

# TRANSIENT BOILING OF LIQUEFIED CRYOGENS ON A WATER SURFACE

## I. NITROGEN, METHANE and ETHANE

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**Abstract**—An experimental study of the transient boiling rates of pure liquefied nitrogen, methane, and ethane on a water surface is reported. Measured heat fluxes were lowest for nitrogen and highest for ethane. The former is believed to film boil on a water-ice surface while ethane nucleate boils on a solid ice or hydrate crust formed very early in the run. Liquefied methane data fall between those of nitrogen and ethane. For spills of all three cryogenes, the water temperatures several mm below the surface did not change appreciably but only decreased very slowly during a test. Significant vapor superheat was noted for liquid nitrogen spills but not when methane or ethane boiled on the water-ice surface.

### NOMENCLATURE

- $k$ , constant in equation (2);  
 $M$ , mass of liquid cryogen in test vessel [ $\text{g}/\text{cm}^2$ ];  
 $M_0$ , mass of liquid cryogen spilled [ $\text{g}/\text{cm}^2$ ];  
 $Q_{\text{latent}}$ , heat-transfer rate based on rate of mass loss and enthalpy of vaporization [ $\text{kW}/\text{m}^2$ ];  
 $Q_{\text{sensible}}$ , enthalpy removal rate based on the degree of superheat of the evolved vapor [ $\text{kW}/\text{m}^2$ ];  
 $t$ , time [s].

### INTRODUCTION

CRYOGENIC liquids are commonly transported in bulk within insulated tankers and barges. Liquefied petroleum gas (LPG), liquefied natural gas (LNG), ammonia and chlorine are common examples. The hazards associated with an accidental spill of such fluids on water is a cause of concern as these liquids would readily vaporize and produce toxic and/or flammable clouds downwind. Any realistic evaluation of the hazards resulting from a real or hypothetical accident requires data on the rate of boiling from the water surface as this information is a necessary input into any vapor dispersion calculation.

The transient boiling of a volatile liquid on the surface of a second, hot liquid has received relatively little attention compared to the more common phenomenon of boiling on a solid, heated surface. The former is less readily characterized in a quantitative manner as the hot surface is mobile and capable of internal heat transfer by both eddy and conductive mechanisms. In addition, if the volatile fluid boils at a temperature below the freezing point of the hot fluid, there is the possibility of a solid phase forming at the surface and extending into the hot fluid. Finally, any real spill of a cryogenic liquid on water will lead to a highly transient situation with the possibility of rapid variations in the heat flux.

In the present paper, boiling rates of pure methane, ethane, and nitrogen vaporizing from a water surface are reported. In a subsequent paper, the study is extended to hydrocarbon mixtures typical of liquefied natural gas.

### PREVIOUS WORK

It is surprising that so few studies have been published wherein a liquid boils while in contact with the free surface of another hotter liquid which acts as the heat source. Should the temperature difference be sufficiently large that film boiling occurs, one might expect the common film boiling correlations to be applicable since, for such a regime, the characteristics of the hot surface play only a minor role. If, however, the situation is such that nucleate boiling should result, then the situation is quite different since the hot liquid surface may have few, if any, satisfactory nucleation sites. It is entirely possible that the volatile liquid may be effectively prevented from boiling and become quite superheated in the thin layers adjacent to the surface. Just such a mechanism has been proposed [1-7] to explain rather violent vapor explosions which sometimes result when a volatile liquid is contacted with a hot liquid.

Boiling of one liquid on the surface of a second, hotter liquid represents an extreme case of employing a very smooth, polished solid heating surface. As shown by Corty and Foust [8] and Berenson [9], the nucleate boiling region is expanded and the transition boiling region compressed for very smooth heating surfaces though the Leidenfrost temperature (lowest temperature for stable film boiling) and film boiling regimes are not greatly affected.

Early studies of contact boiling between two immiscible liquids were limited to cases where water was boiled on solid surfaces covered with thin oil films [10]. Large vapor bubbles formed and the vapor evolved was probably superheated [11]. Later, Bonilla and Eisenberg [12] vaporized butadiene under pressure

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on a water surface. By refluxing the hydrocarbon and heating the water, experiments were conducted in a steady-state mode. The presence of the more volatile liquid effectively reduced the bulk water temperature and enhanced the net rate of heat transfer from the solid surface. Similar experiments were made by Bragg and Westwater [13]. A number of boiling experiments have been conducted using hot mercury and different volatile organic liquids; these are summarized by Sideman [14]. As mercury possesses a high thermal conductivity, the boiling heat transfer characteristics would be expected to be intermediate between those represented by a solid surface and a typical organic liquid (or water). Significant scatter between results of different investigators was, however, noted.

Only a few previous studies have been made wherein cryogenic liquids were boiled on water. Those pertinent to the present investigation are noted briefly below but the results are introduced later when a comparison can be made with the new results reported in the present paper.

