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Prepared for

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Research Applications Directorate
Division of Advanced Energy Research and Resources Technology
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U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environment
Division of Environmental Control Technology

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CONFINED BOILING RATES OF LIQUEFIED PETROLEUM GAS ON WATER

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SUMMARY AND CONCLUSIONS

Spills of liquefied petroleum gas, propane, ethane, ethylene, and n-butane on water were carried out and the rate of vaporization measured as a function of time. The tests were made in an adiabatic calorimeter and the mass vaporized measured by an analogue load cell; data acquisition was accomplished by coupling the load cell to a real-time computer. All liquefied hydrocarbons were, initially, saturated liquids at one bar. Water temperatures varied from 22 to 24°C. The LPG used contained from 0-0.2 moles ethane/mole propane and from 0-0.11 moles n-butane/mole propane. The calorimeter area was 191 cm^2 and the quantities of LPG (and other liquids) spilled varied from about 150 to over 600 g. If no boiling were to have occurred, these masses would correspond to initial liquid depths of about 1.5 to 6.3 cm.

Two special series of tests were also made. In one, liquid propane was spilled onto a solid ice substrate (at -0.5°) and, in the other, liquid propane was spilled on an agar-agar water gel at 22°C. The propane-ice results were well correlated by a one-dimensional semi-infinite slab model and the heat flux is given by

$$\dot{Q}/A \quad 49.6\ t^{-1/2}\ \mathrm{kW/m^2},\ t \text{ in s}$$

LPG or propane spills on water led to a very violent initial reaction with ice thrown onto the calorimeter walls and, in some instances, an ejection of both LPG and water from the calorimeter. Within a few seconds, however, there formed a coherent ice sheet over the water surface and the subsequent vaporization was well described by a model which assumed that the ice shield would grow into the water. This moving-boundary value hypothesis agreed well with experimental data, and it could be expressed as

$$\dot{Q}/A = 154\ t^{-1/2}\ \mathrm{kW/m^2}\quad (t \text{ in s})$$

No effect of adding small amounts of ethane or butane to the liquid propane to form LPG could be discerned; i.e., LPG could be well represented by pure liquid propane.

The agar-agar water gel tests with liquid propane showed no initial violent boiling and the heat flux was correlated by the relation

$$\dot{Q}/A = 126\ t^{-1/2}\ \mathrm{kW/m^2}\quad (t \text{ in s})$$

The coefficient of 126 is significantly below that found for water (154) while theory predicts it should have been equal to it if the thermal properties of the gel were equal to those of liquid water.

The few ethane and ethylene runs could not be correlated satisfactorily by an analytical model. There is, apparently, a significant surface thermal resistance for a short (circa 5-15 s) period following the spill. Techniques to handle such a surface resistance (that is, in fact time variant) have not been developed. An approximate analysis was, however, developed which yielded a good correlation to the boil-off data after the first 5-15 seconds. The results of this analysis are:

Ethane:

$$\dot{Q}/A = 238\ t^{-1/2}\ \mathrm{kW/m^2}\quad (t \text{ in s})$$

Ethylene:

$$\dot{Q}/A = 260\ t^{-1/2}\ \mathrm{kW/m^2}\quad (t \text{ in s})$$

n-Butane was found to boil quietly on water with a constant heat flux, i.e.,

$$\dot{Q}/A = 8.9 \quad \mathrm{kW/m^2}$$

It is recognized that these results are applicable only to confined-area tests. Future work will emphasize the vaporization of LPG when spilled in an unconfined mode, i.e., with simultaneous spreading and boiling.

INTRODUCTION

Objectives

The objectives of the current program were, primarily, to measure the rate of boiling of liquefied petroleum gas (LPG) on water surface and to develop an analytical model to describe the phenomena involved. Primary emphasis was placed on liquid propane or LPG mixtures containing small quantities of ethane or butane or both. A few exploratory tests were, however, made with pure liquid ethane, ethylene, and *n*-butane.

The ultimate objective of the program is to provide quantitative data and analytical models to delineate the rate of vaporization, the spread rate and the degree of fractionation, should an LPG tanker suffer an accident leading to a major spill on water.

General Background

Cryogenic liquids are often transported as bulk cargo in large tankers. An accident could result in a serious safety hazard. In order to evaluate and take precautionary measures for these potential hazards, reliable data are required concerning boil-off rates of these cryogenic liquids when spilled on water.

The transient boiling of a volatile liquid on the surface of a second, warmer liquid has received relatively little attention compared to a 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 warm 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 leads to a highly transient situation with the possibility of rapid variations in the heat flux.

Previous Work

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 Fourst (1955) and Berenson (1961), the nucleate boiling region is expanded and the transition boiling region compressed for very smooth heating surfaces although the Leidenfrost temperature 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 (Jacob and Fritz, 1931). Large vapor bubbles formed and the vapor evolved was probably superheated (Jacob, 1949).

Bonilla and Eisenberg (1948) vaporized butadiene under pressure 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 (1970).

A number of boiling experiments have been conducted using hot mercury and different volatile organic liquids; these are summarized by Sideman (1966). 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).

Sciance et al. (1967a,b) studied the nucleate pool boiling and film boiling of liquefied hydrocarbon gases (ethane, propane, and n-butane) on a horizontal gold-plated cylinder at different reduced pressures up to the critical pressures and obtained the corresponding boiling curves.

Only a few previous studies have been made wherein cryogenic liquids were boiled on water.

Burgess et al. (1970, 1972) conducted several experimental boil-off tests with spills of liquid nitrogen, liquid methane, and LNG on water. A similar, but less comprehensive study by Nakanishi and Reid (1971) corroborated the same results.

Jeje et al. (1975) studied the boiling of liquefied nitrogen, methane and typical LNG compositions on water at various temperatures. Measured heat fluxes were found to be relatively low for both nitrogen and for very pure methane. A significant increase in the boiling flux was noted upon the addition of small amounts of heavier hydrocarbons.

No previous work has been reported for spills of LPG or liquid propane on water.

APPARATUS

The calorimeter, shown schematically in Figure 1, consisted of three major parts: the calorimeter itself or boiling vessel, the rapid cryogenic-spill device (RCSD) and the thermocouples. Each is described below:

The boiling vessel was a container with four concentric walls. The three outer walls were made from 127 μm scratch-free cellulose acetate sheets separated from each other by a 2 mm air gap with polyurethane foam spacers. The innermost wall was fabricated from 26 μm Mylar sheets separated from the inner cellulose acetate wall by a 2 mm air gap with polyurethane foam spacers. Experimental tests showed negligible heat leak from the walls (0.014 W/cm^2). This was accomplished by spilling liquid propane up to a height of one cm in the empty calorimeter and the heat leak measured. Then liquid propane was added up to a height of 11 cm and again the heat leak measured. Subtraction yielded the heat leak corresponding to 10 cm - height of walls.

The Mylar film was held in place by pressing each end, at the top and the bottom, between two Acrylic plates and stretching it with the help of four tensors. Leaks were avoided by sealing the bottom joint with silicon rubber.

The overall dimensions of the cylindrical boiling vessel were 15.6 cm internal diameter and 22 cm deep. The heat transfer area was 191 cm^2.

The cryogen distributor had the two-fold function of dispersing the cryogen on the water surface in the fast and homogeneous manner, and of preventing ambient air from entering the vessel during the test.

The RCSD could be attached to the calorimeter at different positions thus allowing experiments with different water depths and distances between

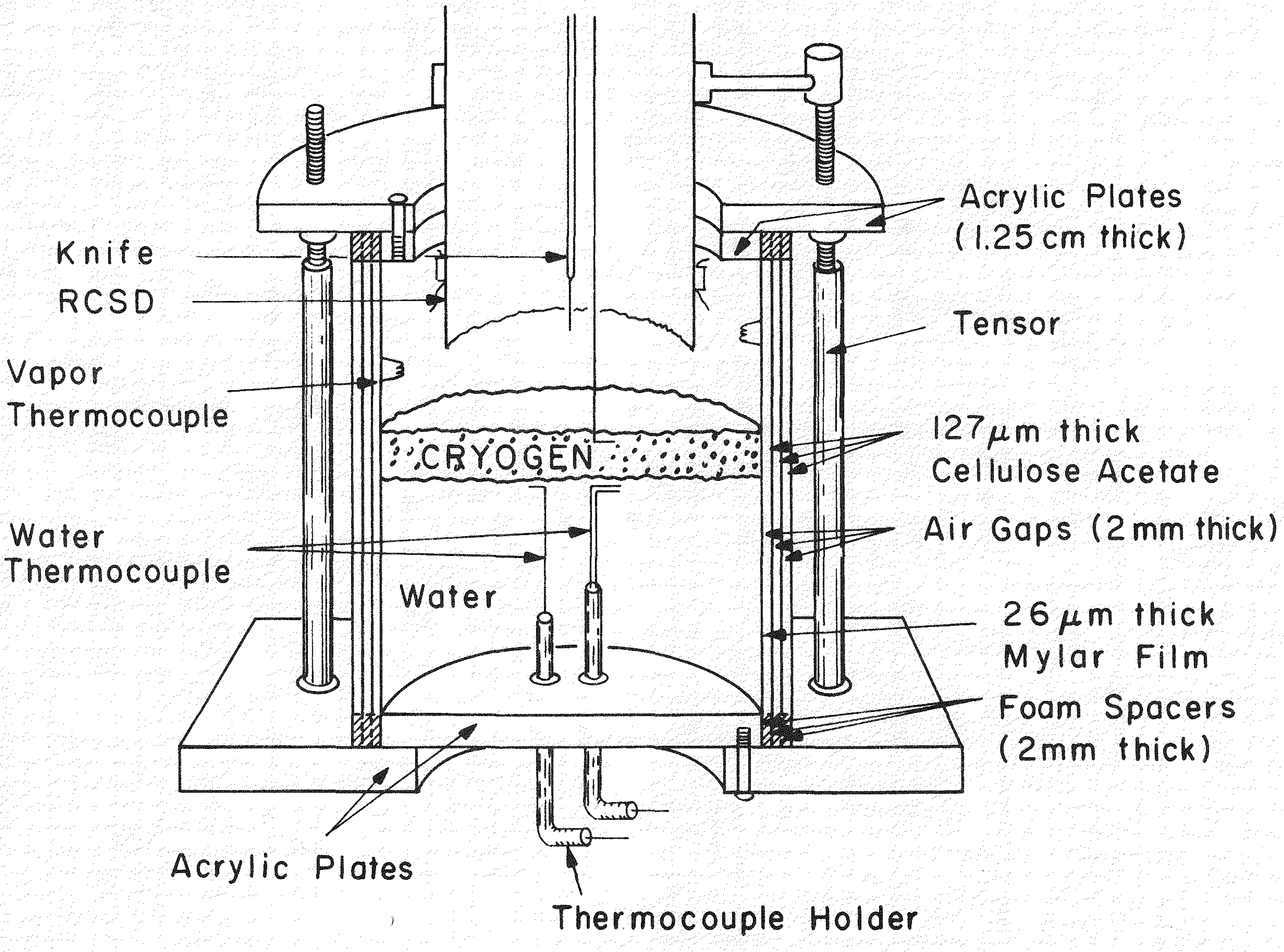

FIGURE 1 CALORIMETER VESSEL

water surface and RCSD. The RCSD entered the calorimeter through the top opening and thus left a small gap (1 cm) between the calorimeter and the RCSD for exhaustion of boil-off vapors.

The RCSD, shown schematically in Figure 2, consisted of Plexiglas tubing 9.4 cm I.D., 10.1 cm O.D. and 18.5 cm long. An elastic-rubber membrane was stretched and placed to cover the bottom end of the tubing and held in place with an adjustable "O"-ring. The membrane, in its stretched form (4-5 X relaxed form), was capable of retaining its elasticity as low as -60°C. When the membrane was punctured, it broke and uncovered completely, in a fraction of a second (∿0.1 s), the tubing opening. This allowed the cryogen to fall in a plug-like fashion and contact the water. The RCSD worked well for LPG ($T_b \sim -40°C$) but, with liquid ethane ($T_b = -88.7$) or liquid ethylene ($T_b = -103.8$), rupture was sometimes incomplete or slow.

Water, cryogen and vapor temperatures were monitored by a set of six chromel-constantan thermocouples. All thermocouples were heat-stationed, i.e., a section of bare thermocouple wire was exposed to the same temperature to minimize axial heat conduction. Two vapor thermocouples entered the top of the vessel; one was located at 4.2 cm, the other at 6.2 cm above the water level, i.e., the water level was constant at 6.8 cm.

