Limits of Superheat and Explosive Boiling of Light Hydrocarbons, Halocarbons, and Hydrocarbon Mixtures

The limits of superheat of thirteen light hydrocarbons and four light halocarbons were experimentally measured at one atmosphere using a superheating column. While there was some variation in the number of degrees to which a compound could be superheated before boiling explosively, in all cases the reduced limits T_L/T_c were close to 0.88. The measured superheat limits of three binary hydrocarbon systems and several ternary mixtures were close to mole fraction averages of the limits of the pure components. The results of both pure components and mixtures paralleled predictions of Beegle (1973), based on thermodynamic stability theory. Limits of pure components agreed closely with limits predicted from homogeneous nucleation theory.

WILLIAM PORTEOUS

Chemical Engineering Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

and

MILTON BLANDER

Chemical Engineering Division
Argonne National Laboratory
Argonne, Illinois 60439

SCOPE

Studies have shown that when no gas phase is present and nucleation sources are removed, liquids held at one atmosphere can be heated to temperatures considerably above their normal boiling point. Studies have also shown that there is an upper temperature limit to which liquids can be heated without vaporization. At this temperature, referred to as the *limit of superheat,* homogeneous nucleation takes place with an extremely rapid liquid-to-gas phase transformation.

While earlier investigations in this area were done primarily out of scientific curiosity, it now appears that superheat phenomena have practical importance. It has been hypothesized that superheating is the initiating cause of liquid natural gas (LNG) vapor explosions. These are nonchemical flameless explosions that sometimes occur when LNG is spilled on a warmer liquid.

In order to determine whether superheating is the cause of LNG vapor explosions, it is necessary to measure the limits of superheat of hydrocarbons and their mixtures. Previous investigators had found that the limit of superheat for a pure component occurred in a narrow temperature range close to 89% of the critical temperature. Only limited data were available for mixtures and only one study had been done on molecules with three or less carbons. This study was undertaken to determine experimentally the limit of superheat of light halocarbons and hydrocarbons and their mixtures. The technique used to measure the limit involved a superheating column in which droplets of a volatile material rise in a denser immiscible medium. This medium is hotter at the top than at the bottom. The droplets increase in temperature as they rise until they nucleate and boil explosively. The temperature at which they nucleate is referred to as the *limit of superheat.*

Thirteen light hydrocarbons, C_2's to C_4's, and four halogenated hydrocarbons were tested. Three binary systems and several ternary mixtures were also studied. These systems included mixtures of ethane, propane, 2-methylpropane, and *n*-butane.

CONCLUSIONS AND SIGNIFICANCE

The compounds studied could be superheated 84° to 117°C above their boiling points at atmospheric pressure, although the reduced temperature limits T_L/T_c of the hydrocarbons and halogenated hydrocarbons varied over the narrow ranges of 0.8805 to 0.8919, and 0.8668 to 0.8886, respectively. There was a weak relation between the reduced temperature limit and the reduced boiling point with compounds with higher reduced boiling points T_B/T_c having higher reduced limits. This small variation in reduced limits paralleled the predictions by Beegle (1973; Beegle et al., 1974) using thermodynamic stability theory. Where physical property data were available, limits of superheat were calculated from homogeneous nucleation theory and shown to be in good agreement with the measurements.

The limits of superheat of binary mixtures of ethane-propane, ethane-*n*-butane, and 2-methylpropane-propane as well as several ternary mixtures of ethane, propane, and butane were determined. The best rule for determining the limits of these mixtures was a mole fraction average of the limits of the pure components. While the propane-2-methyl-propane system followed this rule closely, there was some variation in the ethane mixtures.

Using a superheat temperature limit for methane pre-

dicted from nucleation theory and the experimental values for the other components, one may easily predict the superheat limit of any LNG mixture using the aforementioned mixing rule. Such a mixing rule could be used to calculate the superheat limit profile in a spill provided the concentration profiles were known. By comparing the superheat limit profile with the temperature profile, one could determine if the limit is being reached and thus if homogeneous nucleation is the cause of LNG vapor explosions. Because the temperature and concentration profiles during spills are unknown, it is now necessary to concentrate efforts on obtaining these profiles.

The limit of superheat of pure liquids may be calculated using two different approaches: one involves nucleation theory, which is based on kinetics, and the other uses thermodynamic stability theory. For nonpolymerizing liquids, the homogeneous nucleation rate per unit volume J is given by

$$J = \frac{N_A}{V_L}\left(\frac{3\sigma}{\pi M}\right)^{1/2} \exp\left(\frac{-16\pi\sigma^3}{3kT(P_G - P_0)^2}\right) \tag{1}$$

(Volmer, 1939; Zeldovich, 1943; Kagan, 1960; Katz and Blander, 1973). The pressure within the vapor nucleus P_G which is given by

$$\int_{P_{eq}}^{P_G} V_G dP = \int_{P_{eq}}^{P_0} V_L dP \tag{2}$$

is less than the saturation pressure. This difference, referred to as the *Poynting correction*, occurs because the liquid is at ambient rather than saturation pressure. Methods of evaluating the integrals in Equation (2) will be covered in the Discussion section.

For an isolated volume of liquid, the probability of nucleation is calculated by integrating the nucleation rate of the volume as a function of time over the length of the experiment. From Equation (1), it can be shown that for pure components near the limit of superheat, J is a strong function of temperature varying about three to six orders of magnitude per degree centigrade. Therefore, for volumes of liquid not extremely different in size, most nucleations will take place over a relatively narrow range of temperature. Thus while nucleation theory does not give an absolute superheat limit, it does enable one to calculate the small range of temperatures in which the probability of nucleation becomes very high. Some work has been done on the nucleation theory of mixtures. However, it has been directed toward nucleation of supersaturated gases (Reiss, 1950; Hirschfelder, 1974).

