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## Energetics of Vapor Explosions

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Definitive experiments on large-scale explosive boiling systems have shown that intimate contact between hot and cold liquids, and a temperature upon contact that is greater than the spontaneous nucleation temperature of the system, are two necessary conditions for the onset of large scale vapor explosions. While for certain systems, this knowledge of the necessary conditions may allow the exclusion of explosive boiling from the possible spectrum of events, for other systems it may indicate that such events must definitely be considered. In the latter case, it is necessary to also evaluate the energetics of such explosive interactions. In this paper, a model, based on spontaneous nucleation of the homogeneous type, is proposed to describe the relevant processes and the resulting energetics for explosive boiling systems.

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## ABSTRACT

Definitive experiments on large-scale explosive boiling systems have shown that intimate contact between hot and cold liquids, and a temperature upon contact that is greater than the spontaneous nucleation temperature of the system, are two necessary conditions for the onset of large scale vapor explosions. While for certain systems, this knowledge of the necessary conditions may allow the exclusion of explosive boiling from the possible spectrum of events, for other systems it may indicate that such events must definitely be considered. In the latter case, it is necessary to also evaluate the energetics of such explosive interactions. In this paper, a model, based on spontaneous nucleation of the homogeneous type, is proposed to describe the relevant processes and the resulting energetics for explosive boiling systems.

The model considers that spontaneous nucleation cannot occur either during the acoustic relief time for constant volume heating or until the thermal boundary layer is sufficiently thick to support a vapor cavity of the critical size. These considerations lead to the prediction that, for a given temperature, drops greater than a critical size will remain in film boiling due to coalescence of vapor nuclei and drops smaller than this value will wet and be captured by the hot liquid surface. Once a drop has been captured by a hot liquid surface, it will remain on the surface and store energy until unstable vapor growth within the drop can no longer be restrained by the combination of surface tension, liquid inertia, and condensation within the drop. At this point, vapor will penetrate the entire thickness of the cold liquid drop and expose the immediate surroundings to its pressure. These results are compared to data for well-wetted systems and agreement is obtained between the onset of vapor explosions and the energetics of the events. A consequence of this model is that fine fragmentation must be achieved before a large scale vapor explosion can occur.

When the interface temperature upon contact is considerably greater than the thermodynamic critical temperature of the cold liquid, the model predicts the cessation of large-scale explosions in the free contacting mode considered.

## NOMENCLATURE

A	area
A(T)	preexponential term
C	specific heat
c	velocity of sound
D	bubble diameter
J	nucleation frequency per unit volume
k	thermal conductivity
k <sub>1</sub>	Boltzmann's constant
l	characteristic thickness
m	mass
N	number of nuclei
P	pressure
Q	energy
r	bubble radius
s	entropy
T	temperature
t	time
V	volume
W	work to form a vapor bubble
x	quality
x <sub>1</sub>	distance
y	length of hot liquid expelled
z	length

## Greek

$\alpha$	thermal diffusivity
$\Delta$	change
$\rho$	density
$\sigma$	surface tension

## Subscripts

a	acoustic
atm	atmosphere
c	cold
crit	critical
fg	difference between vapor and liquid
g	growth
H	hot
i	interface
I	interaction
l	liquid
n	nucleation
o	initial condition
v	vapor
w	waiting

\*Work performed under the auspices of the U. S. Atomic Energy Commission.

## I. INTRODUCTION

The possible occurrence and magnitude of vapor explosions has been the subject of many analytical and experimental efforts for a wide variety of industrial applications, i.e., aluminum and steel foundries, liquefied natural gas transportation, the nuclear industry, and the paper industry. Such experimental investigations have resulted in the formulation of a list of necessary but not sufficient conditions for these explosions. These conditions are that (1) two liquids, one hot and one cold, must be present, (2) the liquids must come into intimate contact, and (3) the hot liquid temperature must be greater than some minimum value before these explosions can occur. These investigations have also led to the formulation of several parametric models<sup>1,2,3</sup> which basically assume that fine fragmentation and intimate mixing of the hot and cold liquids have already occurred. After the dispersal and intimate mixing of the two liquids, these models calculate the energy transfer rate via standard heat transfer mechanisms (conduction or convection) and they can be used to determine the sensitivity of the results to variations in the input parameters. One unique discrepancy between the observed vapor explosions and these parametric models is that experimentally a definite thermal threshold is observed, below which no violent explosive interactions occur, whereas the parametric models do not predict this thermal threshold. A proposed explanation for this threshold<sup>4</sup> states that the interface temperature upon contact between the two liquids, as derived in Ref. 5,

$$T_i = \frac{T_H + \sqrt{\frac{k_H \rho_H C_H}{k_C \rho_C C_C}} T_C}{1 + \sqrt{\frac{k_H \rho_H C_H}{k_C \rho_C C_C}}} \quad (1)$$

must be greater than or equal to the temperature for spontaneous nucleation for that particular system.

The purpose of this paper is to begin with the proposal outlined in Ref. 4, and investigate (1) the conditions which must be satisfied before random nuclei can grow within a nonisothermal liquid, and (2) the nature of the heat transfer process at the interface between the hot and cold liquids under explosive boiling conditions. Based on these conditions, a model is formulated to describe the energetics of a vapor explosion and it is compared to experimental data obtained in well-wetted systems.

