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High Pressure Homogeneous Nucleation of Bubbles within Superheated Binary Liquid Mixtures¹

The limits of superheat of some binary normal paraffin mixtures were measured at pressures up to 2128 kPa using the floating droplet method. The variation of nucleation temperature with liquid phase mole fraction was found to be nearly linear for these n-paraffin solutions over the whole pressure range in which the experiments were performed. Homogeneous nucleation theory was used to predict the limits of superheat of the solutions tested. The vapor pressures of the mixtures were estimated by using the Peng-Robinson equation of state to evaluate the liquid and vapor phase fugacities, and the mixture surface tensions were calculated using an empirical adaptation of the van der Waals expression for the surface tension of a pure liquid near the critical point. The predicted and measured limits of superheat were found to be in good agreement over the entire pressure range for all liquid phase compositions. The results of the present work could be useful for predicting liquid phase temperatures and compositions at which the microexplosive or disruptive burning of droplets of fuel blends which are mixtures of volatile and nonvolatile liquids will be initiated during droplet combustion at high ambient pressures.

1 Introduction

The mixing of a cold volatile fluid and a hot nonvolatile liquid can lead to significant superheating, followed by the homogeneous nucleation of bubbles, within the volatile liquid. If the subsequent growth of these bubbles is sufficiently rapid, the resulting bulk phase transition could be manifested by an explosive type of boiling. For example, such explosive boiling has been observed in liquid natural gas spills on water [1] and during the combustion of droplets of certain fuel blends which are solutions of volatile and nonvolatile liquids [2]. Because of the hazards, and possible benefits, attendant to such explosive boiling, the importance of understanding and predicting the factors which initiate the explosive mechanism is self-evident.

In the absence of extraneous nucleation aids such as containing walls and particles, the formation of the initial vapor bubbles which are of a size such that they are in thermodynamic equilibrium with the surrounding liquid occurs by the random molecular processes proposed by homogeneous nucleation theory [3, 4]. The energy, rate of formation, and growth rate of such "critical size nuclei" strongly depends on the physical properties of the liquid in which the bubbles form. For pure liquids the important physical properties are relatively easy to predict, and the limits of superheat of such systems have been studied extensively from both a theoretical and experimental point of view [5, 6]. Experimental work on the homogeneous nucleation of bubbles within liquid-liquid mixtures has received much less attention [7-12], particularly experiments above atmospheric pressure [13], although some measurements of the nucleation pressures of liquid-gas solutions have been reported recently [14-17].

The physical properties of mixtures often cannot be predicted as accurately as the properties of pure liquids. The accuracy of such predictions has a very strong effect on the ability to obtain a meaningful estimate of the homogeneous nucleation temperature [11, 12, 18].

In the present work we report the results of an experimental and theoretical study of the effect of composition and ambient pressure on the limit of superheat of liquid-liquid mixtures. The limits of superheat of some selected binary liquid mixtures were measured over a range of ambient pressures. Methods for estimating the physical

properties required to predict the temperature and pressure at which nucleation of bubbles occurs within these mixtures were also studied. The information obtained was used for predicting the conditions (liquid phase temperatures and compositions) under which the disruptive burning phenomenon or "micro-explosion" of fuel drops which are solutions of volatile and nonvolatile liquids was thought to be initiated during droplet combustion.

The mixtures used in our experiments were binary liquid-liquid solutions of the normal paraffins. Methods for estimating the physical properties of this class of hydrocarbons and their mixtures appear to be among the most well developed. If the homogeneous nucleation temperatures of such simple solutions could be accurately predicted at various liquid phase compositions and ambient pressures, then we believe that we will have established a basis for calculating the limits of superheat of a wider class of multicomponent liquid-liquid solutions.

2 Experiment

2.1 Description of the Apparatus. The experiments performed consisted of heating individual droplets of the test solutions by direct contact heat transfer between the test droplet and a surrounding immiscible field liquid which had a much higher boiling point. A small droplet of the test liquid solution was injected into the bottom of a column filled with a heavier immiscible nonvolatile field liquid. The field liquid was heated to produce a stable temperature profile which was hotter at the top of the column than at the bottom. As the droplet rose, it was progressively heated until it began to boil. By choosing a field liquid with a relatively high surface tension, low vapor pressure, and low mutual solubility with all components of the test solution, the probability for homogeneous nucleation within the bulk of the test droplet would be greater than at the interface between test drop and surrounding liquid [19]. The field liquid then serves only as a medium to transfer heat to the test drop and does not influence the ability of the droplet to intrinsically undergo a phase transition. This concept was first employed by Skripov and Kukushkin [7] for measuring the superheat limits of n-hexane/n-heptane mixtures at atmospheric pressure and by Skripov and Ermakov [20] for measuring the homogeneous nucleation temperatures of some pure liquids at high pressures.

A schematic diagram of the experimental installation is shown in Fig. 1. The test section consisted of a bubble column mounted inside

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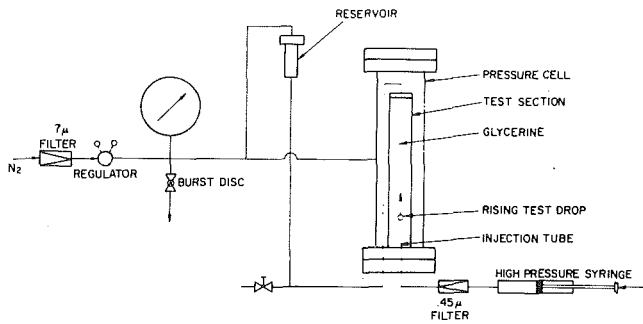


Fig. 1 Schematic of the apparatus

a pressure vessel. The bubble column was essentially a glass tube 55 cm long, 4.5 cm o.d., and 4.1 cm i.d. The tube was heated by an aluminum sleeve with variac-regulated electrical strip heaters and was attached along its length. The sleeve was placed around the glass tube and carefully pressed to the tube by using tie bolts. Vertical slits on opposite sides of the sleeve provided visual access to the interior of the tube. The test section assembly was mounted on the bottom cover plate of the pressure cell and sealed with a stainless steel cap via o-rings. Slotted windows on the pressure vessel with direct back lighting permitted observations of the interior of the test section. (The test section and pressure cell were connected to a small external reservoir in order to help condense vapors generated by both vaporization of the test drops and some vaporization of the field liquid.) Nitrogen gas was used for pressurizing the test section. The pressure was measured by a 0-3447 kPa (0-500 psi) Heise gage which was calibrated to ± 6.9 kPa (1 psi). Temperature was measured by a digital volt meter connected to three thermocouples located at fixed positions in the test section 5.4 cm, 6.7 cm, and 9.2 cm from the top of the glass tube. The thermocouple lead and heater wires were passed through Conax "feedthrough" fittings screwed into the bottom cover plate.