In contrast with the kinetic limit of superheat, the thermodynamic limit of superheat is a true limit. For pure liquids, it is defined as the temperature at which $(\partial P/\partial V)_T = 0$ at an ambient pressure. The thermodynamic limit of superheat is an absolute upper stability limit of a liquid and must be above the kinetic limit.

Because the region in which $(\partial P/\partial V)_T$ approaches zero is metastable, few physical property measurements have been made in this area. Therefore, it is usually impossible to calculate this derivative based on actual experimental data. However, one can use an equation of state to estimate the properties and, thus, the limit.

Unfortunately, each equation of state gives a different limit. For example, the Redlich-Kwong (1949) and the van der Waals (1899) equations predict a limit of $T_L = 0.89\ T_c$ and $0.84\ T_c$, respectively, for $|P| << P_c$. While this method cannot give us an absolute answer, it does tell us that T_L/T_c for different substances should be nearly constant.

The thermodynamic stability theory for mixtures is straightforward, but more involved. The Redlich-Kwong equation of state and the Soave (1972) modification were used by Beegle (1973) and Beegle et al. (1974) to predict limits of binary mixtures. For several mixtures tested, it was found that the superheat limit was essentially the mole fraction average of the limit of the pure components. Furthermore, it was found that when either the Redlich-Kwong equation or the Soave modification was used, the stability criteria could be written as

$$\left(\frac{\partial P}{\partial V}\right)_{T,N_a,\mu_B} \leq 0$$

Superheat temperatures have been determined experimentally for many compounds. The experimental technique used to measure the limits generally involves heating a group or series of droplets suspended in another immiscible liquid (see Experiment section). In this way chance of heterogeneous nucleation on vessel walls is eliminated. Other experimental techniques for measuring the limit include heating liquids in glass capillaries (Wismer, 1922) and rapid heating of a liquid at a glass interface (Sinha and Jalaluddin, 1961).

Individual limits for approximately 45 compounds have been determined. A summary of these limits for hydrocarbons at one atmosphere is given in Table 1. The limits for all compounds occur at about 0.89 of the critical temperature. In a few cases, the reported limit was less than 0.87 T_c. However, in those studies, the superheated liquid was in contact with a glass interface so that there was a high probability of heterogeneous nucleation.

Other types of superheat studies have also been performed. Limits have been measured for some compounds as a function of pressure (Skripov, 1974). The mean lifetime of superheated drops has also been examined (Skripov, 1974).

In addition to pure components, the limits of superheat for various binary hydrocarbon mixtures have been reported. Binary mixtures of *n*-pentane with *n*-hexane, cyclohexane, *n*-octane, *n*-dodecane, and *n*-hexadecane have been studied (Skripov, 1974; Eberhart et al., 1975; Renner et al., 1974; Blander et al., 1971). Propane-*n*-butane mixtures (Renner et al., 1974) and *n*-heptane-*n*-hexane mixtures (Skripov and Kukushkin, 1961) have also been investigated. In all cases, the limit of superheat was fairly close to a mole fraction average of the limits of the pure components.

Jalaluddin and Sinha (1962) studied the limits of superheat of six nonhydrocarbon binary systems. The limit of superheat exhibited a linear relation in only one of the systems studied. However, their studies were done in the presence of a solid surface so they may have been observing heterogeneous rather than homogeneous nucleation.

EXPERIMENTAL METHOD

We utilized a modification of a technique first introduced by Moore (1956, 1959) and Wakeshima and Takata (1958). An emulsion of the fluid to be investigated and an immiscible denser medium is produced in the lower chamber or pot of the

Table 1. Limit of Superheat of Hydrocarbons

Compound	Limit of superheat (°C)	T_L/T_c	Reference
Normal Alkanes			
Propane	53.0	0.882	Renner et al. (1974)
Butane	105.0	0.890	Eberhart et al. (1975)
	104.7		Renner et al. (1974)
Pentane	132	0.863	Sinha and Jalaluddin (1961)
	144.0	0.888	Skripov and Ermakov (1964)
	145	0.891	Skripov and Kukushkin (1961)
	146	0.893	Wakeshima and Takata (1958)
	146	0.893	Skripov (1966)
	146.1	0.893	Sinitsyn and Skripov (1967)
	147.8	0.896	Blander et al. (1971)
Hexane	137	0.808	Basu and Sinha (1968)
	180.0	0.893	Sinitsyn and Skripov (1968)
	182	0.897	Wakeshima and Takata (1958)
	182.3	0.897	Skripov (1974)
	183.8	0.901	Blander et al. (1971)
	184	0.901	Skripov and Ermakov (1964)
Heptane	157	0.796	Basu and Sinha (1968)
	211	0.896	Wakeshima and Takata (1958)
	212.8	0.900	Skripov (1974)
	213	0.900	Skripov and Kukushkin (1961)
	213.5	0.901	Eberhart et al. (1975)
	214	0.902	Skripov and Ermakov (1964)
Octane	239.8	0.902	Skripov and Ermakov (1964)
Nonane	265.3	0.906	Eberhart et al. (1975)
Decane	285.1	0.904	Eberhart et al. (1975)
Branched Alkanes			
2,2-Dimethylpropane	113.4	0.891	Eberhart et al. (1975)
2-Methylbutane	136	0.889	Wismer (1922)
	138	0.893	Wakeshima and Takata (1958)
	139	0.895	Skripov and Kukushkin (1961)
2,3-Dimethylbutane	173.2	0.893	Eberhart et al. (1975)
2,2,4-Trimethylpentane	215.3	0.898	Eberhart et al. (1975)
Cyclic Hydrocarbons			
Cyclopentane	183.8	0.893	Eberhart et al. (1975)
Cyclohexane	216	0.884	Wakeshima and Takata (1958)
	216	0.884	Skripov and Kukushkin (1961)
	218.5	0.888	Skripov (1974)
	219.6	0.890	Eberhart et al. (1975)
Cyclooctane	287.5	—	Eberhart et al. (1975)
Methylcyclopentane	202.9	0.894	Eberhart et al. (1975)
Methylcyclohexane	237.2	0.892	Eberhart et al. (1975)
Benzene	191	0.826	Sinha and Jalaluddin (1961)
	203	0.847	Kenrick et al. (1924)
	225.3	0.887	Skripov and Sinitsyn (1968)
2,3 Dimethylbenzene	235	0.824	Kenrick et al. (1924)
Normal Alkenes and Alkynes			
1-Pentene	144	0.898	Eberhart et al. (1975)
1-Octene	121	0.901	Eberhart et al. (1975)
1-Hexyne	192	—	Eberhart et al. (1975)