## II. NUCLEATION

The mechanism described in Ref. 4 considers spontaneous nucleation upon contact, which may be either heterogeneous or homogeneous nucleation depending on the transient wetting characteristics of the given system.<sup>6,7</sup> Heterogeneous nucleation is a condition where random vapor embryos are generated at the interface between two liquids because of the reduced interfacial tension, and homogeneous nucleation is the condition where these embryos are generated within the bulk of the cold liquid. For simplicity, well-wetted systems will be considered which means that the nucleation is homogeneous within the cold fluid. The frequency of formation for critical size vapor cavities is given by the classic equation for nucleation

$$J = A(T) e^{-\frac{W}{k_1 T}} \quad (2)$$

where  $J$  describes the frequency of nucleation sites per unit volume at a given temperature and pressure. (For the conditions considered in this paper, the pressure at nucleation is assumed to be 1 atm.) The preexponential factor  $A(T)$ , involves all the details of formulating vapor embryos (accommodation coefficients for evaporation and condensation, etc.), but, as will be shown, this term can be in error by several orders of magnitude and have little effect on the temperatures calculated for spontaneous nucleation. In the exponential term,  $k_1$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $W$  is the work required to form a spherical vapor bubble.

$$W = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 [P_L - P_V] \quad (3)$$

At the limit of mechanical stability for a vapor embryo,

$$P_V - P_L = \frac{2\sigma}{r} \quad (4)$$

Substitution of Eq. 4 into Eq. 3 and assuming that  $P_V \gg P_L$  simplifies Eq. 3 to:

$$W = \frac{16\pi\sigma^3}{3P_V^2} \quad (5)$$

Equation 2 exhibits a very strong temperature threshold as illustrated in Table I for homogeneous nucleation of Freon-22. The frequency of nucleation increases many orders of magnitude within a very narrow temperature band. Small scale, definitive experiments have been carried out to verify the temperature threshold predicted by Eq. 2, and excellent agreement has been obtained for a wide variety of liquids at several different pressure levels.<sup>6,8,9,10</sup>

TABLE I  
HOMOGENEOUS NUCLEATION OF FREON-22  
 $J = A(T) \exp(-\frac{W}{k_1 T})$

TEMP. °C	$P_V$ BARS	$\sigma$ DYNES/CM	$r$ Å	NUMBER OF MOLECULES	$J$ $CM^{-3} SEC^{-1}$	WAITING TIME FOR 1 $CM^3$
50	19.8	4.71	46	291	$1.88 \times 10^{-12}$	16.807 yrs
52	20.3	4.46	44	226	$5.52 \times 10^{-3}$	3 min
54	21.2	4.22	40	179	$1.33 \times 10^6$	$1 \times 10^{-6}$ sec
56	22.3	3.97	36	136	$7.96 \times 10^{17}$	$1 \times 10^{-21}$ sec
58	23.2	3.73	32	100	$1.75 \times 10^{16}$	$6 \times 10^{-17}$ sec
60	24.3	3.46	28	79	$4.21 \times 10^{22}$	$2 \times 10^{-22}$ sec
65	27.0	2.91	22	39	$6.2 \times 10^{27}$	$2 \times 10^{-28}$ sec
70	30.0	2.35	16	17	$6.8 \times 10^{37}$	$1 \times 10^{-31}$ sec
75	33.2	1.81	11	7	$1.5 \times 10^{40}$	$7 \times 10^{-33}$ sec
80	36.6	1.30	7	2	$5.0 \times 10^{40}$	$2 \times 10^{-33}$ sec
85	40.4	0.82	4	<1	$9.2 \times 10^{40}$	$1 \times 10^{-33}$ sec

These definitive experiments generally consider systems in which the heating rate of the cold liquid is very slow, i.e., of the order of several seconds. In such systems, the cold liquid is basically in thermal equilibrium with its surroundings and can thus be best classified as isothermal. For the systems considered in this paper, the thermal transients upon contact of the hot and cold liquids cause the temperature of the cold liquid to rise from its bulk temperature to a value greater than the homogeneous nucleation



temperature in time spans of the order of  $10^{-6}$  to  $10^{-8}$  sec. Under these conditions, nucleation cannot proceed until a sufficiently thick thermal boundary layer has been developed to support the growth of the vapor embryos to the limit of their stability. The premise of the model proposed in this paper is essentially that suggested by Hsu<sup>11</sup> for nucleate boiling from wall cavities on a much longer time scale, i.e., nucleation will not occur until the thermal boundary layer is sufficiently thick to support a critical size vapor cavity. Therefore, the difference between small scale definitive experiments used to verify the spontaneous nucleation model and the large scale explosive interactions considered herein is that in the former case the temperature gradients within the cold liquid are insignificant and have no effect on the nucleation process, whereas in the latter set of conditions, the temperature profile in the cold liquid is the primary mechanism for describing the time required for nucleation.

### III. PROPOSED MODEL

Explosive boiling conditions have been experimentally generated in a wide variety of contacting modes including shock tube conditions, where one liquid is impinged upon another at a high velocity, subsurface injections of one liquid into another, and free contacting modes where one liquid is essentially imbedded within an infinite sea of the other liquid as illustrated in Fig. 1. In this particular study, only the free contacting mode is considered.

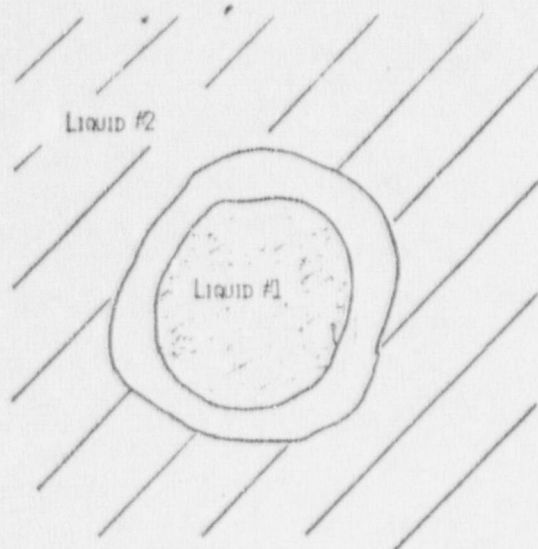


Fig. 1. Free Contacting Mode.