Vapor thermocouples were fabricated from 25.4 μm wire, 2 cm long with 127 μm wire extensions.

Four water thermocouples entered from the bottom so that the cryogen-water interface was not affected. These thermocouples were fabricated from 127 μm wires. Two were placed at the water surface and the other two at 0.5 cm and 1.0 cm below the water surface, respectively. These thermocouples were tested and calibrated independently with a reference junction at 0°C. Accurate readings within ±0.2°C were obtained with a

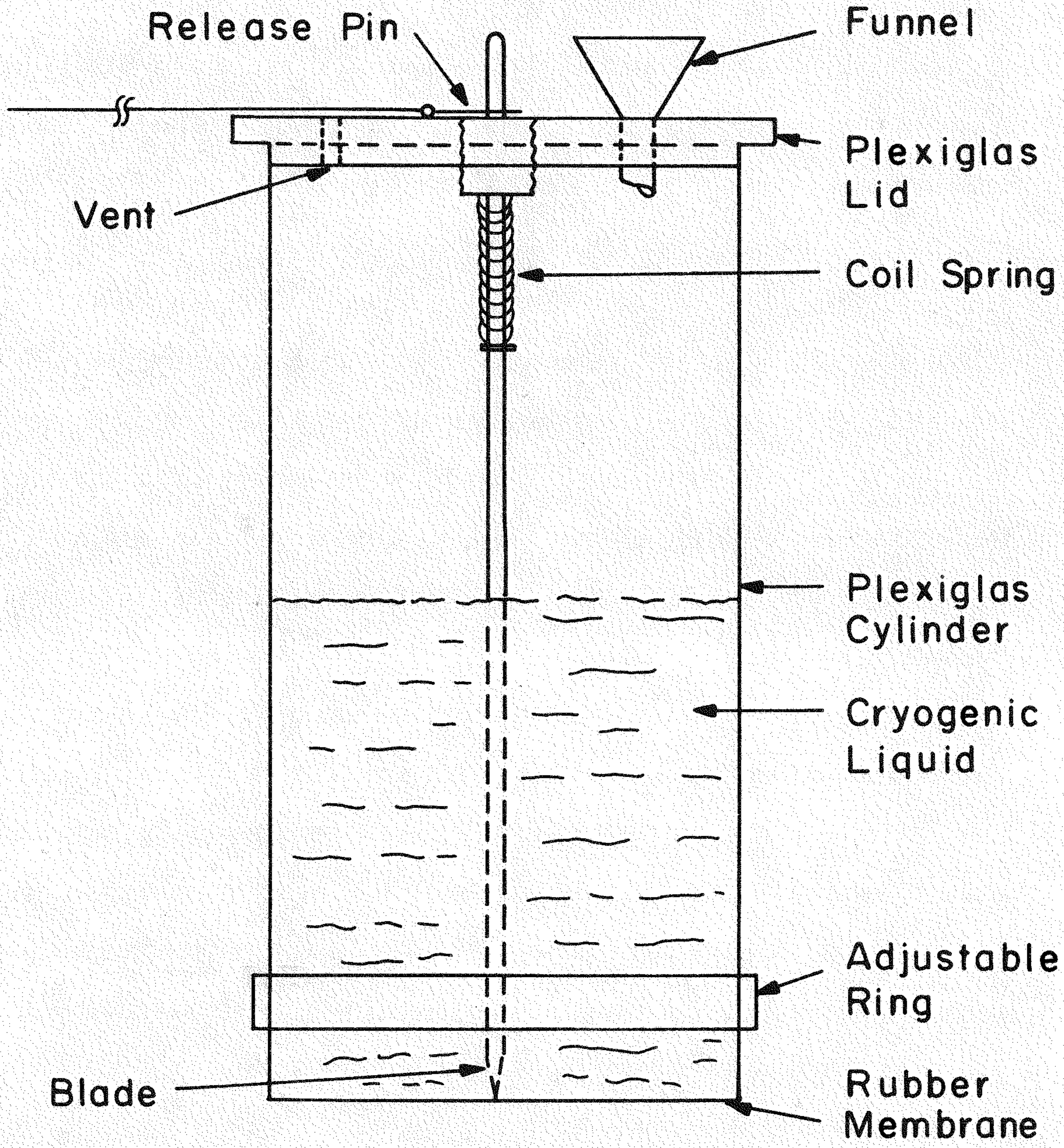

FIGURE 2 RAPID CRYOGENIC SPILL DEVICE (RCSD)

time response of 0.6 s in the air and 0.07 s in liquid nitrogen, ethane, propane and butane. The responses of the vapor thermocouples were about ten times faster than the liquid thermocouples.

The calorimeter vessel, during an experiment, was placed on top of a Mettler PE11 load-cell balance which measured the weight of the system continuously. The response time of the balance was determined by spilling different amounts of water, i.e., 150 g to 320 g, from 3 cm height into the calorimeter. Weight readings were recorded continuously at 0.1 s intervals. For five different runs, recorded values oscillated for less than 0.7 s, after which the oscillations were damped out and a constant value was recorded. In Figure 3 a typical response curve is shown from spilling 320 g of water from a 3 cm height.

The load-cell balance and the thermocouples were connected to a real-time Nova 840 computer which both stored and analyzed data. The schematic diagram of the system is shown in Figure 4.

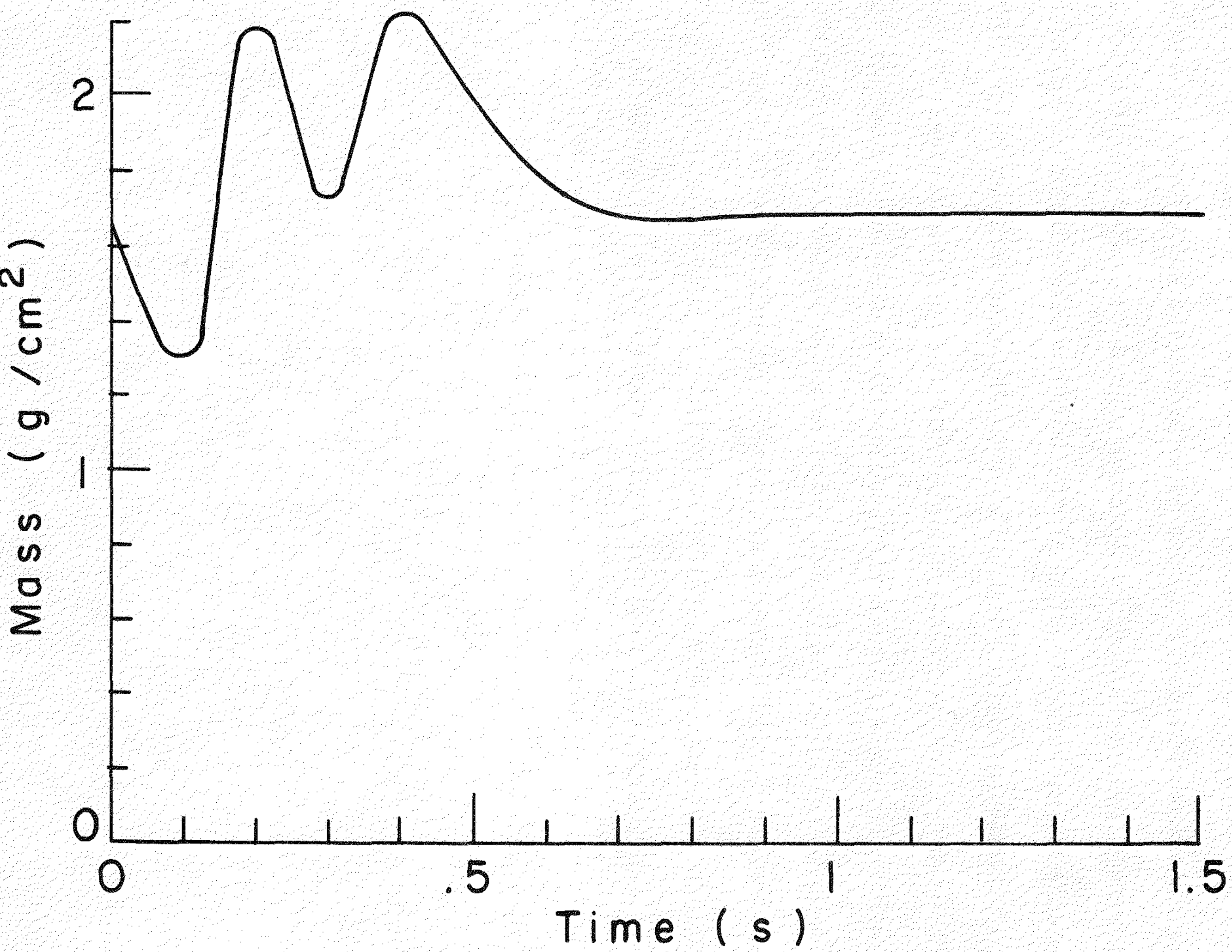

FIGURE 3 RESPONSE CURVE OF THE LOAD CELL BALANCE, SPILL OF 1.68 g/CM^2 WATER ON WATER

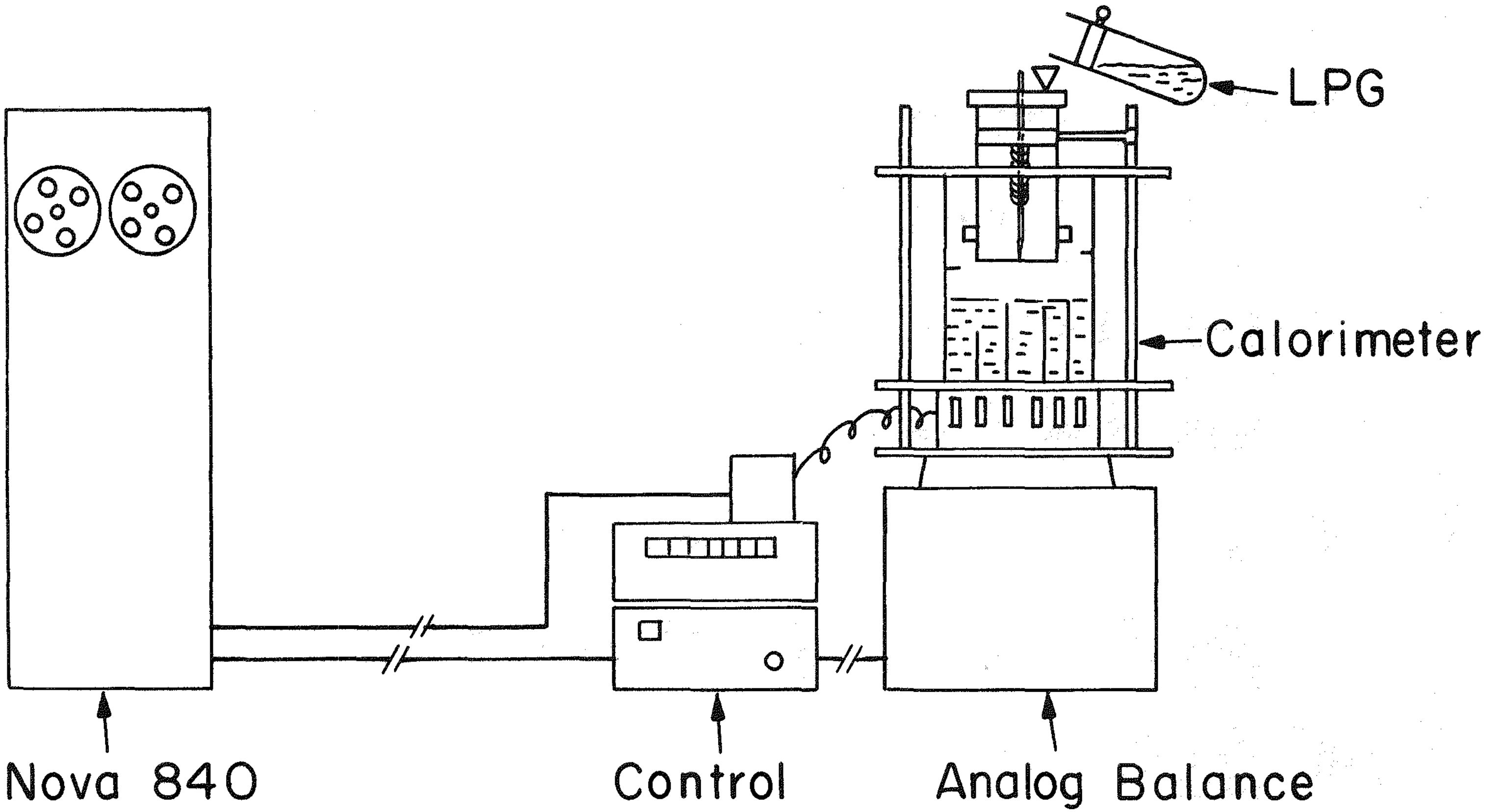

FIGURE 4 EXPERIMENTAL APPARATUS

EXPERIMENTAL PROCEDURE

Hydrocarbon Purity. Ethane and ethylene were supplied as compressed gases while liquid cylinders of propane and *n*-butane were purchased. Purities exceeding 99.5% were stated by the Matheson Gas Co.

