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The Homogeneous Nucleation of Bubbles in Superheated Binary Liquid Mixtures

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It is shown how to apply homogeneous nucleation theory to predict the limits of superheat of multicomponent liquid mixtures. Measurements of such limits for *n*-pentane-*n*-hexane, *n*-hexane-cyclohexane, benzene-cyclohexane, and benzene-*n*-hexane mixtures as a function of composition are presented and compared with theory.

SCOPE

Barriers to the nucleation of bubbles may lead to a superheating of liquids which is so large that when nucleation does occur, they boil with explosive violence. Such explosive boiling tends to occur whenever a low boiling nucleating liquid comes in contact with a much higher boiling host liquid if their temperature difference is sufficiently large. This limit of superheat is therefore readily attained and represents quite a significant hazard to industry.

In a recent review in this journal (Blander and Katz, 1975), it was shown that homogeneous nucleation theory was quite successful in predicting the measured limits of superheat of pure (that is, one component) substances. However, the low boiling liquid is often a mixture of two or more components. It is the purpose of this paper to show how to apply nucleation theory to multicomponent mixtures, to describe an improved version of the rising droplet column used to measure the limits of superheat, and to present results on an ideal and on several somewhat nonideal binary mixtures which were studied to test the validity of the theory.

CONCLUSIONS AND SIGNIFICANCE

The theory for the homogeneous nucleation of a superheated liquid was successfully generalized to multicomponent mixtures by employing the chemical equilibrium approximation; that is, the pressure and composition of the gas in the embryonic bubbles is determined by its being in equilibrium with the surrounding superheated liquid for bubbles of every size. With this approximation, the equation for the rate of nucleation of multicomponent mixtures

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becomes identical in appearance with that for a pure substance [Equation (1)] except for a minor and negligible change in the preexponential. The fact that one is dealing with a mixture enters the equation only via the use of the mixture surface tension and mixture vapor pressure. Given experimental data for these quantities (or reliable estimation techniques), one is thus able to predict the limits of superheat of multicomponent mixtures as easily as that for pure substances.

The theory was tested by comparison with limit of superheat measurements on *n*-pentane-*n*-hexane, *n*-hexane-cyclohexane, benzene-cyclohexane, and benzene-*n*-hexane mixtures. The measurements for the first three mixtures confirm the theoretical predictions to within the joint uncertainty due to the uncertainties in the physical properties and that due to the experimental scatter. The data for the benzene-*n*-hexane mixtures depart somewhat from the theoretical predictions (for example, predicting an excess limit of superheat of 9°K instead of 14°K at a *n*-hexane mole fraction of 0.4) but, nevertheless, still fit the general shape of the limit of superheat vs. mole fraction curve quite well. (The slight but probably not negligible solubility of benzene in the host liquid may account for these deviations.) We conclude that adequate estimates of the limits of superheat can be obtained from this theory even for somewhat nonideal mixtures.

In a recent review article (Blander and Katz, 1975), it was shown that homogeneous boiling nucleation theory was able to quite accurately predict values for the limits of superheat of pure (that is, one component) substances. It was also shown that experiments on ideal binary liquid mixtures (for example, propane-butane) were adequately fitted by a mole fraction weighted average of the limits of superheat of the pure components though no theoretical derivation for this result was provided. However, mixtures which were only slightly nonideal, such as *n*-pentane-*n*-dodecane, showed a small but unmistakable deviation from linearity. For less ideal mixtures, more significant deviations are to be expected. For its practical importance (most fluids of industrial interest are mixtures) as well as for its fundamental scientific interest, we decided to examine the theory to see what generalization was needed to make it applicable to multicomponent mixtures and to make suitable measurements to verify the theory.

There exists a generalization of nucleation theory for the condensation of binary vapor (Reiss, 1950) which was recently generalized further to multicomponent vapors (Hirschfelder, 1974). Since one-component nucleation theory can be derived for both boiling and condensation from a common starting point (Katz and Blander, 1973), one might think the same should be done for multicomponent mixtures. However, as we shall show below, by making the approximation that all embryonic bubbles are in chemical equilibrium rather than the approximation that they are in mechanical equilibrium, not only are the derivation and the final equation greatly simplified, but some hard to obtain data, for example, the composition dependence of the vapor in equilibrium with a liquid mixture as a function of pressure, are no longer required.

THEORY

In a superheated binary liquid mixture of fixed bulk composition at constant temperature T and external pressure P^0, theory predicts that the logarithm of the rate of homogeneous nucleation is proportional to the minimum work of formation of a bubble of critical size, that is, that size at which a bubble is in both mechanical and chemical equilibrium with the surrounding liquid. (Mechanical equilibrium means that Laplace's equation $P = P^0 + 2\sigma/r$ is satisfied. Chemical equilibrium means that the pressure and composition of the vapor inside the bubble are determined by the requirement that the vapor be in equilibrium with the surrounding liquid.) The probability of forming critical sized bubbles (and thus the rate of nucleation) increases extremely rapidly with increasing superheat. This increase is so rapid (typically one order of magnitude for each 0.3°C at observable rates of nucleation) that one can define a limit of superheat as the temperature at which the probability of nucleation goes from a negligibly small number to almost unity.

