Bubble Nucleation in Liquids

Theoretical and experimental aspects of homogeneous and heterogeneous bubble nucleation are reviewed. Recent developments in nucleation theory, which include hydrodynamic and diffusion constraints, gas phase nonidealities, and heterogeneous nucleation are discussed. A large number of the measured limits of superheat of pure components are close to 88 to 90% of the critical temperature. Where calculations can be made, these measurements are in agreement with predictions from classical nucleation theory. Measurements of the limits of superheat of mixtures are useful for understanding one proposed mechanism for the dangerous phenomena known as contact vapor explosions.

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SCOPE

This review covers theoretical and experimental aspects of bubble nucleation. Under some conditions, liquids held at 1 atm. can be superheated to limits of superheat which are about 88 to 90% of their critical temperature. Such homogeneously nucleated liquids boil with an essentially explosive violence which can pose a hazard in industry. Heterogeneously nucleated liquids boil at lower temperatures but may be violent nevertheless. Large superheating may be involved in the dangerous and destructive contact vapor explosions observed in metallurgical and paper smelt processing and pose a potential hazard in the operation of nuclear reactors, in cryogenic systems, and in the transport of liquefied natural gas. An understanding of bubble nucleation phenomena should be significant in fully defining safety procedures for minimizing these explosions. In addition, other nucleation related problems, as in the control of foaming of plastics or even of beer, would be helped by knowledge of the fundamentals of bubble nucleation.

This review covers the thermodynamics and kinetics of the classical theory of nucleation which provides a prediction of the rates of bubble nucleation per unit volume from thermodynamic and kinetic parameters. Recent work on the influences on these rates by factors such as thermal conductivity, viscous and inertial forces, diffusion, and gas nonidealities is included.

Heterogeneous nucleation occurs at temperatures below the homogeneous limit of superheat. Criteria for a high probability of heterogeneous nucleation are also discussed.

Measured limits of superheat of one component systems are generally close to 88 to 90% of the critical temperature, in accord with predictions from nucleation theory. Measurements of mixtures, some of which are discussed, may be significant in understanding contact vapor explosions.

CONCLUSIONS AND SIGNIFICANCE

Classical nucleation theory relates the nucleation rate to the interfacial and surface properties of a volatile liquid in contact with a hot substrate. The better the wetting of the substrate by the fluid, the less probable is heterogeneous nucleation at the interface and the more probable is homogeneous nucleation in the interior of the fluid. One predicts that homogeneous nucleation occurs at the limit of superheat at temperatures (88 to 90% of the critical temperature) which are generally higher than the range for heterogeneous nucleation. A large number of liquids held at an ambient pressure of 1 atm. have been heated close to their predicted limits of superheat where they boil explosively. Liquids nucleated heterogeneously at lower temperatures boil with less violence.

The limit of superheat is a narrow range of temperatures above which fluids will always film boil. Below this temperature range fluids may film boil if the probabilities are high enough for heterogeneous nucleation at an interface between the fluid and its (solid or liquid) surroundings. The criteria deduced from theory for homogeneous and heterogeneous nucleation lead to one plausible mechanism for the initiation of the dangerous and destructive contact vapor explosions. This mechanism could be important in defining safety criteria for minimizing the hazards of these explosions.

Recent developments have extended the theory to cases where bubble growth is limited by diffusion rates and viscous and other hydrodynamic forces. Quantitative expressions for the nucleation rates for these cases have not been tested experimentally.

Barriers to the nucleation of bubbles may lead to a superheating of liquids which is so large that they will boil with an essentially explosive violence. All liquids must be superheated to temperatures above their boiling points in order to boil at a finite rate. Superheats vary from those that are negligibly small to superheats so large that the temperature approaches the critical temperature. The purpose of this article is to describe the concepts underlying the kinetics of bubble nucleation and to indicate the conditions under which the barriers to nucleation of bubbles and to boiling lead to very large superheats.

Under some conditions a liquid held at an ambient pressure of 1 atm. may be superheated to close to 90% of its critical temperature before the probability for the nucleation of a bubble becomes significant. Once boiling is initiated in a liquid so superheated, the liquid will boil explosively. Such explosive boiling presents a safety hazard in industry and may be involved in the dangerous and destructive explosive phenomenon known as contact vapor explosion observed in many metallurgical processes and in paper smelt processing (Blander and Katz, 1973; Bradley and Witte, 1972; Brauer et al., 1968; Flory et al., 1969; Genco and Lemmon, 1970; Long, 1957; Nelson and Kennedy, 1956; Witte et al., 1970). Such explosive boiling also poses a potential hazard in the transport of liquefied natural gas and in the operation of nuclear reactors (Burgess et al., 1970; Enger and Hartmann, 1972; Fauske, 1972; Katz, 1972; Katz and Sliepcevich, 1971; Nakanishi and Reid, 1971). In addition to explosions, smaller barriers to boiling may lead to milder phenomena as in geysers, fountaining of volcanoes, splattering of water as in french frying, or foaming as in beer. An understanding of the fundamentals of bubble nucleation should prove useful in minimizing the bad effects of these phenomena and is essential for fully defining safety criteria in the safe handling of materials which may be capable of producing contact vapor explosions.

The general concept behind the theory of bubble nucleation may be understood if one considers a volatile liquid which is not in contact with a gas phase and which wets (has a zero contact angle with) all surfaces which it contacts. Simple thermodynamic considerations show that bubble nucleation in this liquid will produce bubbles completely within the liquid. Such nucleation is termed *homogeneous nucleation* and is to be contrasted with *heterogeneous nucleation,* nucleation at an interface between the volatile liquid and another phase it contacts. Heterogeneous nucleation can occur only if the the contact angle of the volatile fluid is greater than zero. In this review, we will place emphasis on homogeneous nucleation.

Consider the minimum work to create a bubble in a liquid at its boiling point when the liquid has a zero contact angle with its container surface. The major contributions to this work arise from the positive work to create the surface of the bubble and the work to transfer molecules from the liquid into the bubble, also positive. The total work is always positive and rises to infinity as the bubble volume increases to infinity. Consequently, vapor bubbles in a liquid at its boiling point are always unstable and collapse spontaneously. It is impossible to boil a liquid at its boiling point under these conditions. In order to boil such a liquid, it must be superheated beyond its boiling point so that the minimum work of transferring molecules from the liquid to the gas is negative. When this is added to the surface work, a function as illustrated in Figure 1 is obtained. The minimum work to create a bubble, which is also defined as the negative of the availability (Modell and Reid, 1974; Cole, 1974)*, increases to a maximum at small volumes and then decreases. The maximum constitutes a barrier which must be surmounted at a significant rate before boiling will be observed. The height of the maximum is governed by the surface tension of the fluid and the degree of superheat (that is, the difference between the vapor pressure and the ambient pressure). As one increases the temperature of a pure liquid above its boiling point, the surface tension decreases and the vapor pressure increases. Both factors lead to a lowering of the barrier to bubble nucleation and to an increase of the probability of a bubble surmounting this barrier. In bubble nucleation theory one calculates J, the rate of formation of bubbles which surmount the barrier and continue to grow spontaneously. From this rate (per unit volume per unit time) one may calculate the probability of boiling for any given volume and given heating history.

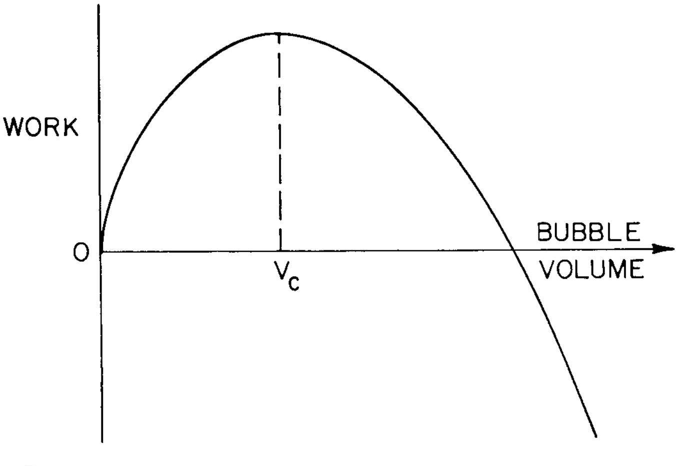

Fig. 1. Schematic of the work, *W*, to make a bubble as a function of the volume, *V*. The bubble with the volume, V_c, at the maximum is termed the critical size bubble.

Boiling initiation for a given ambient pressure does not take place at any particular temperature but can occur over a range of temperatures. The median temperature of this range has been termed the *kinetic limit of superheat.* It is obviously not a true limit and might more properly be termed a *median attainable superheat.* There is a true limit, the thermodynamic limit of superheat, which is the temperature at which the liquid branch of a pressure-volume diagram for a fluid is at a minimum, for example, the point C in Figure 2. Such a minimum point is the border between the metastable and the unstable liquid. The thermodynamic limit of superheat of liquids, except in very esoteric circumstances, is higher than the kinetic limit.

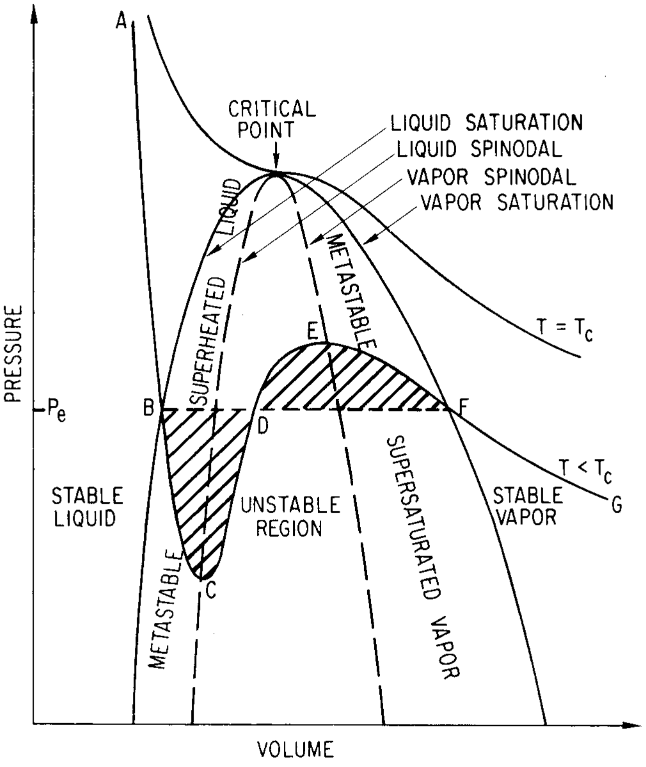

Fig. 2. Schematic of pressure-volume isotherms for a fluid at and below the critical temperature. At $T<T_c$ the curve AB represents the stable liquid; BC, metastable liquid; CE, unstable fluid; EF, metastable vapor; and FG, stable vapor. The shaded area BCD is equal to the area DEF and the line BDF is at the equilibrium vapor pressure.

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* In this review we discuss the minimum work done on the bubble to create it. This is exactly equivalent to the negative of the availability which is a measure of the maximum work which can be extracted from a system.

The theory of nucleation was developed by Volmer and Weber (1926), Farkas (1927), Becker and Döring (1935), Döring (1937, 1938) and Zeldovich (1943). The early work is thoroughly reviewed in books by Volmer (1939) and Frenkel (1946). Recent work by Kagan (1960) and by Katz and Blander (1973) has generalized the theory. Fisher (1948) has examined bubble nucleation at a smooth rigid interface, and Moore (1956, 1959), Apfel (1971*a*), and Jarvis, Donohue, and Katz (1975) have studied nucleation at the interface between two liquids. Cole (1974) has reviewed nucleation at cracks and crevices. In this paper we will describe the concepts involved in these theories with emphasis on homogeneous nucleation, and we will compare theory with experimental data, most of it recent. It will be shown that the available experimental data on boiling are consistent with the predictions of nucleation theory and support the theory.