apparatus. This is connected via a capillary to a column above it which is filled with an immiscible fluid. By exerting a mild pressure on a sidearm connected to the pot, some of the emulsion enters the column and the small less dense droplets rise slowly. The temperature in the column is controlled in such a manner that the top is hotter than both the bottom of the column and the lower chamber. Consequently, the droplets are heated as they rise until they nucleate explosively.

Two variants of this basic column technique were used. Both apparatus were constructed of Pyrex. For fluids whose normal boiling point was below and limit of superheat above room temperature, an apparatus similar to that described by Renner et al. (1974) was used. The pot was immersed in a cold slush bath and the column was wound with nichrome heating wire. The windings were spaced more closely at the top than at the bottom so that the fluid in the top of the column was hotter than the bottom. The overall height of the column was 56 cm and the outside diameter was 3.5 cm. The capillary diameter was 1 mm.

For materials whose superheat limit was below room temperature, a double-jacketed column (see Figure 1) was constructed (Schulze, 1974). The lower chamber contained two ports which could be sealed with ground glass connectors—one had a thermocouple well which dipped into the medium, and the other was connected to a tube through which the pot was pressurized. The pot was immersed in an appropriate slush bath contained in a large Dewar and was connected via a 2-mm capillary to the column. The column was surrounded by two jackets. The inner jacket contained a circulating coolant (glycol-water mixtures) which was also pumped through a copper coil in an appropriate slush bath and then upward through the inner jacket. The pumping rate was slow enough to develop a small temperature gradient. The outer vacuum jacket served as insulation. Temperature was controlled by the flow rate and by setting the temperature of the bath through which the coolant passed.

Temperatures in the heated column were measured by platinum-platinum 10% rhodium thermocouples set in L-shaped thermocouple wells. The wire was NBS certified and a check using an NBS standardized thermocouple indicated that the E.M.F. differed from NBS reference tables by less than 1μV. Temperatures in the jacketed column were measured with copper-copper-nickel thermocouples. The E.M.F. differed from the NBS tables by less than 5μV in the temperature range of interest.

The procedures used were as follows The wire-wound colum was cleaned, clamped in place, and filled with the medium. Line voltage was stabilized by a constant voltage transformer. Voltage fed to the nichrome wires was controlled using a Variac. The temperature was allowed to stabilize for periods as long as several hours. About 5 cc of the liquid to be tested was first condensed and subcooled in a 15-cc graduated test tube, submerged in a slush bath, and then poured into the cooled medium in the lower chamber. The liquid was emulsified in the medium with a wire agitator and the lower chamber

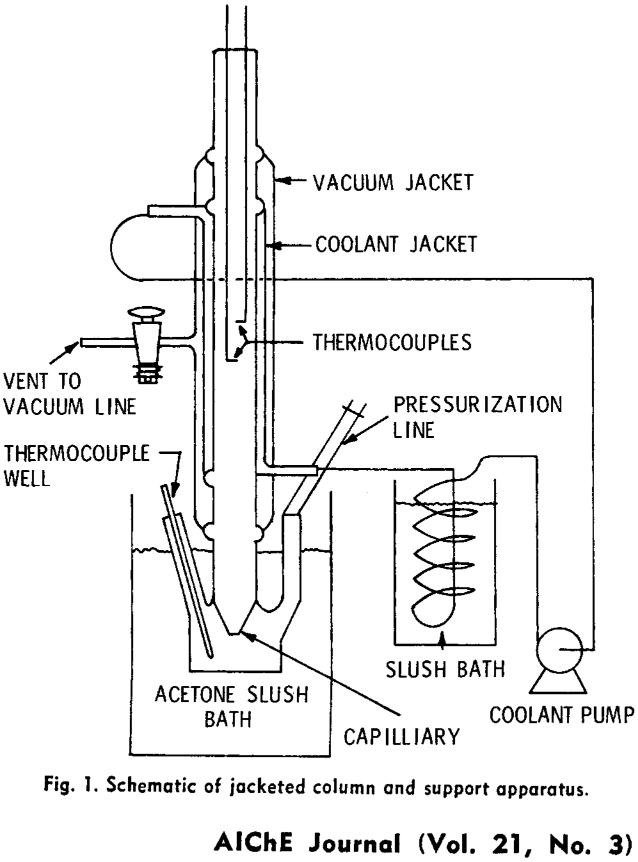

Fig. 1. Schematic of jacketed column and support apparatus.

was pressurized until some of the emulsion entered the upper column. The emulsified droplets rose until they nucleated explosively. Two thermocouples near the top of the column were positioned so that one was just above and the other just below the region where about 95% of the explosions took place. If nucleation took place over a region in the column smaller than 2 cm, the temperature gradient was reduced to increase the accuracy. For each experiment, a minimum of 100 droplets was observed and at least two separate experiments were performed with each substance.