Burgess *et al.* at the Bureau of Mines [15, 16] conducted several preliminary tests where nitrogen, methane, and LNG were boiled from a water surface and the mass change recorded during vaporization. No liquid or vapor temperatures were measured and the data are tabulated as average values over discrete periods of time. The principal result found was that the rates of boiling were such that methane vaporized at a much higher rate than nitrogen. The boiling rate of methane was also found to increase with time, but for nitrogen, the rate either decreased or remained constant. A similar, but less comprehensive study by Nakanishi and Reid [2] corroborated the Bureau of Mines results.

Boyle and Kneebone [17] carried out a few tests using liquid methane spilled on a large tank of water but as will be described later, their results are inconclusive since the quantity spilled was often insufficient to cover the water surface with a continuous film.

#### EXPERIMENTAL

Vaporization experiments were carried out in a well-insulated vessel mounted upon a Mettler load cell balance with a 99 per cent response in less than 20 ms. A schematic sketch of the apparatus is shown in Fig. 1 and a more detailed view of the boiling vessel in Fig. 2.

Some 450–500 g of water at the desired temperature were placed in the boiling vessel. The test was initiated by tipping the cryogenic storage Dewar, allowing liquid to impact on the conical distributor, flow down the walls, and spread over the surface of the water. The change in system mass was monitored from the output of the load cell on a Hewlett–Packard data acquisition system and on Sanborn recorders. As will be described below, liquid and vapor temperatures were also measured during a test. At the completion of a run, when all the cryogen had been boiled away, the residual water was stirred, any ice melted, and a final bulk water temperature measured.

The heart of the apparatus was the boiling vessel (Fig. 2). It was actually a triple walled container. The

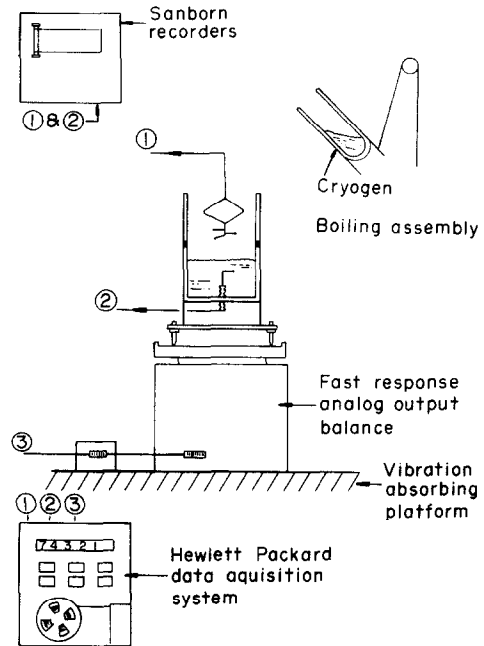


FIG. 1. Apparatus for boiling rate studies.

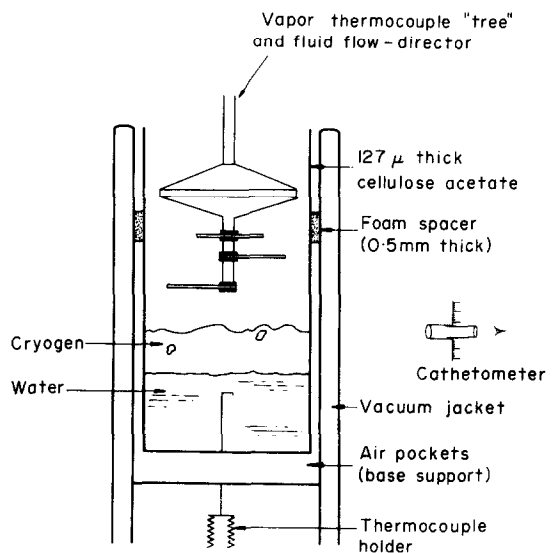


FIG. 2. The boiling vessel.

two outer walls were made from acrylic plastic and the annulus was partially evacuated. The low thermal mass inner wall was fabricated from 127  $\mu$  scratch-free cellulose acetate sheets and separated with polyurethane foam spacers from the inner acrylic wall by a 0.5 mm air gap. This cellulose acetate lining covered both the sides and the bottom. Heat leak from the environment was negligible over the duration of the experiments (*ca* 1 min).

The overall dimensions of the boiling vessel were 9.92 cm i.d. and 17.8 cm deep. The heat-transfer area was 77.3 cm<sup>2</sup>.

An acrylic double-cone (7.6 cm dia) was hung into the open end of the boiling vessel. This device served several functions. As noted earlier, it broke the fall of the

cryogen and thus lessened any initial overshoot reading on the load cell. Also, the cryogen liquid was distributed more evenly over the water surface. The cone also served as the support for the thermocouple tree and, finally, it effectively prevented ambient air from entering the vessel during a test and so the reverse flow patterns noted by Boardman *et al.* [18] did not appear. It did not, however, slow the addition of cryogen appreciably; 100 cm<sup>3</sup> of liquid could be poured into the boiling vessel in about 0.5 s.

