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Bubble Nucleation in *n*-Pentane, *n*-Hexane, *n*-Pentane + Hexadecane Mixtures, and Water

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Bubble nucleation temperatures in pure *n*-pentane and *n*-hexane were measured. Both nucleate explosively with most of the small drops of *n*-pentane (bp 36°) nucleating at $147.8 \pm 0.3^\circ$ and most of the small drops of *n*-hexane (bp 69°) nucleating at $183.8 \pm 0.5^\circ$. These temperatures are somewhat higher than previous measurements and are in excellent agreement with calculations from the steady-state Zeldovich-Kagan theory. Addition of the relatively involatile hexadecane to *n*-pentane raises the nucleation temperature linearly with concentration (weight fraction or mole fraction) to about 197° at 46 wt % hexadecane. The explosive growth phase is slowed in the mixtures because of diffusion control with a high pitched "ping" in the pure *n*-pentane becoming a lower pitched "pong" with 20 wt % hexadecane and a lower pitched "glub" at 46 wt % hexadecane. The mixtures exhibited a significant spread of nucleation temperatures with volume of the droplets. A modification of theory including an extension to diffusion-controlled nucleation was made. We have superheated water to over 265°; however, this is well below the homogeneous limit.

Introduction

Although bubble nucleation is important in many natural and man-made phenomena, only very limited theoretical or experimental work on this subject has appeared. The early quasi-equilibrium theories of homogeneous nucleation of Becker and Döring² and Volmer³ were followed by the steady-state theory of Zeldovich⁴ which was further refined by Kagan.⁵ Most of the few reliable experimental data exist for one-component systems.⁶ It is the purpose of this paper to check previous work on one-component systems (*n*-pentane, *n*-hexane, and water) and to provide new data on a two-component system (*n*-pentane + *n*-hexadecane) to serve as a basis for testing and extending the theory of homogeneous bubble nucleation and to gain a better understanding of the details of the phenomenon. We will discuss the theory of multicomponent systems with one volatile component and take into account the influence of diffusion. The experimental measurements will be discussed in the context of the theory.

Theory

The steady-state theory of Zeldovich⁴ has been clarified and extended by Kagan.⁵ For the case where the influence of viscous and inertial forces is small (which applies to our experiments) Kagan has derived an expression for J , the rate of nucleation, *i.e.*, number of critical size nuclei per unit volume per unit time which continue to grow to macroscopic size.

$$J = \frac{1}{2} N_0 \frac{\beta v_t}{1 + \delta_\lambda} \sqrt{\frac{\sigma}{kT}} e^{-1/\delta_\lambda} \quad (1)$$

where β is a condensation coefficient (here taken as 1) and

$$v_t = \sqrt{\frac{8kT}{\pi m}} \quad (2)$$

is the average thermal velocity of the vapor molecules of mass m , σ is the surface tension of the liquid, and

$$K = \frac{4\pi\sigma r_c^2}{kT} \quad (3)$$

where r_c is the radius of the critical size bubble given by

$$p_c = p_0 + \frac{2\sigma}{r_c} \quad (4)$$

where p_0 is the ambient pressure and p_c is the equilibrium vapor pressure of the liquid. p_c is equal to the pressure inside the critical size bubble.

(1) Correspondence should be addressed to Chemical Engineering Division, Argonne National Laboratory, Argonne, Ill. 60439.

(2) (a) R. Becker and W. Döring, *Ann. Phys.*, **24**, 719 (1935); (b) R. Becker, "Theorie der Wärme," Springer, Berlin, 1955.

(3) M. Volmer, "Kinetic der Phasenbildung," Steinkopff, Dresden-Leipzig, 1939.

(4) Ya. B. Zeldovich, *Zh. Eksp. Teor. Fiz.*, **12**, 525 (1942).

(5) Yu. Kagan, *Zh. Fiz. Khim.*, **34**, 92 (1960); *Russ. J. Phys. Chem.*, **34**, 44 (1960).

(6) (a) H. Wakeshima and K. Takata, *J. Phys. Soc. Jap.*, **13**, 678 (1958); (b) V. B. Skripov and G. V. Ermakov, *Zh. Fiz. Khim.*, **38**, 396 (1964); *Russ. J. Phys. Chem.*, **38**, 208 (1964); E. N. Sinitsyn and V. P. Skripov, *Ukr. Fiz. Zh.*, **12**, 99 (1967); (c) G. R. Moore, Ph.D. Thesis, University of Wisconsin 1956 (University Microfilms Publication No. 17,330, Ann Arbor, Mich.).