The procedure with the double-jacketed column was similar except that the temperature and temperature gradient were altered by adjusting the speed of the coolant pump or by utilizing a different slush bath. With an ammonia-water mixture at very low temperatures, the fluid at the bottom was so viscous that it was occasionally necessary to aid the rise of the droplets. This was done by mild agitation of the fluid at the bottom of the column or by lowering the level of the acetone slush bath, warming the bottom of the column and lowering the viscosity of the medium.

When the liquid to be studied was a mixture, an additional procedure was followed to sample and analyze the mixture. This was done after the temperature measurements had been made. A glass tube was chilled in liquid nitrogen and attached via a stopcock to a 250-cc evacuated sample flask. The tube was then inserted into the pot, the fluid in the lower chamber was agitated and the stopcock on the sample tube was opened, withdrawing about 75 cc of the emulsion. The sample was allowed to come to room temperature. If the column medium was an ammonia-water solution, it was neutralized with concentrated hydrochloric acid. The flask was then vigorously heated to degas the sample. The gas was sampled with a syringe and injected into a gas chromatograph for analysis.

Three media were used. One was an ethylene glycol-water eutectic (47.5 mol % glycol) which could be used for liquids which boil at temperatures as low as −63.3°C. A lithium chloride-water eutectic solution (25.2 wt % LiCl) could be used for liquids which boil as low as −84°C. The reagent grade lithium chloride used contained insoluble impurities which were heterogeneous nucleation sites and caused the droplets to boil prematurely. This problem was eliminated by passing the solution through a 5μ ceramic filter. An ammonia-water eutectic (34.5 wt % NH_3) could be used for liquids boiling as low as −100°C. This eutectic was made by enriching reagent grade ammonium hydroxide obtained from Fisher with 99.99% pure ammonia obtained from Matheson.

With the exception of propadiene, all purities[*] of the compounds studied were at least 99%.

RESULTS

Results for pure fluids are listed in Table 2. All compounds were run at least twice. Some were measured both in an ethylene glycol-water medium and in a lithium chloride-water medium. The measured limit of superheat was independent of medium, with the exception of 1,3 butadiene, which was about 1°C higher in an ethylene glycol solution. This was probably caused by the dissolution of some ethylene glycol in the butadiene, thus raising the limit. The limit listed in Table 2 was obtained with the LiCl solution. More than 95% of the nucleation events took place over a total range of 1°C (±0.5°C) except for ethane which nucleated over a total range of 2°C (±1°C). The limits listed in Table 2 are given to the nearest 0.1° and represent the midpoint of the nucleation range. The temperature gradient in the column at the nucleation temperature was about 0.5°C/cm. Critical temperatures are in degrees Kelvin (IPTS68) and were obtained from Porteous (1975) and Kudchadker et al. (1968).

Butane and propane were the only compounds in Table 2 which had been studied previously (Renner et al., 1974; Eberhart et al., 1975). Our results for propane are consistent with those of Renner et al. (1974). Results for butane were 1.3°C lower than reported by Eberhart et al. (1975), and 1.0°C lower than reported by Renner et al. (1974), who used the same source of butane.

The seventeen substances measured could be superheated about 84° to 117° above their normal boiling points. The reduced limits of superheat ranged from about 0.87 to 0.89 and are generally larger than 0.88. As will be discussed, where calculations may be made, this small range in the reduced limits is consistent with predictions of kinetic limits of superheat from nucleation theory and parallels but is lower than the thermodynamic limits calculated from stability theory (Beegle, 1973; Beegle et al., 1974).

The results for the three binary mixtures are given in Figures 2 to 4. The temperature range of the measurements at a given composition is indicated by vertical bars. The data for the propane-2-methyl propane system in Figure 2 scattered little and the limits of superheat were close to the mole fraction average of the two pure components. The ethane-propane data in Figure 3 exhibited considerably more scatter, and the limits of superheat did not differ much from the mole fraction average of the two pure components. The ethane-*n*-butane data in Figure 4 exhibited even more scatter at low ethane concentrations (as much as 15°C). However, the mole fraction average

TABLE 2. LIMITS OF SUPERHEAT

Compound	Limit of super-heat, °C	Boiling point, °C	Critical temp., K	Limit/ critical, K/K	Reduced boiling point, K/K
Ethane	−4	−88.2	305.43	0.881	0.6055
Propane	53.0	−42.07	369.82	0.882	0.6248
Cyclopropane	77.5	−32.86	397.80	0.881	0.6040
Propene	52.4	−47.7	365.0	0.892	0.6177
Propadiene	73.0	−34.5	393	0.881	0.607
Propyne	83.6	−23.2	402.38	0.887	0.6212
n-Butane	103.7	−0.5	425.16	0.886	0.6413
2-Methylpropane	87.8	−11.7	408.13	0.884	0.6405
1-Butene	97.8	−6.3	419.55	0.884	0.6361
Cis 2-butene	112.2	+3.7	435.55	0.885	0.6357
Trans 2-butene	106.5	+0.9	428.61	0.886	0.6394
2-Methylpropene	96.4	−6.9	417.89	0.884	0.6371
1,3 butadiene	104.1	−4.4	425	0.888	0.632
Chloromethane	93.0	−24.2	416.25	0.880	0.5980
1,1-Difluoroethane	70.4	−24.7	386.6	0.889	0.6427
Chloroethene	100.9	−13.9	431.55	0.867	0.6007
Fluoroethene	16.9	−72.2	327.8	0.885	0.6130

