GAS HYDRATES

CHALLENGES FOR THE FUTURE

Edited by
Gerald D. Holder and P. R. Bishnoi

The New York Academy of Sciences
New York, New York
2009
Methane Hydrate Dissociation Rates at 0.1 MPa and Temperatures above 272 K

SUSAN CIRCONI,* LAURA A. STEEN, STEPHEN H. KIRBY, JOHN C. PENKINS,* AND WILLIAM B. DURHAM* 

*U.S. Geological Survey, 345 Midfield Road, MS 977, Menlo Park, California 94025, USA
*Lawrence Livermore National Laboratory, Livermore, California 94550, USA

ABSTRACT: We performed rapid depressurization experiments on methane hydrate under isothermal conditions above 272 K to determine the amount and rate of methane evolution. Sample temperatures rapidly drop below 273 K and stabilize near 272.5 K during dissociation. This thermal anomaly and the persistence of methane hydrate are consistent with the reported recovery of partially dissociated methane hydrates from oceanic drilling cores.

INTRODUCTION

Naturally occurring methane hydrate has been recovered from numerous oceanic drill cores in a partially dissociated state. Retrieved cores contain several phases: hydrate, fine-grained sediment mixed with altered textures, saline pore water that has beenfreshened by hydrate dissociation, methane gas in excess of its site saturation levels, and occasionally ice. Delft core temperatures measured after recovery are depressed several degrees below the baseline core temperature in zones observed or inferred to contain gas hydrate. Temperatures can be depressed as much as 2 K below the H2O melting point at 273.15 K and are lower than any encountered during core recovery. Such thermal anomalies have been attributed to the enthalpy of dissociation: An experimental study on synthetic methane hydrate dissociation at temperatures above 272 K may provide insights into these observations. Moreover, temporary preservation of hydrate has been observed below 273 K and at 0.1 MPa, first noted in sl methane dodecahydrate and later in sl methane hydrate at high levels (more than 30% of the sample), as well as in all natural gas hydrates. In experiments performed between 204 and 270 K, we observe highly suppressed dissociation rates between 250 and 270 K, and 50-90% of the hydrate remain preserved after 24 hours, based on CH4 evolution and X-ray diffraction analysis of samples. In contrast, below 250 K the time to 50% dissociation is several orders of magnitude smaller. We were interested in investigating methane hydrate dissociation kinetics at temperatures above 270 K following rapid depressurization to 0.1 MPa to better define the regime of anomalous preservation observed at lower temperatures.

*Telecommunications: Voice: 650-329-5674; fax: 650-329-5163. scirconi@usgs.gov

544
The purpose of our study was fourfold: (1) to determine the dissociation rates of methane hydrate above 270 K, (2) to profile sample temperature during dissociation, (3) to identify factors that control dissociation rates in this temperature regime, and (4) to begin a preliminary investigation of the effects of natural impurities (sediment and sea water) on hydrate dissociation.

EXPERIMENTAL METHOD

Hydrate Synthesis

Polycrystalline methane hydrate, with expected stoichiometry CH₄·0.1 H₂O, was synthesized from granular water ice and pressurized CH₄ using the method of Stern et al.⁵ Samples had at most trace amounts of ice remaining after synthesis and a porosity of about 30%. The 30 g hydrate samples were cylinders, 3.56 cm in diameter and approximately 9.3 cm in length. The sample axis was held vertical during synthesis and dissociation (see Figure 1).

Modifications were made to the hydrate synthesis procedure for several samples. A hydrate/sediment aggregate was made by mixing 150 ± 50 μm quartz sand with the ice (volume ratio 3:7) prior to synthesis. After synthesis, methane pressure (P(CH₄) was reduced to 4–5 MPa and temperature was held near 278 K. Sea water (SWCN) pressurized with CH₄ to above 10 MPa was introduced through a port above the sample and partially permeated the samples by gravity. The samples were annealed at 276 ± 1 K, 10 MPa for three days prior to dissociation. Additional hydrate growth did occur based on analysis of identically treated samples.

