

1977 Award Lecture

SUPERHEATED LIQUIDS A LABORATORY CURIOSITY AND, POSSIBLY, AN INDUSTRIAL CURSE

Part 1: Laboratory Studies and Theory

The 1977 ASEE ChE Division Lecturer is Dr. Robert Reid of Massachusetts Institute of Technology. Bestowed annually on a distinguished engineering educator who delivers the Annual Lecture of the Chemical Engineering Division, the award consists of \$1,000 and an engraved certificate. These were presented to Dr. Reid at the ASEE Summer School for Chemical Engineering Faculty held July 31 - August 5, 1977 at Snowmass, Colorado. During the 1977-78 academic year, Dr. Reid will visit three universities to speak on topics related to the subject matter of his award lecture. The 3M Company is supporting this activity in addition to the award itself.

Professor Reid spent his youth in Denver, Colorado and attended the Colorado School of Mines. After a four-year interruption during the second world war, he transferred to Purdue University where he obtained both a B.S. and M.S. in chemical engineering. His doctoral studies were carried out at M.I.T. after which he joined the faculty as Director of the Engineering Practice School at Oak Ridge, Tennessee. He has been active in the AIChE and served as a Director from 1969-71 and as editor of the AIChE Journal from 1970 to 1976. He was the Institute Lecturer in 1968 and received the Warren K. Lewis award in 1976. His research interests have covered a wide range of subjects including kinetics, boiling heat transfer, life support systems, crystallization, properties of materials, cryogenics and thermodynamics. Books include texts on crystallization growth rates from solution, thermodynamics and the estimation and correlation of the properties of gasses and liquids.



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WHAT IS A SUPERHEATED LIQUID? HOW ARE THEY PREPARED?

IF WE PLAN TO DISCUSS superheated liquids, we first need to define them. On Figure 1, there is shown a simple pressure-temperature graph for a pure substance. The area below the saturation curve and above the zero-pressure isobar is normally a stable gas region. If, however, a substance could be maintained as a liquid but still remain in this (shaded) region, it would then be called a superheated liquid; note that, in this case, there is no restriction to positive pressure. Super-

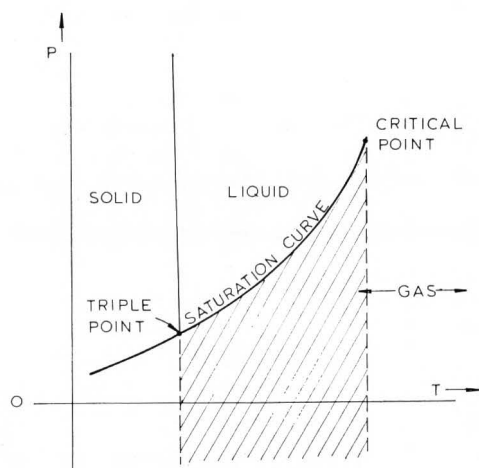


Figure 1

Domain of Superheated Liquids (Cross-hatched) For a Pure Substance

heated liquids at negative pressures (i.e., in tension) are quite common.

In Figure 2, we show the domain of superheated liquids in a different manner. Here we have isothermal sections of a P-V-T surface for a pure substance. The saturated liquid and saturated vapor curves join at the critical point where the critical temperature is shown as T_3 . Tracing an isotherm, say T_1 , beginning in the upper-left corner, subcooled liquid exists until the pressure equals P_1 . This point represents a saturated liquid at a vapor pressure P_1 . If one tries to reduce the pressure further, vaporization normally occurs and the vapor phase is represented by the intersection of T_1 with the saturated vapor curve. If, however, boiling could be suppressed, then by lowering the pressure, while keeping the system at T_1 , one enters the two-phase dome as noted by the dashed curve. As will be described later, there is a limit to how far one can continue this process, and this limit is shown by the spinodal curve where the pressure is P_1' . Thus superheated liquids lie in the region between the saturated liquid curve and the spinodal curve. (A similar phenomenon could be described on the vapor side, but this then would involve us in subcooled vapors—a fascinating subject, but not pertinent to the topic under consideration).