HOMOGENEOUS NUCLEATION

Theory

The thermodynamic limit of superheat

If a fluid exhibits a van der Waals type of loop as in one of the isotherms plotted in Figure 2, then the liquid may exist in two states: the stable and the metastable. The pressure plotted in the ordinate of Figure 2 is the internal pressure of the liquid. The vapor pressure P_e of the liquid is at a level such that the two shaded areas of the loops are equal $\left(\text{that is, } \int_B^F V dP = 0\right)$. The branch AB represents the stable liquid under an ambient pressure greater than the vapor pressure P_e. The curve BC represents the metastable liquid at ambient pressures less than the vapor pressure. The point C is the boundary between the metastable liquid and the unstable fluid represented by the curve CE. The temperature of the isotherm for which a point such as C is at the ambient pressure is the thermodynamic limit of superheat. It is a true limit which might be approached but cannot be reached in a practical sense. The approach to this limit may be made by raising the temperature while the fluid is kept at constant pressure or by stretching the fluid isothermally along the curve ABC of Figure 2. In stretching the fluid, its pressure decreases until the fluid approaches C. [If the temperature of the isotherm is low enough, the pressure can be negative (Apfel, 1970, 1971*b*; Briggs, 1975)]. In either mode of approach, there should be a drastic increase of the constant pressure heat capacity and the isothermal compressibility of the fluid as it gets very close to a point as C. This would provide a simple test of the closeness of the approach to C. However, such a test has not been reported.

If an accurate equation of state were known, one could calculate the thermodynamic limit of superheat (Temperley and Chambers, 1946; Temperley, 1947; Eberhart and Schnyders, 1973; Beegle, 1973; Beegle et al., 1974). At present, despite the calculations which have been made, there is no suitable equation of state for a reliable calculation. In lieu of this, we may use an equation of state, such as the Berthelot equation, which is certainly too simple but adequate for the purpose of illustration:

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT \qquad (1)$$

The calculation of the thermodynamic limit of superheat T_l is particularly simple for the case in which the pressure is close to zero. The result is

$$T_l = 0.919\ T_c \qquad (2)$$

which is obtained by differentiating Equation (1) with respect to V and by setting $(dP/dV) = 0$. This result is higher than, and therefore consistent with, measured kinetic limits of superheat. The limit calculated by using the van der Waals equation is 0.844 T_c which, as will be seen later, is much too low. Other equations of state have been utilized to calculate limits of superheat including a modified Berthelot equation with corrections for volume exclusion effects obtained from scaled particle theory (Eberhart and Schnyders, 1973) and the Redlich-Kwong equation with the Soave modification (Beegle, 1973; Beegle et al., 1974). For pressures other than zero, the reduced limit of superheat T_l/T_c calculated from the Berthelot equation is illustrated in Figure 3. As may be seen in Figure 3, the thermodynamic limit of superheat calculated from the Berthelot equation is considerably higher than the normal boiling point, even at moderately negative pressures. Only for very negative internal pressures (that is, for cases where a liquid is very stretched) might the limit come close to the normal boiling point.

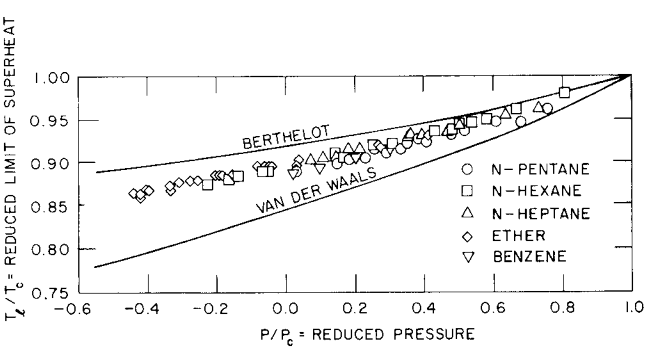

Fig. 3. Reduced limits of superheat as a function of reduced pressure. The thermodynamic limits of superheat calculated from the Berthelot and van der Waals equations are plotted. Calculations from nucleation theory (not plotted) provide a close representation of the measurements. The figure is adapted from Eberhart and Schnyders (1973). The points represent measurements of kinetic limits of superheat by Skripov (1974) and coworkers and Apfel (1971b).

For mixtures, the stability criterion is complex. A sophisticated discussion has been given by Beegle et al. (1974).

Kinetic limits of superheat

Classical theory. The classical theory of kinetics of nucleation may be ascribed to several authors including Volmer and Weber (1926), Farkas (1927), Becker and Döring (1935), and Zeldovich (1943). The starting point is to calculate, at constant temperature, the minimum work (that is, the negative of the availability) W required to form a bubble of gas of volume V_G from the homogenous liquid phase. To create a gas free cavity, one must expend work equal to σA to create the new surface. However, in creating a cavity containing x gas molecules, part of this surface work is done by the gas entering the cavity. The maximum possible work that the x gas molecules vaporizing into the cavity can provide would be that obtained along a reversible path. The entire process is isothermal, so if one wants to vaporize x molecules from the liquid reversibly, it must be done at the vapor pressure P_V. If we vaporize x molecules at a constant pressure P_V into a semipermeable membrane of constant area submerged in a medium at pressure P_L and kept under an external counterforce per unit area $(P_V - P_L)$, then the work W_1 done by the gas on the environment providing that counterforce is $(P_V - P_L)V_G'$. V_G' is the volume inside the membrane enclosing x molecules at the pressure P_V. If the gas volume inside the membrane is then changed from V_G'

to V_G while the number of molecules inside the membrane is kept constant, the maximum work done on the environment W_2 is given by

$$W_2 = \int_{V_G'}^{V_G} (P - P_L)\,dV = P_G V_G - P_V V_G' - P_L(V_G - V_G') - \int_{P_V}^{P_G} V\,dP$$

$$= P_G V_G - P_V V_G' - P_L(V_G - V_G') - x(\mu_G - \mu_L) \quad (3)$$

where P is the pressure inside the membrane during the change in volume from V_G' to V_G. We have used the relation $d\mu = (V/x)dP$ and utilized the fact that the chemical potential of the gas at the pressure P_V is the same as that of the external liquid. The maximum work obtainable from vaporizing the gas to a volume V_G at a pressure P_G is therefore $W_1 + W_2$. The minimum work needed to form a bubble is therefore[*]

$$W = \sigma A - W_1 - W_2$$

$$= \sigma A - (P_G - P_L)V_G + x(\mu_G - \mu_L) \quad (4)$$

Equation (4) is the fundamental equation in nucleation theory. A detailed derivation was given here since it is normally stated without derivation. The work to make a bubble from a metastable liquid increases to a maximum and then decreases as the volume increases. When P_G is equal to P_V, and when the volume of the bubble is such that the radius r is given by

$$P_V = P_L + \frac{2\sigma}{r_c} \quad (5)$$

then the bubble is often termed the *critical bubble*, and r_c is termed the *critical radius*. Since $P_V = P_G$, such a bubble is in chemical equilibrium with the liquid. Equation (5), known as Laplace's equation and also as the Laplace-Kelvin equation, is a statement of the fact that the critical bubble is also in mechanical equilibrium with the liquid. Gibbs (1961) has given an exact derivation of the minimum work to create a critical bubble. For any given fluid and temperature, such a bubble has a unique volume and value of W. For bubbles of any other size, the value of W is not a unique function of the volume, and one other variable (P_G or x) must be fixed.

Bubbles smaller than the critical tend to collapse, and bubbles larger than the critical tend to continue to grow spontaneously. Since bubbles can grow to critical size only from subcritical sizes which tend to collapse, critical size bubbles can form only by the relatively improbable fluctuation up the barrier represented by the increase of W on the left-hand side of Figure 1.

In the usual versions of nucleation theory, that is, those calculated without taking hydrodynamic constraints into account, it is customary to approximate P_G by an expression similar to that in Equation (5):

$$P_G \cong P_L + \frac{2\sigma}{r} \quad (6)$$

In other words, the use of Equation (6) presumes that the bubble is close to mechanical equilibrium. In such a case one can show (Kagan, 1960; Katz and Blander, 1973) that

$$W \approx \frac{4}{3}\pi r_c^2 - 4\pi\sigma[r - r_c]^2 B + \ldots \quad (7)$$

where, for mechanical equilibrium only

$$B \approx 1 - 1/3(1 - P_L/P_V)$$

Since usually $P_L << P_V$, the factor $B \approx 2/3$. On the other hand, if one assumes that the bubble is in chemical equilibrium, that is, $P_G = P_V$ (but not necessarily in mechanical equilibrium), the only difference in the result is that the factor B does not appear in Equation (7) (equivalent to $B = 1$). Whether a bubble in a real case is in chemical or mechanical equilibrium or something in between (which is actually the case) depends on the relative relaxation times for the change of the bubble radius and for the change of the number of molecules in the bubble. If the bubble radius readjusts rapidly to mechanical forces, mechanical but not chemical equilibrium will obtain. If the molecules evaporate rapidly and the liquid is too viscous for the radius to readjust, then chemical and not mechanical equilibrium will obtain. In any case, it is usually of little significance, since, as shall be shown, the only effect of changing B from 2/3 to unity will be to change the rate of nucleation by the factor $B^{1/2}$, and an error in the predicted rate of a factor of $(2/3)^{1/2}$ is negligible. For cavitation, it should be noted that B is always equal to unity, as Kagan (1960) and Zeldovich (1943) have shown.

Consider now the formation of a bubble. Bubbles are formed as density fluctuations in the liquid. A localized region temporarily has a lower than average density, and we describe that by considering it to be a bubble of a given radius r containing a certain number of molecules x. Such a bubble can grow or shrink owing to motions of the surrounding molecules. It can also add or lose molecules; for example, if a molecule in it goes to its boundary, we can picture it as having condensed at the bubble wall. The number n of bubbles per unit volume containing x molecules is related exponentially to the minimum work W required to form the bubble as given in Equation (4); for example

$$n = \mathrm{N} \exp(-W/kT) \quad (8)$$

where we make the usual assumption that the prefactor **N** is the number density of the liquid. There is no rigorous justification for this assumption. However, such an approximate value is probably justified, since large errors in this prefactor lead to very small errors in predictions of the superheats needed to cause homogeneous nucleation.