The parameter δ_λ is related to the heat flow during the growth of a bubble and involves the enthalpy of vaporization and thermal conductivity of the liquid. In the cases given here δ_λ is small relative to unity. However, for multicomponent systems with one volatile constituent, our calculations indicate a similar factor, δ_D , which takes into account the steady-state diffusion of molecules through the medium into the nuclear bubbles. The result of the calculations⁷ includes the factor δ_D

$$\delta_D = \frac{\beta v_t}{2DkT} \frac{\sigma}{p_c - p_0} \left(\frac{dp}{dC} \right)_{p_c} \cong \frac{\beta v_t \sigma}{2(C - C_0)DkT} \quad (5)$$

where the last expression on the right holds where Henry's law is obeyed and $dp/dC = p/C$. C is the bulk initial concentration of the volatile solute, C_0 is the equilibrium concentration at a vapor pressure equal to the ambient pressure p_0 , and D is the diffusion coefficient of the volatile solute in the solvent. The rate of nucleation is lowered from J (eq 1) to J' when diffusion is significant where

$$J' = J/(1 + \delta_D) \quad (6)$$

If $\delta_D \gg 1$, then where Henry's law is valid

$$J' \cong N_0 D (C - C_0) \sqrt{\frac{kT}{\sigma}} e^{-1/\delta_D} \quad (7)$$

and the nucleation rate is diffusion controlled.

In addition to the nucleation rate, diffusion will also control the rate of growth of the bubble. As will be seen from the experiment we describe, the rate of growth in a pure material is so rapid that it produces a sharp explosive report. In a dilute multicomponent solution in an involatile solvent, diffusion control slows the rate of growth considerably and changes the character of the growth process. We show below that for bubbles much larger than the critical size, the rate of growth is proportional to the concentration of the volatile constituent in solution and inversely proportional to the radius.

The total number of moles of gas, n , in a bubble of radius $r \gg r_c$ is

$$n \cong \frac{4/3 \pi r^3 p_0}{RT}$$

and the average thickness, l , of the shell of liquid surrounding the bubble which is partly denuded of the volatile solute for the case where $p_c \gg p_0$ is approximately given by

$$4\pi r^2 l \cong L \frac{n}{C - C_0} = \frac{4/3 \pi r^3 p_0 L}{(C - C_0)RT} \quad (8)$$

where L is a proportionality factor of order unity. The rate of diffusion of molecules into the bubble, \dot{n} , is proportional to the product of the area of the bubble surface ($4\pi r^2$) and the concentration gradient which is proportional to $1/l$. Thus the rate of growth of the radius of the bubble

$$\dot{r} \propto \frac{\dot{n}}{4\pi r^2} \propto \frac{C - C_0}{r} \quad (9)$$

(If the diffusion equation is solved for a stationary boundary and the rate of diffusion per unit area is set equal to $(p_0/RT)\dot{r}$, then $\dot{r} \cong (RT/p_0)((C - C_0)/r)D$ and when $r \gg r_c$, $r \cong \sqrt{(2DRT/p_0)(C - C_0)t}$.) These considerations show that if diffusion is the limiting factor, the rate of growth of bubbles much larger than critical size is proportional to the concentration and inversely proportional to the size of the bubble. At low concentrations growth is slow and increases with increasing concentration. Thus, while bubble growth in a one-component system is explosive, the addition of an involatile diluent slows the rate. The smaller the concentration of the volatile solute the slower the growth. Our measurements demonstrate this change in the character of the growth with dilution.

We also must examine an important correction to the theory first considered by Skripov and coworkers.^{6b} Measurements of vapor pressures are made when a substance is under a pressure equal to its own pressure (p_e). Our measurements on these liquids were made while they were metastable at (or close to) ambient atmospheric pressures, which are much lower. Consequently, the actual vapor pressure in our experiments, p_c (*i.e.*, the vapor pressure of the liquid when the ambient pressure is p_0 , see eq 4) at a given temperature differs from the measured vapor pressure (p_e). This may be estimated from the relation

$$\left(\frac{\partial \ln f}{\partial p} \right)_T = \frac{v_1}{RT} \quad (10)$$

where f is the fugacity and v_1 is the molar volume of the liquid.