The droplet injection system consisted of a high pressure syringe (High Pressure Equipment Co. pressure generator) connected to a glass capillary tube (a length of 3 mm o.d. pyrex tube about 3.8 cm long which had been drawn to an outside diameter of 0.1 to 0.15 mm at one end). This injection tube was mounted on the bottom cap of the test section by a Conax vacuum fitting. A high pressure Millipore filter holder containing a 0.45 micron filter was used to remove solid particles from the test liquid prior to introducing a drop into the test section. Individual droplets were introduced into the bottom of the test section by turning the handle on the syringe until a drop began to form on the tip of the capillary. Then, by suddenly withdrawing liquid in the capillary, droplets of any diameter in the range of 0.1 to 3 mm could be made to lift off of the capillary tip. In this manner it was possible to control reasonably well the size of the droplets entering

the test section.

Power to the heaters was controlled in a manner such that rising droplets boiled at the vertical position in the column corresponding to the middle of the three thermocouples. When this procedure proved too time consuming, the temperature gradient in the field liquid was adjusted so that the droplets boiled between the top two thermocouples. The temperature at which boiling was observed was estimated by assuming a linear temperature gradient between the two thermocouples. The vaporization temperatures of ten droplets ranging in diameter from 0.5 to 1 mm were recorded for each mixture at a given pressure, and an average of the ten measurements was taken to be the limit of superheat of the test solution at the pressure on the field liquid. The pressure was then increased and the procedure repeated. In this way it was possible to measure the variation of nucleation pressure with temperature for a liquid solution of given composition. By changing the liquid phase composition of the mixture the variation of boiling temperature with composition at a given pressure could also be measured. Further discussion of the apparatus and procedure for obtaining the data are described in more detail elsewhere [19].

2.2 Selection of Liquids. The availability of physical property data for the pure liquids and mixtures we used was a major consideration in their selection. For this reason we used mixtures of the normal paraffins in our experiments. The most relevant physical property data are surface tension and bubble point pressures. However, no high temperature (>400 K) surface tension data could be located for such mixtures, and only limited vapor pressure data could be found at high temperatures. The only normal paraffin mixture whose components are liquid at room temperature for which equilibrium vapor pressure data up to the critical mixture point could be located were solutions of n-pentane and n-heptane [21]. Solutions of n-pentane and n-heptane were therefore used as model fuel mixtures. Some limited measurements above atmospheric pressure were also made using n-pentane/n-octane and n-pentane/n-hexadecane mixtures.

To insure that boiling was initiated by bubble nucleation within the test mixture, the properties of the test liquid and field liquid (in which the droplets were heated) had to be such that nucleation within the bulk of the test droplet would be more probable than at the interface between the test droplet and field liquid. The basis for expecting nucleation of bubbles to occur within the bulk of the test droplet is determined by the interfacial forces acting on the microscopic vapor bubble and the energy of the critical size nucleus. If the surface tension of the nonvolatile field liquid is high enough that the test liquid spreads on the field liquid, bubble nucleation within the bulk of the field liquid will be more probable than at the interface between field and test liquids [19, 22, 23]. The relative success that others [8-10] have had in using glycerine as a field liquid to suppress boiling of droplets of the n-alkanes and their mixtures until the droplets reached temperatures as high as 90 percent of their respective

Nomenclature

a = Peng-Robinson constant, equation (15)	P_0 = ambient pressure of liquid surrounding the vapor nucleus	the liquid mixture
A = constant defined in equation (18)	P_e = equilibrium bubble point pressure of the mixture	x = liquid phase mole fraction
b = Peng-Robinson constant, equation (17)	P_i = partial pressure of component i within the vapor nucleus	y = vapor phase mole fraction
B = constant defined in equation (19)	P_{cm} = mole fraction average of the critical pressures of the components in solution	Z = compressibility factor
d_{12} = empirical binary interaction parameter, equation (16)	s_m = effective characterization parameter of the mixture	β = surface tension proportionality constant, equation (5)
f_i^g = vapor phase fugacity of component i	T = temperature	Γ = growth probability of a critical size nucleus
f_i^l = liquid phase fugacity of component i	T_{bm} = mole fraction average of the normal boiling points of the components in solution	ΔA^* = energy of forming a critical size nucleus
J = nucleation rate	T_c = pure liquid critical temperature	σ = surface tension
k = Boltzmann constant	T_{cm} = true mixture critical temperature	μ = critical exponent
k_f = total molecular evaporation rate	V = total volume	
m_i = molecular mass of species i	v = liquid molar volume of the mixture	
n_i = number of moles of species i	v_{il} = partial molar volume of component i in	
n = total number of moles ($n = \sum_i n_i$)		
N_0 = total number density of molecules within the liquid mixture		
P = pressure of gas within the vapor nucleus ($P = \sum_i P_i$)		
P_c = pure liquid critical pressure		

critical temperatures (such temperatures are close to the theoretical limits of superheat of most liquids at atmospheric pressure) supports this hypothesis. The surface tension of glycerine is higher than that of the n-paraffin, and the glycerine/n-paraffin interfacial tension is low enough that the n-paraffin spreads on glycerine. As a result, glycerine was used as the field liquid in our experiments.

The n-hexadecane, n-heptane, and n-octane were obtained from Humphrey Chemical Co. with a stated purity of 99 percent. The n-pentane and glycerine were Fisher and Eastman "spectrograde" respectively and were used directly as received. The mixtures were prepared by combining appropriate volumes of the two liquids at room temperature to give the selected mole percent solution.