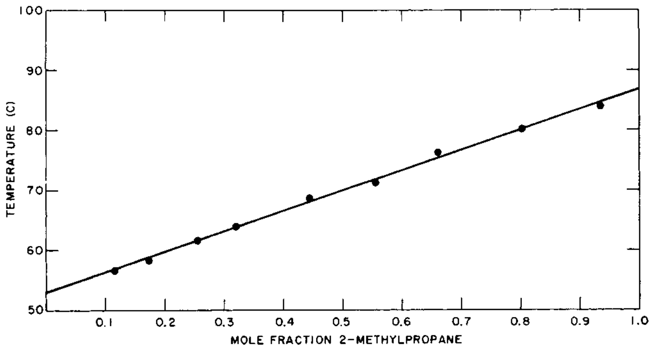

Fig. 2. Measured limits of superheat of propane—2-methylpropane liquid mixtures.

---

[*] The minimum purities are given in the Supplement which has been deposited as Document No. 02593 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N.Y., N.Y. 10017 and may be obtained for $1.50 for microfiche or $5.00 for photocopies.

gives the best correlation with the results. Previous measurements of higher boiling hydrocarbons have exhibited similar results which are essentially linear in mole fraction and when boiling points of the hydrocarbon were very different, scatter was also observed. Small droplets tended to nucleate at higher temperatures than large drops (Blander et al., 1971; Eberhart et al., 1975). The linearity in mole fractions parallels the predictions of Beegle (1973; Beegle et al., 1974) from stability theory.

A number of measurements made on ternary ethane-propane-butane mixtures are listed in column 4 of Table 3. The mole fraction average of the three limits of superheat of the three components are also listed in column 5 of Table 3. The mole fraction average for each composition is within 3°C of the measured nucleation range. Again, the small droplets tended to nucleate at higher temperatures than did large droplets.

TABLE 3. LIMIT OF SUPERHEAT OF TERNARY MIXTURES OF ETHANE, PROPANE, AND *n*-BUTANE

Component Mole Fraction			Limit of Superheat, °C	
Ethane	Propane	*n*-Butane	Observed	Calculated
0.806	0.155	0.039	5.3-8	9.0
0.806	0.073	0.121	7.7-10.3	13.2
0.092	0.811	0.097	50.9-56.7	49.7
0.100	0.771	0.129	52.9-57.8	50.3
0.235	0.433	0.332	51.7-71.1	56.5
0.113	0.652	0.235	56.3-61.6	58.5
0.160	0.299	0.541	64.7-81.3	71.4
0.076	0.403	0.521	69.3-79.9	75.2
0.135	0.160	0.705	71.4-82.7	81.3

DISCUSSION

The size of the droplets varied from about 0.05 mm to 1 mm in diameter. If one considers the sole source of heat transfer within the droplets to be conductive, the temperature at the center of the largest drops would reach 90% of the surface temperature in less than a half of a second. Because convective heat transfer is also taking place, the 90% relaxation time is probably considerably less. Furthermore, most droplets had diameters notably less than 1 mm and the relaxation time decreases with the square of the diameter. Because the heating rate for a droplet is about 1°C/s, the temperature of the droplet can be taken as that of the column fluid within 0.1°C.

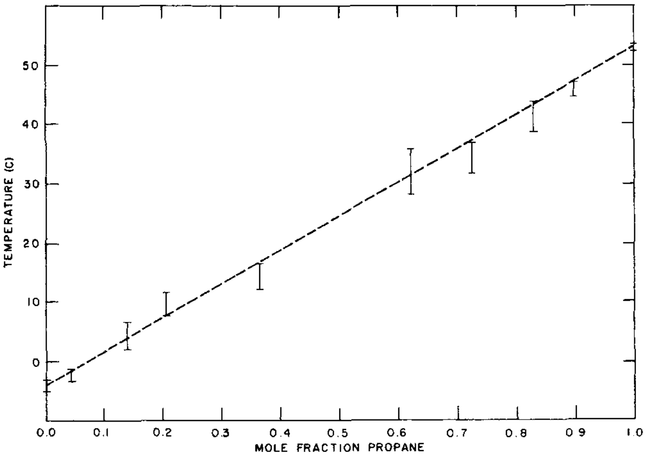

Fig. 3. Measured limits of superheat of ethane-propane liquid mixtures.

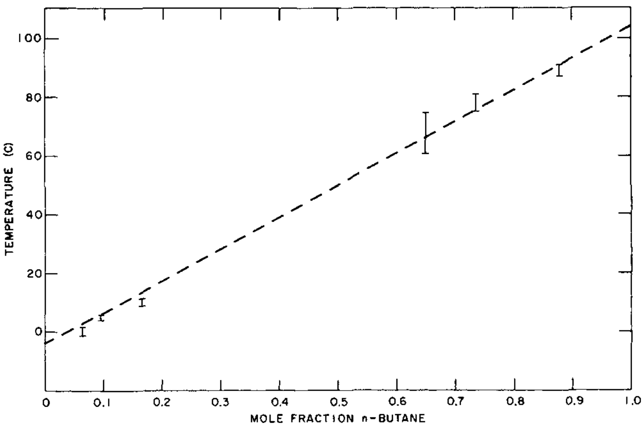

Fig. 4. Measured limits of superheat of ethane—*n*-butane liquid mixtures.