One can obtain an estimate of the proportionality constant connecting the concentration of critical sized bubbles and the logarithm of the rate of nucleation by considering the superheated liquid to contain a distribution of embryonic bubbles of various sizes. This distribution is obtained by calculating the minimum work required to form bubbles of any given size and pressure (for binary mixtures, composition would also be a variable). To obtain the rate of nucleation, it is then necessary to reduce this two-variable problem (that is, size r and pressure p) to one variable. This can be done by assuming that all such bubbles at all times are either in mechanical or in chemical equilibrium. For condensation, the mechanical equilibrium approximation is usually satisfied, but for boiling, chemical equilibrium is probably much closer to reality than is mechanical equilibrium; which approximation is better depends on the relative relaxation times for condensation and for the motion of the interface. For condensation, since the molecules condensing on a cluster do so at its surface, the location of its radius and the pressure exerted by the molecules inside it are related by Laplace's equation. However, the rate of evaporation does not equal the rate of condensation except at the critical size. For boiling, the maintenance of mechanical equilibrium would require a change in the bubble radius every time a molecule evaporated or condensed and thus changed the internal pressure. This is clearly not true for boiling at large negative external pressures, better known as cavitation. Under cavitation conditions, there are at most a few molecules inside each bubble. Typically, these molecules evaporate from one side of the bubble, travel across to the other side, and condense. The bubble radius is in no way related to this process, but the number of gas molecules in the bubble is controlled by the evaporation-condensation process; that is, there is no mechanical equilibrium but there is chemical equilibrium. At higher temperatures (therefore less negative external pressures), the vapor pressure rises and the gas molecules start to interact and interfere with the condensation process. For boiling at temperatures close to the critical temperature, that is, where the density of the molecules inside the bubbles is high, it is no longer obvious which equilibrium is more rapid. But under these conditions it no longer matters since, as shown by Blander and Katz (1975), for pure substances the only difference in predicted rates of nucleation is a multiplicative factor of $(2/3)^{1/2}$.

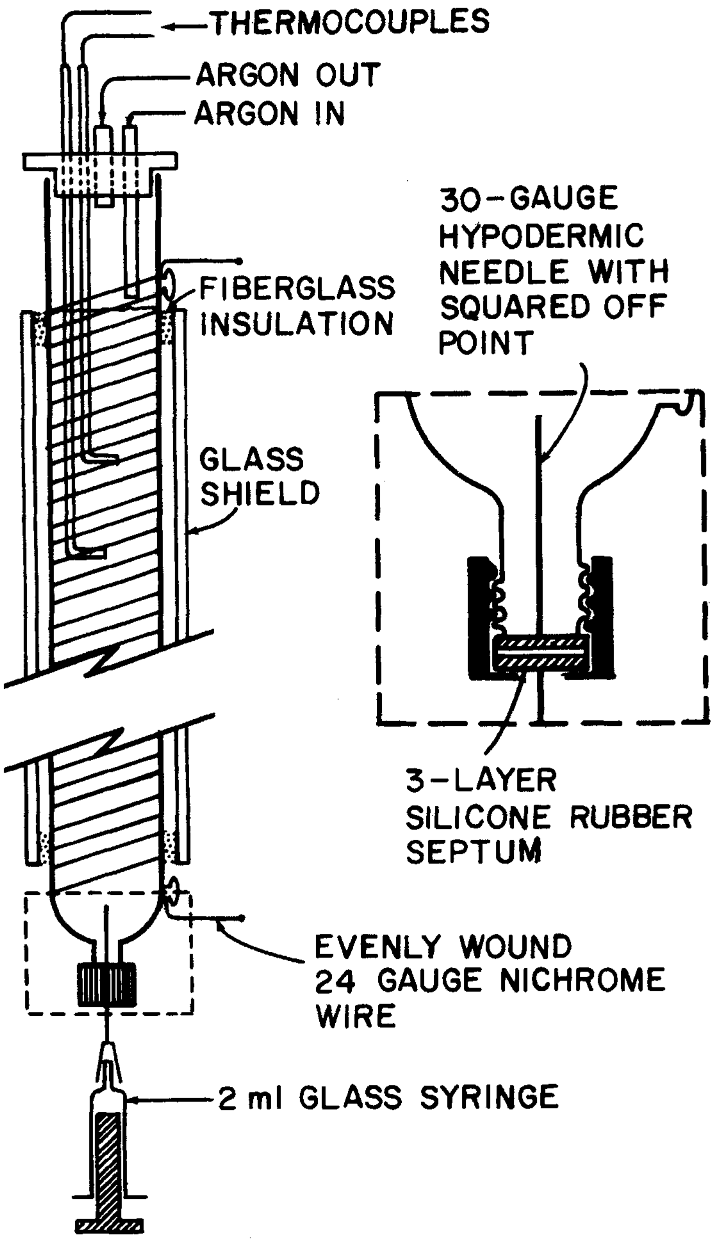

Fig. 1. Low gradient rising droplet column and detail.

For a binary (or multicomponent) liquid, the assumption of chemical equilibrium specifies not only the pressure but also the composition of the vapor. We shall make this assumption; that is, we assume that every possible bubble always contains the appropriate number and composition of molecules to be in equilibrium with the surrounding liquid, and that Laplace's equation (that is, $P = P^0 + 2\sigma/r$) is not satisfied except at the critical size. Thus bubbles smaller than the critical size will have an internal pressure P less than that required for mechanical equilibrium and will tend to shrink, while those larger than the critical size will tend to grow.