2.3 Experimental Observations and Results. Near atmospheric pressure, boiling of the liquid droplets was usually accom-

panied by a "popping" sound which was clearly audible through the walls of the pressure vessel. This effect was indicative of a high bubble growth rate within the droplet. In this case, there was little ambiguity about the vertical position in the column at which boiling was observed. However, between 377 and 653 kPa the bubble growth rate was apparently reduced sufficiently that droplet boiling was not accompanied by any audible sound. The position in the column at which boiling occurred was then detected by a sudden increase in the velocity and diameter of the rising drop. On further increasing the pressure in the test section, it became more difficult to detect the position in the column at which boiling commenced. For example, higher than around 2027 kPa, it was extremely difficult to observe a change in velocity of n-heptane droplets, even above a temperature at which they would have been expected to boil. A similar effect was also observed for dilute solutions of volatile and nonvolatile liquids: it was difficult to discern a change in velocity of n-pentane/n-hexadecane mixtures containing more than 30 mole percent n-pentane at pressures above 1216 kPa. Both these effects are probably due to a combination of high ambient pressure and/or to the possibility that the growth rate of the nucleated bubble is controlled by the rate of diffusion of the volatile species to the bubble surface as the mixture is increasingly diluted by the nonvolatile component. The accuracy of the measurements therefore probably decreased with increasing ambient pressure.

In order to verify our experimental procedures, the limits of superheat of pure n-pentane and n-heptane were measured at various pressures and the results were compared with data reported by Skripov [6]. Figures 2 and 3 show the results on a pressure-temperature diagram. The equilibrium vapor pressure curves of n-pentane

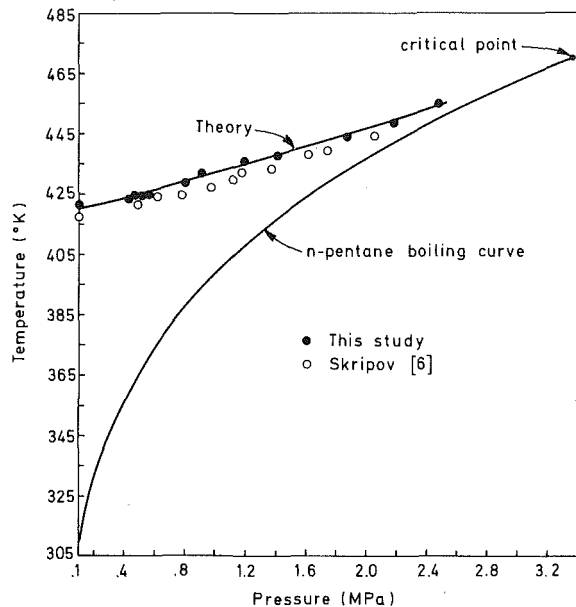


Fig. 2 Variation of the limit of superheat with ambient pressure of n-pentane

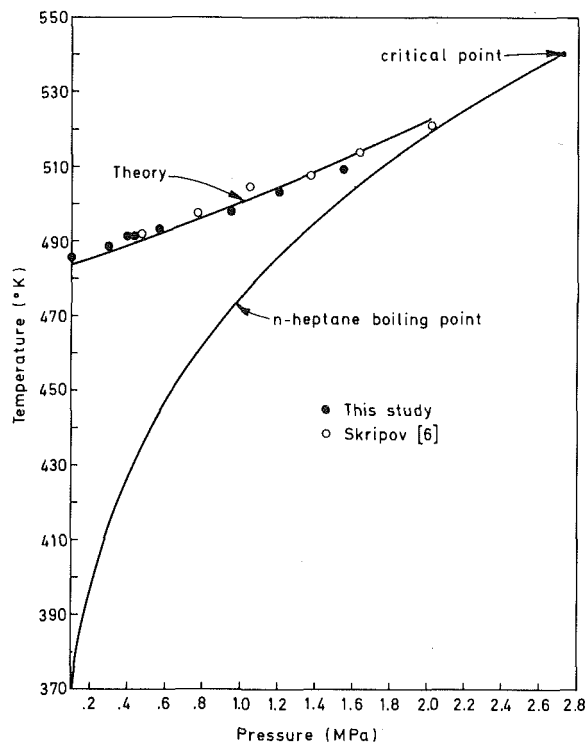


Fig. 3 Variation of the limit of superheat with ambient pressure of n-heptane

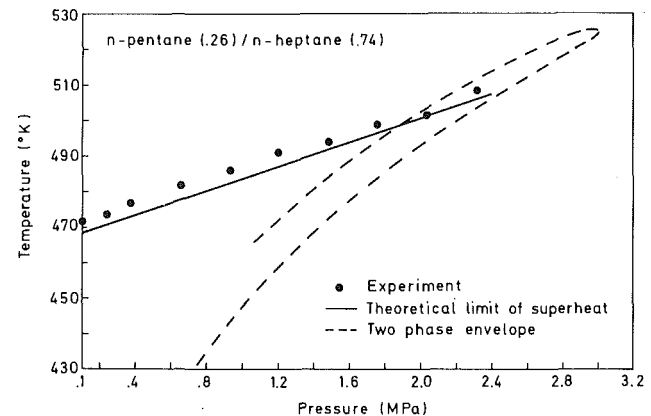


Fig. 4 The limit of superheat of a n-pentane/n-heptane mixture containing 26 mole percent n-pentane. The dotted line represents the locus of saturation states for this mixture which were experimentally measured by Cummings, et al. [21].

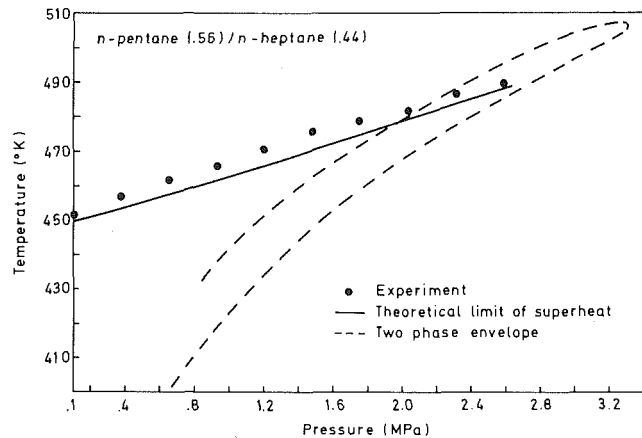


Fig. 5 The limit of superheat of a n-pentane/n-heptane mixture containing 56 mole percent n-pentane. The dotted line represents the locus of saturation states for this mixture which were experimentally measured by Cummings, et al. [21].

and n-heptane [24] are included in Figs. 2 and 3 to illustrate the extent of superheating of the liquid (the theoretical predictions are discussed in Section 3). The present measurements are consistent with Skripov's data. The atmospheric pressure data are also within 2 K of the measurements of Eberhart, et al. [8]. Compared to the variation of saturation temperature with pressure, the limit of superheat of a pure liquid is relatively insensitive to pressure as, for example, previously observed by Skripov [6].