Dissociation Procedure

(1) Maintaining high P(CH₄) each sample was equilibrated at a temperature between 272 and 289 K by immersing the pressure vessel in a heated ethanol bath inside a freezer (Fig. 1). (2) P(CH₄) was reduced over several minutes to at least twice the equilibrium pressure. (3) Sample vessels were rapidly depressurized to 0.1 MPa in about 15 s and then opened to the flow meter. This depressurization rate is an upper limit of the pressure-time pathway encountered during core retrieval. (4) Internal sample temperatures were monitored with one to four thermocouples, and CH₄ evolution was monitored with a custom-built flow meter (see Fig. 1). The external bath temperature (Tbath) was held constant during dissociation.

Temperature Measurement

Both Tbet and internal sample temperatures were monitored during dissociation (Fig. 1, left). Tbet was measured with an RTD located near the vessel. Sample temperatures were monitored using one of two setups. In setup 1, three thermocouples were located along the cylinder axis at the sample top (0.9 cm from sample bottom), middle (4.7 cm), and bottom (0.06 cm). The side thermocouple (4.8 cm) is a few mm in from the sample surface. In setup 2, two thermocouples were located along the cylinder axis, one about 0.5 cm into the sample top and the other 3.5 cm up from the
**FIGURE 1.** Schematic diagram (not to scale) of experimental apparatus showing sample thermocouple configurations used to monitor thermal evolution (left) and the custom-built flow meter that measures the amount of evolved CH₄ (right) during dissociation. Thermocouples, RTDs, load cell, and pressure transducer are interfaced with a data acquisition system.
bottom. The K-type thermocouples measured within ±0.1 K of 273.15 K in an ice/water calibration bath.

Custom-Built Flow Meter

The flow meter is based on the principles of the Toroacelli tube and determines gas flow rate by measuring the change in weight of an inverted, water-filled cylinder as CH4 displaces water (Fig. 1, right). The water column is drawn into the inverted cylinder under vacuum, then prized with flowing CH4 to saturate the water and to minimize solution during measurement. As CH4 displaces water in the cylinder, the external water level is maintained constant by a water priming and drain system. Water temperature and the partial pressure of water vapor in CH4 are incorporated into the data analysis procedure. Becoming our laboratory site is near sea level, we assume that atmospheric pressure is constant at 0.1 MPa. The number of moles of CH4 is calculated using the ideal gas law, which in accurately predicts relative changes over the small pressure range of operation (based on comparison with a noninert equation of state for CH4). A 30 g hydrate sample yields about 6 L of gas. Flow meter volume capacity is about 8 L, and we measured flow rates ranging from 0.01 to 3.00 ml/16.

