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THE EFFECT OF THE PRESSURE-TEMPERATURE HISTORY UPON INCIPIENT-BOILING SUPERHEATS IN LIQUID METALS

by

Robert E. Holtz

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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Reactor Engineering Division

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June 1966

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NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
c	Constant in the equation for surface tension	$\text{lb}_f/\text{in.}-^\circ\text{F}$
h_{fg}	Latent heat of vaporization	Btu/lb
n	Constant in Eq. (7)	dimensionless
P_g	Partial pressure of noncondensable gas phase	psia
P_ℓ	Liquid pressure (system pressure)	psia
P_v	Vapor pressure	psia
Q''	Heat flux	$\text{Btu}/\text{hr-ft}^2$
r	Bubble radius	in.
r'	Equivalent circular radius of cavity	in.
r_c	Radius representing the smallest cavity cross section	in.
R_a	Radius of curvature of liquid advancing into cavity	in.
R_f	Radius of curvature at deepest liquid penetration into cavity	in.
R_r	Radius of curvature of liquid receding from cavity	in.
t	Thermal equilibrium temperature	$^\circ\text{F}$
t_c	Critical temperature	$^\circ\text{F}$
t_ℓ	Liquid temperature	$^\circ\text{F}$
$t_{\ell s}$	Saturation temperature corresponding to liquid pressure	$^\circ\text{F}$
t_v	Vapor temperature	$^\circ\text{F}$
t_w	Wall temperature	$^\circ\text{F}$
$T_{\ell s}$	Saturation temperature corresponding to liquid pressure	$^\circ\text{R}$
T_v	Vapor temperature	$^\circ\text{R}$
V_{fg}	Specific volume of evaporation	ft^3/lb
<u>Greek Letters</u>		
β	Perfect gas constant	$\text{Btu}/\text{lb}-^\circ\text{F}$
σ	Surface tension	$\text{lb}_f/\text{in.}$
θ_a	Advancing contact angle	-
θ_r	Receding contact angle	-

THE EFFECT OF THE PRESSURE-TEMPERATURE HISTORY UPON INCIPIENT-BOILING SUPERHEATS IN LIQUID METALS

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ABSTRACT

The degrees of liquid superheat required to initiate boiling in the alkali metals are found by examining the pressure-temperature history of the system and by using the bubble-equilibrium equation. The calculated incipient-boiling superheats for sodium and potassium are shown to be in agreement with data presented in the literature.

I. INTRODUCTION

Considerable effort has been expended in the study of the boiling of water. Presently, interest is focused on the boiling characteristics of the liquid metals, especially the alkali metals and mercury. This interest is due to the large potential that the liquid metals have for use in various power-reactor applications and to the safety considerations associated with liquid-metal-cooled reactors. Despite the effort expended, the boiling phenomenon in both water and the liquid metals is not sufficiently predictable. One problem area pertinent to this liquid-metal boiling phenomenon, which must be investigated both analytically and experimentally, is the degree of liquid superheat required to initiate boiling in liquid-metal-cooled reactors. This investigation is necessary for obtaining information associated with general reactor technology as well as information pertinent in reactor safety considerations. Establishing all the variables that contribute to the initiation of boiling, and investigating the contribution of each of these variables to the initiation of boiling are the primary purposes of much research presently being conducted. Some of the variables generally accepted as being pertinent to the initiation of boiling are:¹⁻³

1. Thermophysical properties of the fluid,
2. Surface condition (roughness and cleanliness),
3. Heat flux,
4. Gas phase contained in the liquid, and
5. Pressure-temperature history of the boiling surface.

The effect of the thermophysical properties of the heat-transfer fluid upon the initiation of nucleate boiling is discussed in Refs. 4 and 5. Ellison⁴ obtained the expression,

$$t_v - t_{\ell s} = \frac{2\beta T_{\ell s}^2 \sigma}{h_{fg} P_{\ell} r} \quad (1)$$

This thermodynamic analysis of bubble nucleation utilizes the Clausius-Clapeyron equation in solving the bubble-equilibrium equation to obtain Eq. (1). The assumptions used to obtain Eq. (1) are that the vapor behaves as a perfect gas, the latent heat of vaporization is constant, the specific volume of the vapor is large compared to the specific volume of the liquid, and $T_{\ell s} T_v$ is approximately equal to $T_{\ell s}^2$. In this analysis it is assumed that a nucleus that contains vapor and/or gas must be present in the liquid in order to nucleate a bubble, and that this nucleus is held in a stable equilibrium position by a solid particle.