Condensation and Feed Preparation. Each individual hydrocarbon was liquefied by cooling the gas in a dry ice-*n*-butanol slush bath to -90°C and flashing to atmospheric pressure. Mixtures were then prepared by combining the individual components in a graduated cylinder. Prior to each tests, a liquid sample was removed from the filled RCSD with a precooled Teflon thimble. This liquid was vaporized and stored in an elastic balloon for later chromatographic analysis.

Calorimeter Preparation. In most tests, water at 22-24°C was used in the calorimeter. In a few tests, as described later, water was replaced with an agar-agar mix or with solid ice.

As noted earlier, the RCSD was fitted with a new membrane prior to each test. A cutting razor was positioned in the RCSD and locked with a latch pin. When this pin was released, the razor was driven into the stretched membrane and initiated rupture. The razor and RCSD were precooled with a small quantity of the test liquid--which was then allowed to vaporize completely. A predetermined quantity of test liquid was then loaded into the RCSD, the safety hood closed, and the run initiated.

Measurements using a Sanborn recorder of high frequency response (<0.01 s) showed that the membrane broke and unrolled in less than 0.1 s. Recordings of the system weight vs. time did show that, after the membrane ruptured, the mass readings oscillated for brief periods due to inertial forces. These oscillations vanished after about 0.7 s.

The computer was programmed to record data every second during the first 15 s, then every 0.1 s the next 5 s. After that period, data were recorded every second for the rest of the experiment. The spill was made during the period when data sampling frequency was 10 s^{-1}.

RESULTS AND DISCUSSION

Qualitative Observations. For propane or LPG spills on water, immediately following the contact, violent boiling commenced. Ice quickly formed; in most cases, ice was even thrown onto the sidewalls of the vessel. In some instances sprays of water/ice and propane were ejected from the calorimeter.

Within a few seconds, however, the interaction quieted and the surface was covered by a rough ice sheet. The LPG boiled on the surface of this ice, but large gas bubbles occasionally appeared under the ice shield and were trapped. The boiling rate decreased with time with a concomitant increase in the thickness of the ice shield.

In the first second or two, very high boiling heat fluxes were experienced. The mass of LPG lost was approximately half that spilled originally. It is estimated that only 5-15% could have been ejected as liquid if one uses the water loss as a reference. However, since the water surface is very agitated during this period, it is not possible to obtain reliable quantitative values of the boiling flux.

Also, as noted above, the mass lost in the very early time period was approximately proportional to the original mass of LPG used. One may then infer that larger spills lead to more mixing and boiling before the ice shield prevents a direct contact between the LPG and the water.

In Figure 5, boil-off data are shown for a typical spill of liquid propane on 22°C water. 388 g were spilled on an area of 191 cm^2. If no boiling had occurred, this spill would have resulted in a depth of 3.5 cm of propane. Within one second about 90 g of propane had been lost. From energy considerations, each g of propane boiled could produce

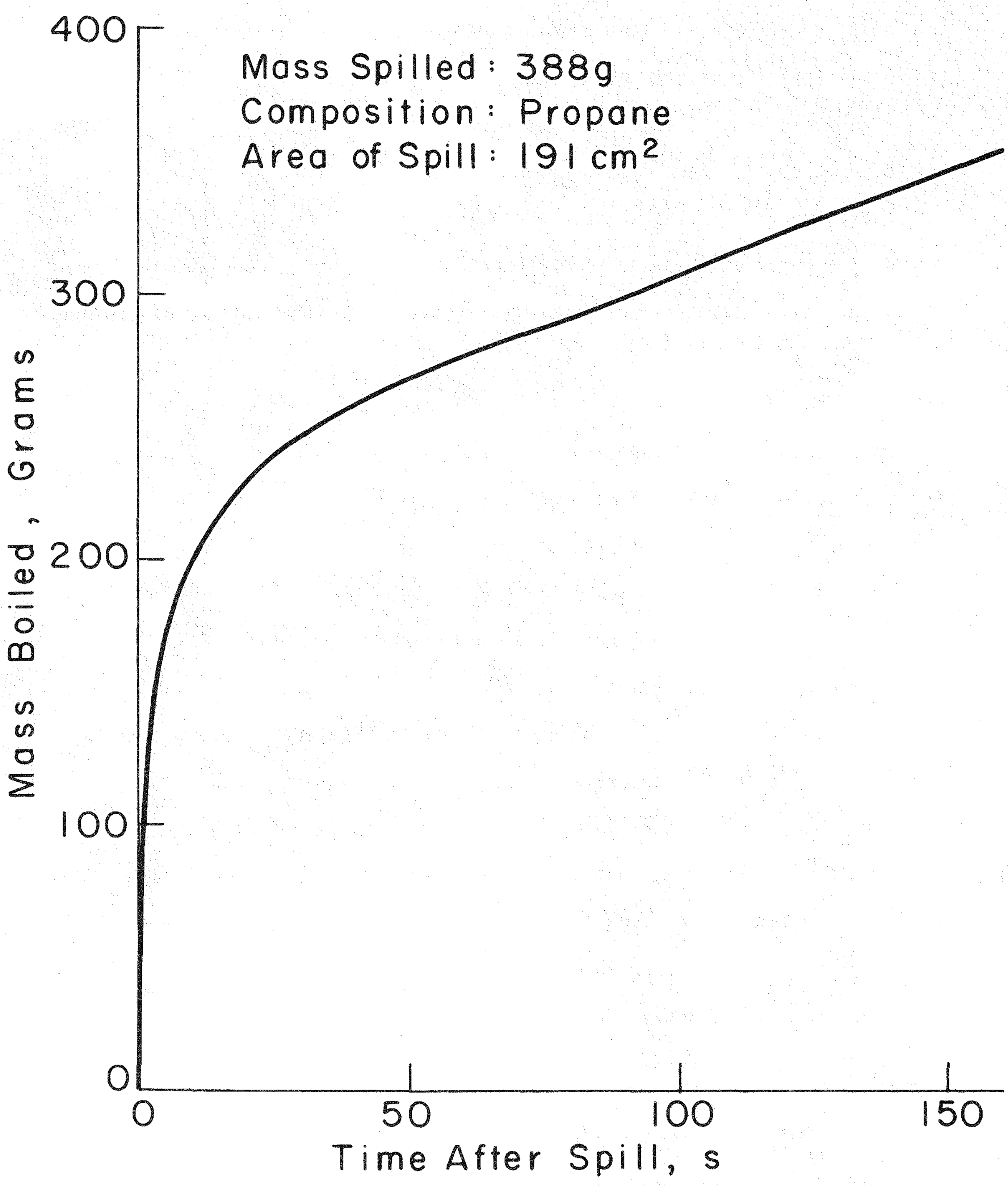

FIGURE 5 BOIL-OFF DATA FOR RUN 7262

about 0.83 g of ice* at -42°C. Then, 90 g of propane could form 75 g or 82 cm^3 of ice. With the calorimeter area equal to 191 cm^2, the equivalent ice shield thickness would be 0.43 cm.

Ice of such a thickness just does not form in the very early stages after a spill. Some ice is evident, but a significant fraction of the energy required to boil the propane (LPG) comes from the sensible cooling of the water as there is vigorous motion of the interface--and the intensity of this surface contact increases with the quantity of propane (LPG) spilled.

For reasons described later, we believe that a coherent, thin ice shield has formed a few seconds after the spill has begun. Visual observation of the boiling process confirms this assertion, but the ice shield is rough with projections rising, in some cases, several cm above the original water surface.

We also note, on Figure 5, that the smooth boil-off curve does not have a continuously decreasing slope (which is proportional to the boiling-heat flux) with time. At about 100 s, there is a small, but detectable, increase in the boiling rate. This phenomenon was not seen in most runs, but, on the other hand, was not rare. We believe that the ice shield, upon cooling, contracted and cracked so as to allow liquid LPG-liquid water contact over a limited area. The crack soon self-heals and the boiling rate again begins to decrease. In a few cases, the crack was sufficiently large to produce, essentially, a discontinuity in the boil-off curve.

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*The enthalpy of vaporization of propane is 426 J/g. To cool one g of water from 22°C to 0°C and freeze and cool to -42°C it requires 92.1 + 333.5 + 81.3 = 507 J. Thus 426/507 = 0.84.

Experimental Tests. In the past year, 63 different spill experiments were carried out. Fifty-one of these tests involved liquid propane or LPG on ambient temperature water. The independent variables were original LPG composition, mass spilled, and initial distance between the RCSD and water.

Temperature measurements in the water did not provide much useful information. The surface temperature always rapidly fell to the boiling temperature of the LPG, and temperatures 1 cm or greater below the water surface showed little change unless the ice thickness became large. Temperatures at intermediate depths (0-1 cm) fluctuated initially, depending upon the severity of the impact, but no trends could be ascertained during the test.

Other tests involved spills of pure liquid ethylene, ethane, and *n*-butane upon water and spills of liquid propane upon water-ice and upon an agar-agar water gel.

Each test series is discussed separately with our present interpretation of the data.

Propane Spills on Solid Ice. A Styrofoam block was cored and filled with water to a depth of about 12 cm. The vessel was placed in a refrigerator maintained at -0.5°C for 24 hours to freeze the water. Thermocouples imbedded in the ice block at various depths indicated the entire block was uniform in temperature before the test.

The Styrofoam block with ice was placed upon the Mettler load cell and liquid propane poured on the surface. The boil-off data from run C3-ICE-518 are shown in Figure 6 for the first 15 minutes. (The data points shown represent but a small fraction of those obtained since mass sampling was done every second.)