If v_1 is independent of pressure

$$\ln \frac{f_c}{f_e} \cong \frac{v_1(p_0 - p_e)}{RT} \cong \frac{f_c - f_e}{f_e} \quad (11)$$

where the expression on the right is valid when f_e/f_0 does not differ greatly from unity. By rearrangement we obtain

$$f_c \cong f_e \left(1 - \frac{v_1(p_e - p_0)}{RT} \right) \quad (12)$$

If the ratios of fugacities do not differ greatly from pressure ratios, then

$$\frac{f_c}{f_e} \cong \frac{p_c}{p_e} \cong 1 - \frac{v_1(p_e - p_0)}{RT} \quad (13)$$

Activity coefficient data⁸ show this approximation to

(7) J. L. Katz and M. Blander, in preparation. (Material in this paper was presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., Spring, 1971, Abstract PHYS 62.)

(8) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Research Project 44, Thermodynamics Research Center, College Station, Texas, 1969.

be valid to within 2.5% for *n*-pentane and a similar precision probably holds for *n*-hexane. Equation 13 may be rearranged to obtain $p_e - p_0$ in eq 4

$$p_e - p_0 \cong (p_e - p_0) \left(1 - \frac{v_1 p_e}{RT} \right) = (p_e - p_0) \left(1 - \frac{zv_1}{v_g} \right) \quad (14)$$

where z is the compressibility factor pv_g/RT . The last expression on the right-hand side with $z = 1$ is the approximate correction factor utilized by Sinitsyn and Skripov. Where data on fugacities *vs.* pressure are available, eq 11 is preferable. The introduction of this factor leads to a significant increase (1.5–2.0°) in the calculated eruption temperatures and accuracy is needed for a correct estimate.

Another correction which must be considered arises from the fact that the derivation of eq 1 was made assuming that the gas phase is ideal. At the pressures involved the gas phase deviates considerably from ideal behavior, especially gases of strongly interacting molecules. We have calculated the corrections for nonideal gases⁷ and find that the exponential term in eq 1 requires no correction and that the only correction is a multiplicative factor which has a negligibly small effect on the temperature we calculate.

Experimental Methods

The method is a modification of the technique of Wakeshima and Takata,^{6a} of Skripov, Sinitsyn, and co-workers,^{6b} and of Moore.^{6c} It consists of the generation of an emulsion of small drops of volatile liquids in an immiscible fluid medium. The individual drops are allowed to rise slowly in a column of the same immiscible medium which is hotter at the top than at the bottom. The drops get hotter as they rise and at high enough temperatures the liquid superheats enough to nucleate and then boils explosively. This boiling can be observed visually and the explosive reports can be clearly heard. For hydrocarbons, sulfuric acid and for water, a silicone oil were used as the immiscible fluid medium in which the droplets rose.

Figure 1 gives a schematic diagram of the Pyrex apparatus used which consisted of a lower vessel 7.5 cm in diameter by 8.5 cm in height connected to an upper column about 5.5 cm in diameter by 46 cm in length with a 1-mm capillary about 3 cm long serving as an opening between the two vessels. The upper column is capped by a Teflon stopper in which is set an L-shaped, thin-walled, small bore thermocouple well, the tip of which can be set at any desired height. The central 28-cm portion of the upper column is wound with 28 turns of nichrome wire, cemented in place with Sauereisen cement and with a total resistance of 45 Ω. The spacing between windings is uneven being about 2 cm at the lower end and about 0.5 cm at the upper end.