The assumption of chemical equilibrium reduces the nucleation calculation to pseudo one component, since the rate of nucleation J is therefore given by the net rate at which bubbles of critical size add and lose molecules of the average gas phase composition. Following a procedure identical to that used by Blander and Katz (1975), (setting $B' = 1$ since we here assume chemical equilibrium), one obtains for the rate of nucleation

$$J = N\left(\frac{2\sigma}{\pi}\right)^{1/2}\left(\frac{Y_1}{\sqrt{m_1}} + \frac{Y_2}{\sqrt{m_2}}\right) \exp\left[\frac{-16\pi\sigma^3}{3kT(P_V - P_L)^2}\right] \quad (1$$

As shown by Blander and Katz (1975), there is a sma but not insignificant correction to the literature value c the vapor pressure P_e because $P_L \neq P_V$. This correction i adequately approximated by

$$P_V = P_L + (P_e - P_L)\left[1 - (\rho_g/\rho_l) + \frac{1}{2}(\rho_g/\rho_l)^2\right] \quad (2$$

Equation (1) differs from that given by Blander and Kat (1975) by the term in Y_1 and Y_2. This arises from th fact that the arrival rate of molecules to a cluster β ha to be replaced in a binary vapor by the sum of the arriva rates, that is, $\beta \rightarrow \beta_1 + \beta_2$. (For multicomponent mixtures $\beta \rightarrow \beta_1 + \beta_2 + \beta_3 + \ldots$) Thus, assuming ideal gases instead of $P/\sqrt{(2\pi mkT)}$, one uses $PY_1/\sqrt{(2\pi m_1kT)}$ + $PY_2/\sqrt{(2\pi m_2kT)}$.

EXPERIMENTAL PROCEDURE

The rising droplet column used to measure the kinetic limi of superheat was similar to the apparatus developed b Moore (1959) and Wakeshima and Takata (1958), which wa subsequently modified by Skripov and Ermakov (1964) an Blander et al. (1971). The technique consists of introducin a small droplet of the liquid to be studied at the bottom of a 60 cm glass column filled with a denser, immiscible, host liquid. The column is wound with nichrome wire, and an electrica current is passed through the wire to heat the column; a stabl temperature gradient is formed with the top of the colum

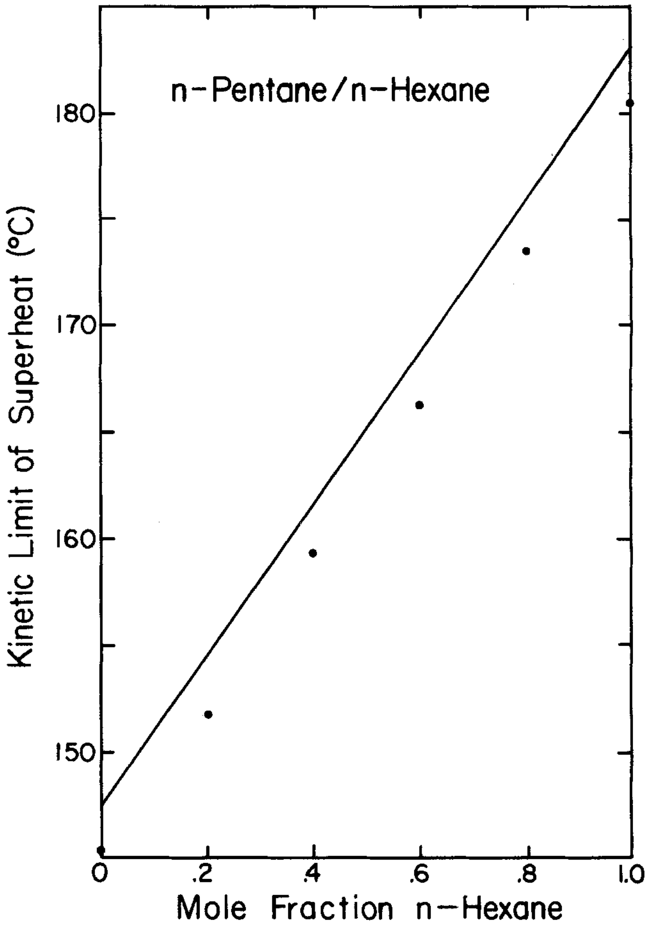

Fig. 2. Comparison of theoretical and experimental limits of superheat for mixtures of *n*-pentane and *n*-hexane.

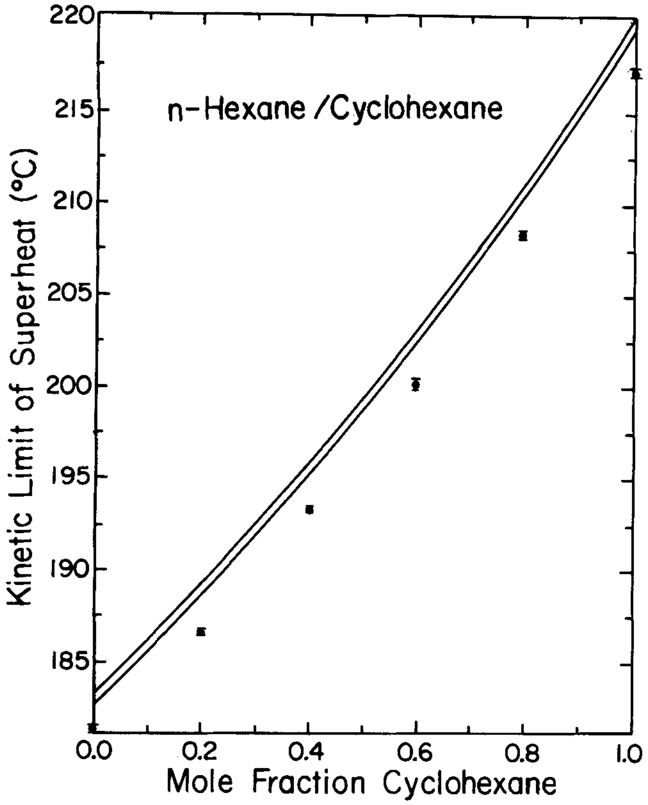

Fig. 3. Comparison of theoretical and experimental limits of superheat mixtures of *n*-hexane and cyclohexane.