The vapor thermocouple tree consisted of three copper-constantan thermocouples fabricated from 25 μm wires. Each was heat-stationed with 10 cm lengths wound in a spider-web perpendicular to the direction of gas flow. Three other heat-stationed 25 μm thermocouples were inserted into the water though, in this case, the wires entered the boiling vessel through the bottom.

Each of the six thermocouples as well as the system mass was sampled every second by the data-acquisition system. The values were digitalized and stored on paper tape for later recall and analysis. Sanborn recorders were used to obtain continuous plots of the thermocouple signals and system mass.

The locations of the thermocouples were varied in different experiments. In most cases, however, one thermocouple was located in the water so that its bead (56 μm dia) just touched the water surface. As placed, it effectively rode with the surface and was used to monitor a local water surface temperature.

During a test, an observer recorded the actual height of cryogen at various times. This was accomplished with a side-mounted cathetometer.

Additional experimental details are available elsewhere [19].

**METHANE EXPERIMENTS**

Twenty-one spills were made with high purity liquid methane (99.98%). The quantity vaporized as a function of time depended neither upon the quantity spilled nor upon the initial water temperature except for very small spills. In Fig. 3, data are shown for fourteen of the tests; the quantity spilled varied from 0.33 to 1.01 g/cm<sup>2</sup> (equivalent to initial layer thicknesses of 0.79–2.4 cm) and the initial water temperature ranged from 9.9 to 52.7°C. The scatter of the data for these runs fell within the cross-hatched band.

Of the seven other methane runs not shown in Fig. 3, one (0.36 g/cm<sup>2</sup> spilled upon 29.8°C water) yielded a vaporization-time curve parallel to the one shown but displaced beneath it by about 10<sup>-2</sup> g/cm<sup>2</sup>. A slight bias in the load cell could have led to this result. Another (0.92 g/cm<sup>2</sup> spilled on 9.3°C water) indicated a vaporization-time curve parallel to, but above the data-band in Fig. 3. In this particular run, surface liquid water temperatures dropped well below 0°C very quickly indicating rapid and widespread ice formation. The five other tests not shown were made with spills of only about 0.18 g/cm<sup>2</sup> liquid methane (4 mm). Vaporization-time data clustered but fell well below the band in Fig. 3. It is believed that, soon after the run began, a

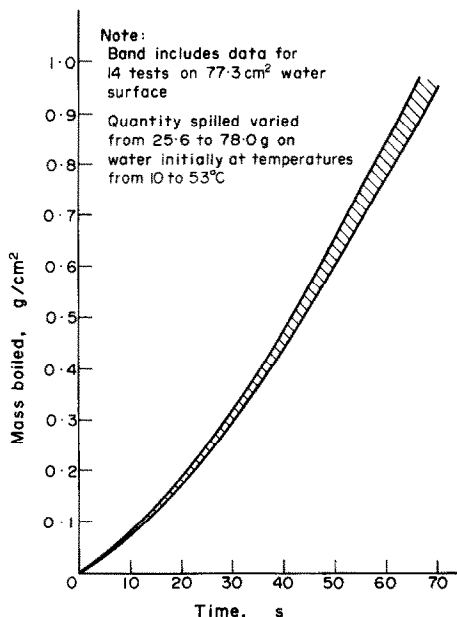


FIG. 3. Pure liquefied methane boiling on water.

continuous layer of methane no longer existed on the water surface and the heat-transfer area was reduced accordingly.

It is interesting to note that the rate of methane vaporized increased continuously with time. By differentiating the data shown in Fig. 3, vaporization rates were found; these are shown in Fig. 4.

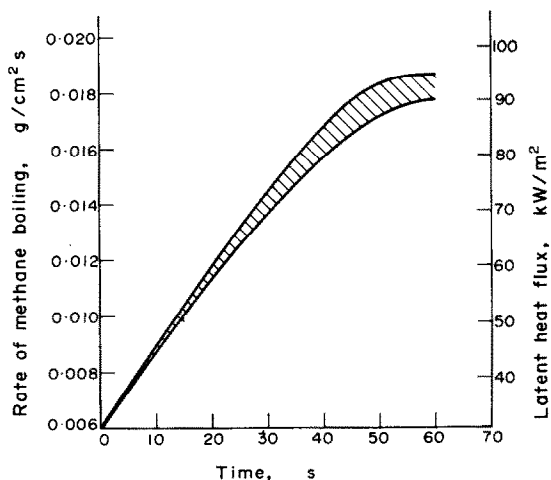


FIG. 4. Rate of vaporization of pure methane on water.

The water temperatures measured during the methane spills revealed some surprising results. Thermocouples placed more than about 5 mm below the surface registered little change in temperature during a run—though on occasion, a rapid drop (*ca.* 2–4°C) was noted, but this perturbation was followed by a quick recovery. For large pours on room-temperature water, thermocouples placed 5–10 mm below the surface did decrease 5–15°C over the course of the test but the decrease was gradual and, in no instance, was 0°C attained. In contrast, temperature

measurements in the first 2–3 mm often fluctuated violently and, in most runs, temperatures well below 0°C were recorded. There was every indication that some ice formed on the surface and this was substantiated by visual observation.