BUBBLE NUCLEATION APPARATUS

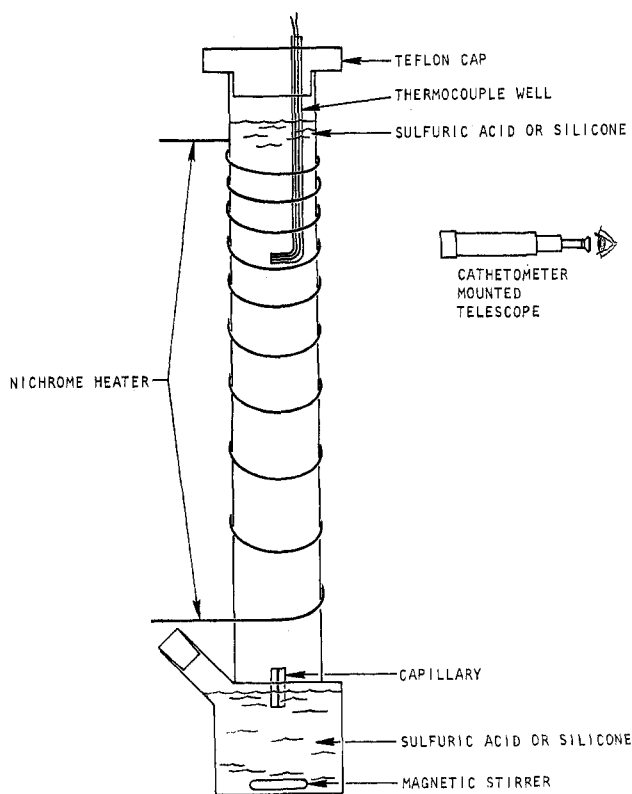


Figure 1. Bubble nucleation apparatus.

A side arm is provided in the lower vessel, and a Teflon-coated magnetic stirrer is used to stir the materials in the lower vessel. A 28-gauge copper-constantan thermocouple, calibrated to 0.1° *vs.* a standard Pt–Pt–10% Rh thermocouple was used for the temperature measurements. The thermocouple was set into the well and was connected through an ice bath to a Leeds & Northrup Type K3 potentiometer standardized *vs.* an unsaturated Eppley standard cell. The current for the nichrome heater was supplied through a constant voltage regulator and a variable autotransformer set to provide a suitable current for the temperature range of interest.

The operation of the apparatus was quite simple. The vessels were filled to appropriate levels with sulfuric acid, and a fixed voltage was set on the heating wires. After about 2 hr the temperatures in the upper vessel stabilized. Temperature was measured at different horizontal positions at any given level by rotating the thermocouple tip. It differed by less than 0.1° within a given level at any position more than about 1/2 cm away from the walls of the vessel. If the liquid was undisturbed, the temperatures and temperature distribution would remain constant to ±0.1° over the time of the experiment (about 0.5 hr). The temperatures and levels were adjusted so that the temperature gradients in the region where measurements were made were about 2–3°/cm. The nucleation of unusually large drops

would temporarily upset the temperature gradients. Frequent checks of temperature were made, and sufficient time (usually about 0.5 hr) was allowed to permit any such temperature fluctuations to decay.

The volatile liquid to be studied was introduced onto the surface of the sulfuric acid in the lower vessel and partly emulsified by mechanical mixing with a stirring rod followed by rapid stirring with a Teflon-coated magnetic stirrer bar. The sulfuric acid level was about 0.25–1 cm above the bottom of the capillary and by careful manipulation individual drops could be sent through the capillary into the upper tube. These drops floated upward slowly and nucleated when sufficiently superheated.

The liquids used were as follows: *n*-pentane and *n*-hexane were Pure grade obtained from the Phillips Petroleum Co. (Special Products Division), 99 mol % minimum with a stated boiling point of 96.9°F (36.06°) for *n*-pentane and 155.8°F (68.78°) for *n*-hexane. Two grades of *n*-hexadecane from Matheson Coleman and Bell were used in a separate series of measurements; one grade was ASTM grade olefin free of 99+ % purity with a minimum melting point of 18.0°, and the other grade was Practical grade with a melting point range of 17–18°. No significant differences were found between experimental results from these two grades indicating that impurities have little influence on the measurements. Only results from the purer grade are reported here. The sulfuric acid was Du Pont Reagent grade 95–97%, specific gravity 1.84 min. The water was triply distilled, and the silicone oil was Dow Corning No. 710 silicone fluid with a viscosity of 500 cSt at 25°.

Nucleation in Pure *n*-Pentane and *n*-Hexane. A small quantity of one of the pure hydrocarbons (about 5 cm³) was introduced into the side arm of the lower vessel where it floated on the surface of the sulfuric acid in the vessel. Each experiment consisted of several hundred measurements and was repeated at least once using a fresh batch of sulfuric acid in both the upper tube and the lower vessel each time. The organic was emulsified with the sulfuric acid. By a variety of means, including manipulation of the stopper in the side arm or by stopping the stirrer, individual droplets of the organic compound could be made to enter the upper column. The sizes varied from droplets which were so small that they were not visible through the four-power telescope of the cathetometer to some as large as 2 mm. The sizes were estimated by comparison with a scale set in the line of sight of the telescope. The scale served to measure the height at which droplets nucleated and the height of the thermocouple. Any given droplet rose slowly in the cooler lower portion of the tube and accelerated in the hotter upper portion of the tube with large droplets rising more rapidly than small ones. The droplets got hotter as they rose and reached levels where the temperatures were considerably higher than their