The growth or decay of bubbles is considered to occur by the evaporation or condensation of molecules at the gas-liquid interface. The net rate at which bubbles go from those containing $x \rightarrow x + 1$ molecules is equal to the difference between the forward rates governed by vaporization and the backward rates governed by condensation. At steady state, this rate is independent of x, and the rate of formation of bubbles per unit time per unit volume J can be then shown to be an integral of n

$$J = \beta / \int [nA]^{-1}\,dx \quad (9)$$

where β is the rate per unit area at which a bubble surface gains or loses molecules, accurately approximated as $\beta = P/(2\pi mkT)^{1/2}$. Since W can be approximated as a quadratic, the integral in Equation (9) can be readily evaluated with the result

$$J = \beta A(r_c) n(r_c) Z \quad (10)$$

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[*] Following Gibbs (1961), the total volume of the system has been kept constant to obtain this result. If the external phase is infinite in extent, then there is only an infinitesimal increase in pressure. If the external phase were kept at constant pressure, a term $xP_L v_L$ should be added to Equation (4), where v_L is the volume per molecule of the external phase. This derivation can be readily generalized for the formation of any new phase.

where $A(r_c)$ and $n(r_c)$ are the surface area and number density of critical bubbles, and Z, known as the Zeldovich factor, is given by

$$Z = (\sigma kT/B)^{1/2}\,[P_V A(r_c)]^{-1} \qquad (11)$$

and where P_V, the vapor pressure, is equal to the pressure inside the critical bubble. The rate J represents the net rate of bubbles that grow from $x \rightarrow x + 1$ molecules which, in this steady state solution, is also the rate at which bubbles grow beyond critical size and continue to grow spontaneously. The solution of Equation (9), represented by Equation (10), depends on the fact that the largest contribution to J from the integral occurs at radii close enough to the critical radius so that the work to make a bubble is adequately represented by the quadratic function of $(r - r_c)$ given in Equation (7) (Cohen, 1970), and the contributions from terms of order higher than $(r - r_c)^2$ are negligible. In a sense, this implies that most of the impedance governing the steady state rate J occurs near the critical size. This is evidenced in Equation (10), where it can be seen that the rate of nucleation is proportional to the equilibrium number of critical size bubbles. The Zeldovich factor Z is a correction to the rate which arises from the fact that the steady state concentration of critical size bubbles is less than the equilibrium number given by Equation (11). Combining Equations (7) to (11), one obtains

$$J = \mathrm{N}\left[\frac{2\sigma}{\pi m B}\right]^{1/2} \exp\left[\frac{-16\pi\sigma^3}{3kT\,[P_V - P_L]^2}\right] \qquad (12)$$

The pressure inside the critical bubble P_V is equal to the vapor pressure of the liquid at a total hydrostatic pressure equal to the ambient pressure P_L. However, the equilibrium vapor pressure P_e is measured on a liquid under a hydrostatic pressure equal to its vapor pressure. It is necessary to correct for this. In the Appendix we show that this Poynting correction can be expressed by

$$P_V - P_L \cong (P_e - P_L)\delta \qquad (13)$$

where for moderate pressures the correction factor for the effect of pressure on the vapor pressure δ is given by the equation

$$\delta \cong 1 - \left(\frac{d_G}{d}\right) + \frac{1}{2}\left(\frac{d_G}{d}\right)^2 \qquad (14)$$

where d is the density of the liquid and d_G the density of the gas. Combining Equations (12) and (13) and expressing the result in terms of common laboratory units, one obtains

$$J \approx 3.73(10^{35})\left[\frac{d^2\sigma}{M^3B}\right]^{1/2} \exp\left[\frac{-1.182(10^5)\sigma^3}{T[P_e - P_L]^2\delta^2}\right] \qquad (15)$$

where $B \approx 2/3$, except for cavitation in which case $B \approx 1$, and where the units are $J(\mathrm{cm}^{-3}\mathrm{s}^{-1})$, $P_V(\mathrm{atm.})$, $P_L(\mathrm{atm.})$, $T(K)$, $\sigma(\mathrm{erg\ cm}^{-2})$, $d(\mathrm{g\ cm}^{-3})$, $M(\mathrm{g\ mole}^{-1})$. We have also neglected a term close to unity which corrects for the effect of nonideality of the gas inside the bubble (Katz and Blander, 1973).

Let us examine the implications of Equation (15). The preexponential terms vary slowly with temperature. However, any temperature change inside the exponential will have a very strong effect on the rate of nucleation. Consider nucleation at an ambient pressure P_L of 1 atm. One observes experimentally that nucleation occurs at about 0.89 T_c. On substituting experimental values (or values extrapolated from experimental) for surface tension, vapor pressure, density, and molecular weight into Equation (15), one finds that at 0.89 T_c, the predicted rate of nucleation is about $10^4 - 10^6$ bubbles $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ and that its value changes about three to four orders of magnitude per degree Celsius. The major reason for this extreme sensitivity to temperature is that, so close to the critical temperature, the exponential is of the order of 10^{-30} and the fractional change in the magnitude of the surface tension is very large per degree, that is, $d \ln \sigma^3/dT = -0.07$ to -0.09; increasing T by 1 deg. decreases σ^3 by about 7 to 9%. In addition to this, the denominator of the exponent contains T and $(P_V - P_L)^2$, both of which increase with increasing temperature; the vapor pressure P_V especially so. Thus, these factors also decrease the argument of the exponent. On the other hand, for conditions typical of cavitation, for example, two-thirds the critical temperature and very large negative ambient pressures P_L, the temperature dependence of the rate of nucleation is greatly reduced. This is due to both the decreased dependence of the surface tension on temperature, that is, $d \ln \sigma^3/dT = -0.01$ to -0.03, and to the fact that since $|P_L| >> |P_V|$, the temperature dependence of the vapor pressure has no effect. To summarize, at ambient pressures it is meaningful to speak about the limit of superheat, since the rate of nucleation changes so rapidly with temperature that one can imagine a narrow temperature range below which homogeneous nucleation does not occur and above which it will effectively occur instantaneously. At very negative pressures, that is, nucleation far below the critical temperature, it is useful to speak about the tensile strength of the liquid, that is, the negative pressure that must be exceeded to cause homogeneous nucleation, since now the exponent is a strong function of the ambient pressure P_L which occurs squared in the denominator of the exponent but is a relatively weak function of temperature.

Hydrodynamic constraints on nucleation rates. Kagan (1960) has presented an important extension of nucleation theory which takes into account hydrodynamic and transport constraints on the rate of nucleation. His calculations lean heavily on the fact that the rate of nucleation is largely dependent on the rates of growth and collapse of bubbles close to the critical size. Bubbles grow or shrink with the addition or subtraction of individual molecules, and the net rates of the transfer of molecules to or from the bubble are slowest near the critical size. Figure 4 schematically indicates the processes involved in bubble growth. The net rate of vaporization of molecules into a bubble, dx/dt, is given by

$$\dot{x} \equiv (dx/dt) = \frac{A}{(2\pi m\ kT)^{1/2}}\,[P_V(T_S) - P_G] \qquad (16)$$

where $P_V(T_S)$ is the vapor pressure of the liquid at the temperature of the interface. At the critical size, the average rate of vaporization $\dot{x}$ is zero, and $P_G = P_V(T_S)$ and $T_S = T_o$, the temperature of the surrounding liquid. At sizes other than the critical size, $[P_V(T_S) - P_G]$ and $(T_S - T_o)$ are both nonzero.

Kagan first considers the temperature T_S. If there is a net flux of molecules vaporizing into the bubble, there is also a net flux of enthalpy across the interface into the bubble, since the enthalpy of the vapor is higher than that of the liquid. In the steady state there must be an equal flux of enthalpy to the interface from the body of the liquid, so that

$$\lambda_e\left(\frac{\partial T}{\partial R}\right)_{R=r} = \frac{\dot{x}\Delta H_V}{A} \qquad (17)$$

Near the critical size, Equation (17) can be solved for $(T_S - T_o)$. From this, $P_V(T_S) - P_V(T_o)$ can be calcu-

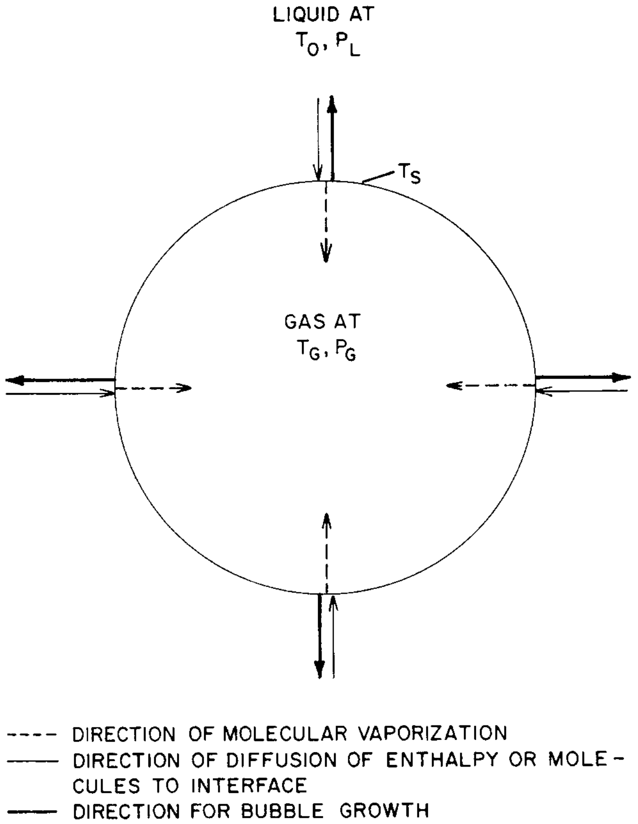

Fig. 4. Processes involved in bubble growth. The rate of nucleation is related to the rate of vaporization of molecules from the liquid-gas interface into the bubble. Since the vaporization carries enthalpy from the liquid at the interface into the gas, a corresponding transfer of enthalpy to the interface from the bulk lqiuid is required. The impedance for this enthalpy transfer is a factor which slows the rate of vaporization and decreases the rate of nucleation. For mixtures, the diffusion of more volatile constituents from the bulk liquid to the interface provides a similar impedance which lowers the rate of nucleation.

With the transfer of a molecule into the gas, the bubble tends to grow. This growth is impeded by viscous and inertial forces which, if large, can impede the vaporization of molecules and thus control the rate of nucleation. If viscous or inertial forces control the bubble growth rate (and the nucleation rate), then the pressure inside the bubble will be close to the vapor pressure.

lated, which, when substituted in Equation (16), leads to the result

$$\dot{x} = \frac{A}{(2\pi m\, kT)^{1/2}\,(1+\delta_\lambda)}\,[P_V(T_o) - P_G] \quad (18)$$

where

$$\delta_\lambda = \left(\frac{\Delta H_V}{kT}\right)^2 \frac{\sigma}{\lambda_e} \left(\frac{2k}{\pi m T}\right)^{1/2} \left(\frac{P_V}{P_V - P_L}\right) \quad (19)$$

As shown by Kagan, the nucleation rate is given by

$$J_\lambda = J/(1+\delta_\lambda) \quad (20)$$

where J is given by Equation (15), and J_λ includes the influence of heat transfer on the bubble nucleation rate. The physical significance of this equation may be readily seen if we consider that the rates of vaporization or condensation in the bubble may be viewed as controlled by an impedance to the inward flow of molecules and enthalpy in the radial direction. The finite rate of transfer of enthalpy through the external phase to the interface places another impedance in series with the impedance to molecular flow from the interface into the bubble. An important point in Kagan's derivation stems from the fact that $\dot{x}$ and $T_S - T_o$ are both zero at the critical size and are close to zero near the critical size, where the largest contribution to J from the integral in Equation (9) is made. Consequently, the pertinent surface tension and vapor pressure is that at the bulk temperature T_o.

Since the influence of fairly large changes in the prefactor makes a relatively insignificant change in the kinetic limit of superheat which is calculated for pure liquids, the factor $(1 + \delta_\lambda)$ will not be very important for pure liquids unless it is extremely large. However, for cases, as in mixtures, where the temperature coefficient for J may be small, this factor can be significant.