Vapor temperatures were also recorded. No vertical or radial gradients were detected below the cone but the temperatures were often 10–30°C higher than the boiling point of pure methane. The degree of superheat appeared to be nearly independent of the initial water temperature. For spills with initial depths exceeding 1–1.5 cm, little or no superheat was found. For smaller spills (these runs were noted above to give anomalously low boiling rates), large superheats reinforce the assertion that complete liquid coverage was not attained. For larger spills, when the liquid head had decreased to 0.1–0.3 cm, the surface was probably covered with low-temperature ice and no increase in vapor temperature would have been expected even when the residual liquid methane formed islands rather than existing as a continuous film.

Only two other studies have reported data for boiling rates of liquefied methane on water. Boyle and Kneebone [17] carried out a few very small scale spills on a 9 ft<sup>2</sup> (8360 cm<sup>2</sup>) surface. When scaled, their tests represented spills of 0.16 and 0.27 g/cm<sup>2</sup>. The first is smaller than any carried out in the present work while the second is in the range of the tests that yielded anomalous low rates. The rates reported by Boyle and Kneebone were much lower than those shown in Fig. 4 but agreed reasonably well with the few low mass spills taken in this work. In all such tests, it is believed that there was not a complete coverage of the water surface so that actual numerical values of the boiling rates per unit area are misleading.

The other reported study involving liquid methane was carried out by the Bureau of Mines [16]. In this case, the spill area was 0.80 ft<sup>2</sup> (742 cm<sup>2</sup>) and three sizes of tests were apparently made, i.e. of 2, 3 and 4.5 l. These correspond to 1.13, 1.70 and 2.55 g/cm<sup>2</sup>, values larger than any studied and reported in the present work. Contrary to the results shown in Figs. 3 and 4, the Bureau of Mines found that the boiling rates did depend somewhat upon the initial quantity of methane spilled. Their data are reproduced in Fig. 5 where the mass lost is shown as a function of time. No

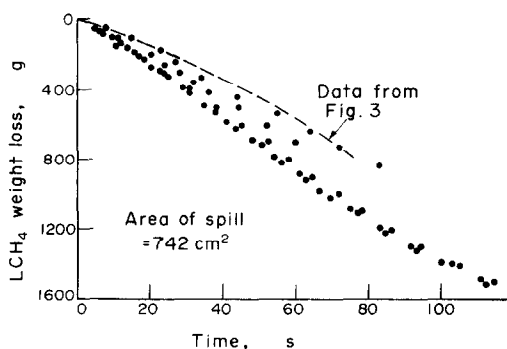


FIG. 5. Liquid methane vaporization on water as reported by the Bureau of Mines [16].

delineation of the spill size is given but it is believed that the top series of data points represents the smallest spill (1.13 g/cm<sup>2</sup>) while the lowest extended set represents the largest spill (2.55 g/cm<sup>2</sup>). The few points in between probably show limited data for the 1.70 g/cm<sup>2</sup> tests. Such results indicate that rates increase with spill size. The data from Fig. 3 are also shown in Fig. 5, after multiplication by the area, 742 cm<sup>2</sup>. The comparison is interesting. As expected, from the trends discussed above for the Bureau of Mines data, the weight loss values from Fig. 3 are less than those of larger mass spills, though the difference is not great for the smallest Bureau of Mines spill (1.13 g/cm<sup>2</sup>) which almost overlaps the largest spill (1.01 g/cm<sup>2</sup>) studied in this work.

The qualitative picture for liquid methane is reasonably clear. The important physical phenomena occur at or near the cryogen–water interface with ice formation; the bulk water phase is not affected. Film and perhaps transition boiling first occur due to the large initial temperature difference; as patches of ice form and cool, nucleate boiling is encouraged thus an increase in boiling rate is noted with time. For every 0.5 g of liquid methane boiled from a 1 cm<sup>2</sup> surface, if ice were to be formed and cooled to liquid methane temperatures, then there results an ice thickness of only about 0.6 mm. Though this extreme in ice formation is not achieved due to concomitant heat transfer into the bulk liquid, clearly, the order of magnitude is correct to explain why the observed energy loss occurs only in the very top layers of water. Ice thicknesses were not measured at the completion of a run, but after stirring and melting the ice, the final water temperature could be employed to verify an overall energy balance since the initial water conditions, the quantity of methane poured, and the temperature of the evolved methane vapor were all known. Such energy balances generally closed within 10 per cent. Photographs of the interface indicated that the vapor bubbles were large and normally between 10 and 18 mm in diameter.

The quantitative picture of methane boiling on water is less satisfactory. The system is highly transient and there are several thermal resistances in series—all of which are probably quite time dependent. The surface boiling coefficient is initially low (film boiling) but increases significantly as ice patches form and cool. As the ice increases in thickness and extent, it too contributes a thermal resistance (ideally one which would reduce heat transfer proportional to  $t^{-\frac{1}{2}}$ ). Finally, continuous melting and freezing at the agitated interface must play an important role in the heat-transfer process. Similar conclusions were stated earlier by Boyle and Kneebone [17].