boiling points before nucleating to produce sharp high-pitched explosions. Except for the largest droplets (>1.2 mm) and a small number of droplets (<5%) which exploded prematurely, essentially all of the droplets of *n*-pentane and *n*-hexane exploded in a narrow range of temperatures (total range of about $\pm 0.3^\circ$ for *n*-pentane and $\pm 0.5^\circ$ for *n*-hexane). The largest droplets (>1.2 mm) rose very rapidly and probably did not reach the ambient temperature of the medium. They usually nucleated at a higher level where the ambient temperature was higher. Many of the drops which nucleated at lower temperatures appeared to have bubbles attached to them before nucleating and probably did not nucleate homogeneously. The range of temperatures in which the large majority of droplets nucleated was so narrow that when the temperature was stable there was a striking illusion that most of the droplets nucleated close to a single plane. No obvious large differences existed between the smallest drops (which formed 1–2-mm bubbles when they exploded) and those which were 1 mm in size as a liquid. As will be discussed, this is consistent with nucleation theory where *J* for these one-component fluids is a very steep function of temperature. Calculation of the rate of nucleation in our experiment of droplets of volumes which vary by about three orders of magnitude reveals that nucleation for these pure materials should occur over a narrow range of temperatures ($\sim 0.6^\circ$) as observed. Only an occasional small droplet exploded at higher temperatures (0.5–1° higher). The temperatures measured are given in Table I.

Table I: Measured and Calculated Temperatures (°C) for Different Nucleation Rates

	<i>T</i> (measured)	<i>T</i> (calculated)	
		<i>J</i> = 10 ⁴ cm ⁻³ sec ⁻¹	<i>J</i> = 10 ⁶ cm ⁻³ sec ⁻¹
<i>n</i> -Pentane	147.8 ± 0.3	147.7 (147.2) ^a	148.3 (147.9)
<i>n</i> -Hexane	183.8 ± 0.5	183.6 (183.1)	184.3 (183.8)

^a Parentheses include compressibility correction.

Nucleation in *n*-Pentane–Hexadecane Mixtures. The experiments were repeated for the purified *n*-pentane diluted with the relatively involatile hexadecane. The mixtures were made up by weight. The observations exhibited very significant qualitative and quantitative differences from those on pure *n*-pentane. Figure 2 gives a plot of the average temperature for the nucleation of these mixtures as a function of weight per cent hexadecane. The nucleation temperature increased with increasing weight per cent of the relatively non-volatile hexadecane. The largest influence on this is probably related to the surface tension of the mixture. Pure *n*-pentane at 147.8° has a low surface tension (3.3

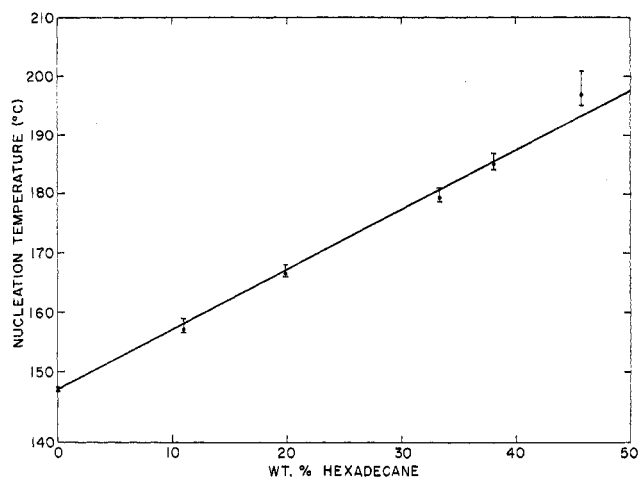


Figure 2. Bubble nucleation temperatures of *n*-pentane + *n*-hexadecane mixtures vs. weight per cent hexadecane. Bars represent spread of data due to different size drops and fluctuations in nucleation temperatures.

ergs/cm²), because it is close to its critical point (196.6°). Hexadecane, which has a much higher critical temperature (444°), should have an appreciably higher surface tension at 147.8° and the mixtures, if they have an intermediate value, should nucleate at higher temperatures. Another (and probably smaller) influence is that the vapor pressure of *n*-pentane is lower in the mixtures than in pure *n*-pentane.