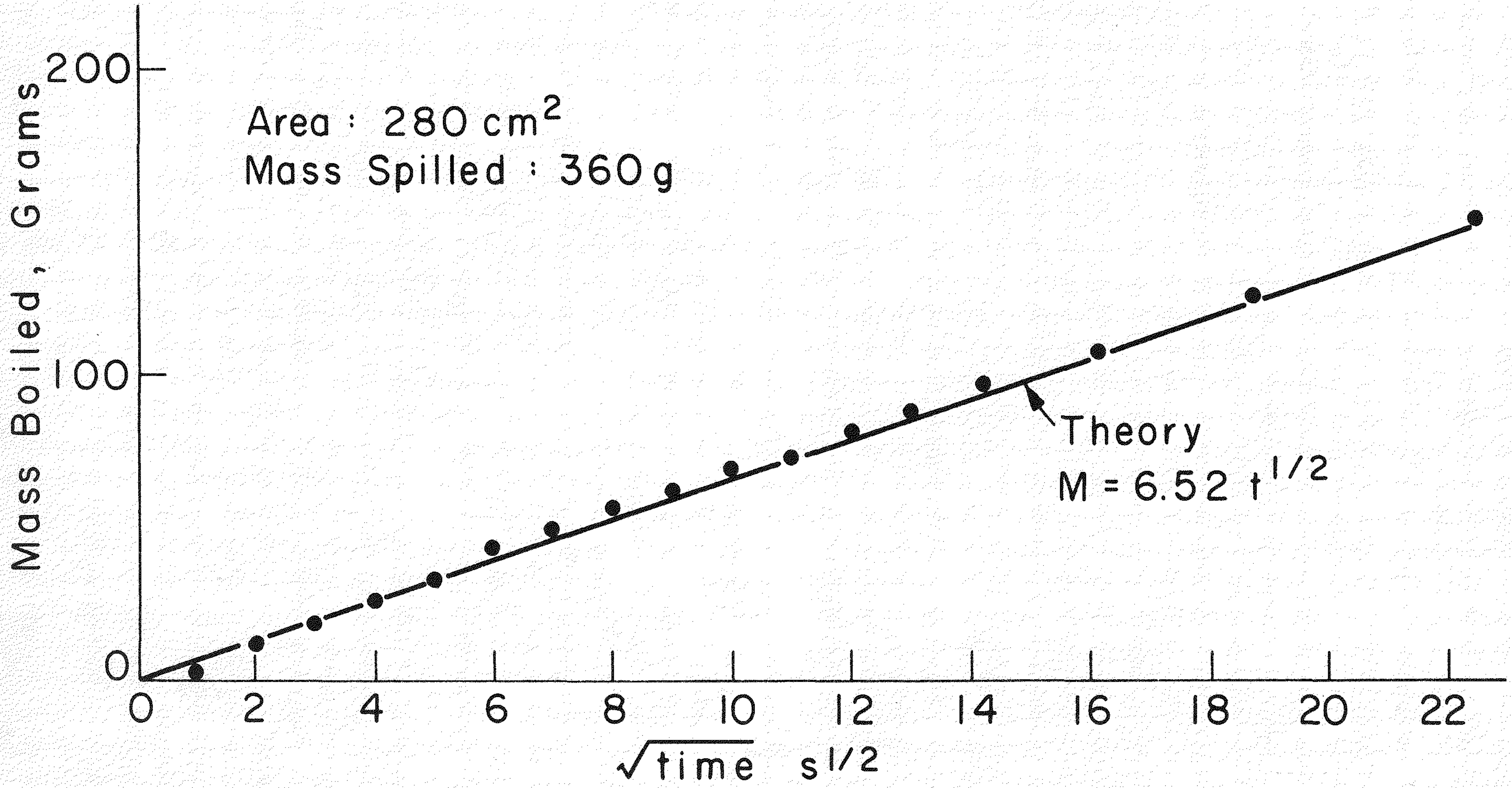

FIGURE 6 BOIL -OFF DATA FOR LIQUID PROPANE ON −0.5°C ICE

Tests in this series were carried out to confirm that propane boiling on ice could be modeled by a simple one-dimensional, semi-infinite slab theory. In such a case, a slab, initially homogeneous at T_i is subjected to a step change in temperature at the surface to a new temperature T_b. The slab is taken to be infinite in depth. No interfacial thermal resistance is assumed. Then the equation to be solved is

$$\partial T/\partial t = \alpha \partial^2 T/\partial x^2 \qquad (1)$$

with the boundary conditions T(x,t) as

$$\left.\begin{aligned} T(x,0) &= T_i \\ T(0,t) &= T_b \quad \text{when } t > 0 \\ T(\infty,t) &= T_i \end{aligned}\right\} \qquad (2)$$

T is the temperature at depth x at time t. α is the thermal diffusivity, in this case of ice. The solution is

$$(T - T_b)/(T_i - T_b) = \mathrm{erf}(x/2\sqrt{\alpha t}) \qquad (3)$$

Then, the heat flux is

$$\dot{Q}/A = -k(\partial T/\partial x)_{x=0} \qquad (4)$$

$$= k(T_i - T_b)/\sqrt{\pi \alpha t} \qquad (5)$$

with k the thermal conductivity.

Assuming the properties of ice may be chosen at the arithmetic mean temperature between boiling propane and initial ice temperature $[-42.5 + (-0.5)]/2 = -21°C$,

$$k^*_{ice} = 2.43 \text{ W/m K}$$

$$\alpha_{ice} = 1.35 \times 10^{-6} \text{ m}^2/\text{s}$$

and $$\dot{Q}/A = \frac{(2.43)(-0.5 + 42.5)}{(\pi \times 1.35 \times 10^{-6})^{1/2}} \; t^{-1/2} = 4.96 \times 10^4 t^{-1/2} \text{W/m}^2$$

The mass boiled off, M/A, is the integral of the above, divided by the enthalpy of vaporization of propane, 426 J/g.

$$M/A = (2 \times 4.96 \times 10^4/426) \; t^{1/2} = 233 \; t^{1/2} \; \text{g/m}^2$$

The area of the Styrofoam box was about 280 cm^2, therefore theory would predict

$$M = (233)(280/10^4) \; t^{1/2} = 6.52 \; t^{1/2} \; \text{g}$$

The line corresponding to this equation is shown on Figure 6 and the agreement between predicted and experimental data is excellent.

Propane Spills on an Agar-Agar Gel. To eliminate any agitation of the water surface immediately following a spill of propane, the water was "gelled" in two runs with 0.64-0.66% agar-agar in the basic calorimeter. In one test (8251), 214 g of propane were spilled, while, in the other, 456 g were used. Both runs yielded essentially identical boil-off data and these results are graphed in Figure 7 for the first 256 seconds.

The data plot as very straight lines when mass boiled is correlated with $t^{1/2}$. The slope is 11.3 $\text{g/s}^{1/2}$.

No early mass loss is seen (compare with Figure 5). As noted and discussed later, the slope of 11.3 $\text{g/s}^{1/2}$ is less than would have been

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*Ice thermal conductivities were obtained from Ratcliffe (1962).

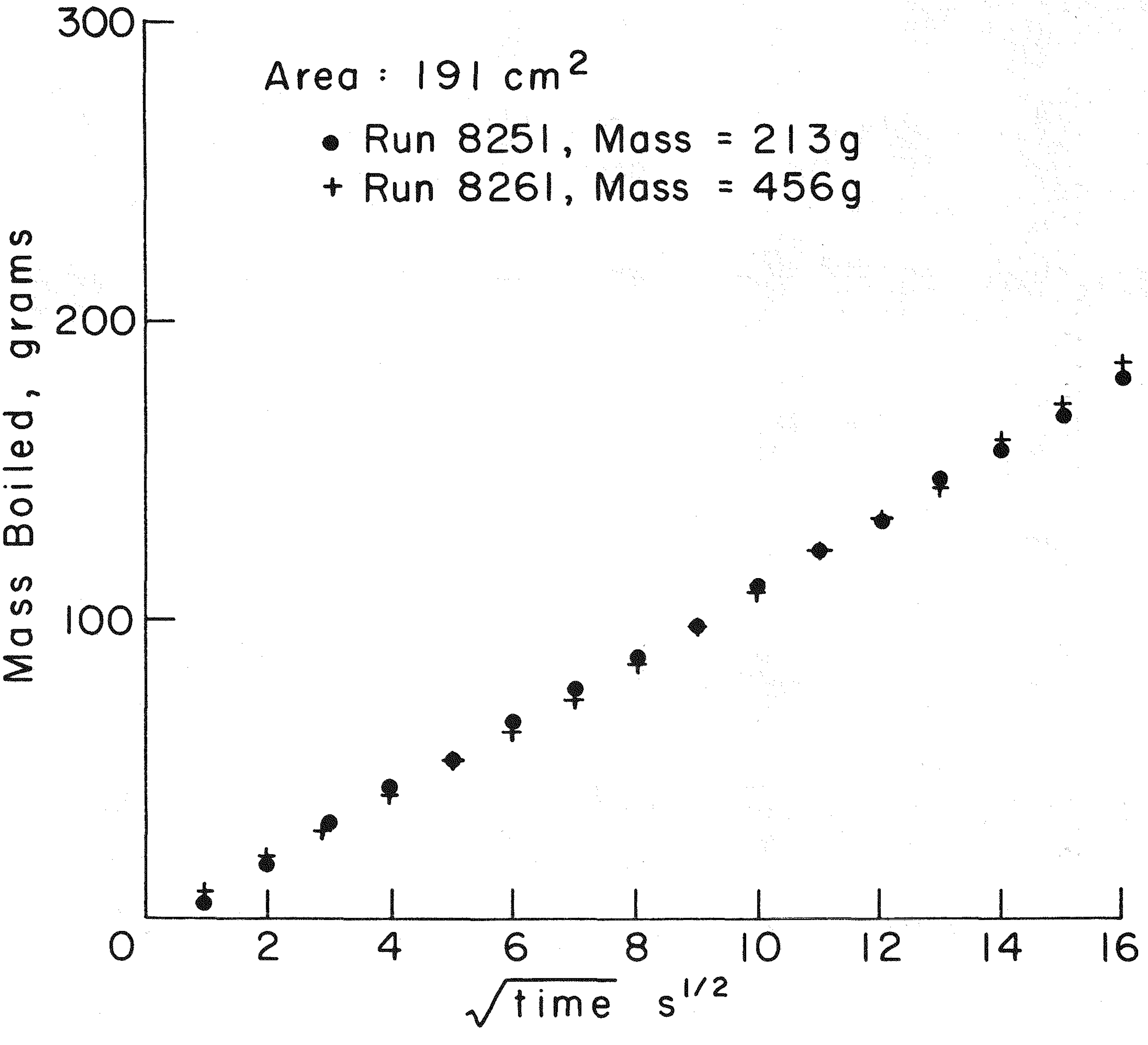

FIGURE 7 BOIL-OFF DATA FOR PROPANE ON AN AGAR-AGAR / WATER GEL

expected from theoretical modelling if the agar-agar gel were assumed to have thermal properties identical to those of water.

The heat flux from the agar-agar gel to the boiling propane is

$$\dot{Q}/A = [(11.3)(426)/(191 \times 10^{-4})(2)]\ t^{-1/2}$$
$$= 126\ t^{-1/2}\ \text{kW/m}^2$$

<u>LPG and Propane Spills on Liquid Water</u>. A typical plot of boil-off data vs. time was shown earlier in Figure 5. A large mass loss is noted in the first few seconds, but the rate then drops to a much smaller value. If these same data are plotted as a function of $t^{1/2}$ instead of t, Figure 8 results. After a short period, the data plot as a reasonably straight line.

This behavior suggested that one might model the linear portion with a conduction model with moving boundaries, i.e., an ice front that proceeded into the liquid-water region.

In such a model, we consider that liquid fills the region $x > 0$ at an initial temperature T_2 in Figure 9. At time $\tau = 0$ the surface is exposed to temperature T_1 which is lower than the phase change temperature T_p. Solidification will start, and the interface separating the solid and liquid phase will propagate to larger values of x. At an time τ, the surface separating the liquid and solid phases is at $X(\tau)$. The bulk temperature of the liquid at large x is T_2 and is constant. Heat is conducted, therefore, from the liquid through the solid phase to the free surface.

At time τ, the region $x < X(\tau)$ is a solid phase with constant properties k_1, α_1, ρ_1, c_1; t_1 is the temperature in this phase and it must satisfy the equation,