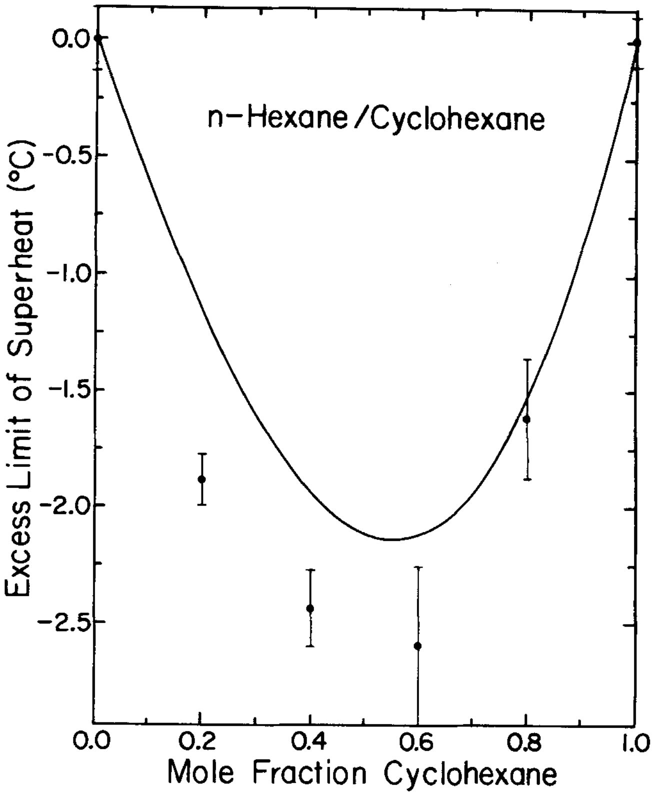

Fig. 4. Comparison of theoretical and experimental excess limits of superheat for mixtures of *n*-hexane and cyclohexane.

hotter than the bottom. The droplets which are introduced at the bottom rise up and are heated until the limit of superheat is reached and explode. The range of temperatures over which the explosions occur is measured with two thermocouples.

In the apparatus used in these experiments, a close fitting glass cylinder was slipped over the heated section of the column (Figure 1) with fiber glass insulation sealing off the annular region, which greatly reduced the heat losses to the environment and allowed much finer temperature control. The nichrome wire windings were made as even as possible and ended about 2 cm above the bottom of the column. This caused the entire heated section of the column to be within about 30°C of the maximum temperature, and in the top 15 cm, the temperature change was only about 0.5°C and very linear. This low gradient section at the top of the column allowed the location at which the droplets exploded to be spread out vertically, increasing the accuracy with which the nucleation temperatures could be measured, and helped to insure that the droplets were isothermal. It was found that the temperature in the low gradient section was so sensitive to changes in the voltage setting of the variable transformer used to supply the current (used in series with a constant voltage transformer to eliminate line voltage variations) that a small adjustment would move the boiling range well out of the desired section. To remedy this problem, a 1.15Ω, ten turn precision rheostat was placed in series with the column; when the rheostat's resistance was varied from zero to full scale, the column temperature would decrease about 5°C, providing more than enough sensitivity to control the column temperature precisely.

Instead of using an emulsion chamber to introduce droplets into the host medium (for example, glycerol) as used in most previous investigations, a 2 ml glass syringe and a 30 gauge hypodermic needle with a squared off point was inserted through a silicone rubber septum at the bottom of the column. By carefully manipulating the syringe plunger, single droplets of virtually any size desired could be injected. The silicone rubber septum was held in place with the drilled out cap of a screw top bottle, the threaded section of which was attached to the bottom of the column by the glassblower; this arrangement allowed easy, leakproof changing of the binary mixtures.

Since glycerol tends to oxidize at high temperatures, argon was continuously but slowly flowed over the surface of the glycerol at the top of the column. Whenever the column was heated up from room temperature, argon was bubbled through a hypodermic needle stuck through the septum to flush out any

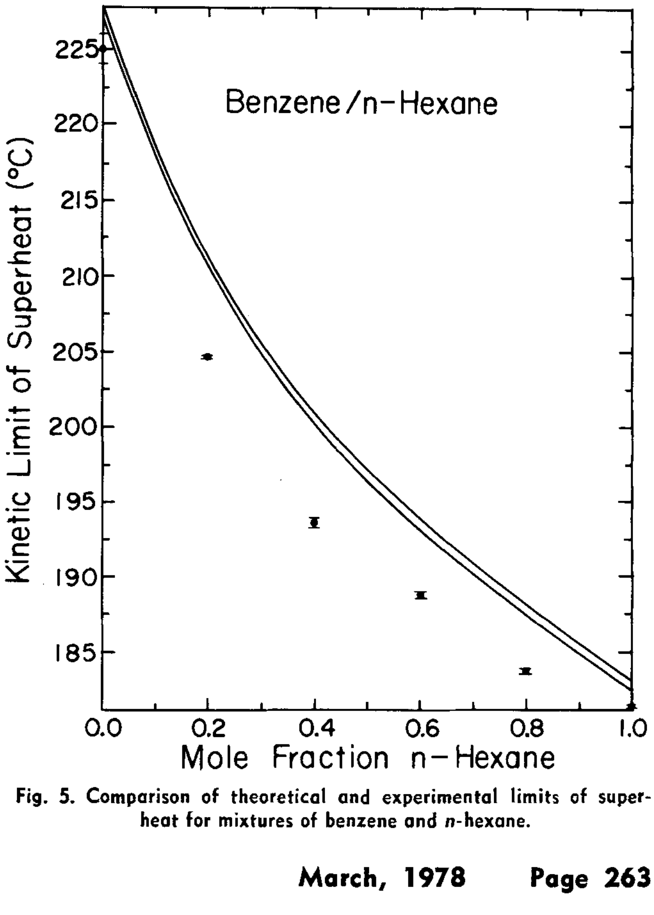

Fig. 5. Comparison of theoretical and experimental limits of superheat for mixtures of benzene and *n*-hexane.

