Theory and Measurement of Hydrate Dissociation

Experimental data on the rate of dissociation of methane hydrates are presented. The data were obtained from hydrate mass loss measurements using an electrobalance. A resistance heater with a known heat flux was used in the dissociation experiments. A mathematical model describing the dissociation process is also presented. The model, based upon first principles, assumes that the water formed during dissociation is blown away by the methane gas produced so that the dissociation process may be regarded as a moving-boundary ablation problem. Agreement between the model and the data is within 10%.

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Introduction

Natural gas hydrates are solid inclusion compounds in which a natural gas molecule smaller than *n*-butane is encapsulated by a cage of water molecules. These cages, which form either of two different crystal structures, diamond or body-centered cubic, prevent guest molecule translation and inhibit rotation and vibration to some degree. The properties of hydrates are reviewed in detail by Davidson (1973).

Since the Russians discovered *in situ* reserves of hydrates in the late 1960's, hydrates have been considered a potential natural gas resource, as indicated by the U.S. Department of Energy *Handbook of Natural Gas Hydrates* (Lewin Assoc., 1984). Substantial amounts of hydrates have been determined to be at the ocean bottom and in permafrost regions of the earth (Kvenvolden and McMenamin, 1981). In order to recover gas from hydrate reserves, it is necessary for heat to flow in order to dissociate the water bonds in the hydrate structure. The source of the energy given to the molecules may be the reserve itself, the surrounding earth, or hot fluids such as steam or geothermal brines. Holder et al. (1982) calculated that the recovery of gas from hydrates was energy-efficient from a thermodynamic standpoint. McGuire (1981) and Bayles et al. (1984) suggested that thermal stimulation techniques are most attractive for gas hydrate dissociation.

The purpose of the present work was to measure the rate of hydrate dissociation and to formulate an *a priori* model that would predict such data with no adjustable parameters. Such a result would be an important first step toward predicting the dissociation rate of hydrates in sediments, ultimately needed for the recovery of gas from hydrate in the reservoir.

Physical Model

In the present work, a mathematical model for hydrate dissociation under thermal stimulation was based upon a planar, one-dimensional semiinfinite system. Generalization to cylindrical, spherical, or finite geometry presents no difficulty. Furthermore, a radiant heat source, as a means for thermally dissociating the hydrate, was selected for ease of experimental control; generalizations to other heating conditions pose no problem.

Consider the physical situation presented in Figures 1a and 1b. Initially the hydrate body is at a uniform temperature T_i and occupying the semiinfinite region $0 < x < \infty$. At time $t = 0$ a constant heat flux q_s is applied to the boundary surface at $x = 0$. The temperature of the boundary surface rises from T_i to T_s, which is the temperature in equilibrium with the prevailing pressure as shown in Figure 1a. Thereafter, dissociation starts and the boundary surface moves in the positive x direction as shown in Figure 1b. Meanwhile, the temperature of the moving boundary remains constant at T_s, the dissociation temperature in equilibrium with the constant pressure prevailing outside the hydrate body. To simplify the analysis, it is assumed that the water resulting from the dissociation process is completely removed from the surface immediately on formation. Effectively, the gas blows the water away from the surface. Such an assumption is usually encountered in ablation problems (Goodman, 1958). There will therefore be no liquid phase over the dissociation surface and we need only consider the heat transfer problem in the undissociated solid phase.

Let t_{sd} be the time required for the boundary surface to reach the equilibrium temperature T_s. Thus, for $t < t_{sd}$ the problem may be regarded as a fixed-boundary problem, while for $t > t_{sd}$