Krakoviak⁵ utilized Eq. (1) and calculated by comparison with water, the degree of liquid superheat required to initiate nucleate boiling of a liquid metal from surface cavities. The following equation used in these calculations was obtained by rearranging Eq. (1) and applying the perfect-gas law:

$$\frac{t_{vw} - t_{\ell sw}}{t_{vx} - t_{\ell sx}} = \frac{\sigma_w T_{vw} V_{fgw} h_{fgx} r_x}{\sigma_x T_{vx} V_{fgx} h_{fgw} r_w} \quad (2)$$

The additional subscripts x and w in Eq. (2) refer to liquid metal and water, respectively. In solving Eq. (2), we assume that r_x is equal to r_w . This analysis shows that considerably higher liquid superheats may be required to initiate boiling in the alkali metals than are required for water. The predicted higher superheats for the liquid metals in this analysis are due only to differences in the thermophysical properties of water and the liquid metals. For example, comparing the alkali metals to clean, distilled water, where liquid superheats of 90°F are required to initiate nucleate boiling at 1 atm, Krakoviak has calculated that liquid superheats of 375, 774, 203, and 201°F are required to initiate nucleate boiling at 1 atm in potassium, sodium, rubidium, and cesium, respectively.

The contribution of the surface condition to the nucleation of bubbles has been experimentally examined by Griffith and Wallis⁶ for water, methanol, and ethanol. This study showed that the surface condition affects both the liquid superheat required for bubble initiation and the stability of boiling, once it is initiated.

Marto and Rohsenow⁷ examined the effect of surface conditions upon the nucleate pool boiling of sodium. This analysis showed that the surface

condition can significantly affect the liquid superheat required for bubble initiation, the steady-state nucleate-boiling wall superheat, and the slope of the boiling curve.

The basic reason for examining the role of the surface upon the liquid superheats required for bubble initiation is that the largest surface cavity that does not fill with liquid will determine the minimum wall superheat required to nucleate a bubble from a given surface. Almost all the studies attempting to determine the role of the surface condition upon the initiation of boiling have used the bubble-equilibrium equation,

$$P_v - P_\ell = \frac{2\sigma}{r}, \quad (3)$$

and attempted to correlate the bubble radius with the geometries and sizes of the surface cavities.

The surface condition (both roughness and cleanliness) has been shown to affect the degree of liquid superheat required to initiate nucleate boiling of water. However, accounting for the size, shape, and number of cavities on a surface, both before and during boiling, appears to be an extremely difficult task. Also, despite every effort to obtain as clean a boiling surface as possible, it may be difficult to remove all traces of contamination from within all the surface cavities.

The effect of the heat flux upon the degree of liquid superheat required to initiate nucleate boiling is not clearly established. The uncertainty as to the effect of the heat flux upon the incipient liquid superheat is due primarily to difficulties in measuring the temperature of the liquid adjacent to a surface when high heat fluxes are being applied. However, it has been observed that in steady-state boiling, the degree of liquid superheat tends to increase with increasing heat flux. This effect is expressed in the Jens-Lottes⁸ equation for steady-state boiling of water,

$$t_w - t_{\ell s} = 60 e^{-P_\ell/900} (Q''/10^6)^{0.25}. \quad (4)$$

It has also been observed that removal of most of the gas phase from the liquid increases the degree of liquid superheat required to initiate nucleate boiling in water.^{1,3,5} Removal of the gas phase from the liquid leaves less gas phase which may be entrapped by surface cavities. When a significant amount of gas phase has been entrapped by a surface cavity, the equilibrium equation for a bubble nucleating from the cavity must be written to account for the gas phase present in the bubble. Thus Eq. (3) must be written

$$P_v + P_g - P_\ell = \frac{2\sigma}{r}. \quad (5)$$

Equation (5) shows that the larger the amount of gas phase entrapped by a surface cavity prior to bubble nucleation, the lower the liquid superheat required to initiate a bubble of radius r from that cavity. The inherent properties of most of the alkali metals are such that a gas phase, other than the noble gases and nitrogen, will form compounds with the alkali metals. For example, sodium is inert to only nitrogen and the noble gases helium, argon, neon, krypton, and xenon.⁹ The solubility of argon gas in sodium is of the order of 0.01 ppm.¹⁰ Hence, both Krakoviak⁵ and Holtz³ have utilized a comparison of the nucleate boiling characteristics of the alkali metals with those of distilled, degassed water in order to postulate the degree of liquid superheats required for bubble initiation in the alkali metals.

Marto and Rohsenow,⁷ Griffith and Snyder,¹¹ and Fabric¹² report that the pressure-temperature history of the boiling surface does significantly affect the degree of liquid superheat required for bubble initiation. Also, Buchberg *et al.*¹ have experimentally shown that the pressure-temperature history of a system has a significant effect upon the degree of liquid superheat required to initiate nucleate boiling in water.

As the previous discussion indicates, many variables contribute to the degree of liquid superheat required to initiate nucleate boiling from a surface. However, in any given system, once the working fluid, materials (surface condition), and cover gas (if any) have been determined, the system assembled, and operating conditions set, the remaining significant factor that will determine the degree of liquid superheat required for bubble initiation is the pressure-temperature history of the boiling surface. In the remainder of this report, the effect of the pressure-temperature history of a boiling surface upon the initiation of nucleate boiling is examined.