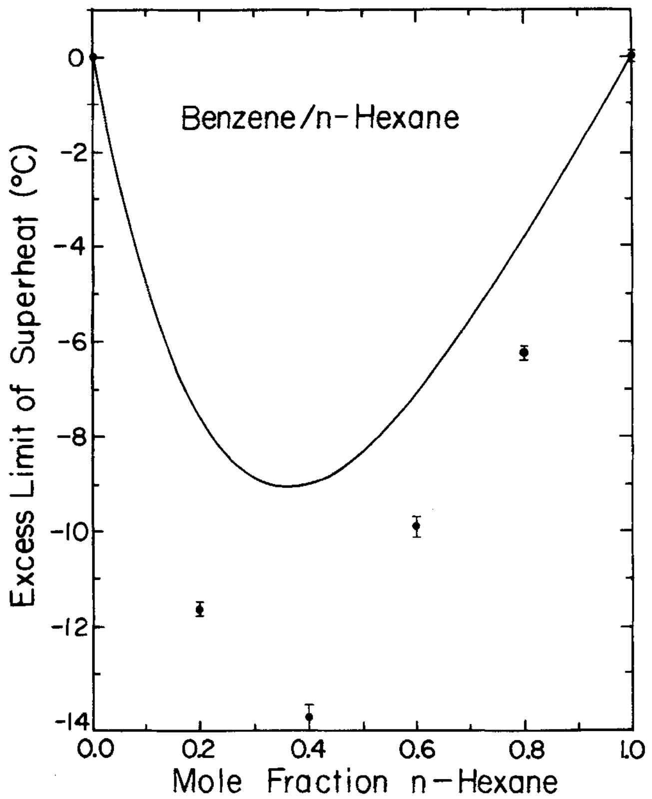

Fig. 6. Comparison of theoretical and experimental excess limits of superheat for mixtures of benzene and *n*-hexane.

oxygen. Once the column had come up to temperature, it could be left running continuously for several days, if needed, without any discoloration of the glycerol.

For each pair of substances, mixtures of mole fractions 0.0, 0.2, 0.6, 0.8, and 1.0 were studied. About fifty droplets were injected for each composition. One thermocouple was placed at the lowest level,* and another was placed at the highest level where droplets were observed to explode. These two readings were recorded, and study of the next composition begun. Figures 3 to 8 show both the mean explosion temperature and the range of temperatures over which the droplets exploded.

The mixtures studied were *n*-pentane-*n*-hexane, benzene-*n*-hexane, benzene-cyclohexane, and *n*-hexane-cyclohexane. The benzene and *n*-hexane were pure grade from Phillips Petroleum Company (99 mole% minimum), and the cyclohexane was ACS Reagent grade from Eastman Kodak. The *n*-pentane was Baker grade (99% minimum), and the anhydrous glycerol used as a host liquid was Baker Analyzed grade (99.8% assay), both from J. T. Baker. The purities were considered adequate since use of technical grade *n*-pentane (95% purity) gave identical results to those obtained with Baker grade.

DISCUSSION

During the course of this study, it was observed that droplets of pure benzene less than about 0.2 mm in diameter dissolved totally in the glycerol without nucleating. Mixtures containing high concentrations of benzene were also observed to dissolve but to a lesser extent; that is, small droplets would decrease slightly in size but not enough to disappear before exploding. This poses a problem, since the concentrations of mixtures containing benzene may change somewhat as they are superheated, causing the droplets to act like those containing a lower concentration of benzene. The effect of leaching benzene out of the droplets should be to bring the experimental points closer to the theoretical curves, since benzene has the higher limit of superheat in the mixtures studied. We have no reliable estimate for the magnitude of this systematic error but think (because of the similarity of the figures and their agreement with theory) that it is small and probably within the scatter of the data.

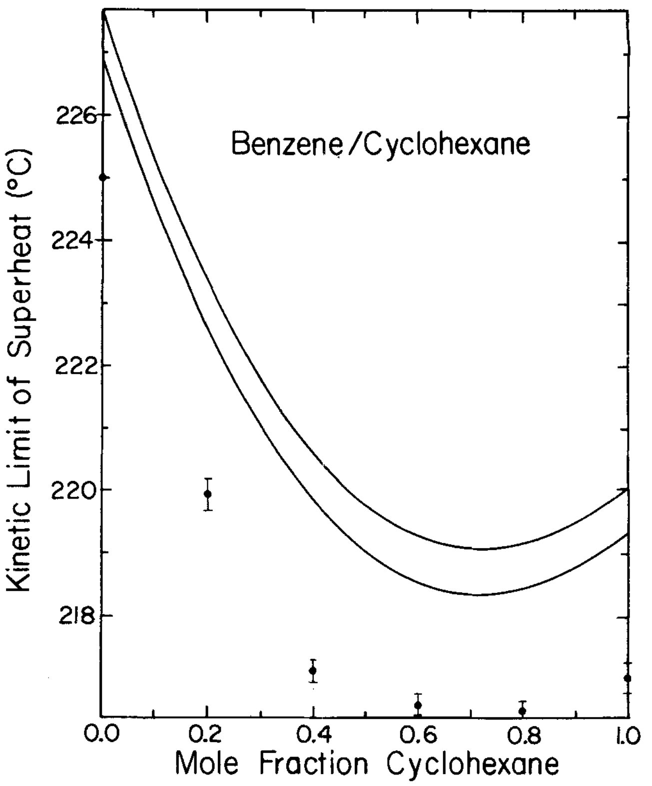

Fig. 7. Comparison of theoretical and experimental limits of superheat for mixtures of benzene and cyclohexane.