When compared to methane film boiling on solid surfaces, with a temperature difference near 170°C, experimental fluxes of about 35 kW/m<sup>2</sup> have been reported [20, 21]. As shown later in Table 1, this value is lower than the fluxes measured in this work except at the very initial portion of the experiment. Nucleate boiling is apparently important except in the early stages. Also, film boiling heat fluxes estimated from

standard correlations such as those of Berenson [9] are even lower ( $\sim 27 \text{ kW/m}^2$ ) so such relations do not appear applicable for the case of methane boiling on a water surface.

**ETHANE EXPERIMENTS**

Eight spill experiments were made with pure ethane (0.16% *n*-butane was present as an impurity). Spill sizes ranged from 0.30 to 1.06 g/cm<sup>2</sup> (0.55–2 cm) on water whose initial temperature varied from 8 to 49°C.

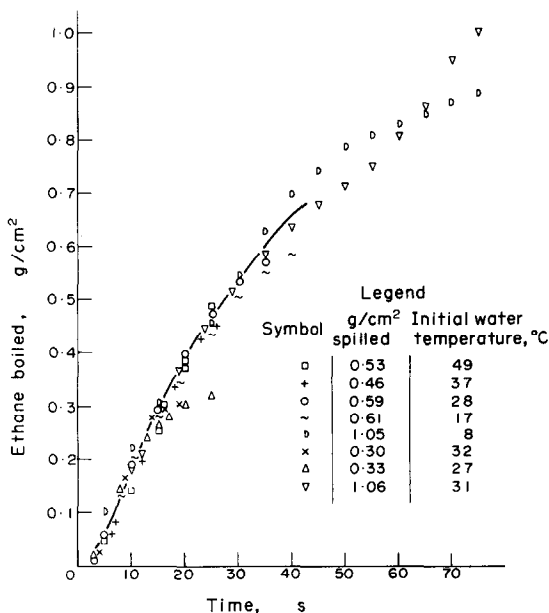


Fig. 6. Liquefied ethane boiling on water.

Vaporization-time data for the various runs have been plotted in Fig. 6. There is clearly an induction period early in the run where the rate of vaporization is low. Following this period, the rate increases significantly and then, later, decreases slowly. Visual observation indicated that ice formed extremely rapidly and, the lower the initial water temperature, the more rapid the ice formation. It is believed that the induction period shown in Fig. 6 results because a finite time is required to create a cold, solid ice surface that would promote efficient nucleate boiling. The only experiment in which no induction period was observed was one wherein the initial water temperature was only 8°C. Presumably, ice formed very quickly in this case. The more pronounced rate of ice formation for liquid ethane is also probably the reason why the rate of boiling decreased at longer times, i.e. the solid ice crust acted as an effective thermal resistance.

The assertion of a rapid build-up of ice is further strengthened by experimental vapor temperature data which indicated essentially no superheat. Water temperatures in the first few mm below the surface dropped quickly to near liquid ethane temperatures whereas 1 cm below the surface, there was only a very slow decrease in temperature over the duration of the run.

To compare the rates of boiling between methane and ethane, assuming that both evolve saturated vapor, approximate heat-transfer rates for both cryogenics are shown in Table 1 as a function of time. Initial rates

Table 1. Approximate heat-transfer rates for pure methane and ethane boiling on water

Time (s)	Boiling flux (kW/m <sup>2</sup> )	
	Methane	Ethane
5	37	60
10	45	120
15	52	105
20	59	80
30	71	70
40	83	60
50	90	45
60	~90	30

for ethane are larger even though the temperature difference between boiling ethane and water is appreciably less than for methane. The more rapid ice formation with a concomitant shift to nucleate boiling could cause this difference. For ethane runs, at long times, a solid ice crust has apparently formed and the heat flux decreases significantly. For both hydrocarbons, the heat fluxes are higher than for liquid nitrogen as shown below.

**LIQUID NITROGEN**

Sixteen spills were made with liquid nitrogen. Initial water temperatures were varied from 6.3 to 52°C and the quantity spilled from 0.31 g/cm<sup>2</sup> (0.38 cm) to 1.0 g/cm<sup>2</sup> (1.25 cm). As in the methane and ethane experiments, weight loss-time data were obtained as were vapor and liquid (water) temperatures.

In a qualitative sense, the results were quite different from the pure hydrocarbon tests. Some ice normally appeared early in the run but often it broke up and allowed fresh contact between the liquid nitrogen and water. Any ice formed was usually transparent in contrast to the milky, opaque form that was found with methane or ethane spills. Small white solid particles were observed to accumulate in the residual liquid nitrogen phase, and the water surface, when not covered with ice, was rough and agitated. The vapor bubbles were somewhat smaller than noted for pure methane and ranged from 7 to 10 mm in diameter.

As with hydrocarbon experiments, the water temperatures showed little or no change except within a few mm of the surface and, only at the very interface did the temperatures drop below 0°C during most runs.