Fig. 1. Typical Surface Cavities

II. EQUIVALENT-CAVITY MODEL

Consider a surface cavity similar to the cavities shown in Fig. 1. Each cavity has one cross section that is smaller than all the other cross sections of that cavity. The arrows in Fig. 1 point out these smallest cross sections.

The surface inside a cavity may be expected to be somewhat irregular.¹² Since the irregular cross sections in various cavities are all somewhat different in geometry, and since irregular openings

are impossible to deal with in theory, an equivalent-cavity cross section is defined as that cross section of a cavity represented by an equivalent circular cross section of radius, r' . Also, an equivalent-critical-cavity radius, r_c , is defined as that radius of a cavity equivalent to the smallest cross section in that cavity. These equivalent radii will be used to approximate the actual irregular cross sections that cavities generally possess.

There are two fill modes for cavities in liquid-metal systems. A wetting condition requires that a gas phase be present in the cavity to have a stable cavity at fill, and a nonwetting condition does not require a gas phase for a stable cavity at fill. Hence, if an insignificant amount of gas phase is present in the cavities at fill or if the gas phase contained in the surface cavities becomes insignificant at steady-state heating via thermal diffusion, only the nonwetting condition at fill gives stable cavities, i.e., zero or finite liquid superheats. It may be expected that all entrapped gases will be removed from surface cavities by thermal diffusion in liquid-metal systems. Since this pumping of entrapped gases from wetted cavities will ultimately result in the filling of these cavities, the cavities that remain unfilled (the nonwetted cavities at fill) will determine the degree of liquid superheat required to initiate nucleate boiling.

For the case in which the liquid metal wets all cavities, this model predicts an infinite liquid superheat. Where an infinite superheat is required for surface boiling, nucleation will result from nucleation sites (gas particles) contained in the bulk of the liquid. These nucleation sites may be treated as an extension of the boiling surface and handled as a nonwetted cavity.

In a reactor safety analysis, it is important to know the maximum degree of liquid superheat which may occur. This maximum superheat will occur when all the entrapped gases have been pumped out of all the surface cavities. Hence, in this analysis, the cavities that contain no entrapped gases ($P_g = 0$) will be examined.

Fig. 2. Wetting Liquid Entering a Surface Cavity

Prior to examination of the equivalent cavity model, the symbols used in the model will be more clearly defined by use of figures. Figures 2-5 show the liquid advancing into the cavity, and Fig. 6 shows the vapor pressure within the cavity attempting to push the liquid from the cavity. The symbols P_v and P_l represent the vapor pressure and system pressure, respectively. The figures also show the equivalent-critical-cavity radius (r_c), the equivalent

Fig. 3. Nonwetting Liquid Entering a Surface Cavity

Fig. 4. Liquid Wetting Surface Cavity When $P_v \geq P_\ell$

Fig. 5. Subcooled Liquid Entering a Surface Cavity

Fig. 6. Superheated Liquid Inside a Surface Cavity

circular cross sections (r'), the radius of curvature of the liquid advancing into the cavity (R_a), and the radius of curvature of the receding liquid (R_r).

The basic assumption in this analysis is that cavities are required as bubble-nucleation sites, and that although any given surface has many cavities, nucleation occurs at only a very few of them. Examinations of a cavity and the surrounding liquid before bubble nucleation should determine whether or not the cavity will fill with liquid. A cavity that fills with liquid cannot serve as a nucleation site.

When a system is filled with a liquid metal, the liquid metal may or may not wet the cavity surface. The following possible events may occur:

- (A) Liquid wets at fill.
- (B) Liquid does not wet at fill.
 - (1) Liquid wets while liquid is subcooled.
 - (2) Liquid does not wet (even when heated to the point of bubble expulsion from the cavity).
 - (3) Liquid wets when $P_v \geq P_\ell$.

These possible occurrences will be examined individually.

A. Liquid Wets at Fill

In this case (shown in Fig. 2), the surface-tension force acts downward toward the bottom of the cavity. Assume sufficient cleanup of the surface and the liquid metal so that an insignificant amount of gas phase is present. Then, if

$$P_v < P_\ell + \frac{2\sigma}{r_c},$$

the cavity will fill with liquid and never be a nucleation site. Since the cavity will fill for the above condition, it will fill for all $P_v < P_\ell$. Thus, for all fill pressures above the saturation vapor pressure corresponding to the surface temperature, all cavities will fill and no nucleation sites will be available. Then, according to the basic assumption that cavities are required for bubble nucleation, an infinite liquid superheat will be required. This is plainly contrary to fact. Hence, if $P_g = 0$, nonwetting at fill is a condition for finite liquid superheat.

B. Liquid Does Not Wet at Fill

1. Liquid Wets While Liquid Is Subcooled

This situation is basically the same as the situation in which the liquid wets at fill. If the liquid wets the cavity surface while the liquid is subcooled ($P_v < P_\ell$), the cavity will fill with liquid and cannot serve as a nucleation site. Thus, if $P_g = 0$, nonwetting while the liquid is subcooled is a condition for finite liquid superheat.