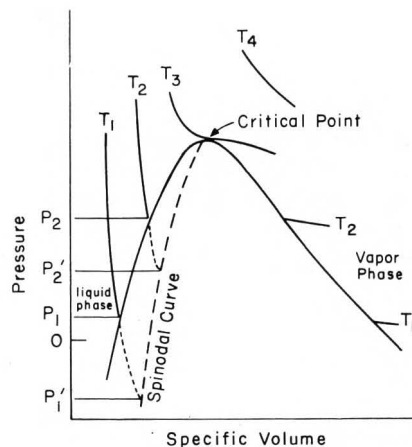


FIGURE 2 SUPERHEATED LIQUIDS LIE BETWEEN THE SATURATED LIQUID CURVE AND THE SPINODAL CURVE

Figure 2 is also useful in pointing out possible experimental techniques to obtain superheated liquids. The process described involved an isothermal depressurization. Alternatively, starting, say at T_1, P_2' , the liquid could be heated in an isobaric manner at P_2' . The limit, in this case, would be the state at T_2, P_2' .

Before learning how one might prepare a superheated liquid, there are several fundamental concepts in boiling that need emphasis. Normally, boiling is carried out on a hot, solid surface whose temperature exceeds the bubble point of the liquid.

Referring to Figure 3, when the solid temperature is only slightly greater than the boiling point, convection currents carry away energy; no bubbles are visible and evaporation occurs at the free surface of the liquid. At somewhat higher solid temperatures, a thin film of liquid becomes slightly superheated and bubbles appear at specific sites on the solid. Irregularities on the surface, such as microcavities, have trapped a small vapor embryo; the superheated liquid film vaporizes into these preformed vapor embryos until bubbles grow large enough to detach and start the cycle again. Increasing further the solid's temperature increases the degree of superheat in the liquid and "acti-

Significant superheating of the liquid is then possible. The drops of the test liquid may begin to vaporize while heating if there is contact with a solid mote or if improperly degassed, but if one attains a sufficiently high temperature, there is spontaneous nucleation. With a sharp noise, a vapor bubble suddenly appears. This event resembles a miniature explosion.

vates" more cavities. The heat flux increases with the temperature difference between the solid and the bubble point of the liquid to some maximum value (peak nucleate flux) where a further increase in temperature actually causes a decrease in heat flux since the bubbles on the surface become effective insulators. This initiates the transitional region, and it continues until the entire

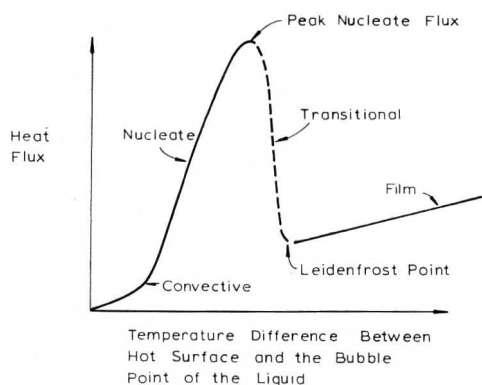


Figure 3
Boiling Regimes

surface is effectively blanketed by vapor. A minimum in heat flux is then attained and is often called the Leidenfrost point. Finally, further increases in the solid temperature increases the heat flux slowly as energy must be driven across a vapor film; i.e., the system is in film boiling.

Returning to the nucleate and transitional region, suppose the hot surface could be made microscopically smooth so as to eliminate any pre-existing vapor embryos. This barrier to "nucleation" would then allow the liquid to superheat. Using a hot, very clean, immiscible liquid as a heat source is the most common way to prepare a superheated liquid.