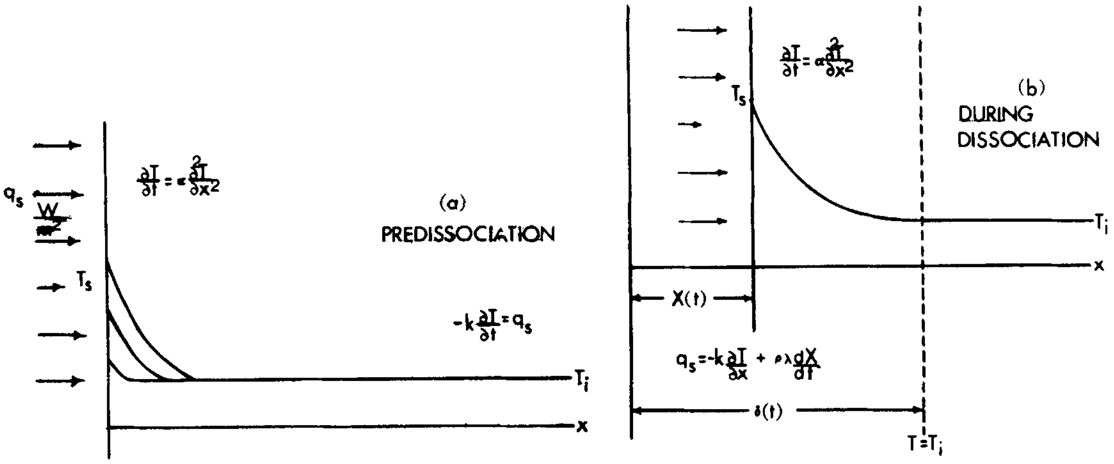

Figure 1. Dissociation process.

the problem becomes a moving-boundary problem. The fixed-boundary problem may then be regarded as a heating problem preceding dissociation. The appropriate differential equations and associated boundary and initial conditions are given by:

For $t < t_{sd}$

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad 0 < x < \infty, t > 0 \tag{1}$$

$$-k \frac{\partial T}{\partial x} = q_s \quad x = 0, t > 0 \tag{2}$$

$$T = T_i \quad x = \infty, t > 0 \tag{3}$$

$$T = T_i \quad 0 < x < \infty, t = 0 \tag{4}$$

For $t > t_{sd}$

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad X(t) < x < \infty, t > 0 \tag{5}$$

$$T = T_s \quad x = X(t), t > 0 \tag{6}$$

$$-k \frac{\partial T}{\partial x} + \rho\lambda \frac{dX}{dt} = q_s \quad x = X(t), t > 0 \tag{7}$$

$$T = T_i \quad x = \infty, t > 0 \tag{8}$$

$$T = f(x) \quad 0 < x < \infty, t = t_{sd} \tag{9}$$

where the function $f(x)$ is obtained from the solution of the fixed-boundary problem.

Goodman (1958) presented an approximate solution to an ablation problem similar to the problem encountered in the present study. This solution utilizes the heat-balance integral method together with a second-degree polynomial approximation for the temperature profile. The method is based on the von Karman-Pohlhausen momentum integral technique used in the analysis of boundary layers (Schlichting, 1968). As pointed out by Schlichting and Ulrich (1942), the use of a higher degree polynomial results in better approximations to the exact solution. It seems natural, therefore, to improve Goodman's method, which is based on a polynomial of the second degree (P2 method) by selecting one of a higher order. In the present study, a polynomial of the fourth degree was used. The additional coefficients were used to satisfy additional compatibility conditions at the boundary surface and at the edge of the thermal layer. As indicated later, results based on a polynomial of the fourth degree (P4 method) represent a significant improvement over those obtained using the P2 method.

The basic steps of the solution are straightforward and have been presented in an earlier paper (Selim and Sloan, 1985). The final results are

$$t_{sd} = \frac{4k^2(T_s - T_i)^2}{5\alpha q_s^2} \tag{10}$$

$$\tau = \frac{1}{St} + (1 - \xi) + (1 + St)\ln\frac{St}{(1 - St) - \xi} \tag{11}$$

$$X^* = (1 - \xi) + St \ln\frac{St}{(1 + St) - \xi} \tag{12}$$

where

$$\tau = \frac{5q_s^2 t}{4\rho\lambda k(T_s - T_i)} \tag{13}$$

$$X^* = \frac{5q_s X}{4k(T_s - T_i)} \tag{14}$$

and

$$St = \frac{\lambda}{C_p(T_s - T_i)}$$

Elimination of the parameter ξ between Eqs. 11 and 12 gives a relationship for the dimensionless position of the moving front X^* as a function of dimensionless time τ. The only parameter appearing in this relationship is the Stefan number St. Graphical results are presented in Figure 2. From this figure we notice