Kagan also considered the influence of viscous and inertial forces on the rate of vaporization of molecules $\dot{x}$. He utilized a hydrodynamic equation for P_G in Equation (16), that is,

$$P_G = d\, r\, r + \frac{3}{2}\, d\, \dot{r}^2 + P_L + \frac{2\sigma}{r} + 4\,\eta\,\frac{\dot{r}}{r} \quad (21)$$

instead of approximating it by Equation (6). When inertial and viscous forces are small, Equation (6) is a reasonable approximation. When viscous or inertial forces are large, P_G will be close to P_V. Kagan's general result thus leads to simple forms for these limiting cases. For example, when inertial terms are relatively small and when the viscosity is high enough so that the factor

$$\omega = \frac{\eta}{\sigma(1+\delta_\lambda)} \left(\frac{18kT}{\pi m}\right)^{1/2} \quad (22)$$

is much larger than unity, then the viscous flow term is the major constraint on the growth of bubbles near the critical size, and

$$J_\eta = N\,\frac{\sigma}{\eta}\left(\frac{\sigma}{kT}\right)^{1/2}\left(1 - \frac{P_L}{P_V}\right)\exp\left(\frac{-\,16\pi\sigma^3}{3\,kT\,(P_V - P_L)^2}\right) \quad (23)$$

For superheated liquids, ω can easily be larger than unity. For very viscous liquids (as, for example, acid volcanic lavas or glasses), Equation (23) leads to calculated values of the nucleation rate which differ significantly from Equation (15). For all these cases where $\omega >> 1$, the pressure inside the bubble probably lies close to the equilibrium pressure P_V, since the rate of vaporization is fast relative to the slow viscous controlled rate of growth of the bubble near the critical size. As mentioned earlier, a constant pressure P_V inside the bubble rather than P_G given by Equation (6) changes the rate of nucleation only in changing the factor B to unity. For cases other than cavitation, or those not controlled by viscous constraints, B is generally about two-thirds. Consequently, the approximation of P_G by Equation (6) leads to an entirely negligible error in the prefactor for Equation (15). For cases in which $\omega >> 1$, one should calculate rates of nucleation from Equation (23) which is for a viscosity controlled nucleation rate.

Similarly, inertial forces become important if the factor ω' given by

$$\omega' = \frac{16\,kTd}{3\,\pi m\,(1+\delta_\lambda)^2\,(P_V - P_L)} \quad (24)$$

is greater than unity and not very small relative to ω^2. In these cases ($\omega >> 1$ or $\omega' >> \omega^2$ and $\omega' >> 1$), the classical equation given by Equation (15) predicts limits of superheat which are low. However, since the exponential term in the theory, which is the same in all cases, varies about three to four orders of magnitude per degree near the limit of superheat of pure substances at ambient pressures of 1 atm., very large values of ω, ω', or δ_λ would be required before the calculated limit of superheat is significantly larger than calculated classically.

Theory for mixtures. The theory for bubble nucleation from mixtures has been examined only for the case in which one component is volatile. If one considers the steady state solution of the equation for $\dot{x}$, then the diffusive flux of molecules into the bubble is given by Equation (16). This is expressed by

$$D\left(\frac{\partial C}{\partial R}\right)_{R=r_c} = \frac{(P_V - P_G)}{\sqrt{2\pi mkT}} \tag{25}$$

Thus, at steady state, molecules which vaporize into the bubble are replaced by molecules diffusing to the interface. This diffusion is an impedance in the steady state process. Equation (25) has been solved in a manner similar to the solution of the heat flow Equation (17) to obtain the rate of nucleation J_D (Blander et al., 1971):

$$J_D = J/(1 + \delta_D) \tag{26}$$

where δ_D, which corrects for the impedance arising from the diffusion of the volatile component to the interface, is given by

$$\delta_D = \frac{2\sigma(dP/dC)_{P_V}}{D(2\pi mkT)^{1/2}\,(P_V - P_L)} \tag{27}$$

As in the derivation of Equation (19) for δ_λ, $\dot{x}$ is zero at the critical size. Consequently, since the largest contribution to J comes from near the critical size, where $\dot{x}$ is very small, the pertinent vapor pressures and concentrations are those of the bulk solution.

The significance of Equation (25) can be understood if we take the case where the solution is ideal or dilute enough for Henry's law to be obeyed so that $(dP/dC) = P/C$ and

$$\delta_D = \frac{2\sigma}{D(2\pi mkT)^{1/2}\,(C_V - C_L)} \tag{28}$$

For typical values of the parameters ($\sigma \sim 3$ erg/cm^2, $D \sim 10^{-5}$ cm^2/s, $m = 10^{-22}$ g, $T = 500$K), δ_D is always larger than unity and may be very large for very dilute solutions. If δ_D is large, the rate of nucleation is diffusion controlled and is given by the equation

$$\begin{aligned} J_D &= \mathrm{N}\,D(P_V - P_L) \\ &\quad (dC/dP)_{P_V}\,(kT/\sigma)^{1/2}\exp[-16\pi\sigma^3/3kT(P_V - P_L)^2] \\ &\cong \mathrm{N}\,D(C_V - C_L) \\ &\quad (kT/\sigma)^{1/2}\exp[-16\pi\sigma^3/3kT(P_V - P_L)^2] \end{aligned} \tag{29}$$

where the second expression in Equation (29) holds when Henry's law is obeyed. Although no measurements have been made which permit a test of this equation, its properties are important for understanding nucleation in mixtures. Consider the extreme case of a solution of a volatile gas in an involatile solvent (water in a volcanic magma, carbon dioxide in beer) dilute enough so that σ essentially depends only on the solvent properties. If σ depends weakly on temperature, then the variation of the exponential term with temperature depends largely on the variation of P_V. This variation is a function of the enthalpy of solution of the volatile solute. If the enthalpy is negative, J_D will increase with temperature, and if positive enough, J_D will decrease with temperature. Consequently, for mixtures there can be upper limits of superheat as one finds with pure one-component liquids as well as lower limits of superheat. For example, solutions of water in volcanic magmas exhibit positive enthalpies of solution. For such cases, the rate of nucleation increases with cooling of a magma, and one should observe a lower limit of superheat. This is opposite to the usual intuitive expectation that outgassing and nucleation increase with an increase of temperature.

For the case in which the two components of a binary mixture are volatile, the phenomenon behaves in a manner which is intermediate between the behavior for pure materials and the behavior for mixtures containing one volatile constituent, with the exact behavior depending on the relative differences in volatility and the solution properties. No solution to the kinetic equations has yet been made for this case.

Experimental Confirmation of Theory

Techniques

All of the techniques depend on understanding conditions under which homogeneous nucleation is possible. For nucleation of a heated liquid to be homogeneous, conditions must be such that the probability for nucleation and vaporization in the interior of a liquid exceeds that at its surface. A necessary condition for this to occur is that the heated liquid not be in contact with a vapor phase. Another condition which is sufficient (but not necessary) is that the liquid wet any other phase it contacts. From thermodynamics, it can be readily shown (Jarvis et al., 1975) that if the volatile liquid spreads (that is, has a zero contact angle with) any body it contacts, then a bubble in the interior of the liquid is more stable than a similar size bubble at the interface, and, as a consequence, the probability of homogeneous nucleation is always higher than that for heterogeneous nucleation. As will be seen later, the prefactor for heterogeneous nucleation is smaller than that for homogeneous nucleation. As a result, the rate of homogeneous nucleation can be greater than that for heterogeneous nucleation, even when the wetting angle is somewhat greater than zero. These conditions can be met when the liquid is completely enclosed by a high surface tension material with a smooth surface, as, for example, a glass or another liquid which is involatile.

Moore (1956, 1959) and Wakeshima and Takata (1958) have pioneered a technique which has proven to be successful for a large number of organic liquids. Skripov and co-workers (Skripov (1974) reviews the large number of papers by these workers) and Blander and coworkers (1971) have utilized this technique for a variety of organic liquids. It consists of introducing small droplets of a volatile liquid into the bottom of a column of a denser immiscible liquid medium. The immiscible medium is heated nonuniformly so that it is hotter at the top and cooler at the bottom. As the droplets slowly rise, they get hotter and hotter until they attain the limit of superheat, they nucleate, and they explode with a sharp report. Figure 5 illustrates an apparatus for accomplishing this. The nonuniform heating of the medium in the upper tube is achieved by varying the spacing of wires wound about the upper tube. The density gradient stabilizes the column against convection, and temperatures can be kept uniform at a given level in the tube. A capillary connects the upper tube to a lower chamber, where the volatile fluid is emulsified in the liquid medium. Small amounts of the emulsion are then forced into the medium in the upper chamber by mild pressure. With this technique, it is possible to introduce very small drops. Another variation is to introduce droplets into the column by injection from a syringe inserted through a membrane in the base of the column. The measurement consists in noting the approximate size of the droplet and the temperature at the level where the droplet boiled explosively. Media which have been used successfully for organic materials are sulfuric acid, glycer-

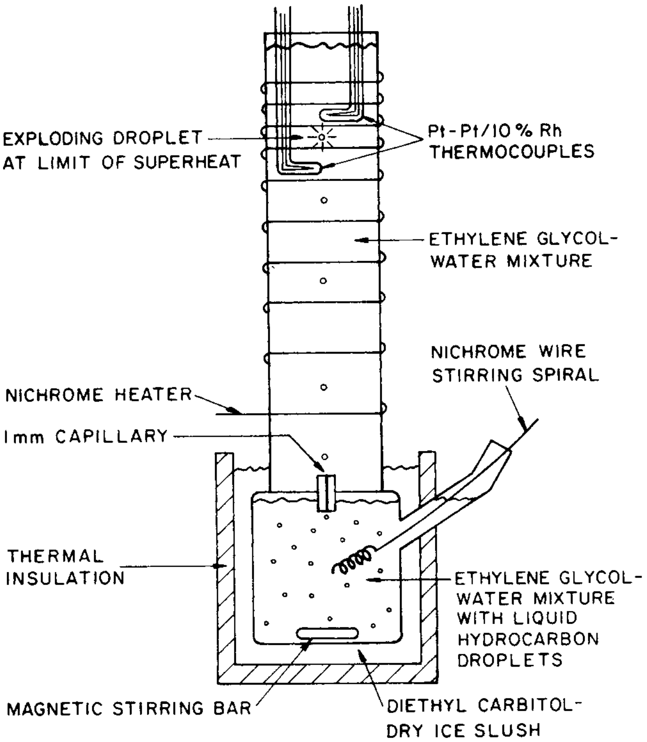

Fig. 5. Schematic of apparatus for measuring limits of superheat (after Renner et al. (1974)). This particular configuration is used for measurements of organic liquids which boil below room temperature but nucleate at temperatures above room temperature.

ine, ethylene glycol, lithium chloride-water mixtures, and ammonia-water mixtures.

To relate such measurements to nucleation theory, one must analyze the nucleation probabilities from the kinetic equations. If one has a collection of N_o droplets, all of the same volume being heated at a rate (dT/dt), then the number of droplets which nucleate and boil per unit time is

$$(dN/dt) = -NVJ(T) \qquad (30)$$

As was discussed previously, J varies about three to four orders of magnitude per degree and over a large range of values can be represented by the form $J = J_o \exp(LT)$. Using this form one can solve Equation (30) to obtain

$$\ln \frac{N}{N_o} \cong -\frac{VJ(T)}{L(dT/dt)} \qquad (31)$$

where (N/N_o) is the probability that a droplet of volume V heated at a rate (dT/dt) will survive to a temperature T. Thus, there is not a unique nucleation temperature but a range of temperature for the nucleation of droplets. This range is very narrow when J varies strongly with temperature and L is large.