Consider the apparatus in Figure 4 (Moore, 1959; Wakeshima and Takata, 1958). A dense, hot liquid fills the vertical column. Heating wires are wrapped about this tube in such a way as to insure that there is a temperature gradient with the hottest liquid on top. The bottom of the column is kept cool (below the bubble point of the test liquid). Small drops of this test liquid are injected and rise into the warmer zones. Heat transfer is rapid and the bulk temperature of a drop (circa 0.5 mm or less) is close to the "host" fluid temperature at any height. Significant superheating of the liquid is then possible. The drops of the test liquid

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A logical question to ask is why carry out such an experiment? What is learned? At best, after many trials, we learn just how high we can heat a liquid before it undergoes a phase transition to vapor. This temperature is important because we associate it with a point on the spinodal curve (Figure 2). We also believe that this limit (often termed the superheat limit temperature or SLT) represents the temperature where extremely rapid homogeneous nucleation occurs, i.e., when vapor bubbles appear spontaneously in the bulk liquid.

There have been numerous modifications to the basic "bubble column" just described. Apfel (1971) levitated his test drops in an acoustic field while Forest and Ward (1977) held their test drops in a flow field and varied the temperature of the host liquid. Besides the bubble column there are other ways to measure the superheat limit

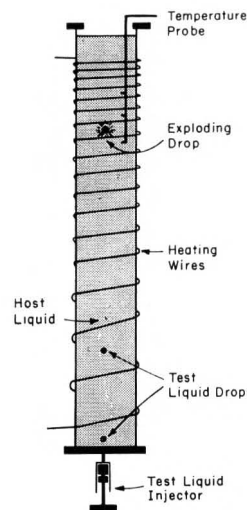


FIGURE 4 BUBBLE COLUMN TO MEASURE THE SUPERHEAT-LIMIT TEMPERATURE OF A TEST FLUID

temperature. Heating may be accomplished using very clean, very smooth glass surfaces (Briggs, 1955; Wismer, 1922; Kendrick et al., 1924; Field, 1977), but it is difficult to attain temperatures as high as found in bubble columns. Skripov (1974) and Skripov et al. (1977) describe a pulse-heating

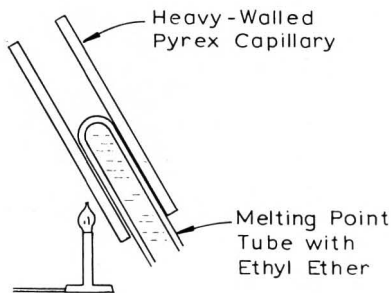


FIGURE 5
WOODBRIDGE MICRO (SUPERHEAT-) ROCKET

technique which shows promise. A programmed current is imposed across a platinum wire in the liquid. The voltage drop is monitored and the calculated resistance is related to the surface temperature of the wire. A thin film of liquid is very rapidly heated. Spontaneous nucleation is recognized by a sharp rise in voltage. The key is to heat the liquid so fast that surface nucleation on the wire surface occurs slowly relative to bulk heating and nucleation in the adjacent liquid film.

A most unusual demonstration of the rapidity of homogeneous nucleation was described by Woodbridge (1952). He selected fresh melting-point capillary tubes about 1.5 mm in diameter and 6-7 cm in length. These were filled about 3/4 full with ethyl ether. The ether tubes were placed loosely within a 15 cm, heavy-walled Pyrex capillary tube as shown in Figure 5. When heated gently, the ether expanded until liquid reached the open end when "with a noise like a pistol shot, the rocket takes off. . . ." Flights of 40-50 feet were obtained.

Typical data showing measured superheat limit temperatures are shown in Table 1 (Blander and Katz, 1975; Patrick, 1977). Note the rather amazing constancy of the ratio of the SLT to the critical temperature.

Most data for mixtures have been limited to binary systems of hydrocarbons; Figure 6 from Blander and Katz's review paper shows some typical data for the *n*-pentane—*n*-hexadecane

system. In our laboratory, we are beginning to measure the SLT for polar mixtures.

THERMODYNAMIC APPROACH

THE PREDICTION OF the SLT from thermodynamics is, in essence, a problem of predicting stability limits. Gibbs (1876, 1878) first discussed stability in a paper published a century ago. Considerably more recently Beegle et al. (1974) reconsidered the problem from Legendre transform theory and derived a very general criterion to indicate the limit at which a superheated liquid becomes unstable.