Upon contact between two semi-infinite slabs with constant thermal properties, the interface temperature, as given in Eq. 1 and derived from the parabolic heat conduction equation, is invariant in time. If it is assumed that the hyperbolic heat conduction equation governs the transient response of the liquids, the results given in Ref. 12 show the heat flux at the interface should approach the value dictated by the parabolic solution at approximately  $10^{-12}$  sec, which, as will be subsequently seen, is several orders of magnitude less than the time of vapor formation. Therefore, the parabolic solution is adequate for this description. Since the temperature at the interface

is constant, the transient temperature distribution throughout both liquids is predicted by the standard error function solution, which for small values of the argument, can be approximated by:

$$\frac{T_i - T}{T_i - T_c} = \frac{x_1}{2\sqrt{\alpha t}} \quad (6)$$

The instantaneous increase in the interface temperature is accompanied by a pressurization due to the local expansion of the liquid. This single phase pressurization, which is capable of producing pressures greater than the thermodynamic critical point of the cold liquid, persists until acoustically relieved. Such behavior has been observed in the aluminum-water shock tube studies described in Refs. 13 and 14. These results show that this pressurization is sustained until it is acoustically relieved by a pressure wave traveling to the free surface of the cold liquid and the refraction wave returning to the interface.

$$t_a = \frac{2l}{c} \quad (7)$$

where  $l$  is the characteristic dimension to the free surface of a given liquid mass and  $t_a$  is the acoustic relief time. During this time, since the local pressure is extremely high, the spontaneous nucleation can be suppressed, but the thermal boundary layer will continue to grow as dictated by the error function solution. Following acoustic relief, the pressure in the liquid will be essentially atmospheric and the pressure within vapor embryos will be determined by the local temperature distribution of the thermal boundary layer. The limit of mechanical stability, or critical size, of a vapor embryo is given by Eq. 4 and is shown in Fig. 2 for  $P_0 = 1$  bar and  $P_v$  the corresponding saturation value. If the acoustic relief time is so short that the thermal layer has not become thick enough to support a vapor bubble of the critical diameter, embryos will collapse before they reach the critical size. Such conditions are shown for  $10^{-9}$  and  $10^{-8}$  secs in Fig. 2 where the initial Freon temperature is assumed to be its normal boiling point. If the acoustic relief time is quite long, the thermal boundary layer will be capable of supporting a vapor embryo not only at the critical size, but also at much larger sizes as shown by the profile for  $10^{-7}$  secs. Given this condition, once an embryo is formed it can continue to grow to a considerably larger size.

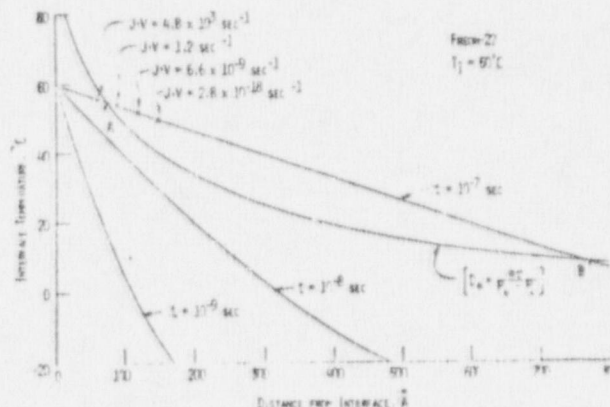


Fig. 2. Thermal Boundary Layer Development and Critical Cavity Size for Freon-22.

The frequency of unstable vapor nucleation, once the thermal boundary layer is sufficiently developed, is given by the product of the frequency per unit volume which is a function of the local temperature, and the volume of fluid (V) having a temperature equal to or greater than that value. This product (per cm<sup>2</sup> of contact) is shown in Fig. 2, for the temperature profile at 10<sup>-7</sup> sec, and clearly indicates the most likely place of vapor formation is the smallest critical diameter.

Once the system is depressurized due to the rarefaction wave, the cold liquid has a waiting time until the first nucleation that is specified by the reciprocal of the product discussed above.

$$t_w = \frac{1}{J \cdot V} \quad (8)$$

During this waiting time the thermal boundary layer will continue to develop, and as it does so, the waiting time for nucleation will be decreasing as the frequency of nucleation increases. When the first critical embryo is formed, and because of its higher frequency it is assumed that this embryo is formed at the smallest critical radius (point A on Fig. 2), the bubble will attempt to grow from this radius to its next stable radius indicated by the intersection of the mechanical stability line and the thermal boundary layer (point B on Fig. 2). This growth cannot proceed until the pressure gradient is developed within the cold liquid, which requires the traverse of another pressure wave from the interface to the free surface and a rarefaction wave back again. This allows continued development of the thermal boundary layer. After the return of this rarefaction wave from the surface, the vapor bubble may grow from its inception size to the value where the mechanical stability line intersects the thermal boundary layer. An interesting aspect of the thermal boundary layer is that after approximately 10<sup>-5</sup> sec, the mechanical stability line and the thermal boundary layer no longer intersect as illustrated in Fig. 3. Therefore, if the cold liquid must wait for 10 usec before a vapor bubble can be formed, this bubble can grow without bound until it exceeds the thickness of the liquid layer. This particular aspect will be employed later in the discussions on vaporization rates.