This is illustrated in Table 1 for a typical value of $L = 7$. The temperature T_m is the median nucleation temperature where $N/N_o = ½$. It can be seen that when L is 7/deg., the probability is high that most droplets of a given size will nucleate in a narrow temperature range. For example, 98% of a collection of droplets will nucleate in a total range of 0.88 deg. and 80% in a range of 0.44 deg. On the other hand, when L is small, one expects a larger range of temperatures since the temperature spread $(T - T_m)$ is proportional to $(1/L)$.

Table 1. Probability of Survival of a Droplet to a Temperature T ($L = 7K^{-1}$)

(N/N_o)	$J(T)/J(T_m)$	$(T - T_m)K$
0.999	1.4×10^{-3}	−0.94
0.990	1.4×10^{-2}	−0.61
0.900	1.5×10^{-1}	−0.27
0.500	1	0
0.100	3.3	0.17
0.010	6.6	0.27
0.001	10.0	0.33

In addition to the natural temperature spread for droplets of a given size, there is also a spread which is a function of the size. For example, in the column technique, the rate of rise of droplets is proportional to the reciprocal of the radius, so that relative values of $V/(dT/dt)$ in equation (31) vary as $V^{2/3}$. Consequently, an increase in the volume of droplets by a factor of a thousand leads to a decrease of the median temperature T_m by about 0.66 deg. when $L = 7$. Increases in the rate of heating by a factor of 1000 leads to an increase of only 1 deg. It can be seen that for one-component liquids the median temperature is relatively insensitive to very large differences in volume or heating rate. It is this property which lends validity to the concept of a kinetic limit of superheat, since one predicts and observes in all column measurements of homogeneous nucleation of one-component liquids that when a large number of droplets are nucleated in the column almost all explode very close to a single plane, essentially independent of the droplet volume. Even for differences in the experimental techniques, where volumes and heating rates may differ significantly from the column technique, the median temperatures will not be very different. As will be noted, observations for some mixtures indicate that the temperature coefficient of J is not as large as for one-component liquids.

Another technique used by Kenrick et al. (1924), Sinha and Jalaluddin (1961), Jalaluddin and Sinha (1962), and Eberhart et al. (1973) is to heat a liquid contained in a glass capillary (or glass vessel) until it boils explosively. If the column of liquid in the capillary extends out of the heating bath to where the temperature is below the boiling point, and if it wets the glass, then the limit of superheat can be attained.

Skripov and co-workers (1974) have developed techniques in which liquids in capillaries or droplets held in place by a glass plate in a column as shown in Figure 5 were held at constant temperature. The time of explosion of many droplets will follow the decay equation, Equation (30). Since the temperature is constant, the integration of Equation (30) leads to the expression

$$\ln \frac{N}{N_o} = -JVt \qquad (32)$$

and a plot of the log of the fraction of a collection of drops which survive vs. the function V_t leads to a line of slope J.

Experimental Results

Measurements on a large number of organic compounds have been made which appear to be consistent with nucleation theory. Table 2 lists the boiling points T_b, measured limits of superheat T_l, limits calculated from Equation (15) for $J \cong 10^6$ bubbles cm^{-3} s^{-1}, and reduced limits of superheat. It is clear that the measurements are generally consistent with theoretical predictions. In addition, where reported, the spread in measured temperatures was small for most of the events observed with the droplet technique, as predicted from the theory, generally less than ±1 deg. Nucleation of these pure substances is manifested by a fairly sharp explosion. Measurements with the capillary technique were usually lower than those with the droplet technique or those calculated from theory.

The pressure dependence of the limits of superheat have been measured for pressures above atmospheric by Skripov

TABLE 2. MEASURED LIMITS OF SUPERHEAT AT 1 ATM.

Substance	T_b (°C)	T_l (°C) Meas.	T_l (°C) Calc.	T_l/T_c (K/K) Meas.	Reference
Normal alkanes					
Methane	−161.5	—	−107.5	—	PB
Ethane	−88.6	−4	−3.5	0.881	PB
Propane	−42.1	53.0	55.3	0.882	PB, RKB
Butane	−0.5	105.0	105.2	0.890	EKB, RKB
Pentane	36.0	147.8	148.3	0.896	BHK, S, SJ, WT
Hexane	68.7	184	184.3	0.901	BHK, BS, S, WT
Heptane	98.0	214	214.5	0.902	BS, EKB, S, WT
Octane	125.7	239.8	242.7	0.902	S
Nonane	150.8	265.3	262.0	0.906	EKB
Decane	174.1	285.1	282.8	0.904	EKB
Branched alkanes					
2-methylpropane	−11.8	87.8	87.7	0.884	PB
2,2-dimethylpropane	9.5	113.4	—	0.891	EKB
2-methylbutane	27.9	139	—	0.895	S, W, WT
2,3-dimethylbutane	58.0	173.2	175.9	0.893	EKB
2,2,4-trimethylpentane	99.2	215.3	214.9	0.898	EKB
Cyclic hydrocarbons					
Cyclopropane	−32.9	77.5	—	0.882	PB
Cyclopentane	49.3	183.8	173.2	0.893	EKB
Cyclohexane	80.7	219.6	216.3	0.890	EKB, S, WT
Cyclooctane	148.5	287.5	—	—	EKB
Methylcyclopentane	71.8	202.9	—	0.894	EKB
Methylcyclohexane	100.9	237.2	232.0	0.892	EKB
Benzene	80.1	225.3	—	0.887	KGW, S, SJ
1,3-dimethylbenzene	139.1	235	—	0.824	KGW (c)
Alkenes and alkynes					
Propene	−47.7	52.4	50.3	0.882	PB
Propadiene	−34.5	73.0	—	0.881	PB
Propyne	−23.2	83.6	88.2	0.887	PB
1-butene	−6.3	97.8	100.2	0.884	PB
cis 2-butene	3.7	112.2	—	0.885	PB
trans 2-butene	0.9	106.5	—	0.886	PB
2-methylpropene	−6.9	96.4	99.3	0.884	PB
1,3-butadiene	−4.4	104.1	—	0.888	PB
1-pentene	30.0	144	141.9	0.898	EKB
1-octene	121.3	237.1	—	0.901	EKB
1-hexyne	71.3	192	—	—	EKB
Cyclopentene	44.2	178.2	—	0.892	EKB
Halocarbons					
Chloromethane	−24.2	93.0	—	0.880	PB
1,1-difluoroethane	−24.7	70.4	—	0.889	PB
Chloroethene	13.9	100.9	—	0.867	PB
Fluoroethene	−72.2	16.9	—	0.885	PB
Ethyl chloride	12.3	126	—	0.867	W
Chloroform	61.7	173	—	0.832	KGW (c)
Chlorobenzene	132	250	—	0.827	KGW (c)
Bromobenzene	156	261	—	0.797	KGW (c)
Hexafluorobenzene	74.5	194.7	195.4	0.905	RK, S
Perfluoropentane	27.0	108.3	108.9	0.904	S
Perfluorohexane	50.9	136.6	137.4	0.915	S
Perfluoroheptane	70.9	161.6	161.2	0.916	S
Perfluorooctane	94.8	183.8	185.2	0.910	S
Perfluorononane	114.5	205.3	205.7	0.913	S
Perfluorodecane	133.0	223.9	223.1	0.917	S
Methanol	65.0	186.0	186.5	0.896	EHB, KGW (c), S
Ethanol	78.5	189.5	191.8	0.896	EHB, KGW (c), S
Acetone	56.2	174	—	0.879	KGW (c)
Carbon disulfide	46.3	168	—	0.803	KGW (c)
Sulfur dioxide	−10	50	—	0.750	KGW (c)
Aniline	184.1	262	—	0.766	KGW (c)
Diethyl ether	34.5	147	145	0.901	KGW (c), S, W, WT

All measurements were by the droplet technique unless noted by a (c) in the last column.

BS	Basu and Sinha (1968)	RKB	Renner et al. (1974)
BHK	Blander et al. (1971)	SJ	Sinha and Jalaluddin (1961)
EHB	Eberhart et al. (1973)	S	Skripov (1974)
EKB	Eberhart et al. (1975)	WT	Wakeshima and Takata (1958)
KGW	Kenrick et al. (1924)	W	Wismer (1922)
PB	Porteous and Blander (1975)		

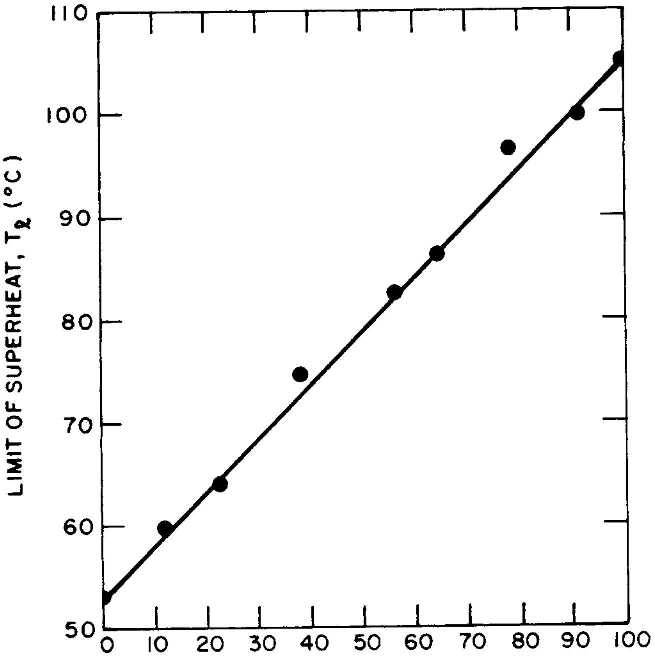

Fig. 6. Limits of superheat of propane-butane mixtures (after Renner (1974)).

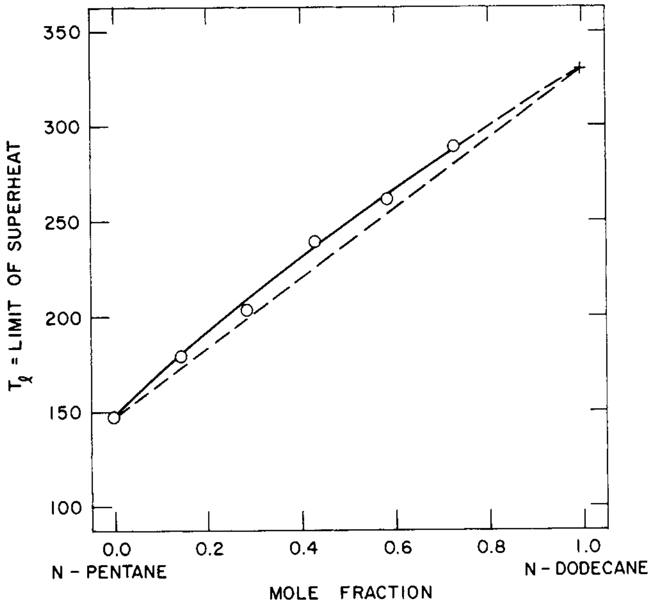

Fig. 7. Limits of superheat of ethane-*n*-butane mixtures (after Porteous and Blander, 1975). Vertical bars represent spread in measurements with small droplets tending to nucleate at the high end and large droplets at the low end of the range.