The effect of ambient pressure on the limit of superheat of two n-pentane/n-heptane mixtures is shown in Figs. 4 and 5. The compositions of these two mixtures were chosen to coincide with the molar compositions used by Cummings, et al. [21] in their phase equilibrium measurements in order to understand more clearly the location of superheated liquid states on a phase diagram for a binary mixture. The boiling curves shown in Figs. 4 and 5 were obtained from their experimental results. (The locus of saturated states for a binary mixture separates into two branches on a pressure-temperature diagram—the dew point and boiling curves—which intersect at the mixture critical point.) The variation of limit of superheat with ambient pressure is similar to the variation of limit of superheat with ambient pressure observed for the individual components (Figs. 2 and 3). The nucleation temperature of the solution depends less strongly on pressure than does the mixture boiling curve, and the variation of nucleation temperature with pressure is nearly linear.

As the volatile component in the mixture is diluted, the limit of superheat increases at a fixed pressure. This behavior is illustrated on the temperature-composition diagrams displayed in Figs. 6 to 8. The variation of limit of superheat with liquid phase mole fraction is nearly linear over the whole pressure range in which the experiments were run. This observation, previously observed only at atmospheric pressure [7–10, 25], appears to be a characteristic for solutions of liquids from this homologous series.

3 Discussion

3.1 Theory of Homogeneous Nucleation. A homogeneous liquid-vapor phase transition is initiated by the formation of the aforementioned critical size nuclei within the bulk of a liquid. Such bubbles form within the liquid lattice structure by random fluctuations of density [3, 4] which produce cavities or holes within which the molecules are gas-like in terms of their molecular spacings and potential energies. The resulting vapor nuclei or bubbles are then considered to grow or decay in a more or less random manner by the ac-

quisition or loss of single molecules until a critical size nucleus is produced which is in thermodynamic equilibrium with the surrounding liquid. These microscopic bubbles are unstable in that their energy is an extremum relative to larger or smaller nuclei [19], and they are the seeds which initiate the liquid-vapor phase transition. The onset of homogeneous nucleation of bubbles within a liquid is governed by the rate of formation (i.e., nucleation rate), or waiting time, of the critical size bubbles. The kinetic limit of superheat is usually defined as the mean temperature in the range in which the

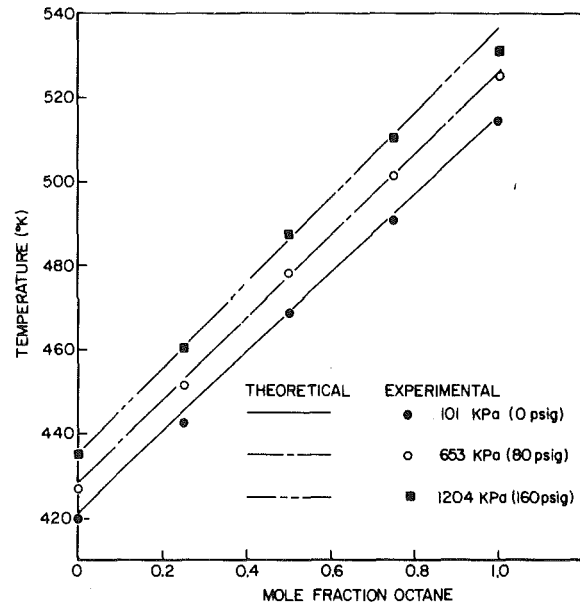


Fig. 7 The variation of limit of superheat of n-pentane/n-octane mixtures with liquid phase mole fraction at ambient pressures of 101 kPa, 653 kPa, and 1204 kPa

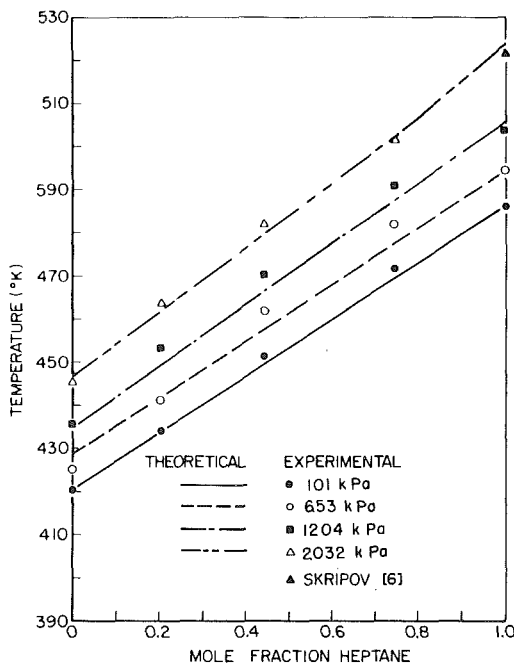


Fig. 6 The variation of limit of superheat of n-pentane/n-heptane mixtures with liquid phase mole fraction at various ambient pressures

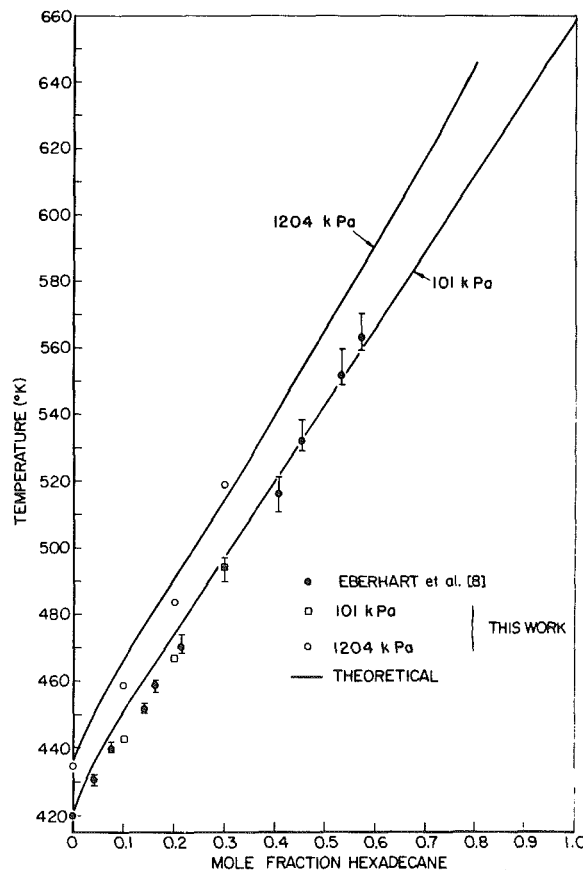


Fig. 8 The variation of limit of superheat of n-pentane/n-hexadecane mixtures at ambient pressures of 101 kPa and 1204 kPa.

nucleation rate changes from a negligible value to a very large value.