The nucleation rates at the experimental limits of superheat may be calculated using Equations (1) and (2). Physical property data to do the calculation were only available for eight of the substances studied.* Surface tensions had to be obtained by extrapolation for all compounds except the normal alkanes (Porteous, 1975).

An exact solution of Equation (2) involves a trial and error procedure. Assuming constant compressibility of the gas and an incompressible liquid P_G may be approximated by

$$P_G \cong P_{eq} \exp \frac{V_L(P_{eq} - P_0)}{ZRT} \quad (3)$$

or

$$(P_G - P_0) \cong (P_{eq} - P_0) \left(1 - \frac{V_L}{V_G} + \frac{1}{2}\left(\frac{V_L}{V_G}\right)^2 + \dots\right) \quad (4)$$

with an error of less than 0.1°C in T_L compared with the numerical integration which follows.

Because integration of the right-hand side of Equation (2) takes place over a metastable region, no liquid volume measurements were available. Therefore, in our numerical solution of Equation (2), incompressibility of the liquid was assumed. However, the integration of the left-hand side takes place over a stable region and compressibility of the gas was calculated using the Redlich-Kwong equation of state, as modified by Soave (1972).

Nucleation rates and values of $d \ln J/dT$ at the experimental limits are given in Table 4 based on the numerical calculations. The wide spread variations in the calculated values of J probably represent uncertainty in the extrapolation of physical properties, especially of surface tensions. The calculations are very sensitive to small errors in surface tensions.

Equation (1) can be used to calculate a nucleation rate at a given temperature for a particular droplet. However, one cannot use Equation (1) to calculate the limit of superheat of a group of drops unless one knows what rate is commensurate with a limit of superheat for the given experimental conditions. Because nucleation is a stochastic process, one can only calculate a temperature at which a given fraction of drops will be left.

For a group of droplets the rate of droplet loss is given by

$$\frac{dn}{dt} = -nVJ \quad (5)$$

---

* Physical property references and details of the extrapolation procedure are available in the Supplement.

TABLE 4. CALCULATED AND MEASURED LIMITS OF SUPERHEAT

Substance	Theory T_L (K) @ $J = 10^6$ (cm^3·s)$^{-1}$	Measured T_L (K)	ΔT (K)	J(cm^3·s)$^{-1}$ Calc. @ $T = T_L$ (expt.)	$d\ln J/dT$ (K^{-1})
Methane	165.5	—	—	—	13.8
Ethane	269.7	269.2	0.5	3.06×10^{-3}	10.6
Propane	328.5	326.2	2.3	2.79×10^{-4}	10.6
2, Methylpropane	360.8	361.0	−0.2	4.05×10^{6}	7.5
n-Butane	378.3	376.9	1.4	8.60	8.7
Propene	323.5	325.6	−2.1	3.32×10^{12}	6.4
2, Methylpropene	372.4	370.0	2.4	1.98×10^{-5}	10.1
1 butene	373.4	371.0	2.4	1.16×10^{-3}	9.6
Propyne	361.4	356.8	4.6	9.50×10^{-15}	12.7

An analytic solution to this equation is impossible for J is an involved function of temperature, which is varying with time. However, for our purposes it is sufficiently accurate to approximate J as a simple exponential function of temperature. Thus, for a constant heating rate, integration of Equation 5 leads to (Eberhart et al., 1975)

$$J = -\ln\left(\frac{n}{n_0}\right)\frac{(dT/dt)(d\ln J/dT)}{V} \qquad (6)$$

By choosing a value of n/n_0, one may obtain a value of J from Equation (6) and back calculate a temperature limit using Equation (1).

To calculate a J commensurate with our experimental conditions, the following values were chosen. A median drop diameter of 0.2 mm was taken. Actual drop sizes varied from about 0.05 to 1 mm in diameter. The rate of rise of the 0.2-mm droplets was about 1 cm/s, and, based on a typical temperature gradient in the nucleation region of the column of 0.5°C/cm, the value of dT/dt is 0.5°C/s. A value of 9/°C for $d\ln J/dT$ was arrived at by taking an average of the values at the experimental limit (see Table 4). The fraction of drops remaining n/n_0 was chosen to be 0.5. Using these values and Equation (6), the order of magnitude estimate of J is 10^6(cm^3 · s)$^{-1}$.

Using this value and Equation (1), theoretical limits were calculated for the various compounds studied. The results of these calculations are given in Table 4. As can be seen in the last column of this table, nucleation rates are strong functions of temperature and vary by three to four orders of magnitude per degree. Therefore, even if the nucleation rate which is commensurate with our measurements were somewhat different, the calculated temperatures would not differ much (for example, about 0.3 degrees different per order of magnitude). As shown in Table 4, the limits of superheat calculated from nucleation theory are in good correspondence with all but one of the measured values. For propyne, the difference of 4.6 degrees probably reflects uncertainties in extrapolation of surface tension data.