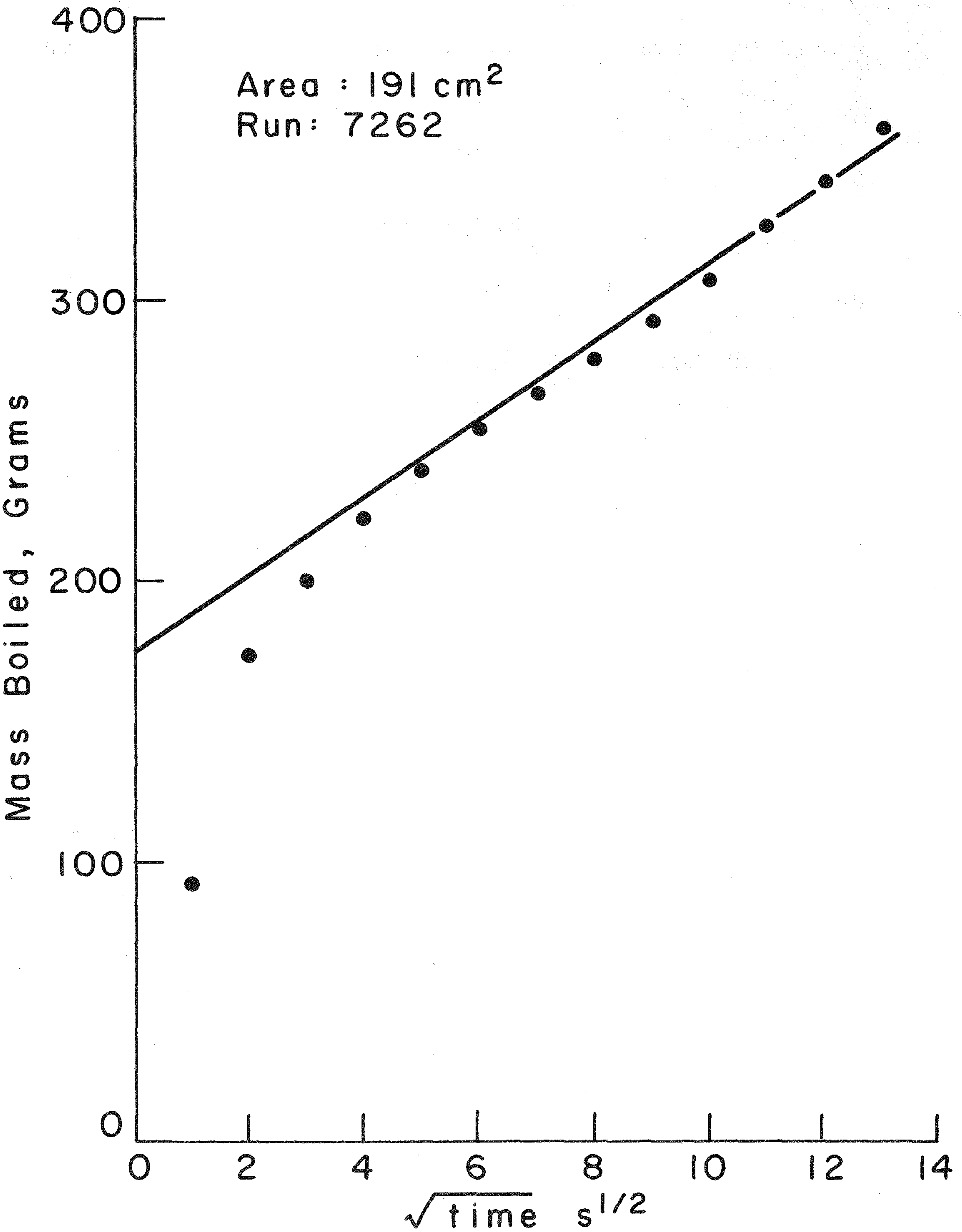

FIGURE 8 BOIL-OFF DATA FOR A PROPANE SPILL ON 22°C WATER

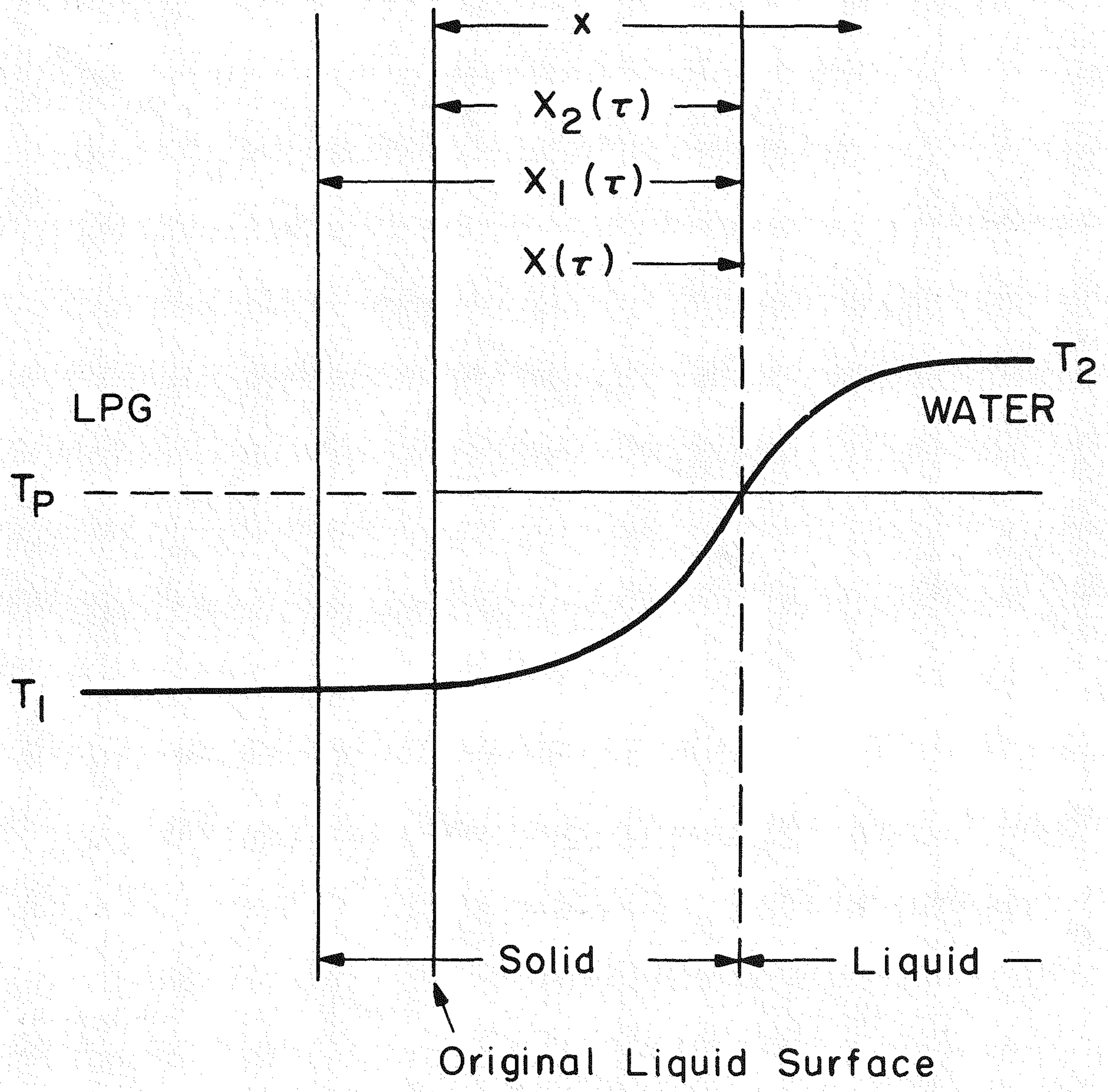

FIGURE 9 HEAT CONDUCTION DURING SOLIDIFICATION OF A LIQUID

$$\frac{\partial^2 t_1}{\partial x_1^2} - \frac{1}{\alpha_1}\frac{\partial t_1}{\partial \tau} = 0 \tag{6}$$

with $t_1 = T_1$ at $x_1 = 0$.

At any time τ, the region $x > X(\tau)$ is a liquid phase with properties k_2, α_2, ρ_2, c_2; t_2 is the temperature in this phase and it must follow the equation

$$\frac{\partial^2 t_2}{\partial x_2^2} - \frac{1}{\alpha_2}\frac{\partial t_2}{\partial \tau} = 0 \tag{7}$$

with $t_2 = T_2$ at $x \to \infty$.

In the solidification of water to ice, there is an increase in volume and the ice surface will move away from the original surface according to the density of each phase. This can be accounted by

$$\frac{X_1}{X_2} = \frac{\rho_2}{\rho_1} = \beta \tag{8}$$

At the interface between liquid and solid, $t_1 = t_2 = T_p$ at $x_1 = X_1(\tau)$, or $x_2 = X_2(\tau)$. Given the above conditions, Eckert and Drake (1972) and Carslaw and Jaeger (1959) describe a solution which leads to the following temperature profiles in the solid and the liquid phases, respectively,

$$\frac{t_1 - T_p}{T_1 - T_p} = 1 - \frac{\operatorname{erfc}(x/2\sqrt{\alpha_1\tau})}{\operatorname{erfc}(K/2\sqrt{\alpha_1})} \tag{9}$$

and

$$\frac{t_2 - T_p}{T_2 - T_p} = 1 - \frac{\operatorname{erfc}(x/2\sqrt{\alpha_2\tau})}{\operatorname{erfc}(K/2\sqrt{\alpha_2})} \tag{10}$$

in which K is calculated from

$$\frac{(T_p-T_1)k_1\ \exp(-K^2\beta^2/4\alpha_1)}{\sqrt{\pi\alpha_1}\ \mathrm{erf}(K\beta/2\ \sqrt{\alpha_1})} - \frac{(T_2-T_p)k_2\ \exp(-K^2/4\alpha_2)}{\sqrt{\pi\alpha_2}\ \mathrm{erfc}(K/2\ \sqrt{\alpha_2})} = \frac{Q_L\rho_1K\beta}{2} \tag{11}$$

The heat transfer from the ice surface is given by

$$\frac{q}{A} = -\ k_1\left(\frac{\partial t_1}{\partial x}\right)_{x=0} \tag{12}$$

where q/A is the heat flux. Differentiating the temperature profile with respect to x and substituting the heat flux equation; Eq. (12),

$$\frac{q}{A} = -\ \frac{(T_p\ -\ T_1)k_1\tau^{-1/2}}{\sqrt{\pi\alpha_1}\ \mathrm{erf}(K\beta/2\ \sqrt{\alpha_1})} = \varepsilon\tau^{-0.5} \tag{13}$$

The values of ice and water properties are shown in Table 1.

The value of K is found numerically to be about 6.2675×10^{-4} m/s $^{1/2}$. Then

$$\dot{Q}/A = \frac{1.54 \times 10^5}{t^{1/2}}\quad \frac{W}{m^2}$$

and

$$M = 13.8\ \tau^{1/2}\ g$$

for an area of 191 cm^2. The slope, 13.8, is, in fact, that plotted in Figure 8 as the solid, straight line. The same procedure was employed in all other propane and LPG spills and the results were similar. A rich ethane/butane LPG test is shown in Figure 10. Again, the straight line has been drawn with a slope of 13.8.

The effect of either ethane or n-butane added to propane was not discernible; the LPG tests were similar to the pure propane spills.

TABLE 1

Physical Properties of Ice and Water

Ice (at -21°C)	Water (at 20°C)
$k_1 = 2.43$ W/m K	$k_2 = 0.580$ W/m K
$\rho_1 = 913$ kg/m^3	$\rho_2 = 1 \times 10^3$ kg/m^3
$c_1 = 1.93 \times 10^3$ W s/kg K	$c_2 = 4.181 \times 10^3$ W s/kg K
$\alpha_1 = 1.354 \times 10^{-6}$ m^2/s	$\alpha_2 = 1.388 \times 10^{-7}$ m^2/s
$Q_L = 3.335 \times 10^5$ W s/kg	
$\beta = 1.087$	