In its most elementary form, the nucleation rate is expressed by the product of the rate at which individual molecules evaporate into a critical size nucleus times the concentration of such nuclei, the latter usually being considered to follow a Boltzmann distribution. In this approximation, the kinetic limit of superheat can be written in the following form

$$T = \Delta A^* \left[k \ln \left(\frac{N_0 \Gamma k_f}{J} \right) \right]^{-1} \quad (1)$$

where the energy of the critical size nucleus is

$$\Delta A^* = \frac{16\pi\sigma^3}{3(P - P_0)^2} \quad (2)$$

The number density of molecules within the liquid solution, N_0 , was approximated as

$$N_0 \approx 6.023 \times 10^{23}/v \quad (3)$$

where v is the liquid molar volume of the mixture. k_f is the total evaporation rate of the individual molecular species. In a multicomponent liquid solution within which a spherical vapor nucleus forms, k_f was approximated as the sum of the ideal gas collision frequencies:

$$k_f = \frac{8P\sigma^2}{(P - P_0)^2} \left(\frac{2\pi}{kT} \right)^{1/2} \sum_i \left(\frac{y_i}{m_i^{1/2}} \right) \quad (4)$$

Γ essentially expresses the probability that a nucleus of critical size will grow by the evaporation of a single molecule of any chemical species within the liquid solution. In the above approximation $\Gamma = 1$ (i.e., all critical size nuclei continue to grow), but it may be more reasonable to expect that $\Gamma < 1$, and various approximations for Γ expressing this fact have been derived [12, 19]. The values of Γ so obtained typically range from 1 to 0.01. None of the expressions for Γ have yet been verified experimentally because of the microscopic dimensions of the critical size nuclei. However, differences in Γ of a few orders of magnitude will have an insignificant effect on the solution of equation (1) for the kinetic limit of superheat because the argument of the logarithmic term is on the order of 10^{29} to 10^{31} . Therefore, $\Gamma = 1$ was used in our work.

The limit of superheat is, however, very sensitive to the value of the energy of the critical size nucleus, ΔA^* , which in turn is strongly dependent on the vapor pressure and surface tension of the nucleus. These physical properties depend on the liquid phase composition as well as on temperature and ambient pressure, and must be estimated accurately to obtain a meaningful value of the homogeneous nucleation temperature. A major difficulty is that of estimating the relevant properties at a temperature which is higher than the critical temperature of one or more of the volatile components within the mixture. In the case of the vapor pressure, the problem is more computational than theoretical [26]. However, the problem of estimating the surface tension of a mixture of liquids requires further development as described in the next section. (These problems were recently addressed by Avedisian and Andres [11] and Holden and Katz [12] who presented the first accurate calculations of the limit of superheat of some binary liquid mixtures at atmospheric pressure.)

3.2 Surface Tension. If the surface tension of a liquid mixture is expressed in terms of the pure component surface tensions, the surface tension of the component whose critical temperature is exceeded is undefined and thus the method becomes unsuitable. The parachor mixing rule of Weinaug and Katz [27] is very sensitive to the value of the parachors of the components in solution and is sometimes difficult to use because of a lack of accurate vapor phase composition and density data of the mixture.

An empirical method which in principle avoids these difficulties is to apply to liquid solutions the functional dependence of the surface tension on temperature originally developed by van der Waals [28] for pure liquids. From the corresponding states principle, the surface tension of a pure liquid near its critical temperature can be written

$$\sigma = \beta P_c^{2/3} T_c^{1/3} \left[1 - \frac{T}{T_c} \right]^\mu \quad (5)$$

where the critical exponent μ is a constant which varies between 1.2 and 1.4 for a wide variety of nonpolar liquids. β should be a constant for all pure liquids which follow the corresponding states principle. However, examination of the available surface tension values of many pure nonpolar liquids reveals that β is not constant. This observation led Brock and Bird [29] to search for an empirical correlation for β in terms of some parameter characteristic of a liquid. They found that β could be correlated with the Riedel parameter, defined as

$$\frac{T_c}{P_c} \left(\frac{d \ln P}{dT} \right)_{T_c, P_c}$$

However, use of various mixing rules in their correlation did not produce estimates of the surface tension of liquid mixtures sufficiently accurate for solving equation (1).

It was found that in some cases β could be correlated better with the characterization parameter which we defined for a mixture as

$$s_m = \frac{T_{cm} \ln(P_{cm})}{T_{cm} - T_{bm}} \quad (6)$$

This parameter represents the slope of a straight line connecting an appropriately defined normal boiling point and critical point of the mixture. It has been utilized in the past [24] to correlate the vapor pressure of pure nonpolar liquids. A correlation for β in terms of s_m was obtained by using mole fraction average values of T_{bm} and P_{cm} , and the true critical mixture temperature T_{cm} (as, for example, estimated by methods recommended by Reid, et al. [30]). The results of this approach for correlating β with s_m are shown in Fig. 9. The abscissa was obtained from available experimental surface tension data by taking an average value of β over the temperature range of the reported data for each substance at constant liquid composition. The critical exponent was held constant at a value of 11/9. The data were correlated by a second degree polynomial as

$$\beta = -0.4412 + 0.2003s_m - 0.00516s_m^2 \quad (7)$$

A limited test of the accuracy of equations (5) and (7) was made by

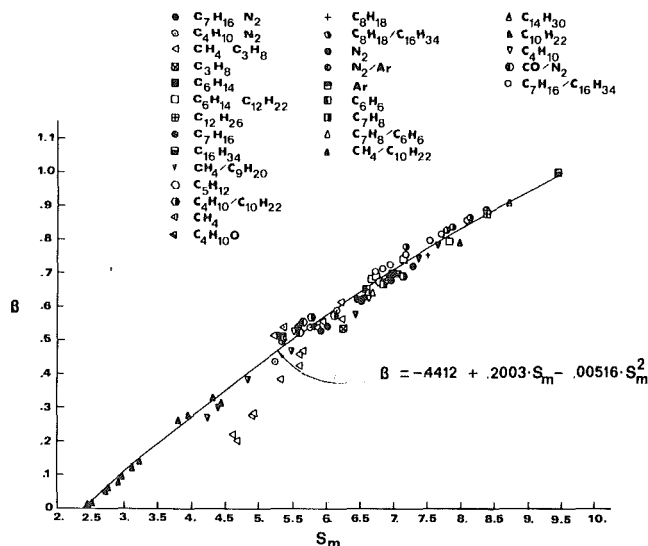


Fig. 9 Correlation of β in equation (5) with the characterization parameter for several nonpolar liquids and their mixtures.