In addition to this, another significant observation was made on the mixtures. With increasing hexadecane content it was observed that there was an increasing tendency for small drops (<0.1 mm) to nucleate at higher temperatures than large drops. At the highest concentrations of hexadecane (~46 wt %) the difference was about 5°, *i.e.*, drops of about 0.5-mm diameter usually exploded from 196 to 198° whereas small drops (≤0.1 mm) usually exploded from 197 to 201°. This would result if *J* were to become less strongly dependent on temperature with increasing dilution. As will be discussed, this can probably be ascribed largely to the relatively weaker dependence of surface tension on temperature of the mixtures as compared with the pure *n*-pentane. This wide variance of average nucleation temperature with volume should be a general feature for mixtures, especially those dilute in volatile solutes in a solvent far from its critical temperature. The points recorded in Figure 2 are those for drops ~0.2 mm. The bars about the points indicate the ranges where more than 90% of the drops nucleated. Since the size distribution was not uniform for all compositions, the range does not exhibit a regular change with composition.

A third observation of significance is on the nature of the explosive nucleation. For pure *n*-pentane, the sharp explosive report was high pitched and could be best described as a "ping." With dilution, the sound became lower pitched so that with 20% hexadecane it

might be characterized as a "pong." At the highest dilutions of the *n*-pentane (35–46% wt % hexadecane) the rate of growth of bubbles was so slowed that only very low pitched sounds were produced (characterized as a "glub"). These differences are related to the process of bubble growth which is diffusion controlled in the mixtures. These characteristic sounds reflect the smaller rate of growth of a postnuclear bubble with greater dilution of the volatile constituent. This is consistent with the discussion in the Introduction.

Nucleation of Liquid Water. The behavior of water was not as simple as that of the hydrocarbons, and nucleation may not have been homogeneous. However, the nucleation temperatures were quite high, and our observations seemed to be of sufficient interest to report.

The water utilized was triply distilled, but no special precautions were taken to degas it. Small amounts of gases such as CO₂ at the high temperatures and water fugacities involved probably make little difference in the nucleation temperature. The ambient fluid was Dow Corning No. 710 silicone oil. Although the water and silicone are immiscible at low temperatures, significant miscibility was observed at high temperatures (>200°). The miscibility places limitations upon the interpretation of the results. Droplets were made by emulsifying water and silicone oil in the lower vessel and a large number of drops up to 3 mm in diameter were introduced one at a time into the upper column.

It was quite apparent that water was somewhat soluble in silicone at the higher temperature. Small droplets (<0.1 mm) which rose slowly left a refractive index contrast trail behind them and disappeared before nucleating. Larger droplets (0.1–0.5 mm) partly dissolved in the silicone and silicone appeared to dissolve in the droplet. These droplets tended to nucleate at high temperatures 265–280° with fairly sharp explosions. However, it is questionable whether any of these contained pure water. Some of these drops (as well as larger ones) appeared to nucleate bubbles at the water-silicone interface at lower temperatures (200–240°) and a stream of bubbles rose rapidly from the surface of the slowly rising droplets. This indicated heterogeneous nucleation in at least some of the droplets. Most droplets from 0.5 to 1.0 mm nucleated in a range of temperatures from 250 to 275° with occasional droplets exploding at higher temperature up to 280°. These droplets rose fairly rapidly and from the appearance of the index of refraction contrast with the silicone probably had a core of pure water. Droplets from 1 to 3 mm in size rose rapidly at high temperatures and had little time to dissolve. The cores had a high index of refraction contrast with the silicone and were probably pure water. Most of these droplets exploded in the range 240–265° with an occasional explosion at higher temperatures (270°). These droplets exploded quite sharply and pushed the vessel against its support with a strong thud.

The wide range of temperatures and the erratic nucleation behavior may be partly the result of heterogeneous nucleation as postulated by Apfel,⁹ who has performed similar measurements with water. However, some of our observations do not support this. For example, some large (1 mm) drops evolved a continuous train of bubbles from their surface as they rose until they reached a high temperature where they exploded. Clearly, two separate kinds of nucleation are involved: the train of bubbles coming from a heterogeneous site and the explosive nucleation beginning in an unknown way. (The train of bubbles indicates that the surface tension of the silicone is less than that of the water. A reversal of the relative values of the surface tensions would change the mode of release and nucleation.)