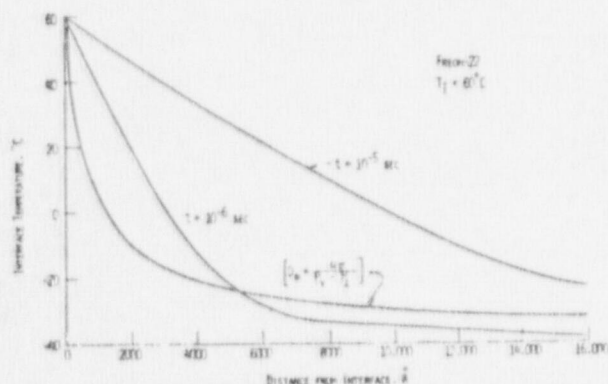


Fig. 3. Thermal Boundary Layer Development and Critical Cavity Size for Freon-22.

The time to nucleation is then the sum of two acoustic relief times and the waiting time for a critical size cavity to appear.

$$t_D = 2t_a + t_w = \frac{3}{J \cdot V} \quad (9)$$

For simplicity, the waiting time is evaluated from the thermal profile at the end of the first acoustic relief time. If the time to nucleation is less than 10<sup>-6</sup> sec, the boundary layer will be composed of a region of stable growth for the vapor bubble and an unstable region where condensation will occur. The time for the vapor bubble to grow from its inception size to the limit of its stable region can be calculated from the inertial growth equation because of the high superheats and small dimensions involved. This time is the minimum lifetime of the bubble under these conditions and is given by

$$t_E = \frac{\Delta r}{\sqrt{\frac{2}{3} \frac{\Delta P}{\rho_L}}} \quad (10)$$

where  $\Delta P$  is the average driving pressure between the minimum and maximum stable limits for the vapor bubble. If many additional bubbles can be formed during the lifetime of a single bubble, there is a possibility that they could coalesce at the larger diameter and vapor blanket the interface between the cold liquid drop and the hot surface. Such behavior would cut off the heat transfer to the cold drop and prevent that particular liquid mass from escalating into an explosive vapor release at that point in time. The number of additional bubbles that can be formed during the minimum lifetime of one bubble is equal to the product of  $J \cdot V \cdot t$ . However, the number of vapor bubbles that can be instantaneously formed within the boundary layer is basically determined by the compressible aspects of the liquid. If large number of bubbles are formed before the liquid can be displaced radially, mutual pressurization will occur and prevent the formation of further vapor sites. This site density can be determined from the compressibility of the liquid phase, which can be related to the sonic velocity by

$$c^2 = \frac{\Delta P}{\Delta \rho} \quad (11)$$

If the total volume and mass of the liquid drop is assumed to remain constant then the change in density can be specified by

$$\Delta \rho_L = - \frac{\rho_L}{V_L} \Delta V_L \quad (12)$$

The compression of the liquid volume, which is assumed to exist over a depth of one bubble diameter, is equal to the increase in the vapor volume which can be specified by

$$\Delta V_v = \frac{N \pi D^3}{6} v_b \frac{ND^3}{2} \quad (13)$$

Therefore, the increase in density of the liquid phase, per unit surface area of contact, can be related to the number and size of the incipient critical embryos by

$$\Delta \rho_L = \frac{\rho_L}{D} \cdot \frac{ND^3}{2} = \frac{\rho_L ND^2}{2} \quad (14)$$

Consequently the pressure increase within the liquid can also be related to these two parameters and sonic velocity of the liquid phase itself.



$$\Delta T = 1/2 N_D D^2 C^2$$

(15)

The pressurization of the liquid phase itself by the vapor bubbles is indeed a very complex phenomena and depends upon the local temperature, but for simplicity, it will be assumed that an overpressure of 5 bars is sufficient to suppress further nucleation sites within the remainder of the liquid phase. (The analysis is rather insensitive to this assumption, i.e., a value of 2 bars or 15 bars could have been chosen without dramatically altering the results.) A characteristic diameter of 50 Å is assumed for the vapor bubbles and with these two parameters the number of nucleation sites per sq cm of contact area is  $10^9$ . In other words, the first  $10^9$  sites that appear, assuming that they can be generated within the growth time of a single bubble, will prevent any further sites from activating. If the number of sites that can be formed within the growth time of one bubble is considerably less than this value, no significant pressurization will occur within the liquid and each bubble will essentially grow as if it was contained in an infinite sea of liquid. If a characteristic time of  $10^{-9}$  sec is assumed for the growth time, which corresponds to approximately a 250 Å increase in radius with a 12 bar pressure difference, a value of nucleation frequency can be calculated where radial pressurization will become important.

$$J = \frac{N}{V \cdot t} = 2 \times 10^{24} \quad (16)$$

This nucleation frequency corresponds to a temperature of approximately 63°C. For temperatures higher than this value, radial pressurization will essentially limit the number of nuclei to  $10^9$  sites/cm<sup>2</sup>, with the exception, as will be discussed later, when the interface temperature is considerably greater than thermodynamic critical point of the cold liquid.

#### IV. DROP STABILITY

Using the equations outlined above, one can assess the stability of a cold drop impinging upon a hot surface. Upon contact, the interface temperature is established and the thermal boundary layer develops during the acoustic relief time necessitated by single phase constant volume heating, the waiting time for the first nuclei, and the acoustic relief time required before that vapor bubble can grow. As illustrated in Fig. 2, this establishes not only the inception criteria for the vapor bubble but also the maximum diameter to which it can grow in a stable manner. Once this change in radius is evaluated, the time required for that growth can be evaluated from the inertial growth equation. The number of bubbles that can exist simultaneously is obtained by the product of the nucleation frequency determined by the temperature at point A in Fig. 2, the volume per unit surface area between the interface and point A, and the growth time of a single bubble. Because of mutual pressurization effects, the number of simultaneous nuclei is less than  $10^9$  sites per sq cm of contact. If the number of nucleation sites that exist simultaneously result in interference at the maximum stable bubble diameter (point B in Fig. 2), the interface between the two liquids will be vapor blanketed and the energy transfer will be terminated for all practical purposes. This interference site density can be evaluated from the maximum stable diameter at point B by

$$N = \left( \frac{1}{D_B} \right)^2 \quad (17)$$

where N cannot be greater than  $10^9$  sites per sq cm.

