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A New Technique for Hydrate Thermal Diffusivity Measurements[1]

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Thermal property measurements of natural gas hydrates in various sediment mixtures are necessary to describe heat transfer to surroundings during well boring and gas production. An apparatus for measuring thermal diffusivity in various mixtures of hydrates with sediment has been constructed. The apparatus uses a new method for determining thermal diffusivity that has advantages over the von Herzen and Maxwell probe method. The new experiment is simple and inexpensive to construct and appears to be much more accurate than the ±30% reported for an earlier probe. The thermal diffusivity of ice has been measured to determine the uncertainty of the technique, i.e., within ±6% with a 95% confidence level. The thermal diffusivity for pure methane hydrate at various temperatures is reported.

KEY WORDS: hydrate; ice; methane hydrate; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Hydrates of natural gas are pervasive in the seafloor and permafrost regions of the world [1]. These natural hydrates are usually associated with a sediment substrate [2, 3].

Waite et al. [4] have performed thermal conductivity measurements on hydrate sediment mixtures and found a maximum in thermal conductivity within a range of pure sediment and pure hydrate compositions. They

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attributed this nonlinearity to poor contact of high thermal diffusivity sediment grains and cementing properties of lower thermal conductivity hydrates.

The thermal conductivity, along with the heat capacity and density of the medium, can be used to determine the thermal diffusivity; each of these properties can vary with hydrate fraction. Therefore, it is expected that the thermal diffusivity will have a maximum like the thermal conductivity, but for a different hydrate composition.

2. EXPERIMENTAL SETUP

An apparatus was developed to measure the thermal diffusivity of solids. The experimental apparatus, shown in Fig. 1, consisted of a 20-cm long, 5-cm inner diameter stainless steel cell submerged in a cooling bath. The cell had three thermocouples, which penetrated to three different radii within the cell: the center, the wall, and midway between the center and wall. A fourth thermocouple was used to measure the bath temperature. A gas inlet/outlet was located at the top of the cell, along with a filter and pressure transducer. A nickel–chromium heating wire (18 gauge, $1.384\,\Omega \cdot \mathrm{m}^{-1}$) was located through the centerline of the cell. The heating wire was electrically insulated with a thin plastic tube coating. A 3 A, 13.8 V dc power supply was connected to the heating wire, which could supply ~4.7 W of power through the wire.

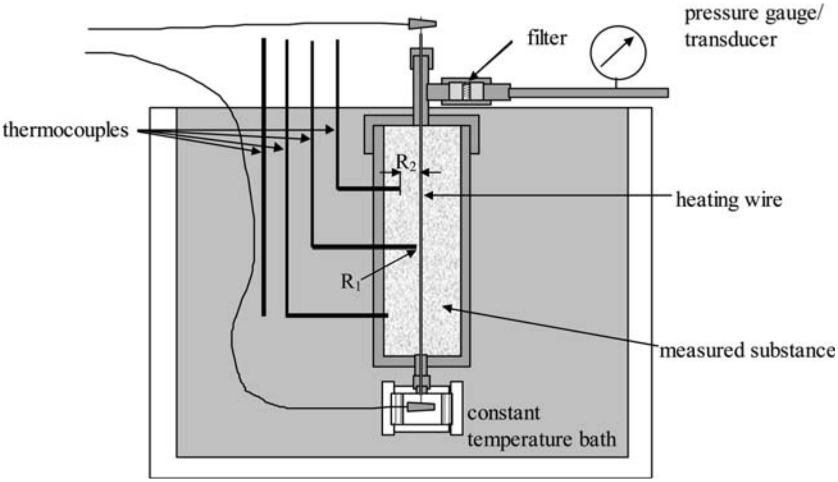

Fig. 1. Thermal diffusivity apparatus.

As discussed in the following section on the thermal diffusivity equation derivation, this cell configuration provided all of the necessary parameters for measuring the thermal diffusivity, α, namely R_1 and R_2 (the distance of the center and midway thermocouples from the cell centerline), T_1 and T_2 at the respective thermocouples, and $[\Delta T/\Delta t]_1$ and $[\Delta T/\Delta t]_2$ at the respective locations. Distances R_1 and R_2 were constant in the apparatus.

The center thermocouple could also be used to ensure that the temperature near the heat source was below the melting point. The wall thermocouple was used to indicate when the heat wave from the heating wire had reached the outer wall.