Discussion

In this section we will calculate temperatures where the expected rates of homogeneous nucleation should correspond to our observations. Calculations for *n*-pentane and *n*-hexane were made using data from Timmermans,¹⁰ the International Critical Tables,¹¹ and the API Table.⁸ Available data on surface tensions were graphically fit to an equation of the form

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^S$$

The best fits of the data were made with values of σ_0 , T_c , and S of 52.72 ergs/cm², 469.77°K, and 1.22 for *n*-pentane, and 52.40 ergs/cm², 507.85°K, and 1.22 for *n*-hexane.

Most of the drops recorded in our measurements ranged from about 0.1 to 1.5 mm with a median at about 0.5 mm. The volume of these median sized drops was about 10⁻⁴ cm³, and they spent about 0.1 sec in the temperature range of about 0.3°. Consequently, a rate of J of about 10⁶ cm⁻³ sec⁻¹ is appropriate ($J = 1/vt$, where v = volume and t = time). Since the rise time of a drop is inversely proportional to its radius, the appropriate rate J is proportional to the inverse of the square of the radius. Consequently, the appropriate J for the 1.5-mm drop is about 10⁴ and for the 0.1-mm drop about 25 × 10⁵. In Table I our calculated temperatures for $J = 10^4$ and 10⁶ are given for *n*-pentane and *n*-hexane. The values given in Table I were calculated for values of $Z = 1$ and $Z = 0.74$ (in parentheses). For *n*-pentane the measured value of Z is 0.74 and it is probably similar for *n*-hexane. The correction for Z lowers the calculated temperatures about 0.5°, *i.e.*, the factor $(1 - (v_1/v_g))^2$ in eq 14 leads to temperatures about 1.5–2.0° higher than without it, whereas the factor $(1 - (Zv_1/v_g))^2$ leads to temperatures about 1.0–1.5° higher than without it.

The range of temperature for the large change of J in Table I is relatively small and is in excellent agreement with our measurements, both with or without the Z correction. The large change of J with a small change of

temperature (one order of magnitude per 0.3°) explains the very narrow range of measured temperatures despite the range of drop sizes. The variance in the measured values is probably real and probably not related to difficulties in measuring temperatures. The range, though small, stems from the probabilistic nature of each eruption and to the differences in sizes. Of hundreds of drops an occasional small drop might be expected to nucleate as much as 0.5–1° higher than the large majority, as was observed. Our measured and calculated temperatures are significantly higher than those given by previous workers.⁶

One must question whether the homogeneous limit has been reached in these experiments. The surface tension of sulfuric acid is much higher than the small values (~ 3 ergs/cm²) for the hydrocarbons. Consequently, the interfacial tension between the hydrocarbon and sulfuric acid is likely to be higher than the surface tension of the hydrocarbons. This will lead to a higher probability for homogeneous nucleation than for nucleation at the interface if the hydrocarbons spread on sulfuric acid. Very few drops appeared to nucleate bubbles at the surface and many of these few appeared to have bubbles attached to them before nucleation was initiated. Both *n*-pentane and *n*-hexane fit the homogeneous theory at two very different temperatures (and probably at two very different values of the sulfuric acid–hydrocarbon interfacial tensions which govern heterogeneous nucleation). It is very unlikely to be a coincidence and much more likely indicates homogeneous nucleation.

The measurements on the mixtures exhibit a much larger size dependence of the eruption temperature. If we combine eq 3 and 4, we obtain

$$K = \frac{16\pi\sigma^3}{kT(p_c - p_0)^2} \quad (15)$$

The temperature dependence of K essentially governs the variation of J with temperature since the preexponential factor in eq 1 is essentially independent of temperature. For pure pentane σ decreases and p_c increases relatively rapidly with increasing temperature. Both of these quantities operate to increase J with temperature. For example, between 160 and 170° σ for pentane decreases from 2.34 to 1.59 ergs/cm². Measured surface tensions for hexadecane^{8,10} were graphically fit to an equation

$$\sigma = 56.54 \left(1 - \frac{T}{T_c}\right)^{1.84} \text{ ergs/cm}^2$$

with $T_c = 717.15^\circ\text{K}$. Values of σ calculated from this

(9) R. E. Apfel, *J. Chem. Phys.*, **54**, 62 (1971).