Table 1. Summary of rapid deprotonation experiments above 273 K

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Hydrate mass (g)</th>
<th>T.C. (°C)</th>
<th>P.bar (MPa)</th>
<th>T degree (°C)</th>
<th>Time, 60% reaction (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C126</td>
<td>29.80</td>
<td></td>
<td>272.8</td>
<td>5.5</td>
<td>14</td>
<td>5.9</td>
</tr>
<tr>
<td>C30</td>
<td>29.80</td>
<td>#2</td>
<td>273.6</td>
<td>5.3</td>
<td>16</td>
<td>-1.7</td>
</tr>
<tr>
<td>C118</td>
<td>29.80</td>
<td>#2</td>
<td>273.8</td>
<td>6.1</td>
<td>12</td>
<td>-4.2</td>
</tr>
<tr>
<td>C77</td>
<td>30.31</td>
<td>#2</td>
<td>275.6</td>
<td>9.3</td>
<td>12</td>
<td>-4.1</td>
</tr>
<tr>
<td>C14</td>
<td>29.80</td>
<td>#2</td>
<td>276.5</td>
<td>7.9</td>
<td>11</td>
<td>-5.3</td>
</tr>
<tr>
<td>C122</td>
<td>29.80</td>
<td>#2</td>
<td>277.1</td>
<td>8.5</td>
<td>12</td>
<td>-5.5</td>
</tr>
<tr>
<td>C120</td>
<td>29.80</td>
<td>#2</td>
<td>278.3</td>
<td>9.5</td>
<td>22</td>
<td>-8.9</td>
</tr>
<tr>
<td>C130</td>
<td>26.33</td>
<td>#2</td>
<td>277.3</td>
<td>7.6</td>
<td>35</td>
<td>-13.8</td>
</tr>
<tr>
<td>C78</td>
<td>36.17</td>
<td>#2</td>
<td>279.1</td>
<td>4.5</td>
<td>12</td>
<td>-7.0</td>
</tr>
<tr>
<td>C116</td>
<td>29.80</td>
<td>#1</td>
<td>281.4</td>
<td>10.2</td>
<td>16</td>
<td>-13.0</td>
</tr>
<tr>
<td>C81</td>
<td>29.92</td>
<td>#2</td>
<td>283.8</td>
<td>11.6</td>
<td>19</td>
<td>-12.1</td>
</tr>
<tr>
<td>C86</td>
<td>29.92</td>
<td>#2</td>
<td>288.8</td>
<td>26.9</td>
<td>17</td>
<td>-16.4</td>
</tr>
</tbody>
</table>

*Final sample temperature change, due to adiabatic cooling from CH4 expansion and the onset of hydrate dissociation.

*Calculated from seed ice weight, assuming 100% conversion to CH4, q, H.C.

High yield probably due to excessive gas saturation in sample after deprotonation step.

*Only one thermocouple, too high reading.

*Hydrate sample contained added sea water. High yield due to hydrate growth in sea water.

*Only one thermocouple, too middle position.

*Hydrateendorption aggregate with no water added. Low total is due to the longer deprotonation step, in which the vented gas included the form of hydrate dissociation.
A summary of the rapid depressurization experiments above 273 K is listed in **Table 1**. Methane gas yields are typically within ±5% of the expected values (based on sample mass and the assumed stoichiometry). This is acceptable given the possible presence of trace amounts of unreacted ice, the uncertainty in expected s (6.1 ± 0.1), and the possibility that pressurized gas remained trapped in pores (high yield) and/or that partial dissociation occurred during the depressurization step (low yield). Breakdown of methane hydrate commences immediately after depressurization, and CH$_4$ evolution is closely linked to the thermal history of the sample (see **Figure 2**). The rate of hydrate dissociation increases systematically with increasing $T_{	ext{fan}}$ (see **Figure 3**). At 272.8 K, the experiment reached 80% reaction after 10 hours. The sample required heating through 273 K to achieve 100% reaction in a reasonable time. Dissociation is complete after three hours at 273.6 to 273.8 K and only 18 minutes at 283.8 K. Above 273 K, the reaction time decreases exponentially with increasing $T_{	ext{fan}}$ (see **Figure 4**). The significantly longer reaction time at 272.8 K links the anomalous preservation region at 250-270 K to the $T_{	ext{fan}} > 273$ K region explored here. Reconnaissance experiments (**Table 1**) show that introducing impurities significantly increases the methane hydrate dissociation rate at about 277 K (**Fig. 4**). Rates increase in the order: porous hydrate < hydrate + sea water < hydrate + quartz sand + sea water, such that the time to 80% dissociation is four and thirteen times shorter, respectively. This trend is seen in a similar suite of experiments at 268 K (unpublished data). Higher dissociation rates drive the system as low as 263 K in the sediment/sea water sample, thermal buffering at 272.5 K (see below) is not observed, and H$_2$O melting is depressed about 2 K due to the presence of sea water.