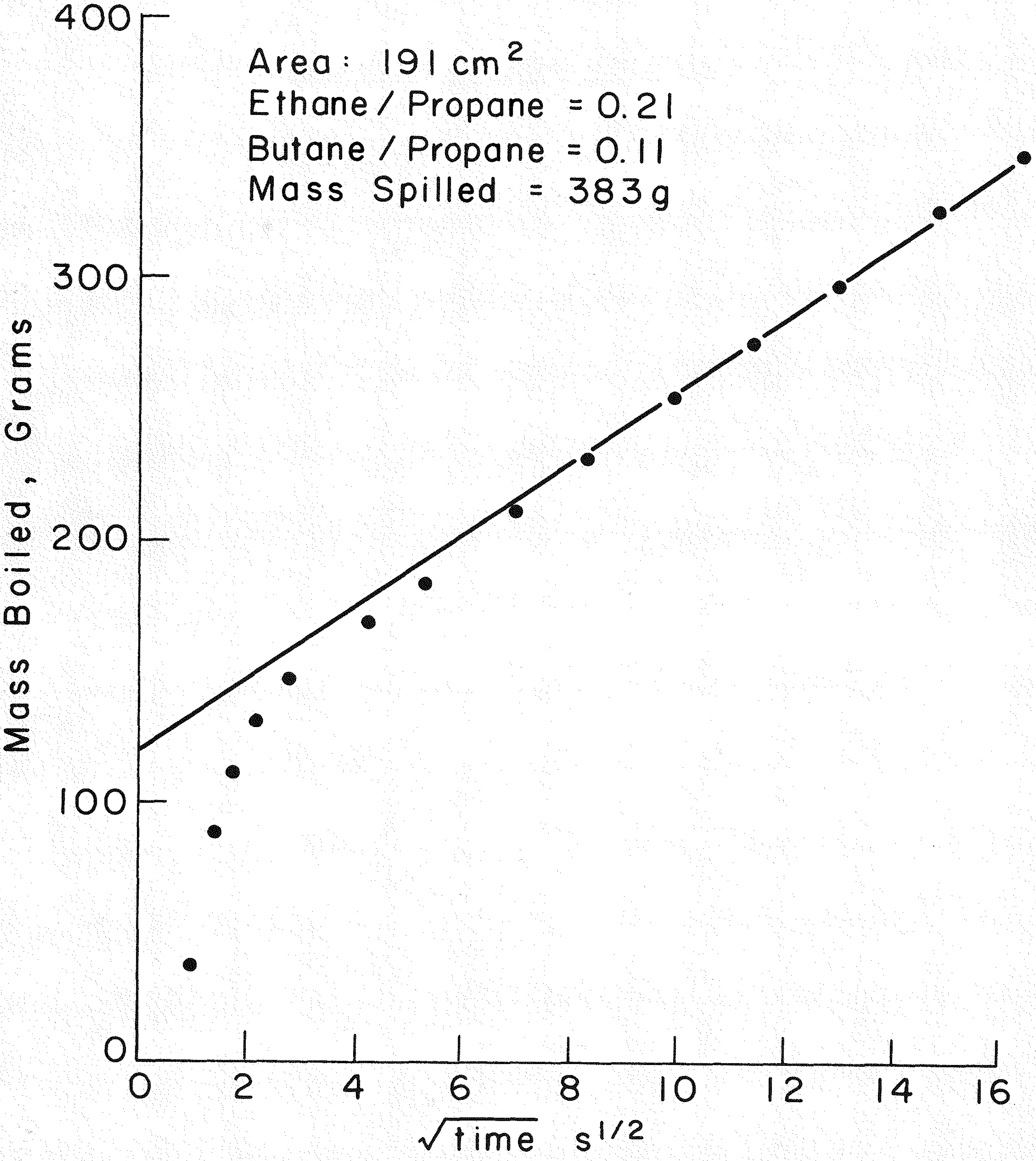

FIGURE 10 BOIL-OFF DATA FOR LPG SPILL ON 22°C WATER

In about 25% of the propane and LPG tests, there was a noticeable "bump" in the data after 30-50 s. The only explanation which we can offer at the present time is cracking of the ice shield with a limited contact between the LPG (propane) and water. The good asympotic fit of most runs with the theoretical prediction does, however, seem to confirm the basic idea that the major thermal resistance resides in the growing ice shield.

The moving-boundary model could be modified to allow even a better fit to the experimental data. The "real" time which should be employed would correspond to the time after spill when a coherent ice sheet just covers the liquid water interface. Let us denote this time as τ^* and approximate it in the following manner. Referring to Figure 10, the best straight line of slope 13.8 is fitted to the data and extrapolated back to time equals zero. Then a horizontal line is drawn to intersect the experimental boil-off curve. The time at this intersection is noted as τ^*. For Figure 8, $(\tau^*)^{1/2} \sim 1.9\ s^{1/2}$ or $\tau^* \sim 3.6$ s. The data can then be replotted as boil-off vs $(t - \tau^*)^{1/2}$. Figure 8, for run 7262, is then shown on Figure 11. There results a very good fit between experiment and theory.

What this modified model indicates is that for a short period following the spill, boiling is rather violent (and probably near the peak nucleate flux). After a few seconds, an ice layer has formed and from this time on, one may analyze the boiling process by a simple moving boundary value model.

The value of τ^* was found to be remarkably constant in all tests although there was a slight reduction if the mass spilled was less than

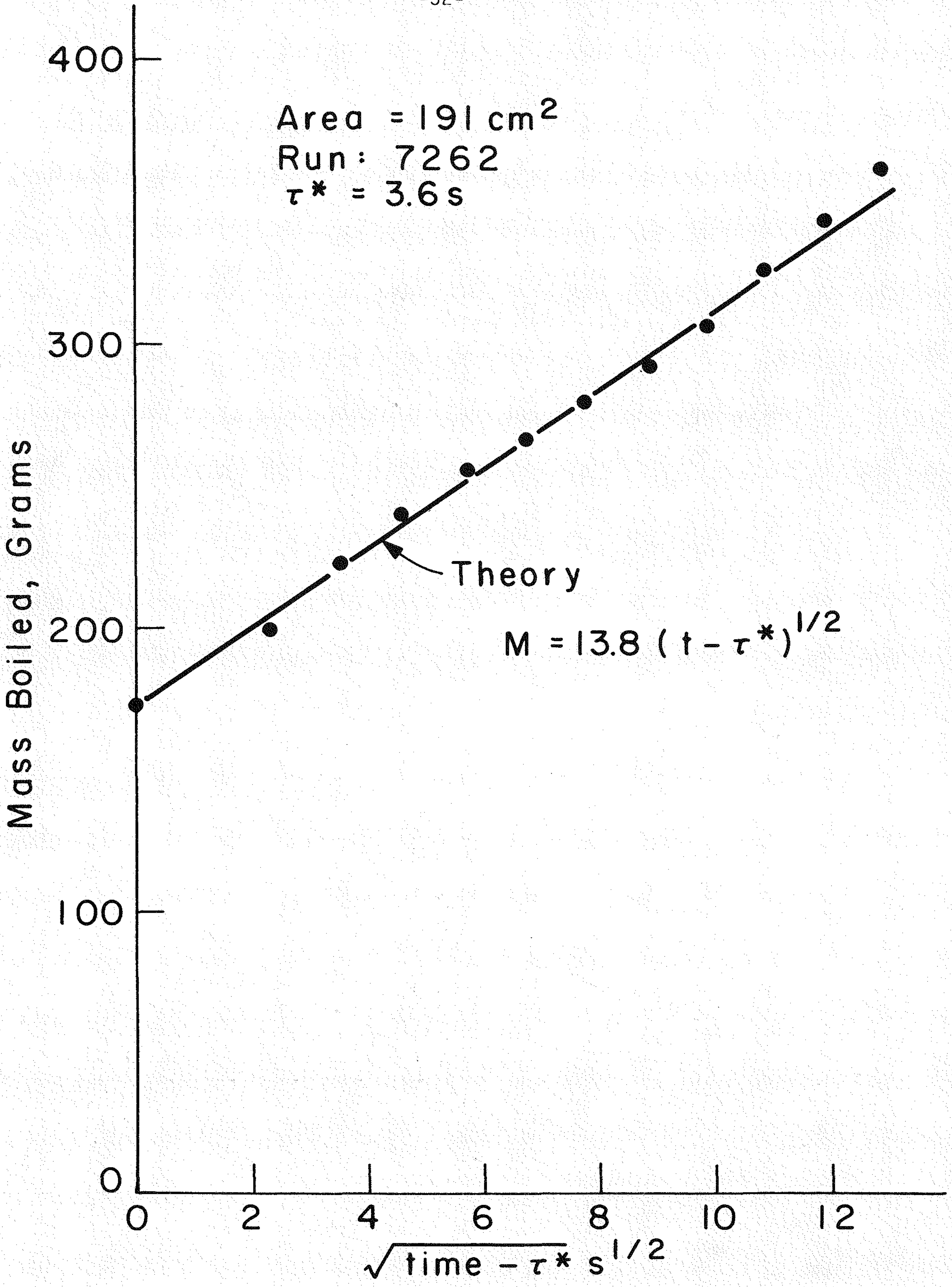

FIGURE 11 BOIL-OFF DATA FOR PROPANE SPILL ON 22°C WATER

200 g ($\sim$1 g/cm^2). τ^* varies from about 2.5-3.6 s for most runs but decreases to about 1.5 to 2.0 s for those with small mass poured.

In one spill of LPG on water, the membrane did not rupture in the expected manner and it required several seconds for the LPG to empty from the RSCD. This malfunction actually provided some very interesting data. There was no violent initial boiling period (or very little) and ice formed rapidly. It might, therefore, be expected that τ^* would be zero. The data shown in Figure 12 are plotted on this basis. While there is some scatter in the data, clearly the general trend supports the moving boundary value model described above as a line with a slope of 13.8 g/s$^{1/2}$ provides a good fit to the data for the first 600 seconds.

Summarizing the experiments involving LPG or propane,

- rapid spills led to an initial violent boiling period with very rapid vaporization of the LPG. The water interface in this period was poorly defined and ice was often thrown onto the walls of the calorimeter. Heat fluxes could not be estimated since the true area of contact between liquid water and LPG was not known.
- within about 1-2 seconds after a rapid spill, a coherent ice layer has formed and subsequent boil-off is well predicted by a moving boundary value model using a time scale beginning at the point ice has formed. Using properties of ice at a temperature averaged between the LPG boiling point (-42.1°C) and freezing water (0°C), a heat flux of about 154 $t^{-1/2}$ kW/m^2 is predicted (t in seconds). For the calorimeter used in this work, the mass boiled off then is predicted to be 13.8 $t^{1/2}$ g.
- there was essentially no effect of adding small quantities of ethane or <u>n</u>-butane to the propane on the heat flux curves. Thus the boiling of LPG may be modelled satisfactorily by using pure propane.

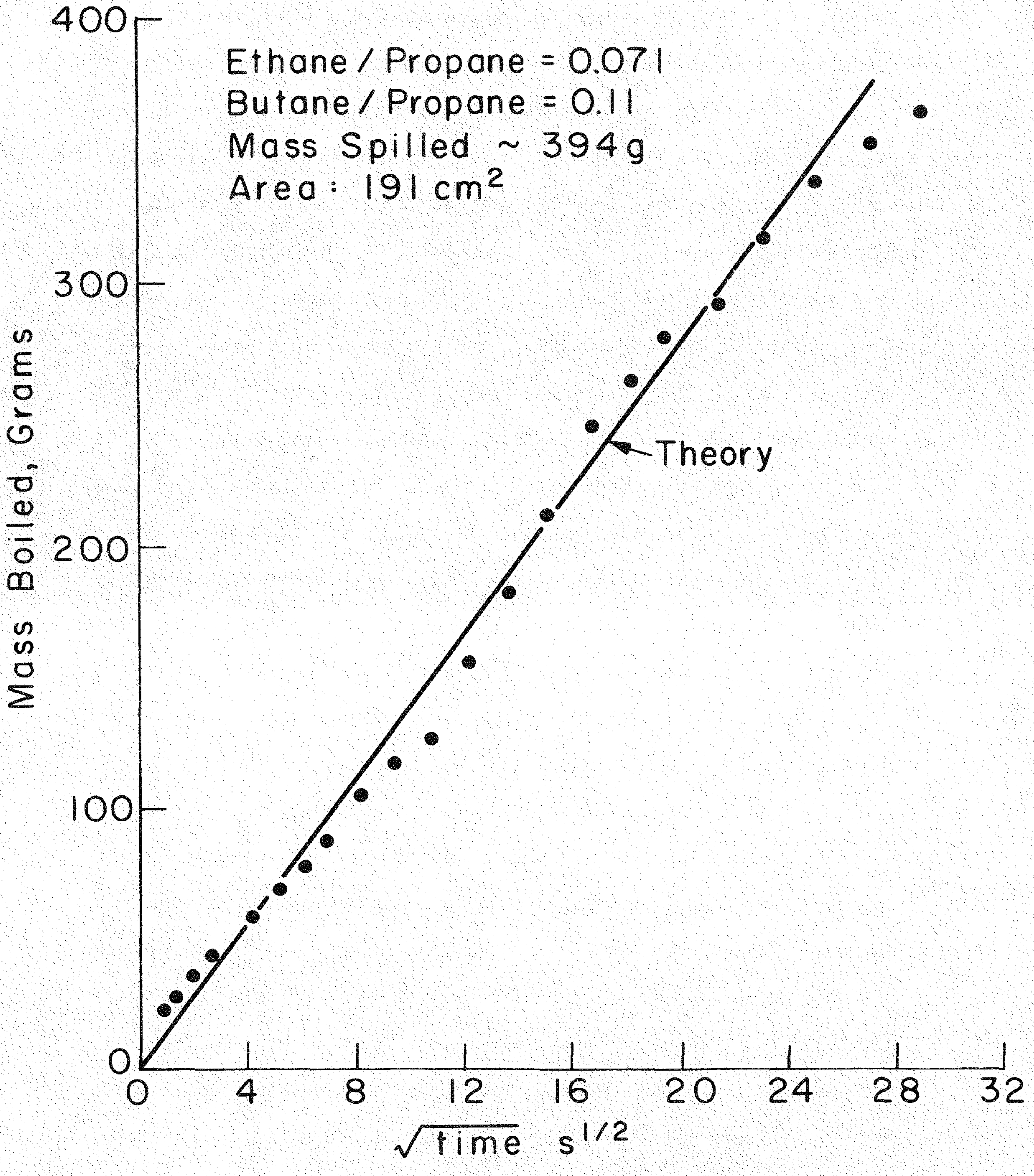

FIGURE 12 BOIL-OFF DATA FOR AN LPG SPILL ON WATER WITH A SLOW SPILL

- little effect of initial water temperature would be expected in estimating the boiling-rate curves for LPG as variations in the water temperature affect only slightly the predicted boiling rate.
- tests with propane boiling on an agar-agar/water gel yield a boil-off curve less than expected if the thermal properties of the agar-agar/water gel are assumed to be identical to those of water. As shown in Figure 7, the slope is about 11.3 $g/s^{1/2}$ rather than the 13.8 found for liquid water.