The most surprising result was the sensitivity of the boiling rate to the initial mass of liquid nitrogen poured on the water. No such trend was evident from the ethane or very pure methane spills. Some typical data points are plotted in Fig. 7. It is obvious that the large pour tests (1.0 g/cm<sup>2</sup>) resulted in a large rate of mass loss as a function of time. All the data taken in this study are shown in Fig. 7 except for the runs with initial spills in the 0.76–0.83 g/cm<sup>2</sup> range. These

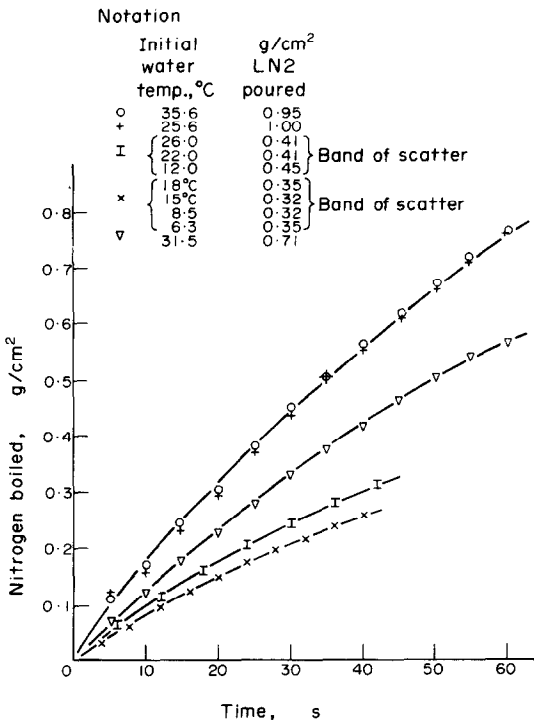


FIG. 7. Liquefied nitrogen boiling on water.

scattered somewhat but even all of these could be plotted in a band between the top two curves.

It was found, however, that all the data could be correlated in the manner shown in Fig. 8. The quantity  $(M_0^{\frac{1}{2}} - M^{\frac{1}{2}})$  is shown to be a linear function of time.  $M_0$  is the initial mass poured and  $M$  is the mass at time  $t$ , both on a cm<sup>2</sup> basis. The vertical rectangles encompass the 0.76–0.83 g/cm<sup>2</sup> spill data noted earlier. Expressing Fig. 8 quantitatively,

$$M_0^{\frac{1}{2}} - M^{\frac{1}{2}} = kt/2 \quad (1)$$

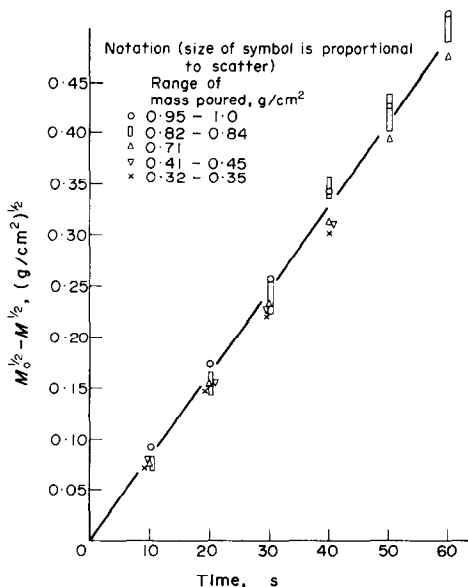


FIG. 8. Correlation for liquid nitrogen boiling on water.

or

$$dM/dt = -kM^{\frac{1}{2}} \quad (2)$$

with

$$k = 0.0163(\text{g/cm}^2)^{\frac{1}{2}}\text{s}^{-1}.$$

Multiplying by the latent heat of vaporization, and introducing the liquid head instead of actual mass/area,

$$Q_{\text{latent}} = 29.2h^{\frac{1}{2}} (\text{kW/m}^2) \quad (3)$$

where  $h$  is the liquid nitrogen head in cm. The range over which equation (3) has been tested is  $0.3 < h < 1.2$  cm.

However, there is an additional, significant correction to be made before one may discuss the heat-transfer rate between liquid nitrogen and water. We noted earlier that for ethane, the evolved vapors were essentially at the saturation temperature and, for methane, the superheat was small, except for very small spills. In the case of liquid nitrogen, the vapors were always superheated. For the larger spills, the degree of superheat was 40–50°C initially but for the small spills, this range increased to 90–100°C. In general, the vapor temperature could be approximated as a linear function of the liquid nitrogen head, i.e. as the head increased, the difference between the actual vapor temperature and the saturation temperature decreased. Combining this relation with the rate of boiling, a term  $Q_{\text{sensible}}$  could be obtained as a function of liquid head.  $Q_{\text{sensible}}$  is shown plotted in Fig. 9 along with  $Q_{\text{latent}}$ . The sum of these two terms yields the total heat transfer between liquid nitrogen and water. At low heads, the vapor is quite superheated and a significant fraction of the enthalpy of the nitrogen vapor is removed as sensible heat. At high heads, the superheat diminishes more than the rate of boiling increases thus there is a net decrease in this term.