Table 1 Correlations of surface tension with temperature

Liquid	$\beta P_c^{2/3} T_c^{1/3}$	μ	T_c (K)
n-pentane [35]	53.3	1.23	469.6
n-heptane [8]	55.13	1.28	540.2
n-octane [8]	55.72	1.30	568.8
n-hexadecane [35]	55.2	1.33	717.0

Avedisian [19]. The average absolute percent error for n-paraffin mixtures not containing methane as a component was under 3 percent. For pure liquids a slightly larger error of 6 percent was found. However, equation (7) was not used for predicting the surface tension of pure liquids because more accurate correlations for the pure liquid components we used were already available in the literature, as summarized in Table 1.

The substances included in the correlation leading to equation (7) were nonpolar mixtures from the same homologous series: n-alkane/n-alkane, aromatic/aromatic, etc. Equation (7) was found not to be very accurate for predicting surface tension of such mixtures as n-alkane/aromatic and n-alkane/alcohol.

3.3 Vapor Pressure. The vapor pressure P within the critical size nucleus was estimated by solving two problems. Firstly, the equilibrium vapor pressure P_e of the mixture was calculated by solving the basic set of phase equilibrium relations

$$f_i^v(P_e, T, y_{1e}, y_{2e}, \dots) = f_i^l(P_e, T, x_1, x_2, \dots) \quad (8)$$

for P_e and the y_{ie} , given T and all the x_i . The fugacities were evaluated from the defining equation [26]

$$f_i^v = y_{ie} P_e \exp \left\{ \frac{1}{RT} \int_{\infty}^v \left[\left(\frac{RT}{V} - \frac{\partial P_e}{\partial n_i} \right)_{T, V, n_j} \right] dV - RT \ln(Z) \right\}. \quad (9)$$

A pressure explicit equation of state, $P = P(T, V, n_1, n_2, \dots)$ is required in order to evaluate the integral in the above equation. The liquid phase fugacities, f_i^l , were determined by replacing y_{ie} by x_i in equation (9). Secondly, with P_e and the y_{ie} now known, the partial pressure of component i within the nucleus, which forms within the bulk of the liquid mixture under an ambient pressure P_0 , was then obtained from the approximate relation (see Appendix)

$$P_i \approx y_{ie} P_e \exp \left[\frac{v_{il}}{RT} (P_0 - P_e) \right], \quad (10)$$

where the partial molar volume of component i in the liquid solution, v_{il} , is defined as

$$v_{il} \equiv \frac{\left(\frac{\partial P_e}{\partial n_i} \right)_{T, V, n_j}}{\left(\frac{\partial P_e}{\partial V} \right)_{T, \text{all } n_i}} \quad (11)$$

The fugacities and partial molar volumes were evaluated by using the Peng-Robinson [31] equation of state:

$$P_e = \frac{nRT}{(V - bn)} - \frac{an^2}{V^2 + 2bnV - n^2b^2} \quad (12)$$

Equations (9) and (11) could then be expanded to yield

$$f_i^v = y_{ie} P_e \exp \left\{ \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_{j=1}^2 a_{ij} y_{je}}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z + 2.414B}{Z - .414B} \right) \right\} \quad (13)$$

and

$$v_{il} = \frac{\frac{RT}{(v - b)^2} (v + b_i - b) + \frac{1}{(v^2 + 2bv - b^2)} \left(\frac{2a(v - b)b_i}{v^2 + 2bv - b^2} - 2 \sum_{j=1}^2 x_j a_{ij} \right)}{\frac{RT}{(v - b)^2} - \frac{2a(v + b)}{(v^2 + 2bv - b^2)^2}} \quad (14)$$

where for a binary mixture,

$$a = a_1 y_{1e}^2 + 2y_{1e} y_{2e} a_{12} + a_2 y_{2e}^2 \quad (15)$$

$$a_{12} = (a_1 a_2)^{1/2} (1 - d_{12}) \quad (16)$$

$$b = y_{1e} b_1 + y_{2e} b_2 \quad (17)$$

$$A = \frac{a P_e}{R^2 T^2} \quad (18)$$

and

$$B = \frac{b P_e}{RT} \quad (19)$$

y_{1e} and y_{2e} are replaced by x_1 and x_2 respectively in equations (15) and (17) to evaluate v_{il} from equation (14).

The parameters a_i and b_i were obtained from the pure component data, and d_{12} is an empirically determined interaction parameter characteristic of the binary 1-2 pair. For hydrocarbon mixtures Peng and Robinson [31] have found that $d_{12} = 0$. The compressibility factor, $Z \equiv PV/(nRT)$ in equation (13), was obtained by rewriting equation (12) in the form

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (20)$$

The largest root of equation (20) is the vapor phase compressibility factor, and the smallest root is the liquid phase value. The molar volume of the liquid mixture, v in equations (3) and (14), was evaluated from a correlation developed by Hankinson and Thomson [32].