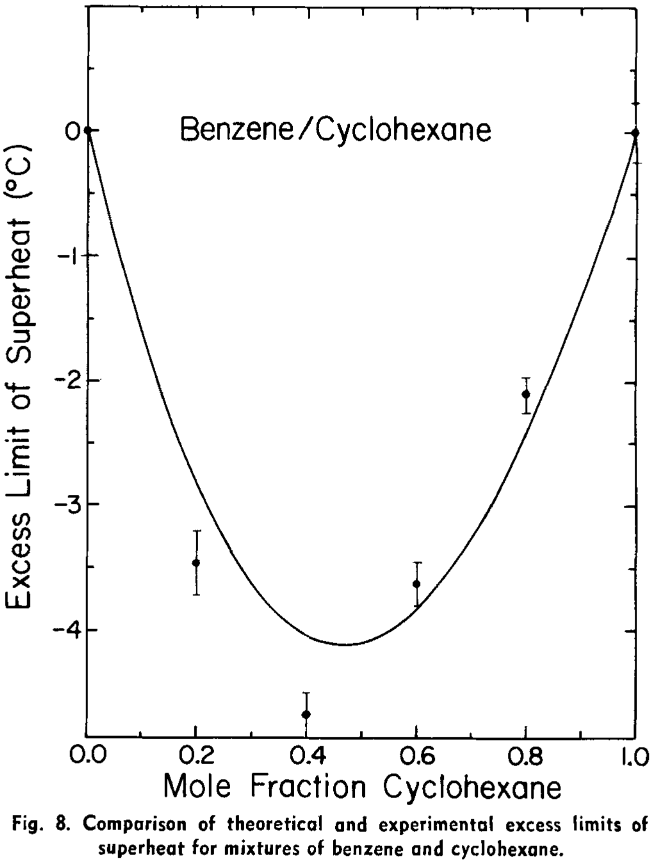

Fig. 8. Comparison of theoretical and experimental excess limits of superheat for mixtures of benzene and cyclohexane.

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[*] About one droplet in fifty exploded at a much lower (and nonreproducible) temperature, almost certainly by a heterogeneous nucleation mechanism. These droplets were not included in our reported values.

TABLE 1. COMPARISON OF THE THEORETICAL KINETIC LIMIT OF SUPERHEAT CALCULATED FOR A RATE OF NUCLEATION OF 10^4 NUCLEI CM^{-3} S^{-1} AND THE EXPERIMENTALLY MEASURED MEAN TEMPERATURE AT WHICH THE SUPERHEATED DROPLETS WERE OBSERVED TO EXPLODE AS A FUNCTION OF MOLE FRACTION OF THE SECOND SUBSTANCE

Mole Fraction	Experiment	Theory
	n-pentane—*n*-hexane	
0.0	145.2	147.5
0.2	151.7	154.5
0.4	159.3	161.6
0.6	166.2	168.8
0.8	173.3	175.9
1.0	180.6	183.1
	n-hexane—cyclohexane	
0.0	181.2	183.1
0.2	186.5	189.3
0.4	193.2	196.0
0.6	200.2	203.2
0.8	208.4	211.3
1.0	217.2	220.2
	Benzene-*n*-hexane	
0.0	225.0	227.8
0.2	204.6	211.3
0.4	193.6	200.9
0.6	188.8	193.9
0.8	183.7	188.2
1.0	181.2	183.1
	Benzene-cyclohexane	
0.0	225.0	227.7
0.2	219.9	223.3
0.4	217.1	220.6
0.6	216.6	219.3
0.8	216.5	219.2
1.0	217.0	220.1

In previous investigations of the limits of superheat using the rising droplet column, a much larger percentage of each droplet's time of rise was spent at low temperatures than in the apparatus used in these experiments. Typically, in earlier columns, droplets may have spent as little as 3 or 4 s at temperatures within 20°C of the limit of superheat. In our apparatus, the droplets were heated to within 20°C of the limit of superheat very quickly and were therefore at temperatures close to the limit of superheat for much longer times. Studies were made to determine the effect of droplet volume on the superheat-limit temperature. The volumes were decreased until the boiling range would no longer change noticeably with droplet size. Large droplets, greater than about 1 mm in diameter, were observed to explode noticeably higher than small droplets. The droplet size which was usually used (about 0.5 mm) allowed each droplet at least 10 s within 20°C of the limit of superheat. As a result, a closer approach to thermal equilibrium was probably achieved in the droplets in our apparatus than in previous investigations, which may explain why the measurements for pure *n*-hexane and cyclohexane fall about 2° to 3°C below the values measured previously [181.2°C[*] vs. 183.8°C (Blander et al., 1971) and 217.2°C vs. 219.7°C (Eberhart et al., 1975)]. The temperatures measured are probably accurate to ±0.2°C or better.