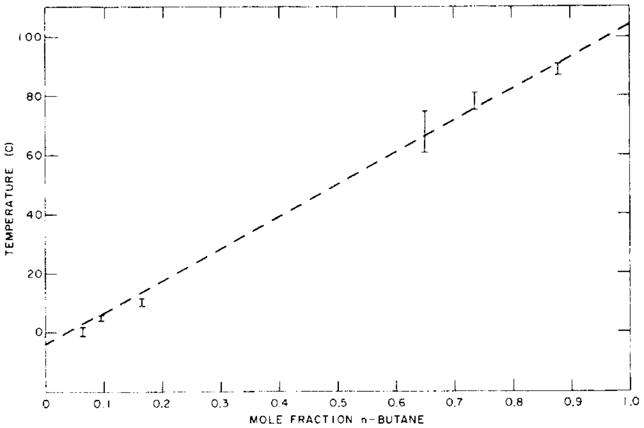

Fig. 8. Limits of superheat of *n*-pentane-*n*-dodecane mixtures (after Eberhart et al. (1975)). The solid line represents the points which deviate somewhat from linear behavior.

and co-workers (1974) and for negative pressures by Apfel (1971). A plot of some of their measurements is contained in Figure 3. All the measurements are consistent with the predictions of theory.

Attempts have been made to measure the homogeneous limit for water. Blander et al. (1971) and Apfel (1971*a*) superheated water in a silicone oil. Most of the droplets observed by Blander et al. nucleated between 250° and 275°C, with occasional droplets exploding at temperatures up to 280°C. Apfel (1972) superheated water to 279.5°C in benzyl benzoate. Since the homogeneous limit is ~300°C, in no case was it attained.

The limits of superheat of mixtures have been measured by Skripov and co-workers (Skripov, 1974), Blander et al. (1971), Eberhart et al. (1975), Renner et al. (1974), and Porteous and Blander (1975) using the droplet technique. Measurements of three systems are exhibited in Figures 6 to 9. The measurements are approximately linear in mole fraction, and for mixtures in which the components do not differ greatly in boiling points, the temperature spread is small and the liquid boils with a fairly sharp explosive report. For mixtures such as *n*-pentane-*n*-hexadecane, where *n*-pentane is a volatile component in an essentially involatile solvent, the addition of solvent not only raises the limit of superheat but also changes the character of the phenomenon. The spread in nucleation temperatures increases with hexadecane content, as plotted in Figure 9, and at high contents of hexadecane, small droplets nucleate at significantly higher temperatures than large droplets. These observations are consistent with a weak dependence of J on temperature. In addition, with an increase in the hexadecane content, the boiling becomes less and less violent so that at 50% hexadecane no sound can be heard. With increased dilution of the volatile constituent, growth of bubbles larger than the critical size becomes increasingly diffusion limited and, therefore, slower and less violent (Blander et al., 1971; Eberhart et al., 1975).

No measurements have been made of mixtures exhibiting large deviations from ideal solution behavior. It has been suggested (R. C. Reid, personal communication) that limits of superheat for such mixtures might deviate considerably from linearity in mole fraction.

HETEROGENEOUS NUCLEATION

Nucleation on a Smooth Rigid Surface

It is straightforward to extend the concepts and method of homogeneous nucleation theory to account for the nucleation of bubbles at a smooth rigid surface. Unscratched glasses may have such surfaces, but nucleation on a crystalline solid is always caused by ever present irregularities, such as grain boundaries, ledges, cracks, and scratches on the surface. Consequently, this case is restricted to glassy materials.

A bubble at a smooth solid-liquid interface is shown in Figure 10. The minimum work needed to form such a bubble is given by an equation almost identical to Equation (4); that is

$$W = \sigma_{LG}A_{LG} + (\sigma_{SG} - \sigma_{SL})A_{SG} - (P_G - P_L)V_G + x(\mu_G - \mu_L) \quad (33)$$

which is derived by an identical procedure to that used

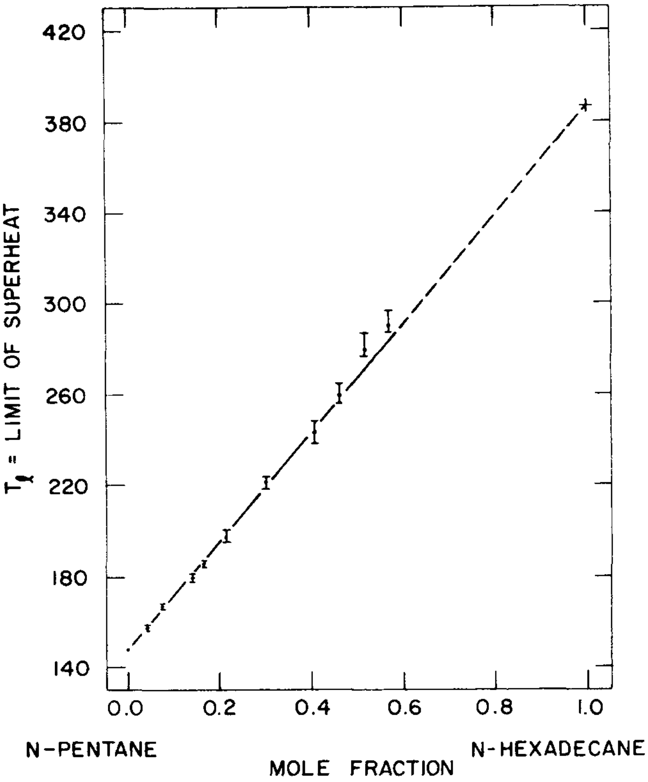

Fig. 9. Limits of superheat of *n*-pentane-*n*-hexadecane mixtures. As in Fig. 7, the vertical bars represent the spread in measurements with small droplets tending to nucleate at the high end and large droplets at the low end of the range.

to derive Equation (4) except that appropriate account is taken of the various areas and surface free energies of the interfaces, denoted by subscript LG for liquid-gas, SG for solid-gas, and SL for solid-liquid. For convenience we shall denotes σ_{LG} as σ. Assuming the bubble is a segment of a sphere, one can express the volume of the bubble V_G and the interfacial areas in terms of its radius of curvature R and the contact angle θ. Defining $m \equiv Z/R$ from the geometry, one can show that

$$m = \cos(\pi - \theta) = -\cos\theta \tag{34}$$

$$V = \frac{1}{3}\pi\,(R - Z)^2\,(2R + Z) = \frac{1}{3}\pi R^3(2 - 3m + m^3) \tag{35}$$

$$A_{LG} = 2\pi r(R - Z) = 2\pi R^2\,(1 - m) \tag{36}$$

$$A_{SG} = \pi r^2 = \pi R^2\,(1 - m^2) \tag{37}$$

Since, by a force balance at the edges of the bubble (known as Young's equation)

$$\sigma_{SL} = \sigma_{SG} + \sigma_{LG}\cos\,(\pi - \theta) = \sigma_{SG} + m\sigma_{LG} \tag{38}$$

then

$$m = (\sigma_{SL} - \sigma_{SG})/\sigma_{LG} \tag{39}$$

A force balance at the edge of the bubble implies that mechanical equilibrium holds, that is, that Laplace's equation

$$P_G - P_L = 2\sigma/R \tag{40}$$

which relates the bubble size to its internal pressure is also satisfied. The chemical potential difference $\mu_G - \mu_L$ can also be expressed in terms of the radius R:

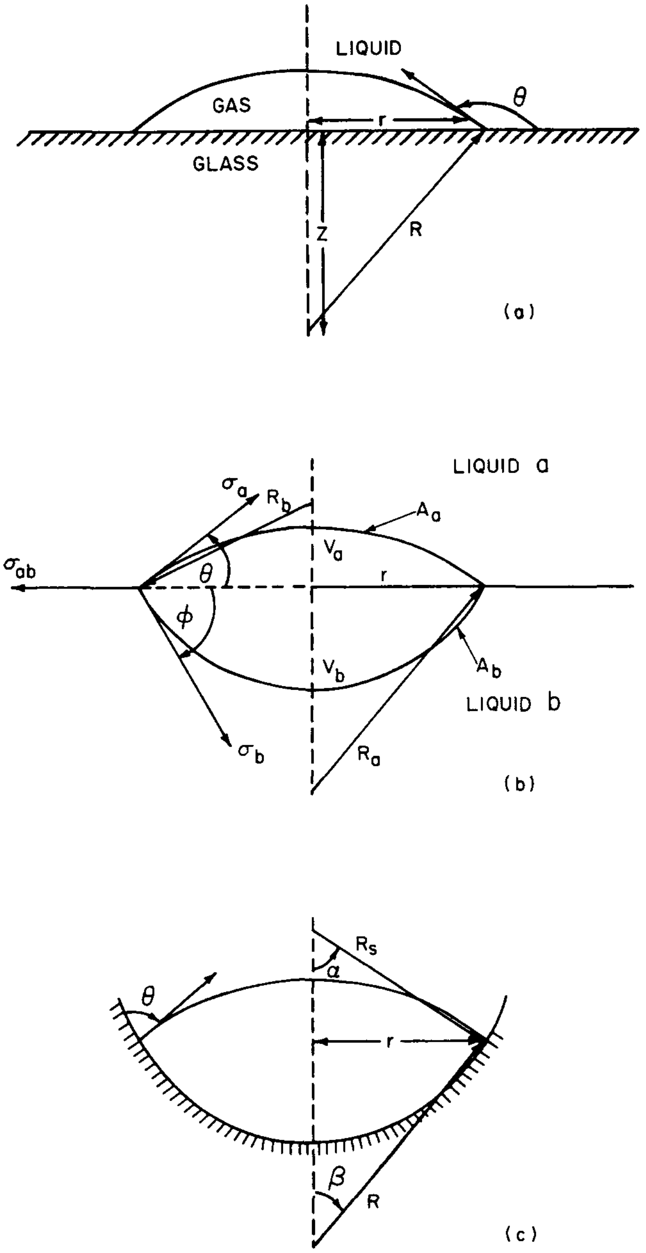

Fig. 10. a. Representation of a gas bubble at a glass-liquid interface. b. Representation of a gas bubble at a liquid-liquid interface. c. Representation of a gas bubble at a glass-liquid interface in a spherical cavity.

$$\mu_G - \mu_L = kT\ln P_G/P_V = kT\ln\frac{P_L + 2\sigma/R}{P_L + 2\sigma/R_c} \tag{41}$$

where R_c is the radius of the critical sized bubble. The number of molecules in the bubble x is related to the radius R via the equation of state

$$x = PV/kT = \left(P_L + \frac{2\sigma}{R}\right)\frac{4}{3}\pi R^3F/kT \tag{42}$$

where $F \equiv (2 - 3m + m^3)/4$. Substituting Equations (34) to (42) into (33), one obtains

$$W = \frac{4}{3}\pi R^2\,\sigma F + \frac{4}{3}\pi R^3F\left(P_L + \frac{2\sigma}{r}\right)\ln\frac{P_L + 2\sigma/R}{P_L + 2\sigma/R_c} \tag{43}$$

The remaining development continues exactly as for homogeneous nucleation, resulting in an equation for the rate of nucleation identical to Equation (10). However, $A(R_c)$ is the surface area of the liquid-gas interface at the critical size and $n(R_c)$, the number density of critical bubbles, is proportional not to N, the number density of the liquid as in Equation (8), but to $N^{2/3}$, since one views each molecule at the surface instead of each molecule in the droplet as a potential bubble. One thus obtains the result

$$J = N^{2/3}\, S \left[\frac{2\sigma}{\pi m B F} \right]^{1/2} \exp \left[\frac{-16\pi\sigma^3 F}{3kT[P_V - P_L]^2} \right] \tag{44}$$

where $S \equiv (1 - m)/2$. Equation (44) for heterogeneous nucleation at a rigid interface may be compared with Equation (12) for homogeneous nucleation. The preexponential term in Equation (44) (which is related to kinetic factors) is smaller than the corresponding term in Equation (12) by a factor of about $N^{1/3}$, which is of the order of 10^7. However, the exponential term of Equation (44) (which is related to thermodynamic factors) is larger than that in Equation (12) when the factor F is less than unity. Since the exponential term with F equal to unity is often of the order of 10^{-30}, a value of $F < 0.77$ may lead to a higher probability for heterogeneous nucleation (if there is 1 cm² of surface per cubic centimeter of liquid) than that for homogeneous nucleation. This corresponds to contact angles (θ) greater than 68 deg. These fairly typical values illustrate the fact that, even though the bubble is thermodynamically more stable at the interface, bubbles will tend to nucleate homogeneously first unless the contact angle is large enough (>68 deg. in this case) to make up for differences in the preexponential kinetic factors.