2. Liquid Does Not Wet (even when heated to the point of bubble expulsion from the cavity)

This condition is shown in Fig. 3. For the nonwetting case, the surface-tension force acts upward (tending to pull the liquid from the cavity) and is opposed by the pressure difference ($P_\ell - P_v$). If

$$P_\ell - P_v > \frac{2\sigma}{R_a},$$

the liquid will be forced deeper into the cavity. However, if

$$P_\ell < P_v + \frac{2\sigma}{R_a},$$

all liquid will be forced from the cavity and bubble formation occurs. For incipient bubble formation,

$$P_\ell = P_v + \frac{2\sigma}{R_a}.$$

For thermal equilibrium at the surface, if P_v^s is the saturated vapor curve and P_ℓ^s is the system pressure in Fig. 3, then the liquid is subcooled. Hence, the bubble will collapse in the bulk of the liquid. It is concluded that P_ℓ^s is the liquid-saturation curve and the vapor is superheated. But again in this situation there is no liquid superheat, and this is contrary to fact. Hence, it must be concluded the wetting is essential for obtaining liquid superheat (net vapor generation).

3. Liquid Wets When $P_v \geq P_\ell$

In this situation (shown in Fig. 4) the liquid is nonwetting until wetting occurs when $P_v \geq P_\ell$, and from then on when

$$P_v \geq P_\ell + \frac{2\sigma}{R_a}.$$

After wetting, the surface-tension force acts downward and is opposed by the pressure difference ($P_v - P_\ell$). If

$$P_v > P_\ell + \frac{2\sigma}{R_a},$$

the bubble will begin to leave the cavity. For incipient bubble escape,

$$P_v = P_\ell + \frac{2\sigma}{R_a}.$$

If the vapor was subcooled, the liquid would be saturated, and no liquid superheat would occur. Since this is again contrary to fact, it may be concluded that the vapor is saturated (or at some quality) and the liquid is superheated.

A boiling surface will contain many surface cavities. All the situations of wetting and/or nonwetting may occur in various cavities on the boiling surface. However, the previous discussion has shown that the situation most pertinent is when the liquid wets the cavity when $P_v \geq P_\ell$ and $P_g \approx 0$. This situation will be examined in order to gain insight into the boiling phenomena of the liquid metals, as well as to predict the liquid superheats required for incipient boiling in the liquid metals.

Examination of surface cavities and the surrounding liquid when the liquid is subcooled and does not wet will determine whether or not these cavities will fill with liquid. The cavity shown in Fig. 5 has an equivalent-critical-cavity radius (r_c) shown within the cavity; actually, it may be either at the cavity entrance or anywhere within the cavity.

A force balance on a liquid entering into any portion of a cavity yields the expression,

$$P_\ell - (P_v + P_g) = \frac{2\sigma}{R_a}, \quad (6)$$

where the surface tension may be expressed in the general form,³

$$\sigma = c(t_c - t_\ell)^n. \quad (7)$$

Equation (6) implies that the liquid-vapor interface is a spherical surface, which is in thermal and mechanical equilibrium with its surroundings.

If an insignificant amount of gas phase is present within the cavity, Eq. (6) may be reduced to

$$P_\ell - P_v = \frac{2\sigma}{R_a}. \quad (8)$$

If $R_a < |r'|/|\cos \theta_a|$ at any time while the liquid is at the cross section represented by the equivalent radius r' , the liquid will pass beyond that cross section further into the cavity. If $|R_a| > |r'|/|\cos \theta_a|$, the liquid will be unable to pass beyond the cross section represented by r' . The liquid penetration into a cavity when $|R_a| > |r'|/|\cos \theta_a|$ is a function of the contact angle, surface tension (σ), and pressure difference ($P_\ell - P_v$).

Furthermore, if $|R_a| < |r_c|/|\cos \theta_a|$ at any time, liquid will pass through the critical cavity opening. Hence, the entire cavity will fill with liquid. Once liquid fills a cavity, that cavity can no longer serve as a nucleation site.

However, if $|R_a| > |r_c|/|\cos \theta_a|$ at all times, liquid will not pass beyond the critical cavity opening. This cavity will not completely fill with liquid; hence, the unfilled cavity may possibly serve as a nucleation site.

Upon wetting of the cavity surface by the liquid metal when $P_v \geq P_\ell$, the surface-tension force tends to keep the liquid metal in the cavity. This situation (shown in Fig. 6) may be expressed by

$$P_v - P_\ell = \frac{2\sigma}{R_r} \quad (9)$$

Equation (9) shows that the vapor pressure (P_v) must always exceed the pressure in the liquid (P_ℓ) before a bubble will nucleate at a surface.