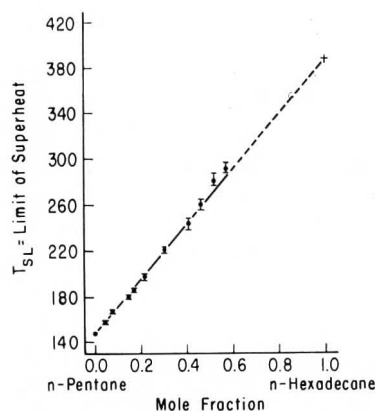


FIGURE 6 SUPERHEAT-LIMIT TEMPERATURES FOR THE BINARY SYSTEM *n*-PENTANE -- *n*-HEXADECANE AT ONE BAR

[M. BLANDER AND J. L. KATZ, *AIChE J.* 21, 833 (1975).]

The derivation is quite straight-forward and is based on the Gibbs criterion that, for an isolated system in a stable equilibrium state, the total entropy is a maximum. With this simple statement, and with Legendre transform theory to vary the independent variables in the system, one arrives at the result for a *n*-component system,

$$y^{(n)}_{(n+1)(n+1)} > 0 \quad \text{for a stable system} \quad (1)$$

Here, $y^{(n)}$ is the *n*th Legendre transform of the system energy and $y^{(n)}_{(n+1)(n+1)}$ represents second-order partial derivative of $y^{(n)}$ with respect to the $(n+1)$ variable.

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SUPERHEATED LIQUIDS: Reid

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If one begins with the system in a stable state, then the limit of stability results when

$$y^{(n)}_{(n+1)(n+1)} = 0 \quad (2)$$

For example, with a pure component ($n = 1$), and with the ordering of variables such that*

$$\underline{U} = U(\underline{S}, \underline{V}, N) \quad (3)$$

then $y^{(1)}$ is identically equivalent to the Helmholtz energy, A , and the variable $(n + 1)$ is V . Thus

$$y^{(1)}_{(n+1)(n+1)} = A_{VV} = (\partial^2 A / \partial V^2)_{T,N} = -(\partial P / \partial V)_{T,N} = 0 \quad (4)$$

for the limit of stability or

$$-(\partial P / \partial V)_{T,N} > 0 \quad (5)$$

for a stable system.

With Eq. (4), one may estimate the superheat-limit temperature provided that an equation of state relating P , V , and T is available for the liquid phase. To illustrate the technique, assume the recent Peng-Robinson equation (1976) is

TABLE 1

Measured Superheat-Limit Temperatures.

- 1 Bar -

Substance	T_b (K)	T_c (K)	T_{SL} (K)	T_{SL}/T_c
Ethane	184.6	305.4	269.2	0.881
Propane	231.1	369.8	326.2	0.882
<i>n</i> -Butane	272.7	425.2	378.2	0.889
<i>n</i> -Heptane	371.6	540.2	487.2	0.902
2,2,4-Trimethylpentane	372.4	543.9	488.5	0.898
Cyclohexane	353.9	553.4	492.8	0.890
Benzene	353.3	562.1	498.5	0.887
1-Butene	266.9	419.6	371.0	0.884
Hexafluorobenzene	353.4	516.7	467.9	0.906
Methanol	337.8	512.6	459.2	0.896
Ethyl ether	307.7	466.7	420.2	0.900
Acrylonitrile	350.5	536.0	474.0	0.884