Ethane Spills on Water. The study of the boiling of pure liquid ethane on water was not the primary focus of this work and only a single test was conducted. The lower boiling point for ethane (-88.7°C) compared with propane (-41.1°C) also caused the membrane in the RSCD to be more brittle and, when cut by the knife, it did not rupture and open rapidly. However, other spill tests in the LNG Research Center have been made with liquid ethane on water so there are additional data for comparison purposes.

Since ice forms reasonably rapidly following a spill of liquid ethane on water, it was hypothesized that a moving boundary model might be applicable in the same manner as employed for propane spills. As the boiling point of ethane is -88.7°C, the properties of ice were selected at -44.4°C.

$$k_{ice} = 2.75 \text{ W/m K}$$

$$C_{ice} = 1800 \text{ J/kg K}$$

$$\rho_{ice} = 915 \text{ kg/m}^3$$

$$\alpha_{ice} = 1.674 \times 10^{-6} \text{ m}^2\text{/s}$$

Water properties at 20°C were chosen; these were equal those noted earlier for liquid propane spills.

The constant K was found to be 9.9717×10^{-4} m/s$^{1/2}$ and the heat flux is

$$\dot{Q}/A = 238\ t^{-1/2}\ \text{kW/m}^2 \quad (t \text{ in s})$$

For a boiling area of 191 cm^2, the boil-off equation is then

$$M = 18.6\ t^{1/2}\ \text{g}$$

This equation is plotted in Figure 13 along with the available experimental data. Clearly this model overestimates the boiling rate in the first few seconds after the spill. At longer times, the fit is much better, but with so few data, no definitive conclusions can be drawn. Theory does predict, nevertheless, that, after an ice shield forms, the heat transfer rate is significantly above that for LPG--although in the very short period following a spill, propane boils at a rate very much faster than ethane.

Ethylene Spills on Water. Four spills of liquid ethylene were made. In all cases, difficulty was experienced in achieving a clean, rapid rupture of the diaphram in the RSCD and, consequently, the exact time that each spill began remains in doubt. The first significant change in a thermocouple reading in the water was chosen to mark the starting time. When this was done, all tests showed an exceptionally low rate of vaporization in the first 5-15 seconds. Boil-off data for run C2 518 are shown in Figure 14 to illustrate this point. The early time data are not too different from the ethane results shown in Figure 13. The boil-off data at later times ($t \gtrsim 10$-15 s) plot, however as unusually

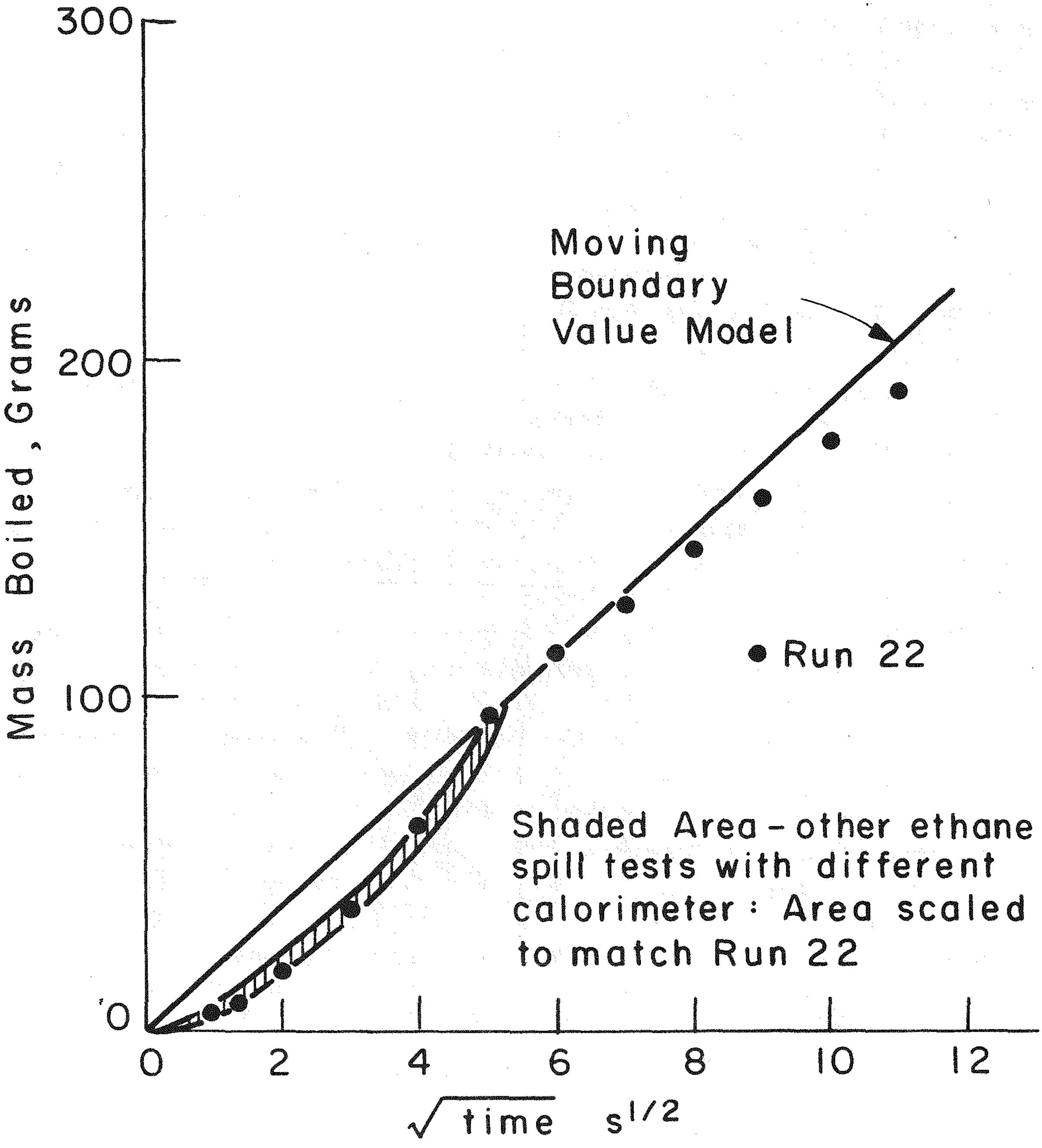

FIGURE 13 SPILLS OF LIQUID ETHANE ON WATER

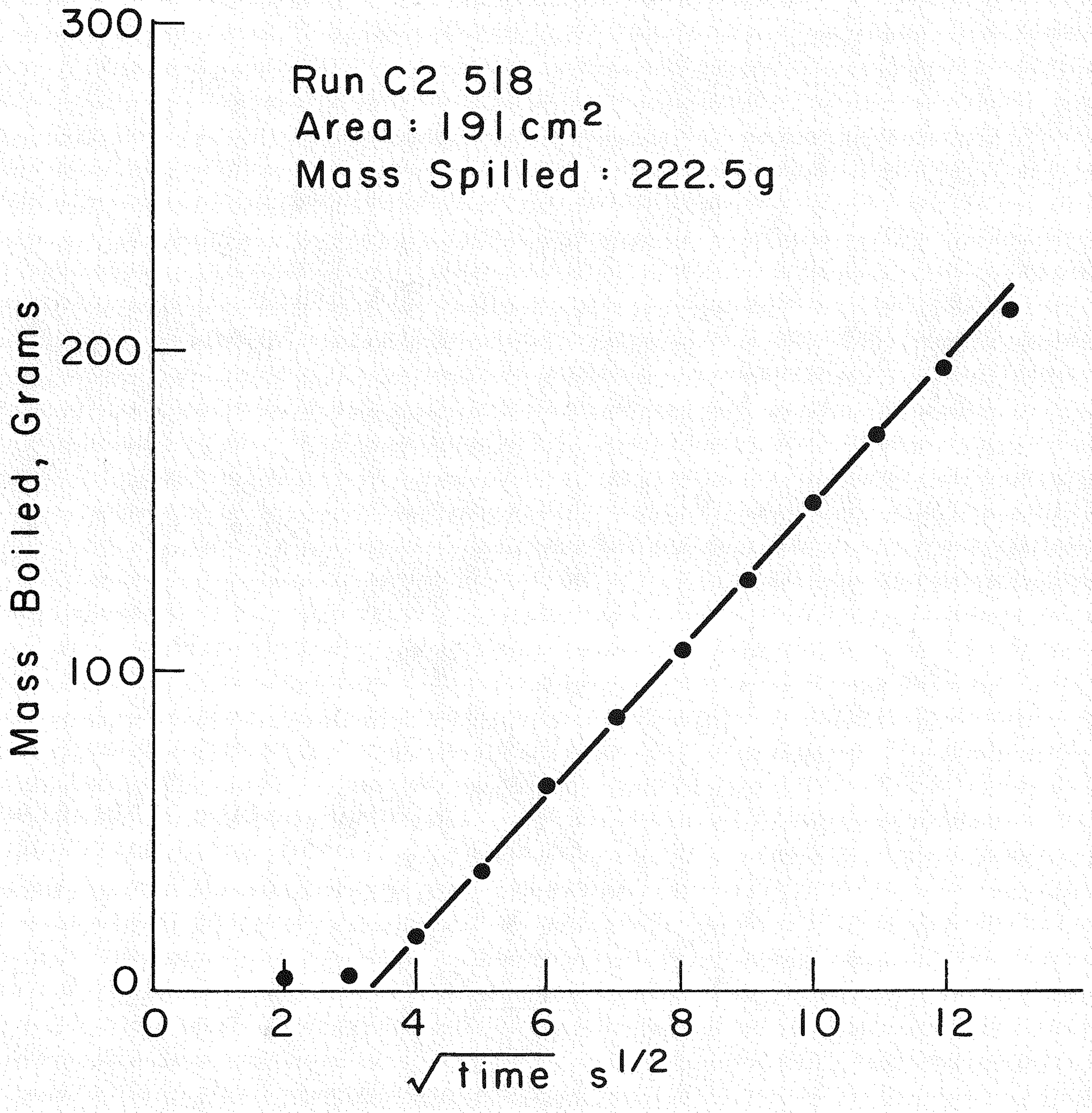

FIGURE 14 SPILL OF LIQUID ETHYLENE ON 22°C WATER

straight lines on the ΔM - $\sqrt{t}$ coordinates. Thus the simple moving boundary model* does not appear to be applicable to correlate boiling rates for ethylene spills.