The fluid properties of most heat-transfer fluids, such as water and the alkali metals, are sufficiently well known. Conversely, sufficient knowledge of the microstructure of the heat-transfer surface before and during boiling appears to be nearly an impossible task. However, the pressure-temperature history of a surface appears to eliminate the need to investigate the microgeometry of a surface in a system where the gas phase entrapped by the surface cavities is insignificant. This is accomplished by utilizing Eq. (8) to determine which size cavities of any surface will fill with liquid when subjected to known pressure and temperature conditions. Upon this investigation of the surface history, an equivalent minimum penetration radius (R_f) may be found. This equivalent penetration radius represents the most severe pressure-temperature condition (highest pressure difference and liquid subcooling) to which the surface has been subjected; thus, R_f results from the deepest penetration of the liquid into the cavity. All cavities where $|r_c|/|\cos \theta_a| > |R_f|$ are filled with liquid, and all cavities where $|r_c|/|\cos \theta_a| < |R_f|$ are possible nucleation sites. Thus, independent of any surface-roughness measurements, the maximum cavity sizes available for nucleation may be found as a function of the system pressure-temperature history.

As the temperature of the liquid increases, the vapor pressure inside the cavity increases. When the liquid takes on excessive superheat, the increasing vapor pressure attempts to push the liquid from the cavity. As the liquid begins to leave the cavity, it moves from the radius r' to some radius larger than r' . With the initiation of liquid movement to a radius larger than r' , a lower degree of liquid superheat is required to sustain an equilibrium condition at this new position. Hence, the combination of the liquid movement caused by the increased vapor pressure due to increased liquid superheat and the requirement of a smaller liquid superheat caused by the movement of the liquid-vapor interface to a larger radius results in additional vapor generation, which expells the liquid and much of the vapor from the cavity.

To calculate the liquid superheat requirements for the initiation of nucleate boiling, consider the condition just before the movement of the liquid-vapor interface. At this time, the interface between the liquid and vapor should be stable (not in motion). This stable volume of vapor in thermal and mechanical equilibrium with the surrounding liquid is shown in Fig. 6. For thermal equilibrium to exist, the superheated-liquid temperature must equal the vapor temperature inside the bubble. If the vapor is saturated vapor or has some quality, the temperature in the bubble represents the saturation temperature corresponding to the pressure inside the bubble. Equation (9) may be used under these conditions.

For water and the alkali metals, the expression for the surface tension [Eq. (7)] may be simplified to³

$$\sigma = c(t_c - t_\ell). \quad (10)$$

When Eq. (10) is used in the bubble-equilibrium equation [Eq. (9)], the liquid temperature (t_ℓ) is equal to the superheated-liquid equilibrium temperature (t). This equilibrium temperature (t) is the temperature of both the vapor in the cavity and the liquid contained in the cavity.

Equation (9) represents the relationship between the bubble radius of curvature, t , P_v , and P_ℓ . The relationship between P_v and t may be expressed by the saturated-vapor curve for the fluid of interest. At this point, there are two unknown functions representing the bubble radius and P_ℓ . If either of these functions can be reasonably postulated or measured experimentally, Eq. (9) can be solved.

Utilizing the equivalent-cavity model, the smallest penetration radius to which the advancing liquid will be forced into the surface cavities (R_f) may be calculated from Eq. (8) by knowing the pressure-temperature history of the liquid. By using this liquid-penetration radius (calculated from the most severe pressure-temperature condition), Eq. (9) may be solved, and the degree of liquid superheat required for the initiation of nucleate boiling may be calculated.

III. APPLICATION OF THE EQUIVALENT-CAVITY MODEL

In this section, the equivalent-cavity model will be utilized to predict the degree of liquid superheat required to initiate nucleate boiling in both sodium and potassium. Before the degree of liquid superheat required to initiate nucleate boiling can be calculated by using the equivalent-cavity model, the saturation curve and the surface tension of the fluids of interest must be known. Figure 7 shows the saturated-vapor curves of sodium and

Fig. 7. Saturated-vapor Curves for Sodium and Potassium

potassium.^{13,14} For sodium, the surface-tension equation [Eq. (10)] may be written^{3,13,15}

$$\sigma = 3.175 \times 10^{-7}(3670 - t_\ell); \quad (11)$$

for potassium, the surface tension may be expressed

$$\sigma = 2.07 \times 10^{-7}(3216 - t_\ell). \quad (12)$$

With this information available, the degree of liquid superheat required to initiate nucleate boiling in sodium and potassium may be calculated using Eq. (9) and the equivalent-cavity model.

Using Eq. (8) and knowledge of both the surface tension and the saturated-vapor curve, the radius to which the liquid will enter the surface cavities may be calculated. Figures 8, 9, and 10 are plots of liquid-penetration radius versus the liquid-saturation temperature at various values of system pressure (P_ℓ) for sodium and potassium. Utilizing these families of curves and knowing the pressure-temperature history of the system, we can calculate the minimum penetration radius (R_f) for either a sodium or a potassium system.