For binary mixtures equations (8) are a set of two nonlinear algebraic equations for the unknowns y_{1e} and P_e . The equations were solved numerically [19], and the accuracy of the results were compared with some binary n-paraffin mixture data available in the literature. Such data are scarce at reduced temperatures typical of homogeneous bubble nucleation within mixtures $-T/T_{cm} > .9$. A relevant test of the accuracy of predicted bubble point pressures could only be made for the n-pentane/n-heptane mixtures we studied. Only for these mixtures could vapor-liquid equilibrium data be located at such high reduced temperatures [21]. As illustrated in Fig. 10, agreement between calculated and experimental vapor pressures is quite good, and

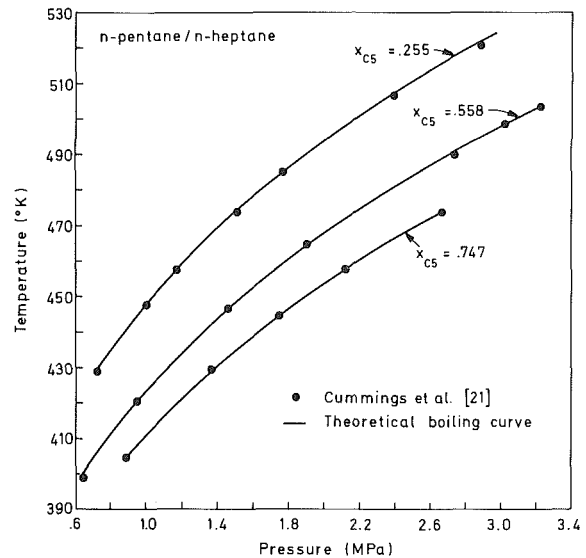


Fig. 10 Comparison of the boiling points of three n-pentane/n-heptane mixtures, as measured by Cummings, et al. [21], with calculated values obtained by solving the set of equations (8).

there is no ambiguity in the method when the critical temperature of n-pentane is exceeded. (The relevant physical constants required in the calculation were taken from Reid, et al. [30].)

No data at high reduced temperatures could be located for the n-pentane/n-octane or n-pentane/n-hexadecane mixtures, although McGlashan and Williamson [33] reported some measurements of bubble point pressures of n-hexane/n-hexadecane mixtures at temperatures up to 333 K. The agreement between bubble point pressures

calculated from equation (8) and their data was also found to be quite good. Notwithstanding the unavoidable criticism of using data at temperatures well below those characteristic of bubble nucleation within mixtures to justify our approach for predicting the gas pressure within the critical size nucleus, we feel that predicted bubble point pressures at high reduced temperatures are as accurate for solutions of volatile and nonvolatile liquids such as the n-pentane/n-hexadecane mixtures as they were found to be for n-pentane/n-heptane mixtures.

3.4 Results. Assuming that droplet boiling is the result of one bubble nucleating anywhere within the droplet, the nucleation rate can be estimated from the approximate expression $J = 1/(v_d t)$, where t is the mean lifetime of a superheated liquid droplet of volume v_d . From our experimental conditions, droplets traveling 4 cm/s over a distance of 1.3 cm spent an average of 0.3 s within a range of 2 K of the observed boiling temperature (a precise value of t is not too important). For droplet diameters ranging between 0.5 and 2 mm, the nucleation rate correspondingly varied from about 10^3 nuclei/cm³-s to 10^5 nuclei/cm³-s. This difference resulted in a less than 1 K change in the predicted limit of superheat.

Using the methods previously described for estimating the relevant physical properties, and a nucleation rate of 10^5 nuclei/cm³-s, equation (1) was solved for T over the pressure range for which $P > P_0$. The results are shown by the theoretical lines in Figs. 2–8. The predicted limits of superheat of pure n-pentane and n-heptane (Figs. 2 and 3) are in very good agreement with both our data and those of Skripov [6] over the whole pressure range.

The theoretical limits of superheat of two n-pentane/n-heptane mixtures of fixed composition are shown as a function of pressure in Figs. 4 and 5. In these calculations, the possibility that the composition of the liquid in the vicinity of the nucleus is different from that in the bulk because of preferential vaporization and local depletion of the volatile species, as discussed by Pinnes and Mueller [18], was neglected. Reid [34] argues that such effects are negligible because the number of molecules within the vapor nucleus is small compared to the enormous number of molecules in the liquid. As shown in Figs. 4 and 5, the agreement between predicted and measured nucleation temperatures is quite good.

The effect of liquid phase composition (mole fraction) on the limit of superheat at fixed pressures is shown in Figs. 6–8 for the n-pentane/n-heptane, n-pentane/n-octane, and n-pentane/n-hexadecane mixtures, respectively. There is again very good agreement between predicted and measured limits of superheat over the whole pressure and composition range of the reported data. This observation shows that homogeneous nucleation was probably the cause of boiling in the majority of droplets tested.

The theoretical limits of superheat of the n-alkane mixtures varied nearly linearly with liquid phase mole fraction at both atmospheric and elevated pressures, as shown in Figs. 6–8. This fact was previously observed at atmospheric pressure [11, 12, 18]. However, this nearly linear variation of limit of superheat with mole fraction is by no means a universal result. Some liquid-liquid mixtures have been found to exhibit nonlinear variations of nucleation temperature with mole fraction. For example, Holden and Katz [12] found that the superheat limits at atmospheric pressure of benzene/n-hexane and benzene/cyclohexane mixtures varied nonlinearly with mole fraction. Those mixtures whose nucleation temperatures do vary nonlinearly with mole fraction are typically nonideal solutions which may exhibit a two-phase miscibility gap (e.g. mixtures of n-hexadecane and ethanol). The ability to correctly predict the limit of superheat of nonideal mixtures requires accurate vapor pressure and surface tension data of the mixture near the mixture critical temperature. Unfortunately, such data are scarce and methods for predicting them are not well developed. This fact is precisely why we choose to use normal alkane mixtures in our experiments. By showing that equation (1) could correctly predict experimentally measured limits of superheat of such relatively simple liquid-liquid mixtures as those made up of the normal alkanes over a range of pressures and liquid phase compositions, and at temperatures which may exceed the critical temperature of one of the components in the solution, we feel that the limits of

superheat of more complicated mixtures may also be correctly predicted by using equation (1) once the required physical properties can be estimated accurately.

The above results may be useful for predicting the internal boiling or micro-explosion phenomenon which has been observed [2] in the combustion of fuel drops which are miscible solutions of volatile and nonvolatile liquids. Concentration gradients produced within the drop as a result of the diffusional processes attendant to droplet vaporization can result in locally superheated regions within the droplet interior. If the droplet burning temperature T_d surpasses the homogeneous nucleation temperature T at any point within the droplet interior, micro-explosions will be initiated by the formation of a critical size nucleus within the fuel blend. The subsequent growth of this initial vapor bubble will lead to the disruptive combustion of the droplet, if the bubble grows fast enough to fragment the drop before completion of burning. As ambient pressure is increased, or the volatile component within the solution is diluted, the bubble growth rate will be progressively reduced. Internal boiling may still be initiated at high pressures by formation of a critical size nucleus within the fuel blend $-T_d > T-$ but growth of this nucleus could be slowed enough that the time for the nucleus to grow sufficiently beyond its initial equilibrium size is longer than the droplet burning time. The method described here for predicting the nucleation temperature of a fuel blend which is a mixture of volatile and nonvolatile liquids may be useful, when coupled with accurate liquid phase temperature calculations of burning fuel droplets, for estimating if, when, and where within the fuel drop disruptive combustion will be initiated.