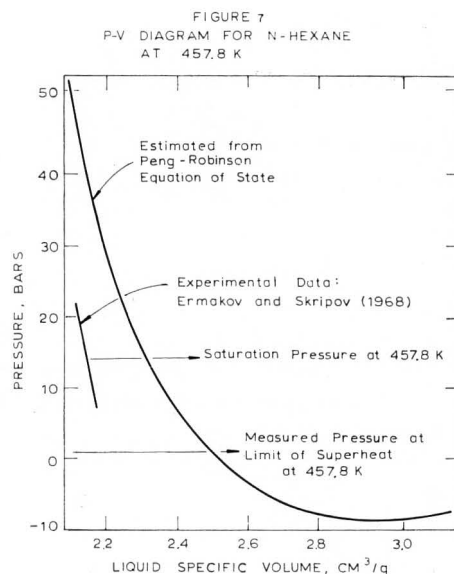
* U , S , and V are, respectively, the system internal energy, entropy, and volume. The underbar represents total, not specific, quantities. N is the system mass (or moles).

applicable to relate P , V , T . Written on a molar basis,

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (6)$$

where a and b are functions of the critical properties; a also depends on the Pitzer acentric factor and upon T . With Eqs. (4) and (6), the limit of stability is predicted when

$$\frac{RT}{(V-b)^2} - \frac{2a(V+b)}{[V(V+b) + b(V-b)]^2} = 0 \quad (7)$$



In Figure 7, we show a graph of Eq. (6) for liquid *n*-hexane at 457.8 K. The branch above the saturation (vapor) pressure of 14 bar represents subcooled liquid. Below this pressure the liquid hexane is superheated. The P - V isotherm shows a minimum at about -8 bar and $3 \text{ cm}^3/\text{g}$; these values are, of course, those that would be found if Eqs. (6) and (7) were solved simultaneously. Also shown in Figure 7 are some measured specific volumes from Ermakov and Skripov (1968) that cover both the subcooled and superheated range. The Peng-Robinson equation predicts specific volume to within a few percent when the pressure and temperature are given; much larger errors result if volume and temperature are the independent variables.

Finally, in Figure 7 the temperature, 457.8 K, was selected since this is the reported SLT for *n*-hexane at one bar. If the Peng-Robinson equa-

Those who take time to follow this procedure soon note that bubble formation rate is essentially zero until a certain temperature is reached where, over a small temperature range, the rate becomes very large.

tion accurately predicts stability limits, then it indicates that one could decrease the pressure to -8 bar before reaching the limit.

The discrepancy between measured values of the SLT and those predicted from thermodynamics is shown in a different way in Figure 8. Here, the reduced SLT is plotted vs. reduced pressure for R-12 (dichlorodifluoromethane). The curve marked Peng-Robinson was calculated from Eqs. (6) and (7), eliminating the volume, and varying the temperature. Curves calculated from three other simple equations of state are also shown, i.e., from the Redlich-Kwong (1949), the Soave (1972), and the Fuller (1976) relations. All give curves similar in shape and all fall below the experimental values. At one bar, the experimental data (Moore, 1956, 1959) indicate a superheat limit temperature of 342 K ($T_r = 0.887$) whereas the Peng-Robinson equation would predict a value of 352 K ($T_r = 0.913$).^{*} Comparison then shows that thermodynamics yields values of the superheat-limit temperature close to, but consistently higher, than those found experimentally. The equations of state are certainly not exact, but the results are reasonable when one remembers that thermodynamics provides the upper limit to the superheat-limit temperature. Experimental values must always be less.

For mixtures, the basic approach is similar but Eq. (7) is replaced by a considerably more complex relation. (See Beegle et al., 1974). For example, with a binary system composed of A and B, the superheat-limit temperature may be calculated from the relation

$$\begin{vmatrix} A_{VV} & A_{VA} \\ A_{VA} & A_{AA} \end{vmatrix} = 0 \quad (8)$$

where $A_{VV} = (\partial^2 \underline{A} / \partial V^2)_{T,N} = -(\partial P / \partial V)_{T,N}$

^{*}In a plot of P_r vs. T_{SL}/T_c , for similar compounds, all experimental data fall on one curve (actually very close to a straight line). This has been shown for the aliphatic hydrocarbons, *n*-pentane, *n*-hexane, and *n*-heptane (Skripov and Ermakov, 1964).