3. DERIVATION OF THE THERMAL DIFFUSIVITY EQUATION

The thermal diffusivity apparatus utilized the Navier–Stokes heat equation for cylindrical geometry applied to a heat wave, which propagates from a line source into an infinite medium [5]. If no volumetric generation occurs, such as hydrate formation or dissociation, if the heat is transferred symmetrically from the center source, if the loss of heat axially is negligible (such as with a long cell), and if no viscous dissipation occurs, the general form of the Navier–Stokes equation greatly simplifies to

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right] \tag{1}$$

where T is temperature, t is time, α is thermal diffusivity, and r is radial distance from the cylinder center.

Although Eq. (1) has an analytical solution, an approximate solution is preferred for our experimental analysis. For small time steps, the change in temperature with time may be linearized in discrete stages;

$$\frac{\partial T}{\partial t} \approx \frac{\Delta T}{\Delta t} \equiv m \tag{2}$$

where m is a constant equal to the change in temperature over a small time increment.

Equation (2) permits us to cast Eq. (1) into the form of an ordinary differential equation. The thermal diffusivity (α) is assumed to be constant for the medium; i.e., the medium is assumed to be homogeneous and the thermal diffusivity is assumed to be a weak function of temperature to combine Eqs. (1) and (2):

$$\left[\frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) \right] = \frac{m}{\alpha} \equiv C \tag{3}$$

where C is a constant.

This ordinary differential equation is integrated once;

$$r\frac{dT}{dr} = \frac{C}{2}r^2 + I_0, \tag{4}$$

where I_0 is a constant of integration.

Assuming that the heat flux from the heating source is constant, the boundary conditions at the centerline are as follows:

$$\frac{dT}{dr} = -\frac{q}{\lambda} \approx \omega, \quad \frac{\Delta T}{\Delta t} = \left.\frac{\Delta T}{\Delta t}\right|_{r=0_1}, \quad @r=0, \tag{5}$$

where q is the heat flux from the wire, λ is the thermal conductivity of the measured medium, and ω is a constant proportional to the heat flux from the heat source at the centerline and the thermal conductivity of the measured medium.

When the constant ω is substituted at the centerline boundary $(r=0)$ into Eq. (4), I_0 is eliminated.

If the temperature is known at some distance (R_1) from the heat source, a boundary condition can be provided at that distance;

$$T = T_1, \quad \frac{\Delta T}{\Delta t} = \left.\frac{\Delta T}{\Delta t}\right|_{r=R_1}, \quad @r=R_1 \tag{6}$$

Likewise, if the temperature is known as some other distance (R_2) from the heating line, another condition is known:

$$T = T_2, \quad \frac{\Delta T}{\Delta t} = \left.\frac{\Delta T}{\Delta t}\right|_{r=R_2}, \quad @r=R_2 \tag{7}$$

From Eq. (4) integrated with boundary conditions Eqs. (6) and (7), with the temperatures measured at two known distances from the heat source, the thermal diffusivity, α, can be calculated (recalling that $\alpha = m/C$).

$$T = \frac{C}{4}r^2 + I_1 \tag{8}$$

where I_1 is a second constant of integration.

When Eq. (8) is applied at the first location, boundary condition 2 follows:

$$T_1 = \frac{C|_{r=R_1}}{4}R_1^2 + I_1 \tag{9}$$

At the second location, a similar equation follows from boundary condition 3:

$$T_2 = \frac{C|_{r=R_2}}{4} R_2^2 + I_1 \tag{10}$$

Elimination of the integrating factor, I_1, gives the following equation:

$$T_2 - T_1 = \frac{C|_{r=R_2} R_2^2 - C|_{r=R_1} R_1^2}{4} \tag{11}$$

From Eqs. (2) and (3) we know that $C_i = (\Delta T/\Delta t)_i/\alpha_i$, where i represents the location of the measurement. Substitution into Eq. (11) for the respective locations, the assumption of a constant thermal diffusivity throughout the measured material results in an expression for the thermal diffusivity:

$$\alpha \approx \frac{\left[\frac{\Delta T}{\Delta t}\right]_{r=R_2} R_2^2 - \left[\frac{\Delta T}{\Delta t}\right]_{r=R_1} R_1^2}{4\,(T_2 - T_1)} \tag{12}$$

A summary of the assumptions in Eq. (12) for thermal diffusivity is as follows:

1. thermal diffusivity does not vary with temperature, time, or distance,
2. the heat source emits a constant energy flux,
3. the measured medium has an infinite radius, which does not allow for the heat wave to reach the cylinder wall,
4. the medium is a long cylinder, i.e., no heat transfer in the axial direction, and
5. the change in temperature with time is linear.