Nucleation at a Liquid-Liquid Interface

While nucleation at a smooth rigid surface is restricted to glasses because crystalline solids are not smooth on a molecular scale, the interface between two liquids is smooth. The calculational procedure is the same, except that in this case there are two curved surfaces, each with its own radius of curvature (Figure 10*b*). The minimum work needed to form such a bubble is given by the equation

$$W = \sigma_a A_a + \sigma_b A_b - \sigma_{ab} A_{ab} - (P_G - P_L) V_G + x(\mu_G{}^a - \mu_L{}^a) \tag{45}$$

Here A_a, A_b are the areas of the newly formed gas to liquid a and gas to liquid b interfaces; A_{ab} is the area of the interface between liquid a and liquid b which is destroyed on forming the bubble; σ_a, σ_b, and σ_{ab} are the surface tensions of a and b and the interfacial free energy per unit area of the ab interface. Furthermore, we have simplified the last term in Equation (45) by assuming that only component a is volatile. Following the same procedure again, one obtains an equation identical to Equation (44) (the algebra is somewhat complicated), except that now instead of σ one uses σ_a and F is now a more complicated geometric factor, that is

$$F = [(2 - 3m_a + m_a{}^3)\,\sigma_a{}^3 + (2 - 3m_b + m_b{}^3)\,\sigma_b{}^3]/4\sigma_a{}^3 \tag{46}$$

where

$$m_a = \cos(\pi - \theta) = (\sigma_a{}^2 - \sigma_b{}^2 + \sigma_{ab}{}^2)/(2\sigma_a\sigma_{ab}) \tag{47}$$

$$m_b = \cos(\pi - \phi) = (\sigma_b{}^2 - \sigma_a{}^2 + \sigma_{ab}{}^2)/(2\sigma_b\sigma_{ab})$$

and

$$S = (1 - m_a)/2$$

The exponential term in Equation (44) was first derived by Moore (1956, 1959) and has been rederived by Apfel (1971), who also included the $N^{2/3}$ dependence. It was put into the above form by Jarvis et al. (1975), where a complete derivation including the proper preexponential is presented.

What actually happens when a liquid is superheated in contact with another liquid depends on the relative magnitudes of the surface and interfacial tensions. There are three different ways for nucleation to occur.

If $\sigma_b > \sigma_a + \sigma_{ab}$, then nucleation occurs as homogeneous nucleation, since it requires less work to form a bubble in the liquid than at the interface. Even if σ_b is somewhat smaller than $\sigma_a + \sigma_{ab}$, nucleation will occur homogeneously, since the rate of homogeneous nucleation is proportional to N while the rate of nucleation at the liquid-liquid interface is proportional to $N^{2/3}$.

If $\sigma_a \geqq \sigma_b + \sigma_{ab}$, nucleation would occur most readily inside liquid b, the host liquid. However, since it is liquid a which is the volatile liquid, some mechanism is needed for injecting molecules of liquid a into a bubble being formed entirely in liquid b. One mechanism is bubble blowing. Here the bubble is almost entirely surrounded by liquid b except for a very small opening which connects it to liquid a. Another mechanism is the diffusion of molecules of liquid a through liquid b. Since diffusion coefficients are small, diffusive nucleation could occur only to embryos formed very close to the liquid-liquid interface.

Only if $\sigma_a < \sigma_b + \sigma_{ab}$ and $\sigma_b < \sigma_a + \sigma_{ab}$ could nucleation actually occur by the mechanism described by Equation (44). There has not been complete experimental confirmation of this equation. Jarvis et al. (1975) have been able to cause nucleation at a liquid-liquid interface, but the surface and interfacial tensions are such that nucleation occurs by the bubble blowing or diffusive mechanism. They superheated water in Freon-E9, a fluorinated ether, and observed nucleation between 220° and 230°C, a temperature which is substantially lower than that observed in most hosts, that is, 265° to 280°C. These measurements are in good agreement with the predictions of the bubble blowing mechanism.

Nucleation at a Liquid Nonsmooth Solid Interface

This case has been discussed in detail by Cole (1974) in his review article on boiling nucleation. The problem is similar to nucleation on plane surfaces except that the geometry is more complicated. For example, if the surface site is a spherical cavity with radius of curvature α and the contact angle of the liquid-solid-vapor interface is θ, the minimum work to form the bubble will depend on α, θ, and β, and on r, the bubble radius (see Figure 10*c*). Cole also considers nucleation from a spherical projection and from a conical cavity, as well as the conditions under which trapping of vapor will occur as a liquid spreads over a surface containing grooves and cavities.

Of direct relevance to our discussions in the next section, where we consider the necessary and sufficient conditions for the occurrence of contact vapor explosions, is Cole's conclusion that just those cavities which are the most effective nucleation sites, that is, steep narrow cracks and crevices which are poorly wetted by the liquid, are also the ones which have the greatest tendency to entrap gas. Sites such as these will almost certainly cause nucleation to occur at temperatures far below the homogeneous limit of superheat. On the other hand, if the fluid has a zero contact angle with the surface, that is, the surface is well wetted, there will be little tendency to entrap gas, and the homogeneous limit of superheat can be reached.

VAPOR EXPLOSIONS

The principles we have outlined provide a basis for examining possible mechanisms for contact vapor explosions which are a hazard in many industrial operations, as mentioned earlier. Such physical explosions can be caused by superheating of volatile liquids and the consequent explosive boiling of that liquid. From theory, one can understand conditions under which such explosions might occur. If enough physical data are available, one may also derive safety criteria for the prevention of these dangerous events.

Nucleation theory leads to the prediction that under certain conditions many fluids may be superheated to a temperature which is close to 90% of their critical temperature before bubbles nucleate homogeneously and grow explosively. Such high limits of superheat may be attained if a volatile fluid wets a hot substrate which it accidentally contacts. The attainment of the limit of superheat leads to the most violent initial explosion possible by this mechanism. The poorer the wetting at the interface between the volatile fluid and the hot substrate, the less violent is the initial explosion. Barriers to nucleation can prevent boiling for a time long enough for a significant enthalpy transfer from the hot substrate into a thin layer of the volatile fluid. The violent eruption of such a thin superheated layer can trigger breakup of the volatile fluid and mixing with hot substrate to produce another stage of more rapid enthalpy transfer and the subsequent superheating of even more fluid because of the larger surface areas. If all other things are equal, the closer the initial triggering superheat is to the limit of superheat, the more violent and rapid the breakup and mixing will be and the more violent the event will be. Wetting characteristics are therefore crucial in determining the relative violence of the initial trigger and of the consequent contact vapor explosions.

When the hot substrate is wet by the volatile fluid such that the wetting angle is zero, then the fluid can reach the homogeneous limit of superheat. For solid surfaces with cracks and crevices, one is less likely to achieve the limit of superheat. Consequently, one expects a higher probability for superheat explosions for liquid-liquid, liquid-glass, and liquid-polymer contacts. With these concepts in mind, we can examine some examples. To simplify the discussion, we consider the case where convection is neglected. If there is no boiling, the temperature T_i at an interface between a hot substrate and a fluid is given by

$$T_i = \frac{T_v \underline{k}_v + T_s \underline{k}_s}{\underline{k}_v + \underline{k}_s} \tag{48}$$

If the volatile fluid wets the hot substrate, film boiling will occur if T_i exceeds the limit of superheat T_l. The boiling will cool the interface, and, if T_i then goes below T_l, the volatile liquid may settle down and wet the substrate. Wetting may also occur if the initial value of T_i is less than T_l but T_s is greater than T_l. If the volatile fluid layer is not too thick (that is, not effectively infinitely thick on the time scale of the observations), then T_i will ultimately rise until T_l is reached, at which time the fluid will nucleate homogeneously and boil explosively. The conditions under which this may occur for a mutually immiscible pair are:

1. $T_l > T_i \geqq T_f$, the temperature at which the substrate freezes. If the substrate freezes, it is likely to contain steep, narrow cracks and crevices and not be completely wetted. This is especially true if the wetting angle is not very small and if the volatile fluid approached the substrate through an intervening gas which could be trapped in the cracks or crevices. Thus, T_l of the volatile liquid should generally be greater than the freezing point (or perhaps the metastable freezing point) of the substrate.
2. θ must be small enough for the probability of homogeneous nucleation to be greater than that for heterogeneous nucleation. If heterogeneous nucleation predominates, the explosion can still be very violent when θ is not very large (that is, $\theta < 90$ deg.).

We may apply this to understanding boiling at a hydrocarbon-water interface. The measured value of T_l for propane, for example, is 53°C. Light hydrocarbons which have been measured (below C_9H_{20}) wet liquid water. Consequently, since $\underline{k}$ for water is larger than for hydrocarbons, one might expect propane to boil explosively when poured on hot water. The explosive boiling of propane on water at temperatures between 53° and 70°C (but not at lower temperatures) has been observed by Enger and Hartman (1972). The lower limit of 53 deg. is equal to T_l. Analogous observations were made for isobutane. Thus, although the limit of superheat was not reached at the interface in the entire range of temperatures, it was approached in these cases, indicating small enough wetting angles. For Freon 22 and propylene, the lower temperature of the range for explosions was about 10 to 15 deg. below T_l, indicating a fairly small nonzero wetting angle. On the other hand, methane and ethane did not explode upon contact with water (Enger and Hartman, 1972). For both methane and ethane, the temperatures T_l are low enough for ice to form at the interface. This nonexplosive behavior can be understood if the ice is not wet or if it contains crevices which are not completely wet and contain gas, as discussed in an earlier section.

When liquid methane or ethane is poured onto a higher hydrocarbon (butane, pentane, or hexane), explosions always occurred (Nakanishi and Reid, 1971). These hydrocarbons have a mutual solubility with methane and ethane, so that there is a continuous range of liquid compositions with each successive layer wetting the layer below it, thereby leading to conditions appropriate for homogeneous nucleation. Explosions may also occur when impure methane or ethane containing propane or butane impurities is poured on water. In some ranges of composition and water temperatures, the initial boiling at the interface will increase the concentration of the higher boiling constituent so that the value of T_l at the composition near the interface is above 0°C. Under these conditions, a vapor explosion may occur. To understand this type of explosive behavior, one requires an understanding of the nucleation properties of mixtures.