(10) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Amsterdam, Vol. I, 1950; Vol. II, 1965.

(11) E. W. Washburn, *et al.*, Ed., "International Critical Tables," McGraw-Hill, New York, N. Y., 1926–1933.

expression varied from 16.34 ergs/cm² at 160° to 15.57 ergs/cm² at 170°. This relatively small change reflects the fact that hexadecane is far from its critical temperature. Consequently, we see that if the mixtures, as expected, exhibit a behavior intermediate between the two components, then the surface tensions will decrease slower than pure pentane with an increase in temperature and J will have a weaker dependence on temperature. Consequently, a larger spread of nucleation temperatures with size should be expected, as was observed. The higher the concentration of hexadecane the more pronounced this effect should be. In very dilute solutions in solvents far from their critical temperature, the major factor influencing the temperature dependence of J is the variation of vapor pressure with temperature which is generally small relative to the variation in $\sigma^3/(p_c - p_0)^2$ for a one-component liquid. Consequently, nucleation temperatures in very dilute solutions should increase strongly with a decrease in size of the droplets and should have a relatively large scatter for any given size.

The influence of the correction term δ_D in eq 6 may be significant even for the high concentrations considered in our experiments. For a dilution of pentane to $1/2N_0$, $\sigma \sim 3$ and $D \sim 10^{-5}$ δ_D is ~ 40 . This is large enough to make eq 7 valid and leads to a value of J smaller by a factor of ~ 40 . This could raise the calculated nucleation temperature several degrees in the 46 wt % mixture (*e.g.*, about two-thirds of the spread in our measurements of small and large drops where a variation in volume of 10^4 leads to about a 5° spread). For large dilutions this correction term for diffusion can be considerably larger.

Quantitative calculations for the mixtures are not possible because thermodynamic data are not available. Crude estimates of surface tensions and partial pressures of pentane in the mixtures were made by several approximations. The highest estimated nucleation temperatures were obtained when surface tensions were assumed linear in mole fraction¹² and partial pressures linear in volume fraction.¹³ Even these led to temperatures lower than measured if the correction term similar to the one represented in eq 14 were not included. This correction analogous to eq 14 is

$$p_0' - p_0 \cong (p_e' - p_0) \left(1 - \frac{p_e' \bar{V}_{C_6H_{12}}}{RT} \right) \quad (16)$$

where $\bar{V}_{C_6H_{12}}$ is the partial molar volume and p_e' and p_0' are the critical and measured partial pressures of *n*-pentane, respectively. If $\bar{V}_{C_6H_{12}}$ is similar to the molar volume for the pure liquid, then this correction becomes quite large near the critical temperature of *n*-pentane (*e.g.*, it approaches $(1 - z)$) and the calculated temperatures are relatively close to those which are measured (for the linear approximations considered). An accurate check of the theory requires measurements of surface tensions, partial pressures, and diffusion coefficients in the mixtures.

As an empirical observation, it might be noted that nucleation temperatures for *n*-pentane and *n*-hexane are about $0.9T_c$. If this holds for *n*-hexadecane ($T_c \sim 717.15^\circ\text{K}$) one would estimate a nucleation temperature of $\sim 645^\circ\text{K}$ in pure hexadecane. A linear plot of temperature *vs.* mole fraction from the measured temperature for *n*-pentane ($\sim 147.8^\circ$) to that estimated for *n*-hexadecane ($\sim 372^\circ$) goes through the measured data on the mixtures.

In any case, the experiments behave, at least qualitatively, as predicted by theory. Dilution of *n*-pentane by hexadecane raises the surface tension and lowers the vapor pressure. This requires heating to higher temperatures in order to overcome nucleation barriers. The influence of the factor δ_D is probably important, even in the fairly concentrated mixtures studied here. We hope to investigate more dilute solutions to observe cases where this term is more important and where bubble growth is slowed more by diffusion control.

Conclusions

Nucleation theory appears to provide accurate predictions for the maximum temperature of eruption of pure liquids. The qualitative and quantitative nature of the process of nucleation and growth of binary mixtures differs significantly from one-component systems. Further investigations are needed to quantify the theoretical predictions for binary mixtures.

(12) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York, N. Y., 1966.

(13) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, New York, N. Y., 1950.