The mole fraction average mixing rule for limits of superheat of hydrocarbons is significant for analyzing proposed nucleation mechanisms for vapor explosions. If the mass flux equations can be solved to give the spatial and temporal variations in concentration of superheated mixtures, one may deduce the spatial and temporal variations of the limits of superheat. Similar near linear behavior for mixtures has been observed for a few hydrocarbon mixtures (Blander et al., 1971; Eberhart et al., 1975; Renner et al., 1974; Skripov, 1974; Skripov and Kukushkin, 1961).

For both the binary and ternary mixtures there was a fairly large scatter in the measurements for mixtures with a low concentration of ethane. For one of the ternaries, the range spanned 20°. One possible explanation is related to the technique. Mixtures low in ethane could not be run in ammonia-water solutions which boil below the limit of superheat. Consequently, they were run in a lithium chloride solution which was kept at −78°C in the lower chamber with a dry ice bath. As this temperature was close to the boiling points of some of the mixtures studied, there was a small amount of vaporization of ethane from the mixture in the neck of the lower chamber during introduction. This may have led to variations in the composition of the individual droplets and to a spread in nucleation temperatures. This evaporation was minimized but not eliminated by subcooling the liquid before introduction to the pot.

A second explanation for the scatter can be deduced from theory if the rate of nucleation is a weak function of temperature. From Equation (6), one may deduce that small droplets will nucleate at a higher temperature than large droplets. For example, if for mixtures, $d\ln J/dT = 1$, 0.1-mm droplets will, on the average, nucleate about 4.6°C higher than 1-mm droplets. In addition, droplets of a given size will nucleate over a large range of temperatures. For example, when $d\ln J/dT = 1$, 80% of droplets of a given size will nucleate in a total range of 3.1° and 98% in a total range of 6.1°. Thus, there should be overlap between the small and large droplets. This is consistent with our observations of a tendency for small drops (0.1 mm) of some mixtures to nucleate at a higher temperature than large drops (0.5-1 mm) with a significant overlap. This phenomenon has been observed before for hydrocarbon mixtures of constituents with large differences in their boiling points (Blander et al., 1971; Eberhart et al., 1975). Since $d\ln J/dT$ is unknown for mixtures, this second explanation is as yet unproven.

A third, but less likely explanation for the spread in temperatures involves solubilization of the more volatile component into the medium during the rise of the droplet in the upper high temperature portion of the column. Since the small droplets rise more slowly, they would lose more of the volatile component and nucleate at a higher temperature. If this were the entire explanation, droplets of any given size should lose about the same amount of the volatile constituent and the spread in temperature observed for a given size should not be observable.

Methods for estimating limits of superheat are necessary for some applications. For hydrocarbon mixtures, the best estimate is the mole fraction average of the limits of the pure components. Where these are unavailable, Equation (1) may be used when data for the calculation are available. If data are not available for pure hydrocarbons, an empirical relation deduced by Eberhart et al. (1974) may be used for hydrocarbons boiling above room temperature

$$\frac{T_L}{T_c} = 0.755 + 0.21\frac{T_b}{T_c} \qquad (7)$$

For the hydrocarbons we studied, variations with the reduced boiling point were smaller and the relation

$$\frac{T_L}{T_c} = 0.8122 + 0.1156\,\frac{T_b}{T_c} \qquad (8)$$

holds with a standard deviation of 0.0025. It is remarkable that the results [represented by Equations (7) and (8)] exhibit a small range in the reduced nucleation temperature T_L/T_c, and reliable values of the reduced nucleation temperature vary from about 0.87 to 0.91. These limits are based on droplet diameters of 0.1 to 1 mm. For systems where the heating rate is constant, the limit is reduced by about 1°C for each order of magnitude increase in diameter.

ACKNOWLEDGMENTS

We would like to thank Myron I. Homa for performing the gas chromatographic analyses and William Schulze for constructing the glass apparatus. This work was performed largely under the auspices of the U.S. Atomic Energy Commission. W. Porteous was supported by a grant from the American Gas Association through the LNG Research Center, Department of Chemical Engineering, Massachusetts Institute of Technology.

NOTATION

J = nucleation rate
M = molecular mass
n = number of droplets remaining
n_0 = number of droplets at beginning of experiment
N_A = Avogadrós number
N_i = moles of component i
P = pressure
P_{eq} = saturation pressure
P_G = pressure within nucleus
P_0 = pressure on system, 1 atm
t = time
T = temperature
T_b = normal boiling point
T_c = critical temperature
T_L = superheat limit temperature
V = volume of droplet
V_L, V_G = molar volume of liquid and gas respectively

Greek Letters

μ_i = chemical potential of component i
σ = surface tension

LITERATURE CITED

Basu, D. K., D. B. Sinha, "A Study of Superheat Property of Liquids," *Indian J. Physics*, **42**, 198 (1968).

Becker, R., and W. Döring, "The Kinetic Treatment of Nuclear Formation in Supersaturated Vapors," *Ann. Phys.*, **24**, 719, 752 (1935).

Beegle, B. L., "Stability Analysis of Multicomponent Systems," S.M. thesis, Mass. Inst. Technol., Cambridge (1973).

Beegle, B. L , M. Modell, and R. C. Reid, "Thermodynamic Stability Criterion for Pure Substances and Mixtures," *AIChE J.*, **20**, 1200 (1974).

Blander, M., D. Hengstenberg, and J. L. Katz, "Bubble Nucleation in *n*-Pentane, *n*-Hexane, *n*-Pentane + Hexadecane Mixtures, and Water," *J. Phys. Chem.*, **75**, 3613 (1971).