To estimate the nucleation rates at which the droplets were exploding, $J = 1/v\tau$ was used. We assumed that one bubble nucleating anywhere within the droplet caused it to explode. Since the droplets rose at about 4 cm/s at the temperature of interest and the length of the isothermal section of the column in which the mixtures exploded was typically about 10 cm long, the mean droplet lifetime (at the limit of superheat temperature) was usually around 1.25 s. For droplets 0.5 mm in diameter, v is about 6.5×10^{-5} cm^3. This gives a value of 1.2×10^4 cm^{-3}s^{-1} for the nucleation rate. A value of 10^4 was substituted into Equation (1) for J, the nucleation rate, and the resulting expression solved numerically for the temperature. In order to get an estimate of the change in nucleation rate with temperature, the expression was also solved for a rate of 10^2 cm^{-3}s^{-1}. From Figures 3, 5, and 7 it may be seen that the nucleation rate changes by two orders of magnitude for a temperature change of about 0.75°C.

In order to solve Equation (1) for temperature, the surface tension, equilibrium vapor pressure, and liquid density must be known as a function of both temperature and composition. *n*-pentane-*n*-hexane form an almost perfectly ideal mixture. Mole fraction averages of the surface tension, equilibrium vapor pressure, and molar volumes at the corresponding temperatures were therefore used. Unfortunately, there is very little data as a function of temperature for the nonideal binary systems which can be studied in the rising droplet column. While systems such as methanol-water, ethanol-water, acetone-ether, and others have well-documented physical property data, they have at least one component which is soluble at the temperatures of interest in all of the liquids we tested for use as the host medium. To circumvent the solubility problem, mixtures of benzene, cyclohexane, and *n*-hexane were studied, even though for these mixtures there is very little physical property data available at high temperatures. The methods and equations used to obtain the needed data are discussed in the Appendix.

RESULTS

The experimental results and the comparisons with theory are presented graphically in Figures 2 to 8. In Figure 2, the kinetic limits of superheat of mixtures of *n*-pentane and *n*-hexane are plotted vs. mole fraction of *n*-hexane. The solid line represents the limits predicted by theory for a nucleation rate of 10^4 cm^{-3}s^{-1}. The dots represent the experimental average nucleation temperatures of the mixtures. The droplet boiling ranges were all less than 0.5°C. For the other binary systems, two graphs are presented. The first is a plot of the kinetic limit of superheat vs. mole fraction of component 2 in the liquid. The two solid lines are the limits predicted by theory for nucleation rates of 10^2 and 10^4 cm^{-3}s^{-1}, the lower line representing 10^2 cm^{-3}s^{-1} and the upper line representing 10^4 cm^{-3}s^{-1} The dots represent the experimental average nucleation temperatures of the mixtures with the droplet boiling ranges indicated by the vertical bars. The second graph for each system (other than *n*-pentane-*n*-hexane) is a plot of the excess limit of superheat vs. mole fraction. The excess superheat is calculated by taking the molar average of the superheats of the pure components and subtracting this from the actual superheat of the mixture. By definition, the excess superheat for the pure components will be zero for both the theoretical and experimental curves. In this manner, the curvatures of the experimental and theoretical superheat curves in the first plot can be compared. The solid lines are the predictions of the theory for 10^2 (lower curve) and 10^4 cm^{-3}s^{-1}, and the dots and

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[*] This number is from our hexane-cyclohexane and hexane-benzene studies. Our hexane-pentane studies were made at an earlier date and with a slightly different column. They give an average value for pure hexane of 180.6°C, that is, 0.6°C lower. This discrepancy is within the joint limits of scatter, that is, 0.5°C for each set of experiments.

bars are the experimental average excess superheat and the temperature range over which the droplets explode, respectively. The fact that the theory lines for 10^2 and 10^4 $cm^{-3}s^{-1}$ coincide on all the excess superheat limit plots indicates that the curvature of the kinetic limit of superheat has little, if any, rate dependence. The values of the kinetic limits of superheat are tabulated in Table 1.

Upon examination of Figures 2, 3, 5, and 7 it is apparent that the shapes of the theoretical curves are always quite similar to those of curves connecting the experimental results, even though the theory predicts values which are 2° to 4°C too high. For *n*-pentane-*n*-hexane, no excess superheat plot is given, since it would be an almost perfectly straight line with no difference (within experimental scatter) between theory and experiment. For the nonideal mixtures, as can be seen from Figures 4, 6, and 8, the curvature of the theory is somewhat smaller than that of the experiment. Nevertheless, the agreement is quite good.

ACKNOWLEDGMENT

Financial support for this work by the Research Corporation is gratefully acknowledged.

NOTATION

J = rate of nucleation per unit volume of liquid
k = Boltzmann's constant
m_1, m_2 = molecular masses of component 1 and 2
N = number density of liquid
P = pressure within a bubble
P_e = equilibrium vapor pressure
P_L = hydrostatic pressure in liquid
P_V = pressure of vapor in equilibrium with liquid at given pressure P_L
P^0 = external pressure on the liquid
r = radius of bubble
T = temperature
v = droplet volume
Y_1, Y_2 = vapor mole fractions of components 1 and 2
ρ_g = density of vapor
ρ_l = density of liquid
σ = surface tension of liquid in equilibrium with vapor
τ = mean droplet lifetime

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APPENDIX

A variety of estimation techniques were used to arrive at values for the physical properties for which no data were available.

The densities of the two pure components were found as a function of temperature, and the excess volume of mixing as a function of liquid composition was calculated at different temperatures by using the theory of Flory (Flory, 1965; Abe and Flory, 1965; Nigam and Singh, 1969). Since the theoretical nucleation rate is fairly insensitive to errors in the liquid density, the accuracy of this estimate of the binary liquid density is more than sufficient for the applications intended here.