4. EXPERIMENTAL PROCEDURE

A medium such as ice, hydrate, or composites with sediment is formed in place around the axial wire in the cell. For ice, deionized water is cooled in the cell until ice forms. For hydrate or hydrate–sediment mixtures, the method introduced by Stern et al. [6], which converts crushed ice into hydrate, can be used.

Initially, no power is supplied to the heating wire. Once the medium for measurement is formed in place, the bath temperature is held constant until all thermocouples have registered identical temperatures. At uniform temperature, power is supplied. As the heat wave moves through the medium, thermocouple temperatures begin to rise. Experiments are conducted until a rise in cell wall temperature indicates the heat wave is at the wall, invalidating assumption 2.

An example of a thermal diffusivity experiment for ice is shown in Fig. 2. The rates of temperature change were measured by averaging the slope of the temperature over the same interval of time for both thermocouples. The interval of time was chosen for each experiment based on the following criteria:

1. the center and midway thermocouples register an increase in temperature,
2. a linear slope was observed in thermocouples at distances R_1 and R_2,
3. the wall thermocouple did not register a rise in temperature, and
4. the center temperature did not exceed hydrate equilibrium.

The temperatures T_1 and T_2 were obtained by averaging temperatures over the time interval. The temperature at which the thermal diffusivity measurement was taken was estimated by the mean of T_1 and T_2 (that is $(T_1 + T_2)/2$).

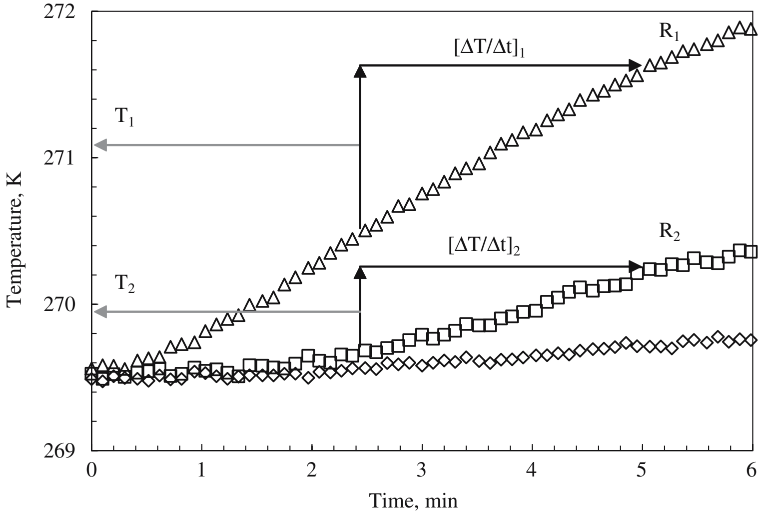

Fig. 2. Example of a thermal diffusivity experiment for ice.

5. UNCERTAINTY ESTIMATES

This new method was tested by conducting experiments with ice in the cell. Five thermal diffusivity points were measured at about 271 K. The thermal diffusivity values for these experiments ranged between 1.10 and $1.20 \times 10^{-6}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$, with a mean of $1.16 \pm 0.07\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$ (95% confidence level), as shown in Table I.

To compare with literature values for ice, the thermal conductivity, λ, was calculated from the thermal diffusivity values by using ice density, ρ, of $920\,\mathrm{kg} \cdot \mathrm{m}^{-3}$ and heat capacity, C_p, of $2040\,\mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$ in the definition for thermal diffusivity:

$$\alpha \equiv \frac{\lambda}{\rho C_p} \tag{13}$$

Comparison of these values is summarized in Table II and shown in Fig. 3. The values from the new technique agree well with those from other sources [7–11].

The accuracy of thermal diffusivity measurements can be estimated from the error propagation of inputs of Eq. (12), namely, the errors in the temperature, distance, and time measurements [12]. The uncertainty of the radius was estimated to be ±0.25 mm, of the time was ±1 s, and of the temperature was ±0.02%. Utilizing the error propagation technique outlined in the Guide to the Expression of Uncertainty in Measurement [12], the uncertainty in the thermal diffusivity is approximately ±4%.

Although different heat fluxes were not tested, it can be seen from Eq. (5) that the temperature gradient increases with increased heat flux. It can be seen in Fig. 2 that the relative magnitude of temperature noise to temperature will diminish as the temperature gradient (or heat flux) increases. However, a practical limit for heat flux is where the temperature rises to the melting temperature of the tested solid.