Now, using Eq. (9), knowledge of the surface tension and the saturated-vapor curve, and a value of R_f found from investigation of the pressure-temperature history of the system, the degree of liquid superheat as a function of system pressure (P_ℓ) may be found. Figures 11 and 12 show the degree of liquid superheat required to initiate nucleate boiling in sodium and potassium, respectively, plotted against the system pressure (P_ℓ) for various values of R_f . The values of R_f selected in this analysis are the minimum points from the curves shown in Figs. 8, 9, and 10.

Using the minimum penetration radius (R_f) calculated from Eq. (8) in Eq. (9) may introduce some error. The possible error introduced by using R_f is discussed in the appendix.

In the application of the equivalent-cavity model, it is essential to have an accurate account of the pressure-temperature history of the boiling surface. Hence, a record of the pressures and temperatures that have been applied must be available so that the minimum penetration radius can be determined. This will involve examining all the pressure-temperature conditions that have been applied in order to determine the most severe condition. Figures 8, 9, and 10 should provide some insight as to which conditions affect the liquid penetration most. For example, these figures show that, for sodium and potassium, system pressure influences the liquid penetration into cavities considerably more than temperature.

Fig. 8. Plot of Liquid-sodium Penetration Radius vs Liquid-saturation Temperature for $P_\ell = 10$, 15, 25, and 100 psia

Fig. 9. Plot of Liquid-sodium Penetration Radius vs Liquid-saturation Temperature for $P_l = 1$, 1.4, 5, and 10 psia

Fig. 10. Plot of Liquid-potassium Penetration Radius vs Liquid-saturation Temperature

Fig. 11: Degree of Liquid Superheat vs System Pressure for Sodium

Fig. 12. Degree of Liquid Superheat vs System Pressure for Potassium

IV. COMPARISON WITH EXISTING DATA

A small amount of experimental information pertaining to the degree of liquid superheat required to initiate boiling in the alkali metals has been published in the literature. The available information that has been located will be compared with the predicted liquid superheats of the equivalent-cavity model.

Comparing the equivalent-cavity-model predictions with the data in the literature required the selection of a minimum penetration radius, R_f . In applying the model, the minimum points on the liquid-penetration curves corresponding to the highest reported operating pressures were selected. These pressures are labeled in Figs. 13 and 15 through 18 as P_ℓ (subcooled).

Figure 13 shows the range of data from Ref. 16 for the incipient boiling superheats in potassium plotted against system pressure. This range of data is compared to the liquid superheats predicted by the equivalent-cavity model for the same range of system pressure. No specific data points were presented in Ref. 16; however, the range of data compares favorably with the predicted liquid superheats.

Data from Ref. 7 for boiling sodium is compared with the predictions of the equivalent-cavity model in Fig. 14. The three data points from Ref. 7 are an average of individual data points obtained. The average superheat data point for the mirror finish was the average of considerably more data than either the Lap F or porous-welds superheat data. The average superheat data for the mirror finish is within 17% of the equivalent-cavity-model prediction; the Lap F and porous-welds superheat data are within 45 and 51% of the equivalent-cavity-model prediction, respectively.

Figure 15 shows superheat data presented in Refs. 17 and 18 compared with the predictions of the equivalent-cavity model. The information from Ref. 17 shows the spread of data as well as the average data point for the initiation of boiling in potassium at a system pressure of 75 psia. This range of data falls directly above the line predicted by the equivalent-cavity model.

The data from Ref. 18 on Fig. 15 are for a condition in which the system was evacuated to as high a vacuum as was obtainable. The liquid metal was then heated to a liquid superheat of approximately 400°F (or greater) above the saturation temperature corresponding to the pressure in the liquid, and no boiling occurred. This point falls below the curve predicted by the equivalent-cavity model for P_ℓ equal to 5 psia.

Figure 16 shows data ranges of liquid superheat required to initiate nucleate boiling in sodium.^{19,20} System pressures prior to the initiation of boiling were between 75 and 100 psia. These data ranges compare favorably with the equivalent-cavity model prediction for values of P_ℓ between 75 and 100 psia.

Fig. 13. Comparison of Model with Data from Ref. 16 for Potassium

Fig. 14. Comparison of Model with Data from Ref. 7 for Sodium

Fig. 15. Comparison of Model with Data from Refs. 17 and 18 for Potassium

Fig. 16. Comparison of Model with Data from Refs. 19 and 20 for Sodium

Figure 17 shows data from Refs. 21 and 22 compared with the predictions of the equivalent-cavity model for initiation of boiling in potassium. No record is available of the pressure-temperature history before these data were obtained. However, in applying the model, we assumed that the system pressure before obtaining the liquid potassium superheats in Fig. 17 was 75 psia. Partial curves assuming pressures prior to the initiation of nucleation of 25 and 100 psia are also shown. Agreement of these data with the equivalent-cavity model appears good.

Figure 18 shows a plot of liquid superheat for boiling sodium from a sintered surface.²² These data compare favorably with curves of 5 and 10 psia using the equivalent-cavity model.