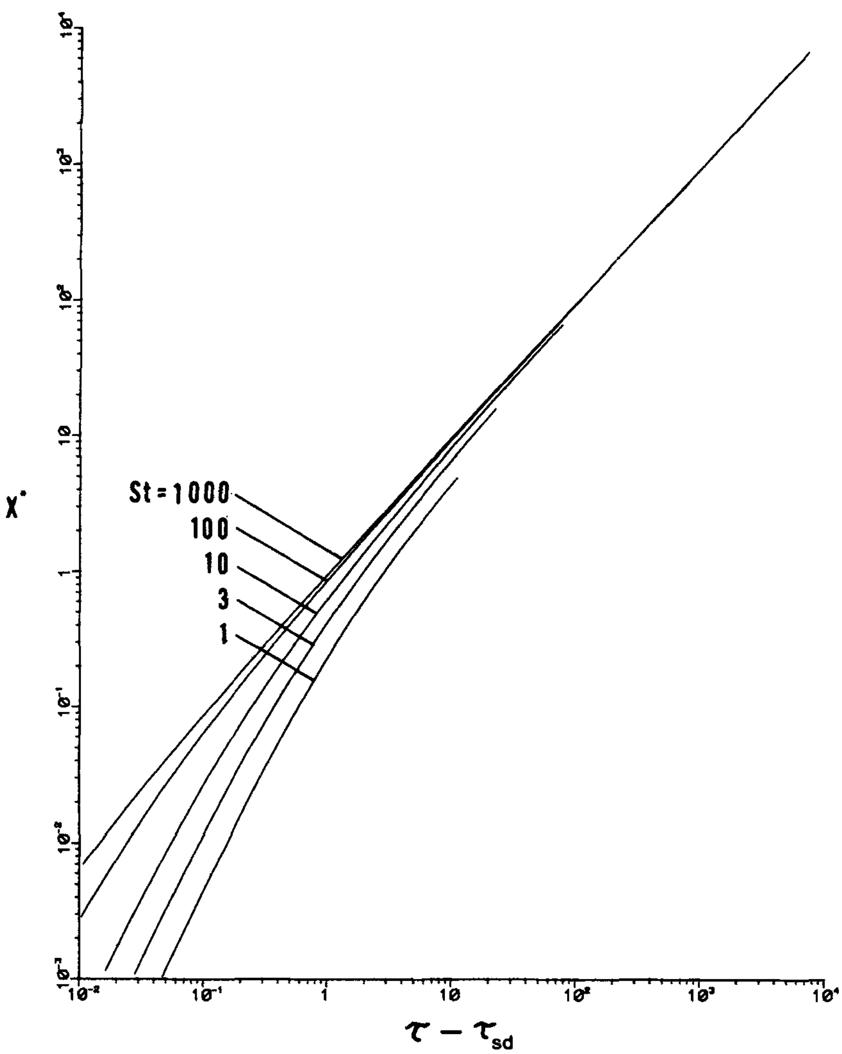

Figure 2. Position of dissociation interface vs. time.

that the speed of the dissociation front decreases with time, eventually attaining a constant value. Thus, a long-time solution is easily found as

$$X^* = \frac{St}{1 + St}\left(\tau - \frac{1}{St}\right) \quad \text{for large } \tau \tag{15}$$

It is also instructive to evaluate the fraction of the incident heat flux that is used in dissociation, f_D, and that fraction which is conducted into the material, f_c. Utilizing the solution of Selim and Sloan (1985), these quantities are easily found as

$$f_D = \frac{\rho\lambda(dX/dt)}{q_s} = \frac{St}{1 + St} \tag{16}$$

and

$$f_c = \left.\frac{-k(\partial T/\partial x)}{q_s}\right|_{x=X(t)} = \frac{1}{1 + St} \tag{17}$$

It is clear that for large St ($St \approx 24$), such as the case of hydrate dissociation without sediment, most of the incident heat is used in dissociation with only a small amount being conducted into the material.