Table I. Thermal Diffusivity for Ice

Experiment No.	Temperature (K)	Thermal Diffusivity, $\alpha (10^{-6}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1})$
1	270	1.20
2	271	1.10
3	271	1.10
4	271	1.20
5	271	1.20
Average	271	1.16 ± 0.07

Table II. Comparison of Thermal Conductivity Values for Ice from Various Sources

Source	Temperature (K)	Thermal conductivity, λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
Lunardini, 1981 [7]	233	2.66
Waite et al., 2002 [8]	253	$\sim$2.12[a]
Incropera and DeWitt, 1996 [9]	253	2.03
Sloan, 1998 [10]	263	2.23
Waite et al., 2002 [8]	263	$\sim$2.01[a]
Cook and Leaist, 1983 [11]	268	2.19
This work	271	2.18[b]
Lunardini, 1981 [7]	273	2.21
Incropera and DeWitt, 1996 [9]	273	1.88

[a] Values are estimated from points on a figure.

[b] Calculated from measured thermal diffusivity data, assuming density = $920\,\mathrm{kg \cdot m^{-3}}$ and $C_p = 2,040\,\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ [9].

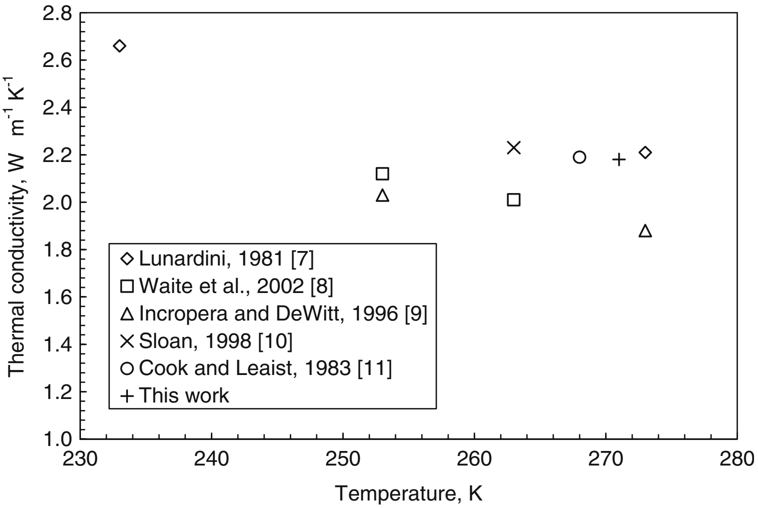

Fig. 3. Comparison of ice thermal conductivity as a function of temperature.

Other sources for uncertainty could exist from heat loss at the cell wall and melting of the measured medium at the heating element. From the ice experiments, the uncertainty with a 95% confidence level is ±6%.

The primary alternative method for thermal diffusivity measurements is that of the von Herzen and Maxwell probe [13], where a heating element and two in-series temperature transducers are located within a hypodermic needle. The needle is inserted into a sample, and heat is emitted from the heating element. The heat rate to the element is known, and the temperature at the element is measured. Since the temperature at the probe is related to how rapid the heat can be dissipated, the thermal conductivity and diffusivity can be determined. The error for the von Herzen and Maxwell probe is reported to be around ±30% [14]. Thus, the experiment described in the current manuscript, with an estimated uncertainty of ±6%, represents a considerable reduction in the uncertainty of the thermal diffusivity measurement relative to the von Herzen and Maxwell probe.

Another disadvantage of the von Herzen and Maxwell method is that heterogeneity of measured samples can lead to inaccurate results. This is because poor contact with the medium could exist at the thermocouple location in the probe needle. The new technique is not as sensitive to heterogeneous samples, since temperatures are measured at multiple locations, and is therefore more appropriate for hydrate–sediment mixtures.

The uncertainty of the current technique can be further reduced by three experimental modifications:

1. thermocouples with higher accuracy,
2. larger diameter cell to allow for a longer measurement, and
3. good insulation around the cell to prevent loss of heat from the wall.

6. HYDRATE THERMAL DIFFUSIVITY MEASUREMENTS

The thermal diffusivity of pure hydrates was measured using the new thermal diffusivity technique. Hydrates were formed in the cell around the heating wire and thermocouples by first filling the cell with crushed ice from deionized water. The porosity of the hydrate in the cell was controlled between 0.40 and 0.42 by sieving the ice particles prior to loading the ice into the cell. Then, the cell was placed into a bath at a temperature below the ice point to prevent ice melting. The cell was pressurized above the hydrate equilibrium pressure at the desired experimental temperature with 99.99 mol% pure methane gas, and the temperature in the cell was raised to 274 K. As ice melted, it was converted to hydrate. To ensure complete conversion of ice to hydrate, the temperature was cycled above and below 273.15 K until no additional gas was consumed, as indicated by a constant pressure.