Eberhart, J. G., W. Kremsner, and M. Blander, "Metastability Limits of Superheated Liquids: Bubble Nucleation Temperatures of Hydrocarbons and Their Mixtures," *J. Colloid Interface Sci.* (1975), to be published.

Farkas, L., "The Velocity of Nucleus Formation in Supersaturated Vapors," *Z. Physik. Chem.*, **125**, 236 (1927).

Frenkel, J., "Kinetic Theory of Liquids," Ch. VIII, Dover, New York (1955).

Hirschfelder, J. O., "Kinetics of Homogeneous Nucleation in Many Component Systems," *Theoretical Chem. Ins.*, Univ. Wisconsin, Madison (1974).

Jalaluddin, A. K., and D. B. Sinha, "Maximum Superheat of Binary Liquid Mixtures," *Indian J. Physics*, **36**, 312 (1962).

Kagan, Yu., "The Kinetics of Boiling of a Pure Liquid," *Russ. J. Phys. Chem.*, **34**, 42 (1960) (Engl. Trans.); *Zh. Fiz. Khim.*, **34**, 92 (1960).

Katz, J. L., and M. Blander, "Condensation and Boiling: Corrections to Homogeneous Nucleation Theory for Nonideal Gases," *J. Colloid Interface Sci.*, **42**, 496 (1973).

Kenrick, F. B., C. S. Gilbert, and K. L. Wismer, "The Superheating of Liquids," *J. Phys. Chem.*, **28**, 1297 (1924).

Kudchadker, A. P., H. A. Ghalib, and B. J. Zwolinski, "The Critical Constants of Organic Substances," *Chem. Rev.*, **68**, 659 (1968).

Moore, G. R., "Vaporization of Superheated Drops in Liquids," Ph.D. thesis, Univ. Wisconsin (1956) (Univ. Microfilms Publ. No. 17, 330, Ann Arbor, Mich.).

———., "Vaporization of Superheated Drops in Liquids," *AIChE J.*, **5**, 458 (1959).

Porteous, W. M., "Calculating Surface Tensions of Light Hydrocarbons and their Mixtures," *J. Chem. Eng. Data*, in press.

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions V," *Chem. Rev.*, **44**, 233 (1949).

Reiss, H., "Kinetics of Phase Transitions in Binary Systems," *J. Chem. Phys.*, **18**, 840 (1950).

Renner, T. A., and G. H. Kucera, "Explosive Boiling in Light Hydrocarbons and Their Mixtures," in Blander et al. Annual Report, Phys. Inorganic Chem. Group, ANL-8123, p. 13, Argonne National Lab., Ill. (1974).

Schulze, W. J., "A Multi-Jacketed Glass Apparatus for Measuring the Limit of Superheat of Ethane and Its Mixtures," *Proc. 19th Symp. on Art of Glassblowing*, Am. Soc. of Scientific Glassblowers (1974).

Sinha, D. B., and A. K. Jalaluddin, "On the Superheat of Liquids," *Indian J. Phys.*, **35**, 311 (1961).

Sinitsyn, E. N., and V. P. Skripov, "Experimental Investigation of the Kinetics of Boiling of a Superheated Liquid," *Ukr. Fiz. Zh.*, **12**, 99 (1967).

———————., "Kinetics of Nucleation in Superheated Liquid," *Russ. J. Phys. Chem.*, **42**, 440 (1968) (Engl. Transl.); *Zh. Fiz. Khim.*, **42**, 844 (1968).

Skripov, V. P., "Statistical Theory of the Spinodal Curve," *Zh. Fiz. Khim.*, **40** (9), 2060 (1966).

———., "Metastable Liquids," Trans. by R. Kondor, Wiley, New York (1974).

Skripov, V. P., and G. V. Ermakov, "Pressure Dependence of the Limiting Superheating of a Liquid," *Russ. J. Phys. Chem.*, **38**, 208 (1964) (Engl. Transl.); *Zh. Fiz. Khim.*, **38**, 396 (1964).

Skripov, V. P., and V. I. Kukushkin, "Limit of Superheat of a Liquid," *Russ. J. Phys. Chem.*, **35**, 1393 (1961) (Engl. Transl.); *Zhur. Fiz. Khim.*, **35**, 2811 (1961).

Skripov, V. P., and E. N. Sinitsyn, "Nucleation in Superheated Liquids and Surface Tension," *Russ. J. Phys. Chem.*, **42**, 168 (1968) (Engl. Trans.); *Zh. Fiz. Khim.*, **42**, 309 (1968).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Van der Waals, J. D., *Die Continuität des Gasformigen und Flüssigen Zustandes*, Barth, Leipzig (1899).

Volmer, M., *Kinetic der Phasenbildung*, Theodor Steinkopff, Dresden (1939); Engl. transl., *Kinetics of Phase Formation;* refer to ATI No. 81935 (F-TS-7068-RE) from the Clearinghouse for Fed. and Tech. Information.

Volmer, M., and A. Weber, "Nucleus Formation in Supersaturated Systems," *Z. Phys. Chem.*, **119**, 277 (1926).

Wakeshima, H., and K. Takata, "Limit of Superheat," *J. Phys. Soc. Jap.* **13**, 1398 (1958).

Wismer, K. L., "The Pressure Volume Relation of Superheated Liquids," *J. Phys. Chem.*, **26**, 301 (1922).

Zel'dovich, Ya. B., "Theory of New Phase Formation: Cavitation," *Acta Physicochim. U.R.S.S.*, **18**, 1 (1943) (In Engl.).

Manuscript received December 17, 1974; revision received January 28 and January 29, 1975.