Thermal Properties of Methane Gas Hydrates

Introduction

Gas hydrates are crystalline solids in which molecules of a “guest” species occupy and stabilize cages formed by water molecules. Similar to ice in appearance (fig. 1), gas hydrates are stable at high pressures and temperatures above freezing (0°C). Methane is the most common naturally occurring hydrate guest species. Methane hydrates, also called simply “gas hydrates,” are extremely concentrated stores of methane and are found in shallow permafrost and continental margin sediments worldwide. Brought to sea-level conditions, methane hydrate breaks down and releases up to 160 times its own volume in methane gas.

The methane stored in gas hydrates is of interest and concern to policy makers as a potential alternative energy resource and as a potent greenhouse gas that could be released from sediments to the atmosphere and ocean during global warming. In continental margin settings, methane release from gas hydrates also is a potential geohazard and could cause submarine landslides that endanger offshore infrastructure.

Gas hydrate stability is sensitive to temperature changes. To understand methane release from gas hydrate, the U.S. Geological Survey (USGS) conducted a laboratory investigation of pure methane hydrate thermal properties at conditions relevant to accumulations of naturally occurring methane hydrate. Prior to this work, thermal properties for gas hydrates generally were measured on analog systems such as ice and non-methane hydrates or at temperatures below freezing; these conditions limit direct comparisons to methane hydrates in marine and permafrost sediment.

Three thermal properties, defined succinctly by Briaud and Chaouch (1997), are estimated from the experiments described here:

- **Thermal conductivity**, \( \lambda \): if \( \lambda \) is high, heat travels easily through the material.

- **Thermal diffusivity**, \( \kappa \): if \( \kappa \) is high, it takes little time for the temperature to rise in the material.

- **Specific heat**, \( c_p \): if \( c_p \) is high, it takes a great deal of heat to raise the temperature of the material.

![Figure 1](image1.png)

Measurements of Thermal Properties

Thermal properties of pure methane hydrate were studied in the laboratory. The formation technique uses a highly reproducible method developed by USGS (Stern and others, 2000, 1996) in which granular ice is packed into the sample chamber of a pressure vessel (fig. 2A). The vessel is then pressurized with methane gas, slowly heated to allow the ice to convert to hydrate, and finally compressed to compact the methane hydrate around the centrally located thermal probe.

Thermal properties were measured by warming the sample with a heater wire in the thermal probe while measuring the temperature change with a centrally located thermal sensor (fig. 2A). The temperature change is linear when plotted as a function of the natural logarithm (ln) of time, as shown by the overlapping blue circles plotting every tenth data point in figure 2B. The sample’s thermal properties are calculated from the slope and intercept of the straight-line fit through the data (A and B, respectively, along the green line in fig. 2B) (Waite and others, 2006). These measurements are repeated over a range of pressures and temperatures.

Thermal Property Results

Equations for calculating thermal conductivity, thermal diffusivity, and specific heat in methane hydrate are given in table 1 (Waite and others, 2007).

Measurements of thermal properties are used in models that can predict changes that methane hydrates undergo during their recovery as a resource or their potential dissociation during warming. Because hydrates displace either ice (permafrost settings) or water (marine settings or beneath permafrost),

![Figure 2](image2.png)
The presence of methane gas hydrates can alter the thermal properties of host sediments. Laboratory efforts by the USGS to measure thermal properties of pure methane gas hydrates

<table>
<thead>
<tr>
<th>Temperature dependence</th>
<th>Temperature dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ ($W/m\cdot K$) = ($2.78 \pm 0.05$) \times 10^{-4} T(°C) + ($0.62 \pm 0.02$)</td>
<td>$\kappa$ ($m^2/s$) = ($5.04 \pm 0.02$) \times 10^{-5} T(K) + ($1.25 \pm 0.05$) \times 10^{-7}</td>
</tr>
<tr>
<td>°C, degrees Celsius; K, Kelvin; °F, degrees Fahrenheit; s, seconds; J, joules; kg, kilograms; P, pressure</td>
<td>°C, degrees Celsius; K, Kelvin; °F, degrees Fahrenheit; s, seconds; J, joules; kg, kilograms; P, pressure</td>
</tr>
</tbody>
</table>

$\kappa$ is approximately four times that of methane hydrate, so the thermal conductivity beneath permafrost or in marine settings is approximately equal to that of methane hydrate. In ice-dominated permafrost can measurably increase the geothermal gradient because the thermal conductivity of ice is approximately four times that of methane hydrate.

$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately equal to that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.


$\kappa$ is approximately that of ice, and water helps gauge the extent to which a host sediment’s thermal properties are altered by the presence of methane hydrate.