Pure methane hydrate thermal diffusivities were measured at temperatures ranging between 265.3 and 281.7 K. The results of the hydrate thermal diffusivity measurements at various temperatures are tabulated in Table III and shown in Fig. 4. As can be seen, hydrate thermal diffusivities remain nearly constant with temperature for the range measured.

Table III. Thermal Diffusivity of Pure Methane Hydrate at Various Temperatures

Temperature (K)	Pressure (MPa)	Thermal diffusivity, $\alpha(10^{-7}\,m^2\cdot s^{-1})$
265	4.34	3.33 ± 0.17
266	4.34	3.34 ± 0.17
269	4.38	3.24 ± 0.16
274	4.38	3.17 ± 0.16
282	6.79	3.12 ± 0.16

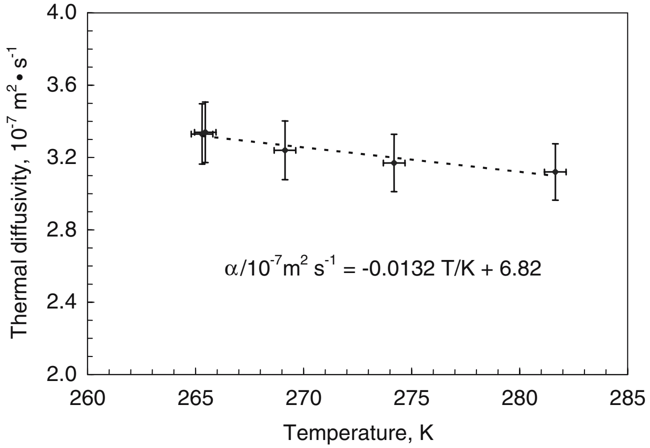

Fig. 4. Thermal conductivity of pure methane hydrate as a function of temperature.

7. CONCLUSIONS

A new hydrate thermal diffusivity experiment was constructed. The experiment was verified by measuring the thermal diffusivity of a known substance, ice. The uncertainty from the experiment appears to be ±6% with a 95% confidence level, which is an improvement from the alternative von Herzen and Maxwell technique (±30%). In particular, the new technique is more appropriate for measuring thermal diffusivity in heterogeneous samples, such as methane hydrate in sediment, since it averages out thermal contact discrepancies. The pure methane hydrate thermal diffusivity for various temperatures has been measured by the new technique. These values ranged from 3.33×10^{-6} to $3.12\times10^{-6}\,m^2\cdot s^{-1}$ at temperatures from 265 to 282 K, respectively.

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REFERENCES

1. K. A. Kvenvolden, *Chem. Geol.* **71**:41 (1988).
2. T. S. Collett, in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, M. D. Max, ed. (Kluwer Academic Pubs., Dordrecht, The Netherlands, 2000), pp. 123–136.
3. M. Kastner, in *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, C. K. Paull and W. P. Dillon, eds. (American Geophysical Union, Washington, D. C., 2001), pp. 67–86.
4. W. F. Waite, B. J. deMartin, J. Pinkston, S. H. Kirby, and C. D. Ruppel, *Geophys. Res. Lett. (2001).*
5. H. S. Carslaw and J. C. Jaeger, in *Conduction of Heat in Solids*, 2nd Ed. (Oxford University Press, New York, 1959), p. 17.
6. L. A. Stern, S. H. Kirby, W. B. Durham, S. Circone, and W. F. Waite, in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, M. D. Max, ed. (Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000), pp. 323–348.
7. V. J. Lunardini, in *Heat Transfer in Cold Climates* (Van Nostrand Reinhold Co., New York, 1981), p. 309.
8. W. F. Waite, J. Pinkston, and S. H. Kirby, *Proc. Fourth Int. Conf. Gas Hydrates*, Yokohama, Japan (2002), pp. 728–733.
9. F. P. Incropera and D. P. DeWitt in *Fundamentals of Heat and Mass Transfer*, 4th Ed. (John Wiley, New York, 1996), p. 838.
10. E. D. Sloan, in *Clathrate Hydrates of Natural Gases*, 2nd Ed. (Marcel Decker, New York, 1998), p. 60.
11. J. G. Cook and D. G. Leaist, *Geophys. Res. Lett.* **10**:397 (1983).
12. International Organization for Standardization, *Guide to the Expression of Uncertainty in Measurement* (1995), pp. 19–22.
13. R. P. von Herzen and A. E. Maxwell, *J. Geophys. Res.* **64**:1557 (1959).
14. Hukseflux Thermal Sensors, *TP02 Non-steady-state Probe for Thermal Conductivity Measurement User Manual*, Version 0107, The Netherlands (2000), p. 39.