The predictions using the equivalent-cavity model show fair agreement with the data in Figs. 13-18. However, an accurate record of the pressure-temperature history of the system was not kept in any of the reporting of these data. Hence, more data must be gleaned to prove the utility of this model as applied to liquid-metal systems.

V. DISCUSSION

Utilization of the equivalent-cavity model enables the calculation of the degree of liquid superheat required to initiate nucleate boiling in the alkali metals. This knowledge of the incipient-boiling superheats is important in fundamental research as well as in reactor safety consideration.

The model utilizes the bubble-equilibrium equation [Eq. (9)]. Thus, the vapor in the unfilled cavity is assumed to be in thermal and mechanical equilibrium with the surrounding liquid. This assumption may be a somewhat idealized case of the actual boiling phenomenon. Utilization of the saturated-vapor curve of the alkali metal of interest and Eq. (9) permits the liquid superheats for incipient boiling to be calculated if the unknown functions representing either the bubble radius or curvature of P_v are known. A previous model³ has postulated P_v as a function of temperature and the amount of dissolved gas content in the liquid by utilizing results obtained from boiling experiments using distilled, degassed water.¹ However, postulating a relationship representing the bubble radius of curvature eliminates the need for using water results to obtain P_v when an insignificant amount of gas is contained in the liquid. Thus, by using the critical-cavity-opening model, and knowing the pressure-temperature history of the system, the incipient-boiling superheats may be calculated directly.

Previous investigators^{11,12} have used a similar modeling approach in attempting to predict the degree of liquid superheat required to initiate nucleate boiling in water. Much of the analysis and some of the arguments

Fig. 17. Comparison of Model with Data from Refs. 21 and 22 for Potassium

Fig. 18. Comparison of Model with Data from Ref. 22 for Sodium

in this report are similar to those utilized by the above authors. However, the application of this type of modeling for liquid metals should be more valid than the use of this model for water because of the large quantities of dissolved gases in water which may not permit the dropping of P_g from Eq. (6). Liquid-metal systems will have less gas phase initially, as well as an increasing thermal-diffusion effect with increasing temperature, which will pump the entrapped-gas phase from surface cavities.

This equivalent-cavity model is presented so that experimenters working with the boiling alkali metals will have some insight as to how they should handle a system after filling it with the liquid metal. For example, heating the system above 1500°F and pressurizing to 100 psia, and then attempting to boil at 5 psia will result in considerably higher liquid superheats than if the system was held at or below a pressure of 5 psia during the period when the liquid was subcooled. It has been experimentally observed^{1,23} that an increase in the system pressure while the liquid is subcooled, increases the degree of liquid superheat required to initiate nucleation from a cavity.

Also, Figs. 8, 9, and 10 show that the liquid penetration into the surface cavities is influenced most significantly by the pressure. This is especially noticeable at higher pressures. Thus, knowledge of the pressure history of the system may be sufficient to obtain reasonably accurate results from the critical-cavity-opening model.

A small-scale experiment was conducted at Argonne using water in glass flasks to gain qualitative information pertaining to the effect of wetting upon bubble nucleation. Both flasks contained distilled degassed water, but the inner surface of one of them had been previously treated with a non-wetting agent (Desicote). These tests showed that the wetted surface had fewer nucleation sites and required higher liquid superheats than the unwetted surface. These qualitative results complement the model in that for the wetted surface more surface cavities filled with liquid. This resulted in fewer nucleation sites. Also, since more cavities were filled with liquid, smaller cavities were forced to serve as nucleation sites. Hence, higher liquid superheats were required for nucleation from these smaller cavities.

The equivalent-cavity model assumes that eventually all noncondensable gases will be removed from the surface cavities. Fabric¹² examined the trapping of noncondensable gases by surface cavities in water systems. This analysis shows that it is unlikely that surface cavities will entrap noncondensable gases and that surface cavities (nucleation sites) will not have an air-water vapor mixture trapped throughout a heating cycle. The solubility of inert gases in the liquid metals increases with increasing temperature, whereas the solubility of air in water decreases with decreasing temperature. Thus, the pumping action (increased solubility with increasing temperature) of the noncondensable gases from surface cavities in liquid-metal

systems, along with the inability of surface cavities to entrap gases, augments the argument that the surface cavities that contain no noncondensable gases are the interesting ones in a reactor safety analysis.

The cavities that have been shown to be nucleation sites when finite superheats occur are those cavities that start out nonwetted but switch to wetting at $P_v \geq P_\ell$. This switch from nonwetting to wetting appears improbable for any given cavity; however, since a boiling surface has many cavities (in the millions) this could explain the extremely small number of sites from which nucleation occurs.

Figure 19 presents a sequence of events postulated as an explanation of this switch from nonwetting to wetting at $P_v \geq P_\ell$. Figure 19a shows a cavity containing a thin oxide layer. Figure 19b shows a nonwetting condition as subcooled liquid metal enters the cavity. When heating is applied to the system (Fig. 19c), a reaction which occurs between the liquid metal and the surface oxides cleans the upper part of the cavity surface causing the switch from nonwetting to wetting at $P_v \geq P_\ell$. Hence, nucleation will be initiated at the radius to which the liquid metal has penetrated the surface cavity.