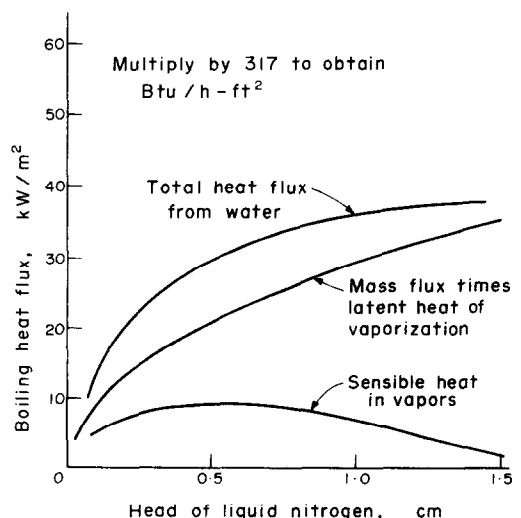


FIG. 9. Heat fluxes from liquefied nitrogen boiling on water.

The only data with which to compare these results were taken by the Bureau of Mines [16]. Little detail is presented in their report, and the data are shown in Fig. 10. In Fig. 10(a), there is appreciable scatter and the authors drew a straight line through the data with a slope of  $0.0167 \text{ g/cm}^2 \text{ s}$ . No correction was made for enthalpy removed by superheated nitrogen vapor. Also, the quantity poured is not given. If a value of about  $1100 \text{ g}$  ( $1.48 \text{ g/cm}^2$ ) were assumed from the tailing of the mass-time curve, then equation (3) yields the dashed curve shown in Fig. 10(a).

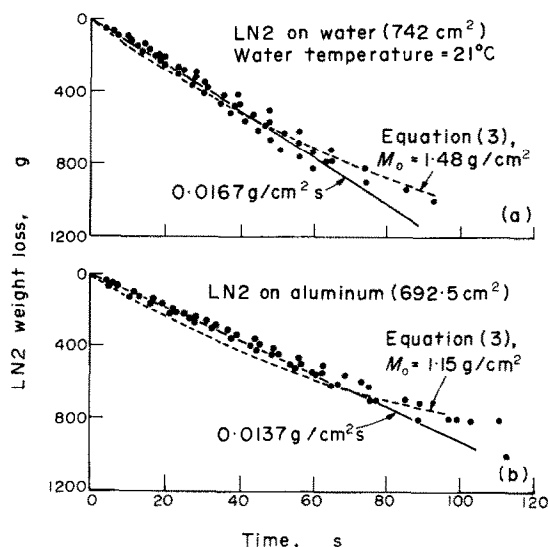


FIG. 10. Weight loss of liquid nitrogen as reported by the Bureau of Mines [16].

It is reasonable to hypothesize that for liquid nitrogen, heat transfer occurs with film boiling. Evidence for this assertion is the agitated surface, the important effect of liquid head, and the large superheat found in the evolved vapors. Also, as indicated in Fig. 10(b), when an aluminum sheet was placed on the water surface, the rate of boiling was not greatly different than on water. In fact, it would appear in this case that about  $800 \text{ g}$  ( $1.15 \text{ g/cm}^2$ ) were spilled. Using this value, the dashed curve in Fig. 10(b) represents equation (3). The good fit indicates that the microstructure of the surface is not important for liquid nitrogen boiling on water, i.e. film boiling predominates.

The experimental boiling fluxes in Fig. 10 may be compared with values of  $25\text{--}30 \text{ kW/m}^2$  reported by Sauer and Ragsdell [22] and Flynn *et al.* [23] for liquid nitrogen film boiling from solid surfaces. Similar values are predicted when correlations such as Berenson's [9] are used. Both experimental and predicted heat fluxes are somewhat less than measured in this work.

The energy removed from the water is probably extracted from a very thin film with rapid ice formation. Though some conduction and convection most certainly occurs in the bulk-water phase, if one neglects

these, an ice thickness of only about  $3 \text{ mm}$  would be necessary to fulfill the energy requirements should  $1 \text{ cm}$  of liquid nitrogen boil on top of a water surface initially at  $20^\circ\text{C}$ . For this size pour, temperatures in the first  $1$  or  $2 \text{ mm}$  did drop below  $0^\circ\text{C}$  indicating ice formation occurred.

## DISCUSSION

All three cryogenic liquids studied behaved differently when boiled on a water surface. Nitrogen film boiled with the lowest heat flux rates and the highest vapor superheat. The rate was found to be proportional to the square root of the liquid head. On the other extreme, ethane was presumed to nucleate boil after rapidly forming a coherent ice crust. The heat flux was the highest measured and there was essentially no superheat noted in the evolved vapor. Temperatures in the first  $\text{mm}$  or so in the water layer dropped rapidly to well below  $0^\circ\text{C}$ ; this contrasted with the much higher temperatures for nitrogen. The rate of ethane boiling appeared to be independent of the liquid head.