This behavior is postulated for interface temperatures up to and including spontaneous nucleation values. As illustrated in Table I for homogeneous nucleation of Freon-22, the number of molecules contained in a cavity of the critical size becomes quite small at temperatures approaching the critical point, and it is not reasonable to assume that continuum theory still applies. It is uncertain what the nucleation behavior would be at these temperatures, but as a first approximation, it is assumed that a minimum of 40 molecules are required to produce a vapor cavity. (This number is arbitrary, but it makes little difference if it is varied by a factor of three.) Therefore, at the very high interface temperatures, nucleation cannot begin until the thermal layer is sufficiently developed to support a vapor cavity containing 40 molecules. This is one area of spontaneous nucleation that has been of little interest in isothermal experiments because, as shown in Table I, any experiments with slow heating rates in the order of  $10^3$ °C/sec or less would be unable to achieve these high temperatures. In fact, from the practical standpoint, they can only be achieved by instantaneous contact. When the interface temperature upon contact is greater than the thermodynamic critical point, the principal consideration is the length of time required to develop a thermal boundary layer capable of supporting a vapor nucleus with 40 molecules. If the interface temperature is sufficiently high so that the thermal boundary layer can support such a nucleus at the critical pressure within the acoustic relief intervals, mutual pressurization is no longer applicable. Under such conditions, film boiling is inevitable. These temperatures can be estimated from

$$\frac{T_i - T_{crit}}{T_i - T_c} = \frac{D_b^3}{\sqrt{8\alpha t_a}} \quad (18)$$

where  $D_b^3$  is the vapor cavity diameter containing 40 molecules at the critical pressure.

Given the above information, the stability of a specified drop size, in terms of wetting and capture by the hot liquid or sustained film boiling, can be evaluated as a function of interface temperature. A prediction for this behavior of Freon-22 is shown in Fig. 4. This figure illustrates the result that drops larger than a critical size for a given temperature will remain in film boiling despite initial, intimate, liquid/liquid contact, whereas those smaller than this value will wet and be captured by the surface. At very high interface temperatures, Eq. 18 basically predicts all realistic size drops will remain in film boiling. Therefore, it predicts that explosions will not occur in the free contacting mode for these temperatures. The stability line given in Fig. 4 should be interpreted as a limiting region because of the approximations in the analysis.

The film boiling behavior as well as the capture behavior are illustrated in Fig. 5. Once the drop is captured by the surface and the vapor bubbles attempt to grow but cannot approach coalescence prior to the onset of condensation, the liquid has established a very efficient means of transporting energy from the interface to the bulk of the drop itself. Depending upon the number of nucleation sites present, this mode of heat transfer can far exceed thermal conduction. The mechanism for energy transfer is vaporization

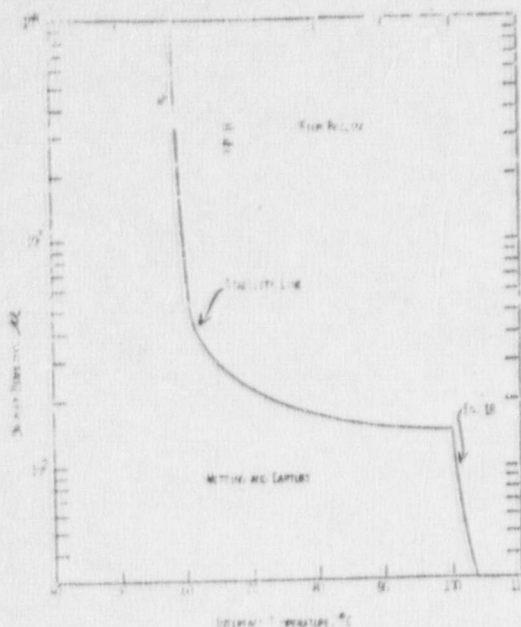


Fig. 4. Liquid Stability Predictions for Freon-22.

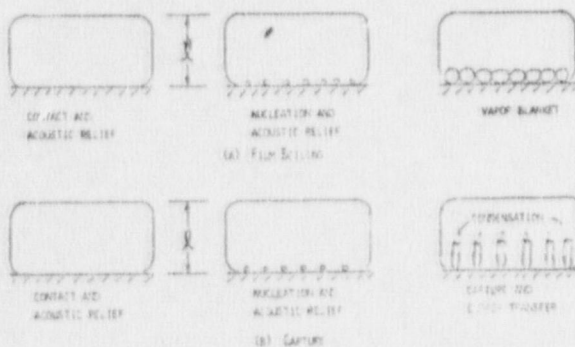


Fig. 5. Drop Behavior Following Contact for (A) Film Boiling and (B) Capture.

within the existing bubbles near the interface and transportation of the vapor molecules through the vapor cavity to the condensing zone. This enhanced heat transfer tends to equilibrate the temperature with the drop in the stable vapor zone and decrease the interface temperature somewhat. However, the interface temperature cannot decrease much without eliminating the basic mechanism for energy transport, spontaneous nucleation, which would allow the interface temperature to increase. Therefore, the energy transport under such conditions is basically determined by the thermal properties and temperature level within the hot liquid. Assuming that the interface temperature remains constant, the energy transport per unit area can be expressed by

$$\frac{Q}{A} = 2k_H(T_H - T_I) \sqrt{\frac{t_I}{\pi \rho_H}} \quad (19)$$

where  $t_I$  is the total interaction time for a given liquid drop. Energy will be stored in the drop until the drop can no longer contain the vapor by surface tension, liquid inertia, and condensation.