It is worth noting that an exact solution to the fixed-boundary problem described by Eqs. 1–4 is available (Carslaw and Jaeger, 1959). Utilizing this solution it is found that our P4 method gives an error of approximately 1% compared with an error of about 9% for the P2 method of Goodman (1958).

Experimental Procedure

Sample preparation and characterization

The hydrate formation procedure was slightly modified from that originally proposed by Holder (1983). In this procedure,

Table 1. Comparative Tests on Laboratory Hydrates

	Hydrate, %		
Run	Bomb Calorimetry	Mass Loss Test	Difference %
1	32.0	31.8	0.63
2	63.9	61.0	4.57
3	31.1	28.8	5.67

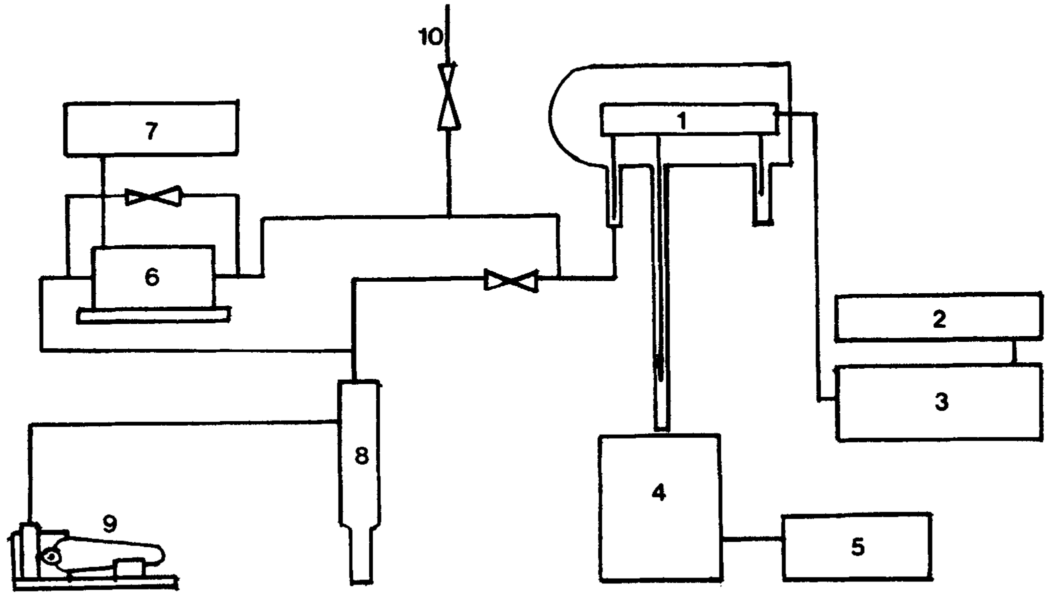

Figure 3. Dissociation apparatus.

1. Electrobalance	6. Barocell
2. Strip chart recorder	7. Electronic manometer
3. Electonic controls for electrobalance	8. Diffusion pump
4. Heater	9. Vacuum pump
5. Variable voltage supply	10. Vent

fine-grained snow was compacted into a stainless steel cell, which was then pressurized to 4.1 MPa with 99.97% methane (Matheson) while the sample was at 230 K. The temperature of the cell was then raised to 274 K where the ice molecules rearranged themselves and formed hydrate by encapsulating gas molecules. After 48 h, when the pressure decrease with time became undetectable, the hydrate was extruded from the formation cell for further testing.

The fraction of hydrates formed in the sample cell was determined via combustion bomb calorimetry. The calorimeter was calibrated by combusting benzoic acid with excess oxygen; it was then tested against napthalene, so that the accuracy was determined to be within 3%. A known weight of a hydrate sample in a chilled cup was placed in the calorimeter and allowed to dissociate. Excess oxygen was added and the mixture was combusted. The temperature rise resulting from combustion was used along with literature values for the heat of combustion of methane to determine methane content in the sample. This experiment was repeated several times to insure that the excess oxygen added was within the limits of methane combustion. The fraction of hydrates in the sample was calculated assuming 91% filling of the cages, as determined by a statistical mechanics model (Sloan, 1985) based upon a revision of that of Parrish and Prausnitz (1972).