Fig. 19. Switch from Nonwetting to Wetting at $P_v \geq P_\ell$

Upon cooling of the surface after boiling, the liquid will again attempt to enter the cavity. The liquid will be able to penetrate the cavity until a nonwetting condition occurs. This nonwetting should occur at the same radius at which the liquid had initially entered the cavity. Hence, the same liquid superheats may be expected to initiate future boiling from this cavity.

The previous analysis has shown that a nonwetted surface requires zero liquid superheat to initiate nucleate boiling. A zero-superheat

requirement for a surface to initiate boiling is an ideal situation for a reactor. This suggests an experimental area for nonwetting surface work.

This equivalent-cavity model also explains the mechanism of bubble formation. Movies and observations showing extremely rapid void formation augment the theory that as the liquid-vapor interface moves to a larger cross section, the vapor pressure caused by the now excessive liquid superheat expels the liquid from the cavity, thus nucleating a bubble.

In general, the calculated incipient-boiling superheats for sodium and potassium are in fair agreement with data in the literature. However, as more data become available, the model should be tested further to prove its utility.

APPENDIX

The Effect of Contact Angle upon Liquid Superheat

The predictions of the equivalent-cavity model do not completely take into consideration the effect of the contact angle upon the liquid superheats required to initiate nucleate boiling. Fabric¹² examined the effect of contact angle upon liquid superheats in water systems. The discussion in this appendix will pertain to the effect of contact angle upon liquid superheats, primarily in liquid-metal systems.

It has been assumed in the equivalent-cavity model that the radius of curvature of the vapor-liquid interface just before bubble initiation is equal in magnitude to the smallest radius of curvature of the liquid being forced into the cavity while the liquid was subcooled (R_f). The validity of this assumption is dependent entirely upon the wetted and nonwetted contact angles of the liquid metal upon the cavity surface. The contact angle as used in this report is measured through the liquid. If the contact angle is between 0 and 90°, the liquid is generally said to wet the surface; if the contact angle is between 90 and 180°, the liquid is said to not wet the surface.

Carlson²⁴ investigated contact angles between liquid metals and stainless steels, and Carlson and Sowa²⁵ investigated contact angles between liquid metals and ceramics. These investigations showed that the condition of the surface is important in determining the contact angle; very slight changes in the composition can make the difference between wetting and nonwetting. This effect of the surface composition upon contact angle makes a theoretical analysis of the contact angle upon liquid superheat extremely difficult to handle. Hence, the effect of contact angle must be examined by utilizing observations of other investigators.

Examination of the nonwetting subcooled liquid entering the surface cavity yields Eq. (8),

$$P_\ell - P_v = \frac{2\sigma}{R_n},$$

which may also be written

$$P_\ell - P_v = 2\sigma \frac{|\cos \theta_a|}{r'} \quad (13)$$

As heat is supplied, the liquid becomes superheated, the liquid wets the surface, and P_v becomes larger than P_ℓ . Equation (9) represents this existing relationship,

$$P_v - P_\ell = \frac{2\sigma}{R_r}.$$

Equation (9) may also be written

$$P_v - P_\ell = \frac{2\sigma |\cos \theta_r|}{r'}$$

Fabric¹² examined the literature pertaining to the angle of contact of liquids advancing into and receding from surface cavities. The advancing contact angle was generally between 105 and 110°, and the receding contact angle was approximately 40° smaller. Using this information, one may assume that $|\cos \theta_a| \leq |\cos \theta_r|$. Since

$$R_a = \frac{r'}{|\cos \theta_a|} \quad (15)$$

and

$$R_r = \frac{r'}{|\cos \theta_r|}, \quad (16)$$

it is seen that

$$R_a |\cos \theta_a| = R_r |\cos \theta_r|; \quad (17)$$

hence,

$$R_a \geq R_r. \quad (18)$$

Thus, with these assumed contact angles, the equivalent cavity model predicts a maximum liquid superheat, providing an accurate accounting of the pressure-temperature history of the system has been obtained.

From the values of contact angle assumed by Fabric¹² for the advancing and receding contact angles of 108 and 66°, respectively, the inaccuracy in using the equivalent-cavity model may be expressed:

$$(P_v - P_\ell)_{\text{actual}} = 1.109(P_v - P_\ell)_{\text{predicted}} \quad (19)$$

The accuracy limits obtained by assuming contact angles for the advancing and receding liquid may be less significant than the inaccuracies caused by the differences in contact angles caused by surface composition and cavity roughness.^{24,25} Also, a qualitative analysis of advancing and receding contact angles appears extremely difficult for liquid-metal systems.

Since sufficient knowledge of the contact-angle phenomena in liquid metals is not available, the possibility of large errors exists. However, the

the agreement of this modeling technique with the data presently available augments the utility of the model.

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