The predicted variation of capture diameter as a function of interface temperature explains why experi-

ments with interface temperatures barely in the spontaneous nucleation range have experienced interactions upon contact, while at higher temperatures, a sustained period of "film boiling" has been observed.<sup>15</sup> A liquid/liquid system is unable to generate film boiling after intimate contact has been experienced if the nucleation frequency is extremely low. On the other hand, for higher temperatures, where the nucleation frequency is much greater, this system will sustain the film boiling mode until the critical capture size is obtained. Once this is obtained, those drops can store energy and explode producing a shock wave that aids in the fragmentation of adjacent drops and increases the local pressure which enhances the capture process.

Such stability considerations also explain the apparent lack of system sensitivity to initial subcooling of the cold liquid as observed in Ref. 15. Film boiling of large drops is determined by the development of the thermal boundary at the interface which is initially affected by subcooling. However, after film boiling is established, the drop would exist as a subcooled body in its own saturated vapor. Given such conditions, the drop will quickly be saturated. For example, standard transient heat transfer calculations would predict that a 1000  $\mu$  drop of Freon-22 initially at  $-116^\circ\text{C}$  would approach saturated conditions in 300 msec if surrounded by its own vapor. Such times are in agreement with those observed in Ref. 15. Therefore, the system that begins in a subcooled state quickly saturates as the fragmentation process proceeds to the critical size.

## V. EXPERIMENTAL APPARATUS

To investigate the explosive nature of well-wetted systems, the apparatus shown in Fig. 6, which is similar to that discussed in Ref. 16, was employed with fluid combinations of mineral oil and Freon-22 and mineral oil-propane. The mineral oil in these tests was reagent grade, and consequently, it is expected that both Freon-22 and propane would have a great affinity for the oil and produce well-wetted systems. A 4 in. pipe was used as the interaction vessel, and it was instrumented with high response, piezo-electric pressure transducers, thermocouples, and a force transducer as shown in the illustration.

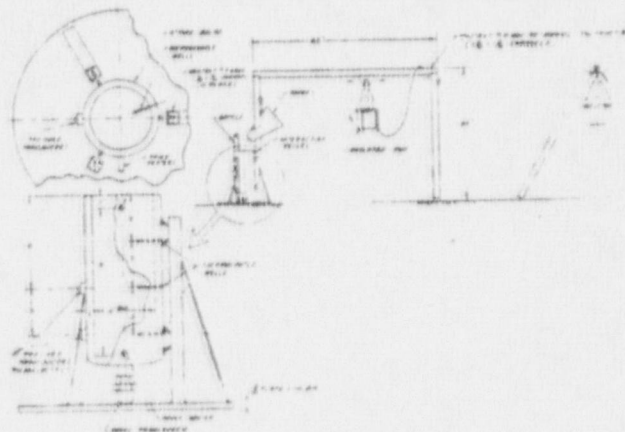


Fig. 6. Experimental Apparatus.

Experiments were conducted by dumping one liquid into the other in the interaction vessel. Contacting modes of hot liquid into cold liquid and cold liquid into hot liquid were run and produced very similar



results for these systems. For these tests, the initial temperature of both the propane and Freon-22 were their normal boiling points. The initial oil temperature was systematically varied from 30°C to 240°C. The interaction was characterized by the maximum pressure, which typically had a rise time of 500 usec under explosive conditions, as illustrated in Fig. 7.

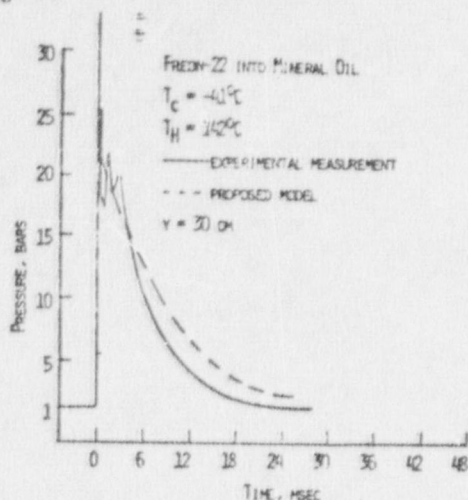


Fig. 7. Pressure Versus Time for an Explosive Interaction.

#### VI. ENERGETICS OF VAPOR EXPLOSIONS

After a system has fragmented itself down to the critical droplet size, the drop will be captured by the surface and begin to spread. On the time scales and temperature levels discussed in this paper, spreading rates are difficult to evaluate, but as a first approximation, it will be assumed that the average contact area of the drop while it is captured by the surface is equal to twice its initial projected area. This would correspond to spreading rates of the order of 1 meter/sec. After capture, the drop of cold liquid can store energy until unstable vapor growth is capable of penetrating the entire drop thickness. However, this energy transfer should occur on a time scale characteristic of the system acoustic relief time if the shock wave is to be sustained. For the experiments discussed in this paper, the acoustic relief time, as dictated by location of the interaction and the acoustic speed of the mineral oil, was approximately 500 usec. Given this interaction time, the drop diameter, and the interface temperature, one can calculate the temperature rise within the cold liquid.

$$\Delta T_{cl} = \frac{2k_H(T_H - T_c)}{\rho_c C_c l} \sqrt{\frac{t}{\alpha_H}} \quad (20)$$

The pressure increase generated by this energy transfer can be determined from the saturation tables. The mixture is assumed to be uniformly fragmented at the capture diameter, and the behavior of one drop is representative of the entire system. Therefore, explosion of one drop initiates the interaction of the remaining mass which has also achieved the stability limit. For large capture diameters, the system will be very sluggish and little, if any, pressurization will occur. However, as the droplet size decreases, the system response will increase and produce vapor on an explosive time scale.