A second method was used to characterize the amount of hydrate formed. This method involved a gravimetric determination of the mass of methane evolved during dissociation. The mass of water that remained could then be measured. With the mass of gas and water known, the percentage of hydrate was calculated using the assumption of 91% cage filling. The calorimeter and mass loss tests were conducted on portions of the same hydrate sample in three experiments. The results of both methods are presented in Table 1. Data from the mass loss test are consistently lower due to two unavoidable experimental conditions. The first is a very small loss of methane during sample transfer to the balance. The second is water condensation on the chilled sample holder. Nevertheless, the mass loss and combustion test data are within 5% of one another, thus confirming the validity of the combustion test.

Hydrate mass loss experiments

Hydrate samples at liquid nitrogen temperatures were suspended by a hangdown wire from a Cahn Electrobalance within

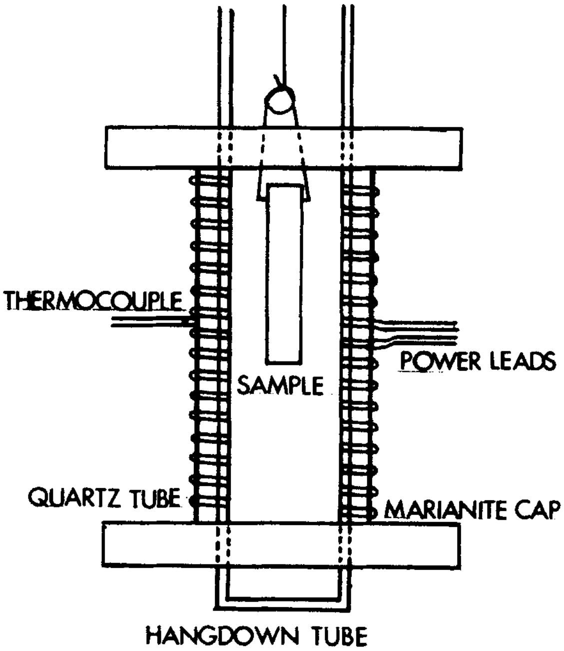

Figure 4. Sample and heater.

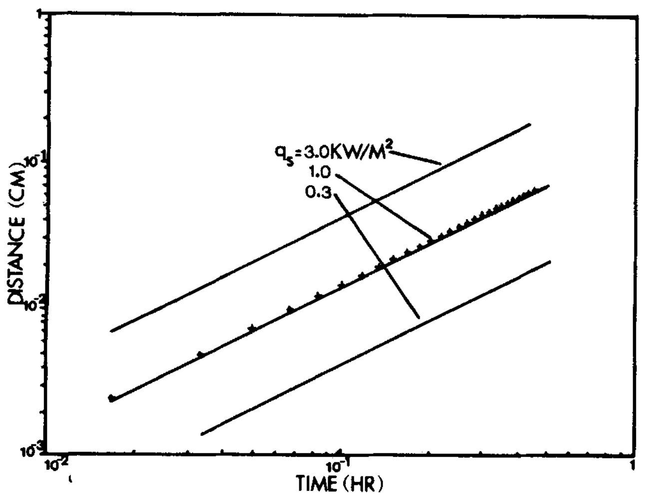

Figure 5. Comparison of moving front location for ice with model predictions.