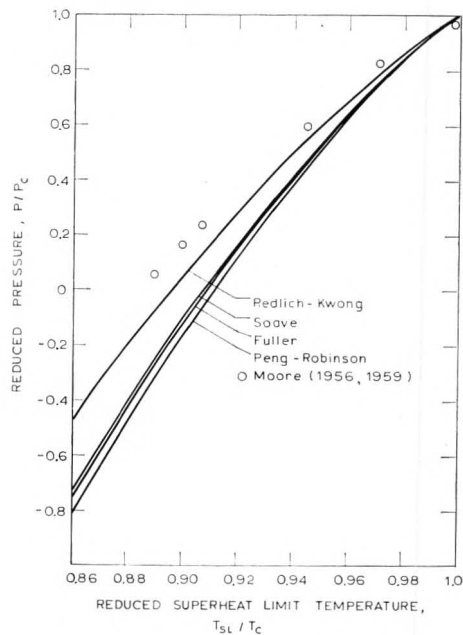
$$A_{VA} = \partial^2 \underline{A} / \partial V \partial N_A = -(\partial P / \partial N_A)_{T,V,N_B}$$

$$A_{AA} = (\partial^2 \underline{A} / \partial N_A^2)_{T,V,N_B}$$

In a pure component case, the comparable equation would be Eq. (5) which can be written as

$$A_{VV} = 0 \quad (9)$$

When heating a binary mixture at constant pressure (or depressurizing isothermally), the limit of superheat is first reached when Eq. (8) is



Estimated Limit of Superheat Temperatures from Equations of State for Dichlorodifluoromethane (R-12)

FIGURE 8

satisfied. At this point, $A_{VV} > 0$. Therefore, the mixture has attained the limit of stability at less severe conditions than would have been expected if the mixture had been treated as a pseudo-pure component and the test limited to Eq. (9) or Eq. (5). A ternary mixture would have even wider limits, etc.

We show in Figure 9 the pressure-volume graph for a 50 mole percent mixture of ethane and *n*-butane as calculated from the Peng-Robinson equation of state. The stability-limit curves from both Eqs. (8) and (9) are shown. Note that the slope $(\partial P / \partial V)_T$ is still negative when Eq. (8) is satisfied. The use of Eq. (9) would be incorrect to define stability limits in this binary system.

At $P = 1$ bar, Eq. (8) is satisfied when $T = 335.5$ K. Constructing graphs similar to Figure

9 for other compositions indicates that, at 1 bar, the superheat-limit temperature is essentially a mole-fraction average of the superheat limit temperatures of the pure components. This result is in agreement with the data of Porteous and Blander (1975).

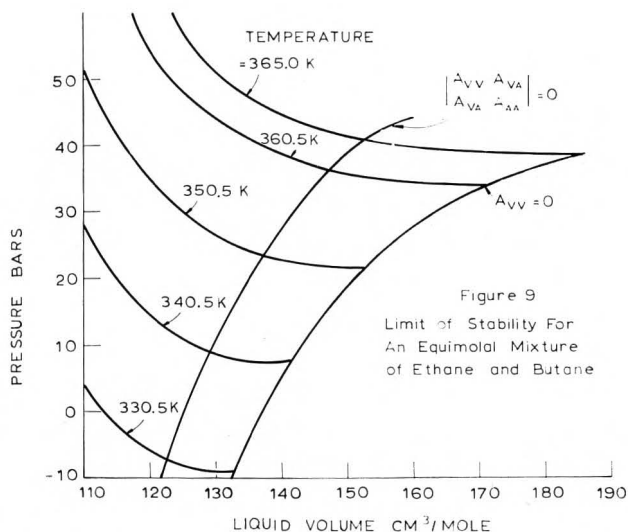


Figure 9
Limit of Stability For
An Equimolar Mixture
of Ethane and Butane

KINETIC THEORY

SUPERHEATED LIQUIDS HAVE also been modelled by using kinetic theory.* In this case, the end result shows the probability of forming a macroscopic vapor bubble from a given quantity of liquid in a given time interval.

