agreement.

Further applications of the principles and methods described should lead to further fundamental knowledge of the processes of bubble formation in boiling, flow cavitation, and evolution of gases from supersaturated solutions. Some of the most promising avenues should be the following:

1. Investigation of the effects of concentration of liquid solutions on bubble evolution.
2. Development of a flow apparatus with liquid interfaces used to eliminate the effects of solid surfaces, such as the annular flow of a superheated liquid within a nonsuperheated liquid through a constriction to produce a region of high velocity and low pressure. Such a condition might be approached with a swirl type of pressure nozzle in which the nonsuperheated and superheated liquid are contacted in the swirl-chamber orifice where an air core normally occurs.
3. Investigation of the effects of suspended particles, as for example very finely divided metals, degassed by boiling the liquid containing them.
4. Investigation of the effects of dissolved gases.

These and similar investigations may help to elucidate how an active center becomes active in boiling, how the nature of the solid surface affects boiling, and how the effects of composition of liquid mixtures on boiling heat transfer can be predicted.

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NOTATION

A = Helmholtz free-energy or total-work function
b = $1 - (p_L/p_k)$
f = fugacity
g = constant in surface-tension correlation, Equation (28)
i = index for summation
j = constant in surface-tension correlation, Equation (28)
J = bubble production rate or nucleation frequency, no./(unit time) (unit volume)
J_{P_A} = bubble formation rate at pressure P_A
k = Boltzmann's constant
m = mass of a molecule
n = number of molecules in a bubble
n_k = number of molecules in a bubble of critical radius
n_s = number of molecules in a bubble large enough to be removed from the distribution
p = pressure
p_n = pressure in bubble with n molecules
p_k = pressure in bubble of critical size
P = vaporization pressure, pressure in liquid at which bubble formation rate is high enough to produce a visible bubble within the time of observation
r_n = radius of bubble with n molecules
r_k = radius of critical bubble
r^* = r_n/r_k
$S(n)$ = effective transfer area of a bubble containing n molecules
t = time
T = absolute temperature
T_c = critical temperature
u = chemical potential, energy/molecule
u_k = chemical potential of vapor molecules in critical bubble
v_k = volume per molecule in the vapor at the transfer surface of the critical bubble
v_L = volume per molecule in the liquid
v_{Lm} = mean value of specific volume of liquid between pressures p_L and p_∞, the vapor pressure over a plane surface ($r = \infty$)
V = volume
V_n = volume of bubble containing n molecules
$W_L(n)$ = probability of vaporization of a single molecule per unit area and time into a bubble containing n molecules
$W_V(n)$ = probability of condensation of a single molecule per unit area and time from a bubble containing n molecules
x = variable of integration, $x \equiv 1 - r^*$
y = mole fraction in vapor phase
z = compressibility factor = pV/nkT
$Z(n)$ = distribution function expressing the number of bubbles containing n molecules in a unit volume of liquid
$\beta(n)$ $\equiv$ $W_L(n-1)/W_V(n)$
Δ = notation for difference or increment
ν = fugacity coefficient = f/p
σ = surface tension

Subscripts

a = molecular species a
A = liquid phase in drop
b = molecular species b
B = liquid phase in field
C = vapor phase in lens
L = liquid phase
k = critical bubble condition
n = number of molecules
0 = bubble containing minimum number of molecules
s = bubble of the size to be removed from the distribution
V = vapor phase
I, II = any two distinct accessible regions of phase space
∞ = condition of thermodynamic equilibrium between two phases separated by a plane interface ($r = \infty$)

Superscript

0 = standard state, the pure component at the temperature and pressure in the vapor

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