Methane seems to represent an intermediate case. The data indicate that both film and nucleate boiling occur, the latter increasing in importance as thin ice patches formed and grew on the surface. The boiling heat flux was intermediate between those of nitrogen and ethane and increased with time. Some superheat was noted in the vapor but this decreased appreciably with the larger spill tests. No effect of liquid head was noted, but for much larger spills, the Bureau of Mines does report an enhancement.

In all three liquids, temperatures measured more than  $5 \text{ mm}$  below the liquid surface decreased only very slowly with time. Boyle and Kneebone's studies [17] also confirm this fact. Though some conduction and convection heat transfer does take place, the predominant energy source would seem to be in freezing thin layers of ice on the surface. One disconcerting conclusion is the fact that ice was found in spills involving all three cryogenics, though the results indicate that film boiling was the predominant regime for nitrogen and also important for methane. Suggestions have been made [17] that water-hydrates may be formed with hydrocarbons. Certainly propane very rapidly forms a hydrate if poured on ambient water. It is possible that some of the ethane and methane "ice" was indeed a hydrate though no direct evidence is available.

The data presented in this paper should allow one to estimate, with engineering accuracy, the rate of boiling of nitrogen, methane, and ethane on water in a fixed container.

These results may not be directly applicable to spills on open water where wave action could prevent any ice from forming at the interface. Removal of such solid nucleation sites probably would shift the heat fluxes toward the lower film-boiling values.

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## EBULLITION TRANSITOIRE DES LIQUIDES CRYOGENIQUES A LA SURFACE DE L'EAU. I—AZOTE, METHANE ET ETHANE

**Résumé**—L'article fait état d'une étude expérimentale des vitesses d'ébullition transitoires d'azote, méthane et éthane purs liquéfiés à la surface de l'eau. Les flux de chaleur mesurés sont les plus faibles dans le cas de l'azote et les plus élevés dans le cas de l'éthane. Le premier est supposé entrer en ébullition en film sur une surface de glace tandis que l'éthane est en ébullition nucléée sur de la glace solide ou sur une carapace d'hydrate formée au tout début de l'expérience. Les données relatives au méthane liquéfié se placent entre celles pour l'azote et celles pour l'éthane. Pour chacun des trois cryogènes répandu en surface, la température de l'eau quelques mm au dessous de la surface n'était pas modifiée de façon appréciable mais diminuait seulement très lentement au cours de l'épreuve. Une quantité importante de vapeur surchauffée a été observée pour les couches d'azote liquide, mais non dans le cas de l'ébullition du méthane ou de l'éthane sur une surface de glace.

## INSTATIONÄRES SIEDEN VON VERFLÜSSIGTEN GASEN AUF EINER WASSEROBERFLÄCHE—I. STICKSTOFF, METHAN, ÄTHAN

**Zusammenfassung**—Es wird über eine experimentelle Untersuchung der Siederaten beim instationären Sieden von reinem, verflüssigtem Stickstoff, Methan und Äthan auf einer Wasseroberfläche berichtet. Die gemessenen Wärmestromdichten waren am niedrigsten bei Stickstoff und am höchsten bei Äthan. Bei dem ersten wird Filmsieden an einer Wasser–Eis-Oberfläche angenommen, während bei Äthan Blasensieden an festem Eis oder einer Hydratschicht, die sich sehr früh im Versuchsablauf bildet, eintritt. Die Daten für verflüssigtes Methan fallen zwischen jene von Stickstoff und Äthan. Beim Einbringen aller drei Flüssiggase änderten sich die Wassertemperaturen einige mm unterhalb der Oberfläche nicht merklich, sondern sanken nur sehr langsam im Verlauf eines Versuchs. Beim Einbringen von flüssigem Stickstoff wurde eine signifikante Dampfüberhitzung festgestellt, nicht dagegen beim Sieden von Methan oder Äthan an der Wasser–Eis-Oberfläche.

## НЕСТАЦИОНАРНОЕ КИПЕНИЕ СЖИЖЕННЫХ КРИОГЕНОВ НА ПОВЕРХНОСТИ ВОДЫ—I. АЗОТ, МЕТАН И ЭТАН

**Аннотация**—Представлены результаты экспериментального определения скоростей нестационарного кипения чистого сжиженного азота, метана и этана на поверхности воды. Для азота получены самые низкие значения тепловых потоков, а для этана — самые высокие. Предполагается, что при нанесении азота на водно-ледяную поверхность происходит пленочное его кипение, в то время как при нанесении этана на твердую ледяную поверхность или гидратную корку, образующуюся в самом начале опыта, происходит пузырьковое кипение. Данные по снижению методу занимают среднее положение между данными для азота и этана. При нанесении всех трех криогенов температура воды несколько миллиметров ниже поверхности значительно не меняется, а только очень медленно снижается в течение всего опыта. Отмечен значительный перегрев пара при нанесении жидкого азота, однако при кипении метана или этана на водно-ледяной поверхности этого явления не наблюдается.