The superheated liquid is visualized as a mixture of continuum liquid molecules with many vapor embryos of different sizes. These embryos probably form from small density fluctuations and grow (or decay) by the vaporization (or condensation) of liquid molecules. Thermodynamic reasoning indicates that for each system (at a given temperature, pressure and composition), there exists a critical-size vapor embryo which is in unstable equilibrium with the bulk liquid. Embryos below this critical size tend to become even smaller while those larger than the critical

*See, for example, Blander and Katz (1975), Kagan (1960), Moore (1956, 1959), Volmer (1939).

size grow even larger—and soon become macroscopic in size.

We are interested in developing means to estimate the rate at which embryos attain the critical size for given experimental conditions. This rate J is then the bubble nucleation rate, and, from theory,

$$J \approx N_L f \exp[-16\pi\sigma^3/3kT(P - P_0)^2] \quad (10)$$

where N_L is the number density of liquid molecules, f is a frequency factor of the order of 10^{11}s^{-1} to account for the rate phenomena of vaporizing—and condensing—molecules in the vapor embryo. σ is the surface tension, P is the pressure inside the embryo and P_0 is the bulk liquid pressure. P is normally very close to the equilibrium vapor pressure at the bulk liquid temperature.

As temperature is increased, the surface tension decreases and the embryo pressure increases. Thus J is a strong function of temperature. In some range of elevated temperatures, the probability of forming critical-size nuclei is not vanishingly small. It is this temperature range that interests us.

The probability calculations then proceed as follows: For any given temperature, the molecular density of molecules is multiplied by the product of the frequency factor times the exponential term. The answer is the “expected” number of macroscopic bubbles one might expect to appear from a given volume of liquid in a given time. Those who take time to follow this procedure soon note that the bubble formation rate is essentially zero until a certain temperature is reached where, over a small temperature range, the rate becomes very large. In the laboratory, this corresponds to heating a liquid well beyond the expected boiling point when, in a small temperature range, vapor bubbles appear so rapidly the event could be labeled as an explosion!

In calculations to estimate the temperature where rapid, homogeneous nucleation occurs, we define some physically reasonable value of the rate and iterate to determine the temperature. To emphasize the rapidity of the events, to define a

... in some cases the agreement is poor, i.e., estimated superheat limit temperatures are larger than those measured experimentally. In these instances, it appears that nucleation occurs at the superheated liquid boundaries from either a vapor pocket or by surface nucleation or nucleation was initiated by the evolution of dissolved gas.

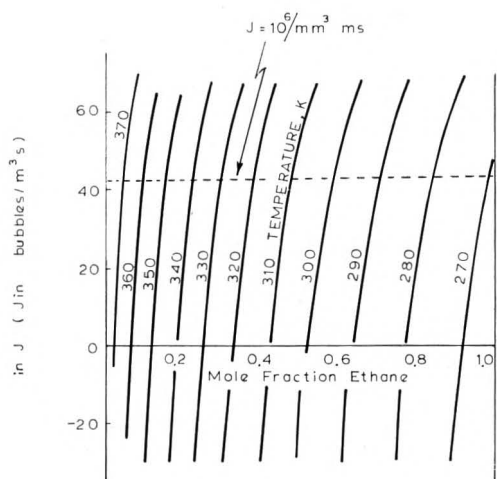


Figure 10 Estimated Rates of Bubble Nucleation For the Ethane - *n*-Butane System at One Bar

vapor explosion, we have chosen a temperature which would produce one million bubbles every millisecond in each and every cubic millimeter. With this, or similar choices, calculated superheat-limit temperatures usually agree within a few degrees when compared with those measured experimentally. Such agreement is rather remarkable in view of the approximations used in the theory and the difficulties of estimating physical properties (e.g., surface tension) for liquids heated well beyond their boiling points.

And, in some cases, the agreement is poor, i.e., estimated superheat limit temperatures are larger than those measured experimentally. In these instances, it appears that nucleation occurs at the superheated liquid boundaries from either a vapor pocket or by surface nucleation (Jarvis et al., 1975), or nucleation was initiated by the evolution of dissolved gas (Mori et al., 1976; Forest and Ward, 1977). In spite of these cases, the use of kinetic theory to provide good estimates of superheat-limit temperatures for many pure materials and simple (ideal) liquid mixtures is well documented (Blander and Katz, 1974).