4 Conclusions

New measurements of the homogeneous nucleation temperature of some binary liquid n-alkane mixtures have been made at high pressures. The results showed that a mole fraction average of the limits of superheat of the individual components in solution at a given pressure could be used to estimate accurately the effect of pressure and composition on the limit of superheat of the mixture.

The theory of homogeneous nucleation of bubbles in liquids, as expressed by equation (1), was successfully used to accurately predict the experimentally measured nucleation temperatures at high pressures and over a range of compositions. Equation (1) was solved for temperature by using both the Peng-Robinson equation of state to evaluate the liquid and vapor phase fugacities of the mixture (and thereby the pressure of the gas within the vapor nucleus), and a new empirically based correlation for the liquid-vapor surface tension (applicable primarily to normal alkane mixtures).

Extension of the general procedures used in this work to other more nonideal liquid mixtures may be made only after the effects of vapor pressure and surface tension of the solution on the liquid phase composition and temperature can be predicted accurately at high temperatures.

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APPENDIX

The vapor pressure P within a critical size nucleus which forms in a mixture under an ambient pressure P_0 (Fig. A-1(a)) is not the same as the equilibrium bubble point pressure P_e of the mixture at the same temperature and liquid phase composition (Fig. A-1(b)). The difference is due primarily to the curvature of the vapor nucleus. Given T, P_0, x_1, x_2, \dots , we wish to estimate the vapor pressure within the nucleus.

Consider Fig. A-1(b). P_e is the equilibrium bubble point pressure of the mixture when the radius of curvature of the liquid-vapor interface is infinite. The fundamental equilibrium condition for component i is that

$$\mu_i^v(P_e, T, y_{1e}, y_{2e}, \dots) = \mu_i^l(P_e, T, x_1, x_2, \dots) \quad (\text{A-1})$$

where μ_i is the chemical potential of component i (not to be confused with critical exponent defined in equation (5)). With fugacity defined by the equation

$$\mu_i \equiv \mu_i^0(T) + RT \ln(f_i), \quad (\text{A-2})$$

equation (A-1) may be expressed alternatively as

$$f_i^v(P_e, T, y_{1e}, y_{2e}, \dots) = f_i^l(P_e, T, x_1, x_2, \dots). \quad (\text{A-3})$$

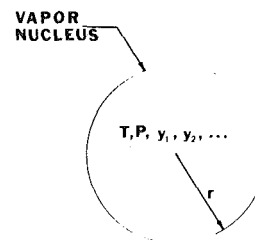
The fugacities in equation (A-3) are experimentally accessible. They may also be estimated from a suitable equation of state (e.g., equation (12)): given T and liquid phase composition the set of simultaneous nonlinear algebraic equations implied by equation (A-3) can be solved numerically for P_e and the vapor phase composition.

A critical size nucleus (Fig. A-1(a)) is defined to be in thermodynamic equilibrium with the surrounding superheated liquid. Therefore, we may also write

$$\mu_i^v(P, T, y_1, y_2, \dots) = \mu_i^l(P_0, T, x_1, x_2, \dots) \quad (\text{A-4})$$

By combining equations (A-1), (A-2), and (A-4), the fugacity of component i within the vapor nucleus $f_i^v(P, T, y_1, y_2, \dots)$, can be related to the fugacity of component i in the equilibrium configuration illustrated in Fig. A-1(b):

$$f_i^v(P, T, y_1, y_2, \dots) = f_i^l(P_e, T, y_{1e}, y_{2e}, \dots) \exp \left[\frac{\mu_i^l(P_0, T, x_1, x_2, \dots) - \mu_i^l(P_e, T, x_1, x_2, \dots)}{RT} \right] \quad (\text{A-5})$$



T, P, y_1, y_2, \dots
LIQUID
Fig. A-1(a)

VAPOR
T, P, y_1, y_2, \dots

T, P, x_1, x_2, \dots
LIQUID
Fig. A-1(b)

Fig. A-1 Physical interpretation of difference between P and P_e

The exponential term in equation (A-5) can be further simplified by integrating the relation

$$v_{il} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, n_i, n_j} \quad (\text{A-6})$$

from P_e to P_0 , assuming v_{il} (e.g., equation (14)) is relatively insensitive to pressure. Combining the result with equation (A-5) gives

$$f_i^v(P, T, y_1, y_2, \dots) = f_i^v(P_e, T, y_{1e}, y_{2e}, \dots) \exp \left[\frac{v_{il}}{RT} (P_0 - P_e) \right] \quad (\text{A-7})$$

The set of simultaneous equations implied by equation (A-7) may be solved numerically for P, y_1, y_2, \dots by first calculating $P_e, y_{1e}, y_{2e}, \dots$ from the set of equations (A-3). However, equation (A-7) may be

further simplified by assuming that

$$\begin{aligned} \phi_i^v(P, T, y_1, y_2, \dots) &\equiv \frac{f_i^v(P, T, y_1, y_2, \dots)}{y_i P} \\ &\simeq \frac{f_i^v(P_e, T, y_{1e}, y_{2e}, \dots)}{y_{ie} P_e} \equiv \phi_i^v(P_e, T, y_{1e}, y_{2e}, \dots) \end{aligned} \quad (\text{A-8})$$

where the ϕ_i^v are defined as vapor phase fugacity coefficients. With this simplification equation (A-7) becomes

$$P_i \simeq P_e y_{ie} \exp \left(\frac{v_{il}}{RT} (P_0 - P_e) \right) \quad (\text{A-9})$$

which is equation (10). The iterative solution implied by equation (A-7) for the nucleus vapor pressure P , once $P_e, y_{1e}, y_{2e}, \dots$, are known is now replaced by equation (A-9) which provides an explicit expression for P_i in terms of P_e and y_{ie} .