Maximum explosive interaction pressures can be calculated from the combination of the capture diameter given in Fig. 1 and Eq. 18 with the heat flux specified by the transient behavior of the hot liquid. These calculations are compared to the experimental data for both systems and contacting modes of cold liquid dumped into the hot liquid and hot liquid dumped into the cold liquid in Figs. 8 and 9. There is good agreement between the onset of explosive interactions, the magnitude of these interactions as a function of oil temperature, and the high temperature cutoff. The existing data for very high temperature oil systems is limited and this particular aspect of both the proposed model and the experimental observations should be examined in detail. The slight apparent shift of the propane data could be the result of small changes in thermophysical properties because of the mutual solubility of the two liquids. However, the proposed analytical model yields a good overall description of the explosive nature for the systems investigated.

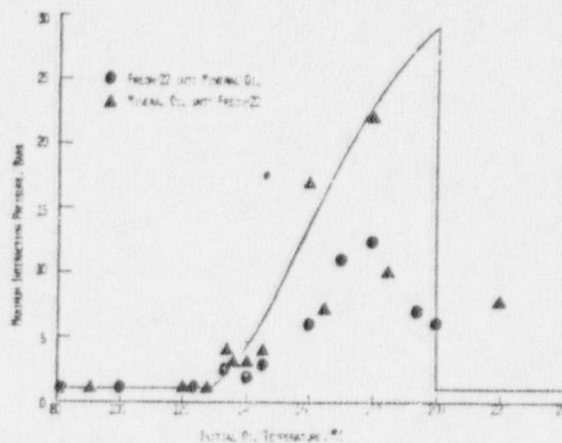


Fig. 8. Explosive Interaction Pressures for Freon-22 and Mineral Oil.

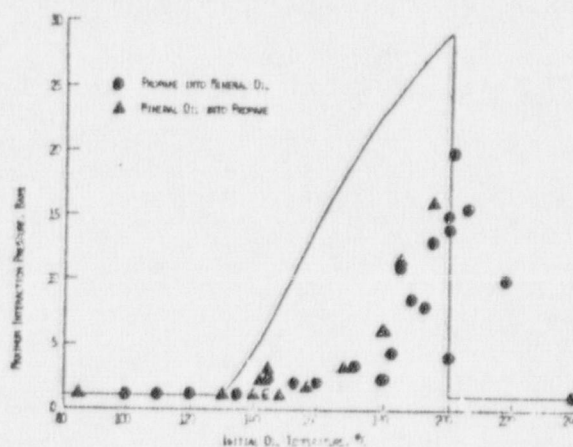


Fig. 9. Explosive Interaction Pressures for Propane and Mineral Oil.

The elimination of explosive interactions at high interface temperatures is a consequence of forming vapor cavities at pressures near the critical point. From such considerations, the proposed model predicts that aluminum-water and nitrogen-water systems are not explosive in a free contacting mode. As observed by Long<sup>17</sup> and Hess and Brondyke,<sup>18</sup> the aluminum-water system requires the presence of a wetted solid wall for explosions to occur. Hence, the system is no



longer in a free contacting mode with explosions begin, but while the fluids were in the configuration, no explosions were observed. Aluminum-water shock tube results<sup>13,14</sup> have also produced explosive events, but again this is not the mode of contact considered herein. Water-liquid nitrogen systems have been observed to be nonexplosive in a free contacting mode but can explode in a shock tube test.<sup>19</sup>

Once the energy deposited in the cold liquid has been determined and the maximum interaction pressure has been obtained, the work potential of the resulting explosion can be evaluated once a model for the expansion is postulated. The work done by the expansion is a very difficult parameter to estimate experimentally, and about the only measurements which can be obtained are photographic observations (which leave considerable doubt regarding the density of the expanding fluid), pressure-time traces, and force-time traces for a given system. The geometry of a system is also very important in determining the work potential and for interpreting the experimental measurements. For the experiments discussed herein, the geometry can be assumed to be one dimensional. Measurements of the amounts of cold liquid added to the system and hot liquid blown out of the system by the interaction were recorded, and these can be utilized to estimate the work potential of the system.

For simplicity the one-dimensional picture shown in Fig. 10 is assumed for the time immediately after nucleation, and the liquid enthalpy and entropy are the saturation values corresponding to the calculated pressure. The proposed model assumes that (1) there is more than sufficient hot liquid to increase the temperature of the entire amount of cold liquid to the calculated temperature and (2) the cold liquid undergoes no further interaction during the expansion and thus expands isentropically. This expansion is opposed by the inertia of the water expelled from the system.

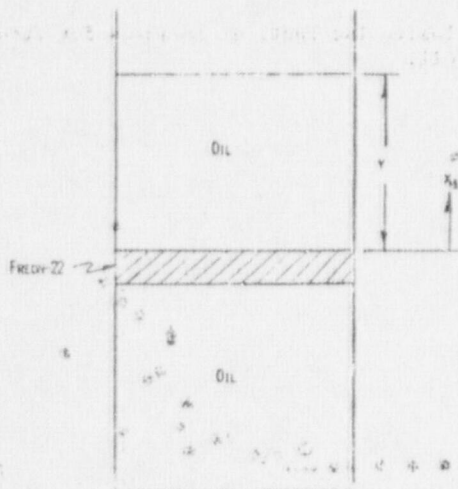


Fig. 10. Assumed Configuration for Work Calculated.

$$P_c - P_{atm} = \rho_H y \frac{d^2 x_b}{dt^2} \quad (21)$$

As the expansion proceeds, the pressure in the Freon decreases as its volume increases according to the isentropic restriction.

$$V_c = A z = m_c [(1-x)v_{lc} + x v_{vc}] \quad (22)$$

$$x = \frac{s_o - s_f}{s_{fg}} \quad (23)$$

This calculation is continued until the bottom of the water slug reaches the top of the interaction vessel. The results of such a calculation in terms of vessel pressure versus time are shown in Fig. 7 for an initial Freon mass of 300 ml and the initial temperatures illustrated. The comparison between the measured pressure decay and the model prediction is very encouraging. Since this result gives a PV relationship for the expansion, the work accomplished can then be evaluated. It is highly recommended that future investigations consider reporting pressure and force versus time measurements so that models like this simplistic approach can be evaluated.