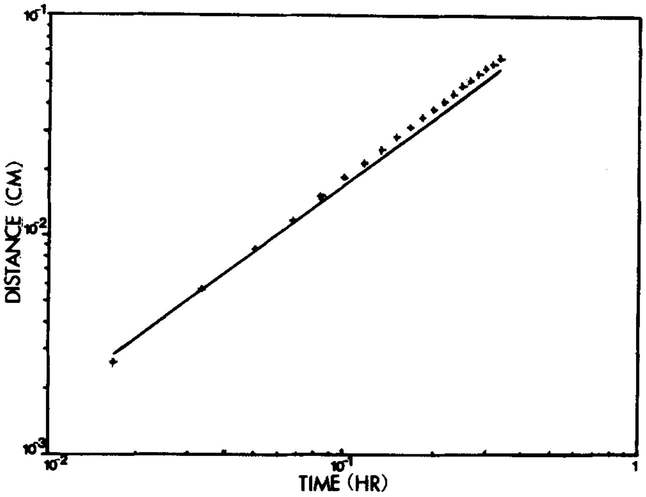

Figure 7. Comparison of dissociation front location for hydrate with model predictions for sample 2.

a glass pressure enclosure. A diagram of the apparatus is given in Figure 3. The pressure in the glass chamber was maintained below 200 Pa (measured by a capacitance manometer) via a vacuum pump. A resistance heater was placed around the hang-down tube, as indicated in Figure 4, and a known heat flux was input to the sample. The electrobalance was used to measure the mass loss, with an accuracy to within 10 μg, as a function of time. The low pressure in the chamber ensured that the heat transfer mechanism was almost entirely radiation, with little or no conduction or convection.

The energy flux from the radiant heater was determined experimentally by dissociating cylinders of ice and carbon dioxide at the same pressure as that of the hydrate studies. For the heater calibration runs, the sublimation of both ice and carbon dioxide was assumed to obey the ablation model presented above. The data of an ice sublimation experiment, presented in Figure 5 along with the model prediction, suggest both the applicability of the long-time portion of the model and that the heat input flux was approximately 1.0 kW/m^2. Eight experiments for the sublimation of carbon dioxide yielded data very similar to those shown in Figure 5. These values gave an energy flux of 1.02 kW/m^2 with a standard deviation of 0.043. Radiation absorptivity for both ice and carbon dioxide (0.97 and 0.98, respectively) were similar, while the transmissivity of both solids was estimated to be zero. It was assumed that the radiation properties for all three substances (ice, carbon dioxide, and hydrates) were similar.

Results and Discussion

Three experimental measurements were made on dissociation of the methane hydrates with data as shown in Figures 6, 7, and 8. In these figures the results of the model are shown along with data represented as crosses. Since the mass loss was linear with time, the data were compared with the long-time solution of the model. Physical properties of hydrate used in model predictions are given in Table 2. The radius decrease of each sample was sufficiently small (less than 10%) such that the curvature of the cylinder could be neglected. Therefore, comparison of the data with the model was applicable.

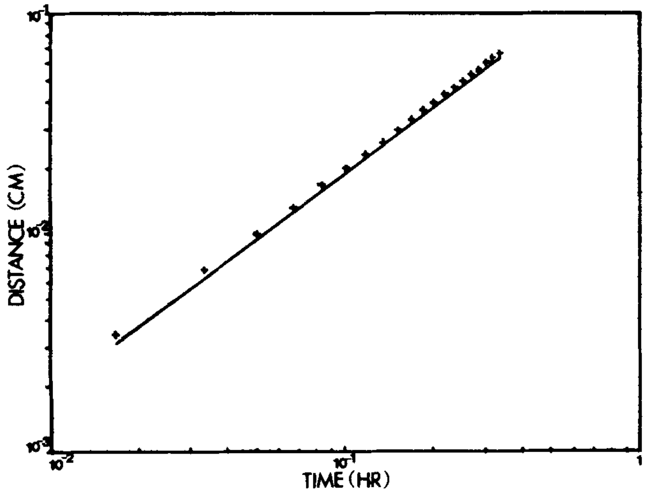

Figure 6. Comparison of dissociation front location for hydrate with model predictions for sample 1.