We are obviously dealing with very complex phenomenon. As a tentative hypothesis, we suggest the ethylene may film boil at short times and, consequently, ice formation would then be retarded. The imposition of a boiling resistance at the interface greatly complicates the analysis. Kreith and Romie (1955) discuss this problem briefly and present some results obtained by using an electrical analogue. Their correlation (presented in a diminutive graph) shows the group Xh/k, as a function of $Q_L/C_1(T_p - T_b)$ and $\alpha_1 h^2 t/k_1^2$. X is the ice shield thickness as a function of time, t. h is the surface boiling coefficient and k_1, C_1, and α_1 are, respectively, the thermal conductivity, the heat capacity, and the thermal diffusivity of ice at the average temperature between the boiling point of ethylene, T_b, and the ice point, T_p. Q_L is the latent heat liberated in ice freezing. For the ethylene case, with an average ice temperature of (0 - 103.8)/2 = -51.9°C,

$$C_1 = 1750 \text{ J/kg}$$

$$\alpha_1 = 1.800 \times 10^{-6} \text{ m}^2/\text{s}$$

$$k_1 = 2.88 \text{ W/m K}$$

The group $Q_L/C_1(T_p - T_b) = 1.84$, and, for this value, the "approximate" Kreith and Romie correlation is shown in Figure 15. (The correlation also assumes that the initial liquid water temperature is 0°C.) While the numerical values are probably not meaningful, it is interesting to

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*The model yields a K of 1.0621×10^{-3} m $s^{-1/2}$ and
$\dot{Q}/A = 275\ t^{-1/2}$ kW/m^2
$M = 22\ t^{1/2}$ g for an area of 191 cm^2

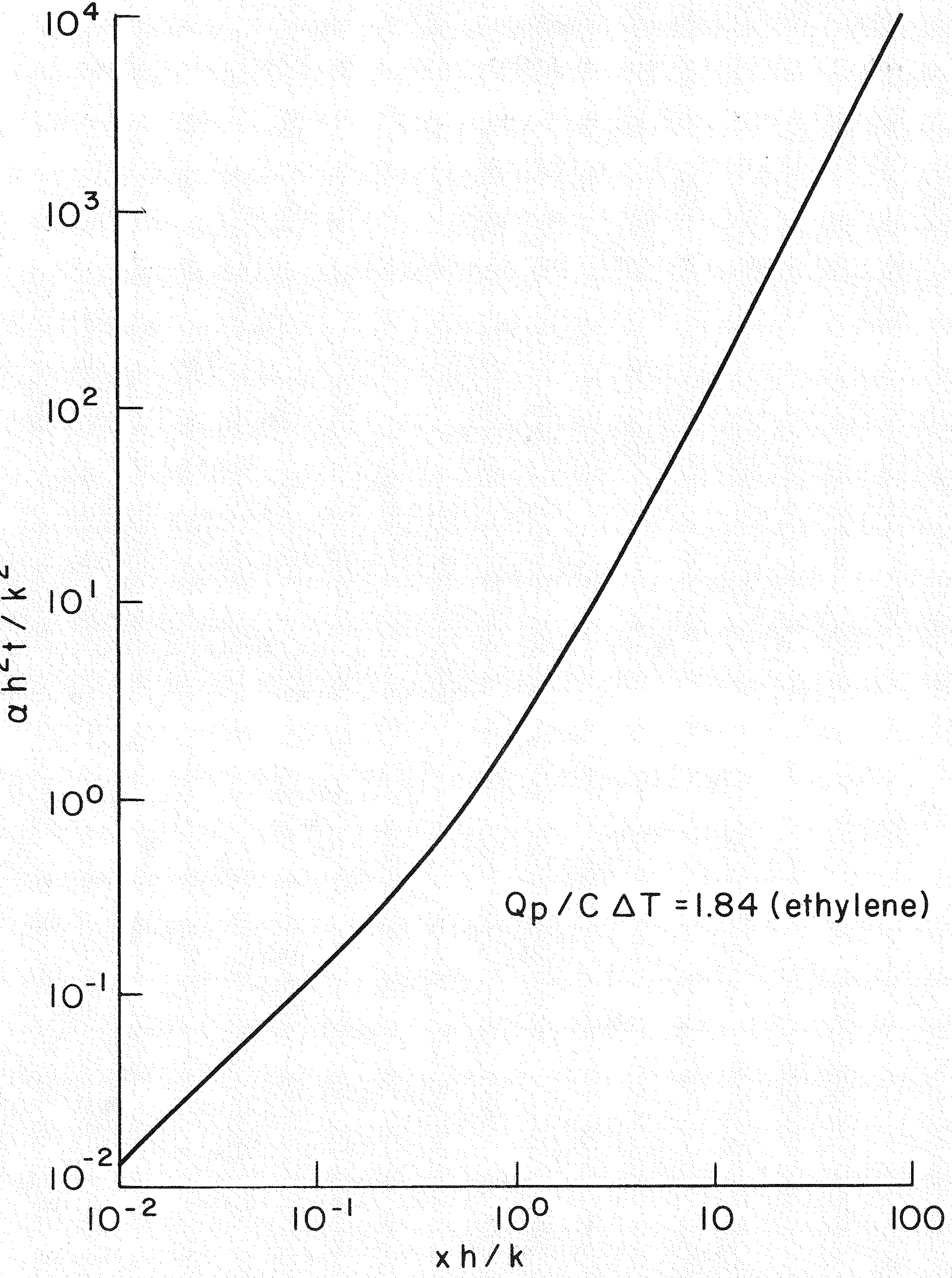

FIGURE 15 KREITH AND ROMIE CORRELATION FOR ICE THICKNESS IN A MOVING BOUNDARY MODEL WITH SURFACE RESISTANCE

note that at low values of $\alpha h^2 t/k^2$ (e.g., short times), X is proportional to t whereas at long times, X varies as $t^{1/2}$. Also, at long times dX/dt is essentially independent of h as would be expected since the predominant thermal resistance would then reside in the ice shield.

At large values of $\alpha h^2 t/k^2$, approximately,

$$\alpha h^2 t/k^2 = (Xh/k)^2$$

or

$$dX/dt^{1/2} = (\alpha)^{1/2} = (1.8 \times 10^{-6})^{1/2} = 1.34 \times 10^{-3}\ \mathrm{m/s}^{1/2}$$

However, the thickness of the ice shield is also related to the total energy removed, assuming the initial water temperature to be 0°C, by

$$\begin{aligned} Q &= Q_L\, \rho_{ice}\, X + \rho_{ice}\, C_{ice}\, X(T_p - T_b)/2 \\ &= X[3.335 \times 10^5 \times 915 + 915 \times 1750 \times 51.9] \\ &= 3.88 \times 10^8\ X\ \mathrm{J/m^2} \quad, X \text{ in m} \end{aligned}$$

or

$$\begin{aligned} \dot{Q} &= 3.88 \times 10^8\ (dX/dt)\ \mathrm{J/m^2\ s} \\ &= 1.94 \times 10^8\ t^{-1/2}\ (dX/dt^{1/2}) \\ &= (1.94 \times 10^8)(1.34 \times 10^{-3})\ t^{-1/2} \\ &= 260\ t^{-1/2}\ \mathrm{kW/m^2} \end{aligned}$$

Dividing by the enthalpy of vaporization of ethylene, 483 J/g,

$$\dot{M} = 538\ t^{-1/2}\ \mathrm{g/m^2\ s}$$

Integrating and using an area of 191 cm^2

$$M = 20.5\ t^{1/2} + C \quad \mathrm{g}$$

Thus, in the boiling period where the primary thermal resistance is in the growing ice shield, the slope of the mass boiled-off vs $t^{1/2}$ curve should be 20.5 $g/s^{1/2}$. This value is not far different from that of the line in Figure 14 which is 22.7 $g/s^{1/2}$. The simple moving boundary value model predicts a slope of 22 $g/s^{1/2}$; at long times this model should agree with the Kreith and Romie solution.

In the early time period, the Kreith and Romie graph indicates that

$$\alpha h^2 t/k^2 = Xh/k$$

or

$$X = \alpha h t/k$$

$$dX/dt = \alpha h/k$$

so

$$\dot{Q} = (3.88 \times 10^8)(\alpha h/k)$$

Choosing a representative but, perhaps, low value for $h = 56.7\ W/m^2\ K$ ($10\ Btu/hr\text{-}ft^2\text{-}°R$), $(\alpha h/k) = 3.54 \times 10^{-5}$ m/s,

$$\dot{Q} = (3.88 \times 10^8)(3.54 \times 10^{-5}) = 13.8\ kW/m^2$$

$$\dot{M} = (1.38 \times 10^4)/483 = 28.5\ g/m^2\ s$$

Integrating and using an area of 191 cm^2,

$$M = 1.1\ t + C \quad g$$

The variation of M with t is initially small, but the slope on a $M\text{-}t^{1/2}$ plot, $dM/dt^{1/2} = 2.2\ t^{1/2}$, increases with time, a trend again noted for the ethylene spill tests as shown in Figure 14.

The present theory is too crude and the existing data too meager to make any definitive conclusions. It does appear, however, that when ethylene (and, perhaps, ethane) is spilled on water, one must include a thermal resistance at the interface in any model. The effect of such a resistance will be to diminish the rate of boiling (and ice formation) at short times, but at longer times it would have little influence on rates. The ideas discussed above are in reasonable agreement with the few available data, but the real problem has not been solved. In fact, a solution would be very complex as the interfacial resistance (noted here by h^{-1}) would surely vary with the surface ice temperature and change from a low value of h with initial film boiling to larger values as the boiling enters the nucleate region.

Spill of *n*-Butane on Water. Only one spill was made with *n*-butane ($T_b = -0.5°C$). Boiling was smooth with little ice formation except at long times. The data are shown in Figure 16. The rate of boiling was a constant = 0.56 g/s in the 191 cm^2 calorimeter. In more general terms,

$$\dot{Q} = (0.56)(302.3)/(191 \times 10^{-4}) = 8860\ W/m^2$$

where 302.3 is the enthalpy of vaporization of *n*-butane in J/g.

The rate of boiling of *n*-butane is, as expected, far less than for the other liquefied hydrocarbons studied in this work.

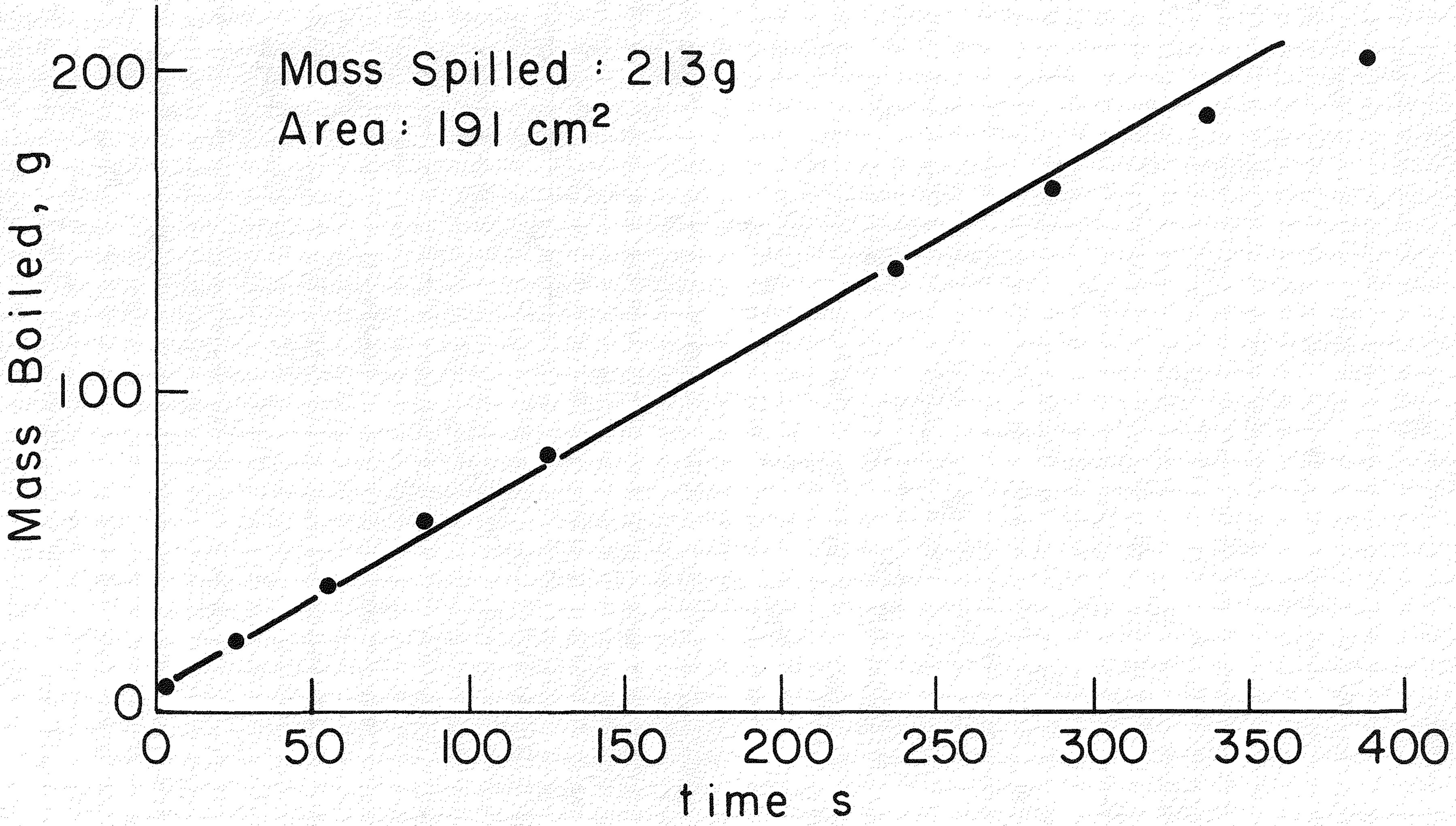

FIGURE 16 SPILL OF N-BUTANE ON 22°C WATER

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