## VII. CONCLUSIONS

A model, based on spontaneous nucleation, has been proposed to describe vaporization potential and behavior upon contact in a liquid/liquid system. This behavior is determined by the size of the liquid mass, single phase pressurization and acoustic relief, nucleation frequency due to random density fluctuations, the initiation of unstable growth and acoustic relief, and the development of the thermal boundary layer in the cold liquid. The proposed model predicts that the stability of a given size drop upon intimate contact with another liquid is extremely dependent upon the interface temperature. For low interface temperatures, large masses will be captured by the hot liquid and the resulting vaporization rates will be extremely low because of the small nucleation frequency. For higher values of interface temperature, large masses will remain in film boiling because of the well-developed thermal boundary layer and the large frequency of nucleation. These masses will remain in film boiling until the critical size is achieved whereupon they will be captured by the hot liquid. For these smaller drops, the vaporization rates of the system can be extremely high, and in fact, can produce vapor on an explosive time scale.

This mechanism proposes that spontaneous nucleation is the mechanism for describing: (1) film boiling in a liquid/liquid system after intimate contact, (2) the limit of stability at a given temperature, (3) the trigger for an explosive interaction, and (4) the propagation of the initiating event in these systems. The model formulated in these considerations provides a good representation of the explosive character for well-wetted liquid systems including the onset of explosive events, the magnitude of these events, and the cessation of explosive interactions at very high temperatures.

## VIII. REFERENCES

1. Cho, D. H., Ivins, R. O., and Wright, R. W., "Pressure Generation by Molten Fuel-Coolant Interactions During LMFBR Accident Conditions," *Proc. of Conf. on New Developments in Reactor Mathematics*, Idaho Falls, Idaho, CONF-710302, Vol. 1, 25 (March 1971).
2. Simon, R., "Computer Model Study of the Smelt-Water Physical Explosions," *AIChE Preprint 15*, presented at the 14th Natl. Heat Transfer Conf., Atlanta, Ga. (Aug 5-8, 1973).
3. Caldarola, L., and Koutsouvelis, G., "A Theoretical Model with Variable Masses for Molten Fuel-Sodium Thermal Interactions," *Proc. Fast Reactor Safety Meeting*, Beverly Hills, Calif., CONF-740401-P2, 964 (April 1974).

- 4 Fauske, H. K., "The Role of Nucleation in Vapor Explosions," Trans. Am. Nucl. Soc., Vol. 15, 813 (1972).
- 5 Carslaw, H. S., and Jaeger, J. C., Conduction of Heat in Solids, 2nd Ed., Clarendon Press, Oxford (1959).
- 6 Skripov, V. P., Metastable Liquids, Halstead Press, Jerusalem (1974).
- 7 Fauske, H. K., "Some Aspects of Liquid-Liquid Heat Transfer and Explosive Boiling," Proc. Fast Reactor Safety Meeting, Beverly Hills, Calif., CONF-740401-P2, 992 (April 1974).
- 8 Blander, M., et al., "Chemical Engineering Division Physical Inorganic Chemistry Semiannual Report, July-December, 1971," ANL-7878 (1972).
- 9 Wakeshima, H., and Takata, K., "On the Limit of Superheat," J. Physical Society of Japan, Vol. 13, 1398 (1958).
- 10 Moore, G. R., "Vaporization of Superheated Drops in Liquids," AIChE J., Vol. 5, No. 4, 458 (1959).
- 11 Hsu, Y. Y., and Graham, R. W., National Aeronautic and Space Administration Report, TN-D-594 (1961).
- 12 Baumeister, K. J., and Hamill, T. D., "Hyperbolic Heat-Conduction Equation--A Solution for the Semi-Infinite Body Problem," Trans. ASME, J. Heat Transfer, Vol. 91-C, 543 (1969).
- 13 Wright, R. W., et al., "Kinetic Studies of Heterogeneous Water Reactors - Annual Summary Report - 1965," USAEC Report No. STL-372-30 (Dec 1965).
- 14 Guest, J. N., Turner, R. G., and Rees, N. J. M., "Al/Water Shock Tube Experiments at A.W.R.E. Foulness since January 1972," FPR-1-74 (January 1974).
- 15 Board, S. J., Hall, R. W., and Brown, G. E., "The Role of Spontaneous Nucleation in Thermal Explosions: Freon/Water Experiments," CEGB Report RD/B/N3007 (1974).
- 16 Henry, R. E., et al., "Large Scale Vapor Explosions," Proc. Fast Reactor Safety Meeting, Beverly Hills, Calif., CONF-740401-P2, 922 (April 1974).
- 17 Long, G., "Explosions of Molten Aluminum and Water," Metal Progress, 107 (May 1957).
- 18 Hess, P. D., and Brondyke, K. J., "Molten Aluminum-Water Explosions," Metal Progress, Vol. 93 (April 1969).
- 19 Anderson, R. P., and Armstrong, D. R., "Experimental Study of Vapor Explosions," Proc. Third Internatl. Conf. on Liquefied Natural Gas, Washington, DC (1972).



# EFFECT OF REWET ON BDHT PERFORMANCE

KV/FT	RESTRICTION ( $T_S - T_{SAT}$ )	PEAK CLAD TEMP., °F		
		BLOWN	E.O.B.	REFLOOD
14.0	300	1356	934	2107
14.0	200	1270	916	
14.0	0	1369	932	2096

CE  
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ECCS 2/21/76.