Skripov (1974), Eberhart, Kremsner, and Blander (1975), and Porteous and Blander (1975) have studied nucleation in hydrocarbon mixtures. The limits of superheat at intermediate compositions are intermediate between the limits of superheat of the end members and do not deviate greatly from being linear in mole fraction. Thus, if one has a pentane layer wetting a substrate such as water at 25°C and pours liquid methane onto it, the two hydrocarbons will form a solution at the interface, and T_l will vary from about 148°C at the water-pentane interface to about −108°C in the pure methane. The initial temperature at the water-pentane interface is, ideally, 25°C and in the methane, about −162°C. Schematic profiles of T_l and T are shown as solid lines in Figure 11 for an idealized initial state soon after the

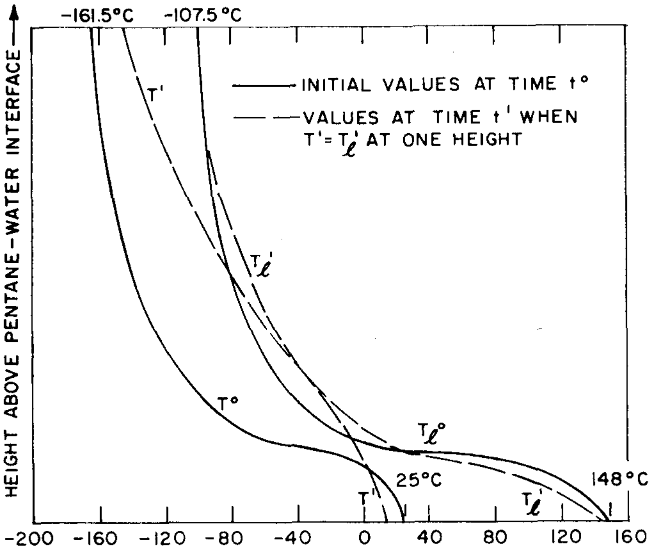

Fig. 11. Schematic idealized profiles of the limits of superheat, T_l, and the temperature, T, at a methane-pentane-water interface. Solid lines represent profiles at an initial time, t_0, and dashed lines represent profiles at a later time, t', when $T' = T_l'$ at one height above the water interface.

methane is poured and as dashed lines for a later time. Since T_l' is fixed by the composition of the hydrocarbon mixture, the straightening of the profile of T_l, if we ignore convection for simplicity, will be a function of the magnitude of the interdiffusion coefficient D of methane in pentane. The straightening of the profile of the actual temperature T will be governed by the magnitude of κ/Cd which is generally much larger than D. Consequently, T will rise and the profile will straighten more rapidly than the profile of T_l, and ultimately, at some depth, the curve for T will become tangent to the curve for T_l. The mixture will nucleate at this depth and initiate the vaporization of that liquid which is metastable. The energy released in this initiating explosion will be a function of the total excess energy stored in the metastable hydrocarbon. This is a function of the thermal histories, properties, and compositions of the fluids.

The mechanism for the destructive water-smelt explosions (Nelson and Kennedy, 1956) caused by leakage of water into a papermaking smelt may be analogous to the mechanism for methane poured on pentane. Smelts are alkali carbonates containing some sulfides. If water in a smelt can form a continuum of liquid solutions ranging from the very hot smelt containing no water to much cooler water containing no smelt (or if there is a compositional gap and the water-rich composition wets the smelt-rich composition), then upon leakage of water into a smelt each successive layer between the two phases wets the one below. If in the state reached (perhaps after some film boiling of the water) the temperature T does not exceed T_l anywhere (300° to 310°C for pure water and increasing with concentration of salt), then the water will not explode. As heat is conducted toward the water, the temperature will rise until, at some intermediate composition, T_l is exceeded. The liquid will nucleate at this point. Sufficient data are not available to check this hypothesis.

A meltdown of a UO_2 fuel element in a reactor excursion in a liquid metal fast breeder reactor can lead to contact between molten UO_2 (uranium dioxide) and liquid sodium. Since T_l for sodium in the system sodium-molten UO_2 is below the melting point of UO_2, the limit of superheat for sodium is probably not reached except in the unlikely case that these two materials are mutually soluble or form compounds that form a continuum of liquids between the two phases. No evidence for this exists at present, and a contact vapor explosion appears improbable in this case unless sodium has a very small or zero wetting angle on solid UO_2.

Even when the limit of superheat is not attained, the explosion can be violent. The violence of the explosion for a given substance is a function of the total enthalpy involved in superheating the liquid before the metastable liquid is nucleated. The closeness of the approach to the limit of superheat will be one factor governing the energy in the initiating explosion. A characteristic of these superheating explosions is the time lag until some portion of the volatile fluid is sufficiently superheated. This time lag permits a large amount of heat to be transferred to the fluid before boiling is initiated and obviates the need for unusual rates of heat transfer. The greater the time lag, the closer to the limit of superheat one gets in a given situation, and the greater the total energy of the initial explosion. Fragmentation after the initial explosive boiling will increase surface areas of the volatile fluid, enhancing the total heat transferred to the fluid in a later stage. Thus, nucleation theory permits one to examine a possible initiating mechanism for contact vapor explosions based on approaching the limit of superheat before boiling is initiated. For some hydrocarbons on water or on other hydrocarbons, this initiating mechanism appears likely. For water-smelt explosions, this mechanism is possible, but adequate data are not available for testing this speculation. For the sodium-molten UO_2 system, it appears less likely that one may achieve the limit of superheat.

If the limit of superheat is reached, then a large fraction of the maximum energy available for an explosion is contained in the metastable layer of fluid before initiation. More energy can be picked up if the initial explosion fragments the fluid, and for any given situation, fragmentation and the enthalpy input are likely to be greater the closer one approaches the limit of superheat. Further detailed studies are required to investigate such hypotheses.

NOTATION

a = constant in Berthelot equation
b = constant in Berthelot equation
c = critical size
d = mass density of liquid
d_G = mass density of gas
k = Boltzmann constant
$\underline{k}$ = $\sqrt{\kappa dC}$ thermal diffusivity (**C** is specific heat)
m = mass of a molecule
$\underline{m}$ = geometric factor $Z/R = -\cos\theta$ (Figure 10)
n = number of bubbles per unit volume which contain x molecules
r = radius of bubble at a planar interface; radius of spherical bubble
r_c = radius of critical size bubble in mechanical and chemical equilibrium with liquid
s = hot substrate
t = time
v = volatile fluid
x = number of gas molecules
$\dot{x}$ = the net rate of increase of molecules in a bubble, (dx/dt)

A = surface area of a bubble

B = coefficient in Equation (7), $\sim 1 - 1/3(1 - P_L/P_V)$

C = concentration of volatile constituent in liquid mixture (number per unit volume)

C = specific heat

C_V = concentration of solute in equilibrium with gaseous solute at pressure, P_V

C_L = concentration of solute in equilibrium with gaseous solute at pressure, P_L

D = diffusion coefficient of volatile constituent in liquid mixture

F = geometric factor defined by $(2 - 3m + m^3)/4$ or Equation (46)

ΔH_V = enthalpy of vaporization per molecule of liquid

J = number of bubbles per unit volume per unit time which grow beyond critical size

J_λ = rate of bubble nucleation with correction for heat conduction

J_η = rate of bubble nucleation controlled by viscous forces

J_D = rate of bubble nucleation controlled by diffusion of volatile constituent

J_0 = value of nucleation rate at a low enough temperature so it is very much lower than the nucleation rate in the region of interest

L = coefficient of T in the equation $J = J_0 \exp (LT)$

LG = liquid-gas interface

M = molecular weight

N = number of droplets

N_o = initial number of droplets

N = number density of liquid

P = pressure

P_e = equilibrium vapor pressure

P_V = vapor pressure

P_L = pressure on external liquid phase

P_G = pressure of gas phase; pressure in bubble

R = distance from the center of a bubble

R = radius of curvature of a bubble at glass liquid interface (Figure 10)

R = gas constant

S = geometric factor $(1 - m)/2$

SG = solid-gas interface

SL = solid-liquid interface

T = temperature

T_l = limit of superheat

T_c = critical temperature

T_i = temperature at interface between two liquids

T_f = crystallization temperature of substrate

T_S = temperature at the bubble interface

T_o = temperature of the bulk liquid

V = volume

V_G = volume of gas phase; volume of bubble

W = minimum work to make a bubble; the negative of the availability where availability is the maximum work which can be extracted from a bubble

Z = Zeldovich factor [Equation (11)]; geometric factor for defining bubble at liquid glass interface equal to $-R \cos\theta$ (Figure 10)

Greek Letters

β = number of gas molecules which strike a surface per area per unit time

δ = Poynting correction factor for effect of ambient pressure on vapor pressure [Equation (13)]

δ_λ = factor correcting for influence of heat transfer on bubble growth [Equations (19) and (20)]

δ_D = factor correcting for influence of diffusion on rate of nucleation [Equations (26) and (27)]

η = viscosity of liquid

θ = contact angle of liquid (Figure 10)

κ = thermal conductivity

λ_e = thermal conductivity of liquid

μ = chemical potential

μ_G = chemical potential of the gas phase

μ_L = chemical potential of the liquid phase

σ = surface tension at liquid-gas interface

ϕ = contact angle (Figure 10)

ω = factor governing relative influence of viscous forces on nucleation rate [Equation (22)]

ω' = factor governing relative influence of inertial forces on nucleation rate [Equation (23)]

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APPENDIX: CALCULATION OF THE POYNTING CORRECTION FACTOR

The metastable liquid is at a pressure P_L which is less than the pressure on it at equilibrium, that is, the equilibrium vapor pressure P_e. To calculate the vapor pressure P_V of the metastable fluid, one may use the thermodynamic relation $d\mu = VdP$ to calculate the difference in chemical potential between the metastable and stable liquids and then equate that difference to the difference between the chemical potentials of the vapors in equilibrium with these two fluids:

$$\mu_L - \mu_e = \int_{P_e}^{P_L} V_L dP = \int_{P_e}^{P_V} P_G V_G d\ln P \qquad \text{(A1)}$$

The molar volume of liquid in the metastable region is usually unknown. One can generally assume that the fluid is incompressible with small error. The gas is stable, and the right-hand side of Equation (A1) can be integrated by using known data or any reasonable equation of state. A useful approximation for the small values of P_L we have considered may be made. Since $P_G V_G$ is approximately constant, then

$$V_L(P_L - P_e) \cong P_e V_e \ln \frac{P_V}{P_e} \qquad \text{(A2)}$$

where V_e is the volume of a mole of gas at equilibrium with the stable liquid. Expanding the logarithm and keeping terms up to second order, one obtains an expression for the correction factor δ:

$$\delta = \frac{P_V - P_L}{P_e - P_L} = 1 - \frac{V_L}{V_e} + \frac{1}{2}\left(\frac{V_L}{V_e}\right)^2$$

$$= 1 - \frac{d_G}{d} + \frac{1}{2}\left(\frac{d_G}{d}\right)^2 \qquad \text{(A3)}$$

Equation (A3) should generally be accurate at values of P_L at least up to 1 atm.

THE AUTHORS

Milton Blander started his career in physical chemistry at Yale with a thesis on the chemistry of aqueous salt solutions. Realizing the evils of water, he switched to the chemistry of molten salts at the Oak Ridge National Laboratory with emphasis on high temperature thermodynamics and statistical mechanics. This set the stage for his work on the origin of meteorites at North American Aviation where he combined nucleation theory and high temperature thermodynamics to deduce a unique and still controversial theory of early processes in the solar system. This interest in nucleation and outer space evolved into an interest in lunar and terrestrial volcanoes which are often driven by the nucleation of bubbles in magmas. At the Argonne National Laboratory, his work on bubble nucleation led him to focus on the mechanism of contact vapor explosions which pose a potential hazard in nuclear reactors.

Joseph L. Katz received his B.S. and Ph.D. in physical chemistry from the University of Chicago, working on the electronic properties of molecular solids. After a year abroad, in 1964 he went to work at North American Aviation where he became interested in nucleation phenomena, initially concentrating on the homogeneous nucleation of a vapor and, more recently, on homogeneous boiling. Since 1970 he has been at Clarkson College of Technology where he is now Professor of Chemical Engineering. At Clarkson he has continued his work on nucleation, including nucleation in solids and nucleation at interfaces.