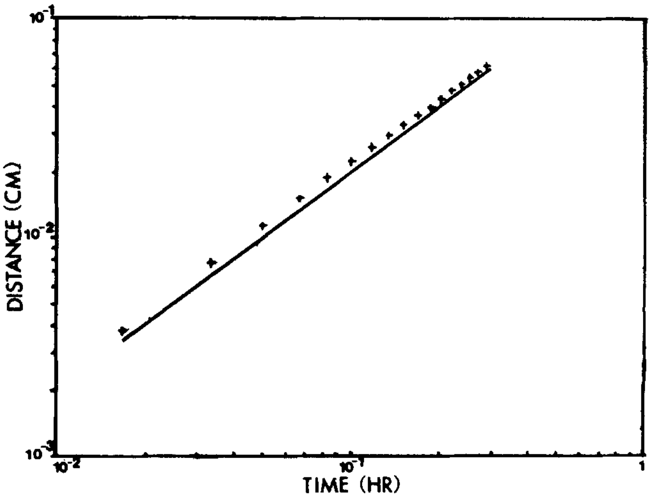

Figure 8. Comparison of dissociation front location for hydrate with model predictions for sample 3.

Table 2. Hydrate Physical Properties

Density (Lewin Assoc., 1984)	0.892 g/cm^3
Heat capacity (Selim and Sloan, 1985)	2.010 W · s/g/K
Thermal conductivity (Stoll and Bryan, 1979)	0.393 W/m/K
Heat of dissociation (Falabella and Vanpee, 1974)	2,618.8 W · s/g

The long-time moving-boundary model underpredicts the data by an average of 6% in Figure 6, 8.5% in Figure 7, and 9.9% in Figure 8. If the uncertainties in the values of the radiant energy flux, as well as the error in the values of the heat of dissociation, are propagated through the moving boundary model, then the error resulting from the predictions should be ±5%. After the sample ice content and end effects are accounted for, we estimate that the data are accurate to within 15%. Such differences between the model predictions and the data are very acceptable, considering the rigor of the model.

Since the thermal conductivity of hydrate is approximately 20% that for ice, the heat conducted into the hydrate mass represents only 4% of the total incident heat; 96% of the heat is spent on hydrate dissociation. For those cases in which hydrates are present with significant amounts of sediment, the higher conductivity of the sediment will cause the conduction mechanism to become very significant.

Conclusion

A mathematical model without adjustable parameters has been developed to describe the dissociation of natural gas hydrates. Experimental measurements with methane hydrates confirm the validity of the model. Agreement between the model and data was within 10%.

In hydrate dissociation without sediments, dissociation is the controlling factor, with thermal conduction only contributing in a minor way. In the *in situ* case of hydrate dissociation in sediments, however, conduction will be much more significant. While sediments are not explicitly considered here, the present model represents a significant beginning to modeling hydrate dissociation within sediment, and suggests directions for future work.

Acknowledgment

The authors gratefully acknowledge the helpful suggestions and contributions of W. R. Parrish and F. H. Poettmann, and also express their appreciation to Hamid Ouar for assistance with the experimental work. This work was made possible by support of the United States Department of Energy through Contract DE-AC21-83MC20693.

Notation

C_p – heat capacity of hydrate, J/kg · K
f_C – fraction of incident heat used in dissociation
f_D – fraction of incident heat conducted into hydrate
k – thermal conductivity of hydrate, W/m/K
q_s – specified heat flux at the boundary surface, W/m^2
St – Stefan number; ratio of latent heat to sensible heat $\rho\lambda\alpha/[k(T_s - T_i)] = \lambda/C_p(T_s - T_i)$
t – time, s
t_{sd} – start of dissociation time, s
$T(x, t)$ – temperature, K
T_i – initial temperature of hydrate, K
T_s – equilibrium surface temperature of hydrate, K
x – spatial position, m
$X(t)$ – position of dissociation interface, m
$X^*(\tau)$ – dimensionless position of dissociation interface

Greek letters

α – thermal diffusivity of hydrate, m^2/s
λ – heat of dissociation of hydrate, J/kg
ξ – parameter, Eqs. 11, 12
λ – heat of dissociation of hydrate, J/kg
ρ – density of hydrate, kg/m^3
τ – dimensionless time, Eq. 13

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Manuscript received May 20, 1986, and revision received Oct. 10, 1986.