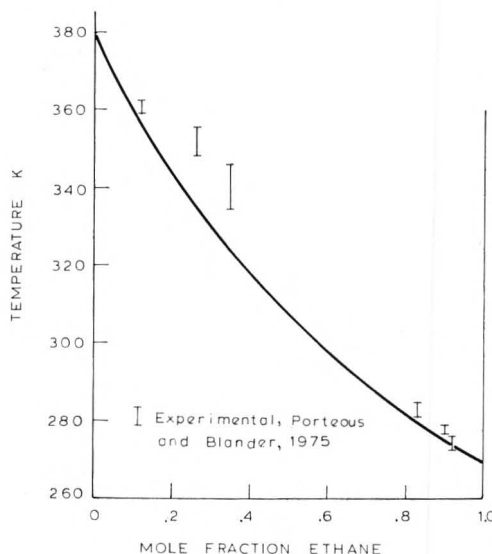
In Figure 10 we show some estimates of the expected rate of bubble formation for the system ethane-butane as a function of temperature and ethane concentration. The external pressure is one bar. The explosion criterion noted above was used. Clearly, both the bulk liquid composition and the temperature significantly affect the "expected" number of bubbles appearing in the superheated liquid. The experimental superheat-limit temperature for pure ethane is about 270 K and, for *n*-

butane, 378 K (Porteous and Blander, 1975).

Crossplotting the temperature and ethane composition when $J = 10^6$ bubbles/mm³ ms yields Figure 11. The smooth curve represents the predicted superheat-limit temperatures for an ethane-*n*-butane binary at one bar. The curve is not linear. The vertical bars show the few existing experimental data (Porteous and Blander, 1975).

We are currently studying the superheat-limit temperatures of highly nonideal liquid mixtures and we expect to find significant deviations from simple mole fraction averages. There is also no well developed kinetic theory applicable to nonideal liquid mixtures and we are in the process of building upon the earlier work of Reiss (1950), Hirschfelder (1974), and Katz (1977).

Figure 11 Predicted and Experimental Superheat-Limit Temperatures of the Ethane - *n*-Butane System at One Bar



Besides the modifications in the mixture kinetic model caused by treating embryos differing in number as well as composition, one may also question whether diffusional limitations enter. For example, in the ethane - *n*-butane case, the vapor embryo is significantly enriched in the more volatile ethane. A "skin" or boundary layer would, therefore, be expected to be enriched in *n*-butane. Blander (1972) argues that such enrichment may not be important since, near the critical size, the subcritical-size embryo has a relatively long life and he solves, approximately, the diffusion equation to predict the effect quantitatively. The principal effect found was a slight change in the pre-exponential frequency factor described earlier.

Another point of view may be presented that possesses some physical meaning. Suppose we select an ethane - *n*-butane mixture containing 96 mole percent ethane.* Figure 10 indicates that the superheat-limit temperature is about 272 K. The pressure difference between that within the embryo and the bulk superheated liquid (at one bar) is estimated to be 21.8 bars. Also the surface tension for this mixture, at 272 K, is estimated to be about 3.7 dynes/cm. Assuming the Laplace equation to apply, the radius of the critical embryo, $r_c = 2\sigma/\Delta P = (2)(3.7 \times 10^{-3})/(21.8 \times 10^5) = 3.4 \text{ nm}$. The number of molecules in the embryo is about 100. To supply this number of molecules to the vapor embryo would require less than a single molecular layer on the surface. Clearly with such a picture, it is difficult to conceive that diffusion could play an important role.

Editor's Note: This paper will be continued in the next issue of CEE.

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*Experiments described in Part 2 indicate that spills of pure ethane on ambient water will not vapor-explode. The addition of 4 mole percent *n*-butane results in quite violent explosions.

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