The vapor pressure as a function of temperature at temperatures close to the critical point is required for the full range of liquid compositions. Since data on vapor pressures at high temperatures of the binary systems in question are very scarce, it was necessary to calculate the mixture vapor pressures. The Riedel-Plank-Millr correlation

$$\log P_{V_r} = -\frac{G}{T_r}\left[1 - T_r^2 + g(1 - T_r)^3\right] \qquad \text{(A1)}$$

was used, where $P_{V_r} = P_V/P_c$ is the reduced mixture vapor pressure, T_r is the reduced temperature, $G = 0.2271 + 0.4525h$

$$g = \frac{\left[\frac{h}{G} - (1 + T_{br})\right]}{(1 - T_{br})^2} \qquad \text{(A2)}$$

$$h = T_{br}\left[\frac{\log P_c}{(1 - T_{br})}\right] \qquad \text{(A3)}$$

and $T_{br} = T_b/T_c$ is the reduced mixture bubble point at 1 atm pressure. Thus, the only properties of each mixture needed are the bubble point and the true critical temperature and pressure.

The mixture critical properties were either taken from the literature (Partington et al., 1960) or were calculated from the theory of conformal solutions (Kreglewski and Kay, 1969; Kreglewski, 1968, 1969). The critical temperatures and pressures as calculated by this theory are probably accurate to better than 1°K and 34 kPa (5 $lb/in.^2$ abs) for the compounds in question, according to the analysis of Kreglewski and Kay (1969). The average maximum error in the Riedel-Plank-Miller correlation was found by Reid and Sherwood (1966) to be about 1.5% for a wide variety of pure compounds.

A limited amount of surface tension vs. composition data was found at temperatures close to ambient for the binary systems studied (Schmidt et al., 1966; Suri et al., 1968; Clever et al., 1963). Since the surface tension of each mixture studied had to be known at temperatures close to the critical temperature, an attempt was made to curve fit the data for each mole fraction of interest, using an equation of the form

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n \qquad \text{(A4)}$$

where T_c is the absolute critical temperature of the mixture, and σ_0 and n are adjustable parameters to be determined by the curve fit. Literature data was found for the surface tensions of *n*-hexane-cyclohexane at 25°, 30°, and 35°C for benzene-*n*-hexane at 25°, 30°, 35°, and 40°C and of benzene-cyclohexane at 20° and 30°C. None of these temperature ranges are wide enough to yield a fit which could be extrapolated over a wide range of temperatures. However, surface tension data were found in Jasper (1972) for the pure compounds (*n*-hexane from 10° to 60°C, cyclohexane from 5° to 70°C, and benzene from 10° to 80°C) and fitted to Equation (A4) to yield a value of n for each component. We therefore assumed a mole fraction average n for each composition and used the binary data and Equation (A4) to obtain σ_0's. The uncertainty in the σ_0's at the various compositions was never more than 0.7 mN/m (about 1%) and were usually about 0.1 mN/m (about 0.2%).

It was found that the prediction of the limit of superheat was most sensitive to errors in the surface tension, as expected, since the cube of the surface tension enters in the numerator of the exponential in Equation (1). A decrease of 3% in the surface tension of a mixture would lower the prediction of the kinetic limit of superheat by about 1°C. The prediction was only a little less sensitive to errors in the vapor pressure; an increase of 4% in the vapor pressure decreased the limit of superheat by 1°C. A 5% change in the molar volume of the liquid did not noticeably affect the prediction of the limit of superheat.

Considering the method used to obtain the values for the surface tension of the mixtures at high temperatures, the surface tensions could easily be about 5% off. Because of errors in the bubble points, critical temperatures, critical pressures, and the Riedel-Plank-Miller correlation, the vapor pressures are probably in error by about the same factor. These sources of errors easily account for the differences between the experimental and theoretical limits of superheat for *n*-hexane-cyclohexane and benzene-cyclohexane. However, the difference between the theoretical curve and the experimental points for benzene *n*-hexane may be partially due to solubility effects.

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Critical Points of Mixtures: An Analogy with Pure Fluids

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The thermodynamic properties of vapor-liquid equilibrium (VLE) states near the critical locus of mixtures are correlated in very close analogy with the techniques used to correlate the properties of pure fluids near a critical point. The only mixture parameters used in the correlation are the values of pressure, volume, temperature, and mole fraction (*PVTx*) along the physical critical locus. We illustrate the power of the present approach by correlating the rather extensive *PVTx* data that exist near the critical loci of the binary mixtures: CO_2-C_2H_6, SF_6-C_3H_8, and C_8H_{18}-C_3H_8. Nearly all the data within 10% of the critical temperature may be described within their accuracy despite the occurrence of critical azeotropy or large regions of retrograde condensation.

SCOPE

The primary objective of this study was to find some relatively simple techniques through which several very general, recent developments in the theory of critical points might be applied to correlating data in the engineering literature. In this work, we apply correlation techniques based on physical ideas of general applicability to experimental data and obtain representations of the data which are economical in terms of number of parameters. Furthermore, we find that the quantity of data needed to describe phase equilibria in the critical region is thereby significantly reduced. The representations may be used with confidence for interpolation, integration, or differentiation. This approach should facilitate the development of new engineering processes by reducing the time and expense required to obtain the VLE data that may be required for a mixture which has not been studied heretofore.

Our approach to correlating data in binary mixtures is adapted from that used to describe He^3-He^4 mixtures by Leung and Griffiths (1973) and by Doiron et al. (1976). We formulate a thermodynamic potential for a binary mixture which has *the same functional form* as the potential which has been used near critical points of pure fluids. The coefficients in this potential (and the critical parameters) are assumed to vary very smoothly as the particular mixture considered is taken from one pure component to the other. This assumption may be considered as an extension of the idea of corresponding states. It should be noted that to be consistent with current theoretical ideas about the critical point (Griffiths and Wheeler, 1970; Leung and Griffiths, 1973), the parameter, which is held constant

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