**Thermal Buffering**

Two-stage thermal buffering is observed in the experiments above 272 K, first at 272.5 K as methane hydrate dissociates and then at 273.15 K as ice reaction product melts (see **Figure 5**). After depressurizing below 273 K on depressurization, temperatures partially rebound and are buffered at 272.5 ± 0.5 K within minutes, regardless of $T_{	ext{fan}}$. When $T_{	ext{fan}} < 274$ K, all thermocouples record thermal buffering, although the effect later disappears along the sample surface while continuing in the interior. The effect is observed only by top and middle thermocouples for $T_{	ext{fan}} > 274$ K. Side and bottom thermocouples show that temperatures plunge below 273 K after depressurization, then climb steadily back through 273 K. The buffering temperature is maintained until dissociation nears completion, is reproducible and distinct from the buffering at the H$_2$O melting point, and is observed in other hydrate dissociation experiments (heating from low 7° through 275 K at 0.1 MPa, unpublished data). The buffering temperature is not constant, increasing very slowly over time from 272.3 to 272.7 K during dissociation. Peters et al. observe similarly depressed temperatures between 272 and 273 K in their experiments. Thermal buffering at the ice point may continue after dissociation is complete, indicating the presence of an H$_2$O ice/water mixture. After dissociation ceased, vessels were opened in
FIGURE 2. Thermal history (a) and CH₄ evolution (b) of a dissociating methane hydrate sample at 277 K (Run CI22, see Tab.8.1). \( T_{\text{init}} \) remains approximately constant. 

Point 1: at time 0, internal sample temperature and \( T_{\text{init}} \) are nearly isothermal. Pressure is then dropped to 0.1 MPa (see text). 

Point 2: sample temperatures plunge within seconds to a minimum below 273 K. At dissociation proceeds, the sample temperature is buffered at about 272.5 K (top and middle thermocouple). Temperature evolves continuously at the bottom and side thermocouple locations as CH₄ evolves and ice (reaction product) melts. 

Point 3: temperatures at the top and middle begin to diverge as dissociation nears completion at the sample top. 

Point 4: as dissociation ends, the sample interior warms above 273.5 K. In the base-thermocouple experiments, the top and middle thermocouples are buffered at the ice point of 273.15 K until the ice melts. Only every fourth point has been plotted for symbol clarity.
FIGURE 3. Methane evolution with time for all experiments, showing that dissociation rates systematically increase with increasing $T_{eq}$. Percent dissociation (the extent of reaction) is the measured amount of CH₄ normalized to the expected amount. Note the reproducibility between the two experiments conducted at 273.7 ± 0.1 K. Every fifth point has been plotted.

FIGURE 4. The exothermic effect of $T_{eq}$ on the time elapsed for 60% dissociation of the hydrate to occur. The scatter in the data is likely due to minor differences in the depressurization procedure. In the early experiments, depressurization was more rapid (under 10 s) and involved a larger pressure drop (more than twice the equilibrium pressure). This difference appears to produce dissociation rates that are initially slightly higher than those in our later experiments. Curves for 50%, 90%, and 100% dissociation (not shown) are shifted up in time but have similar slopes. Preliminary results for hydrate + sea water and hydrate/ice aggregate + sea water samples at about 273 K show the compounding effect of adding impurities (indicated by the arrow).
experiments C114, C116, and C118, revealing a plug of wet, granular ice around the center thermocouples and surrounded by a gas gap. Liquid water had pooled at the vessel bottom.

DISCUSSION

Dissociation Rates and Thermal Buffering

Temperatures in some hydrate-braining drill cores are not depressed below 273 K because the rates of dissociating hydrate is insufficient to depress temperatures to this extent in the surrounding sediments and pore fluids. In our experiments on methane hydrate, the temperature drops below 273 K when the pressure is reduced to 0.1 MPa, regardless of $T_{eq}$, and is self-maintained at not more than 273 K until the dissociation reaction nears completion (above 95%). This thermal buffering effect occurs in actively dissociating parts of the samples. When $T_{eq} > 274$ K, neither buffering at this temperature nor at the ice point controls along the side or bottom surfaces. The sample dissociates and the ice product melts preferentially and quickly along these surfaces. Dissociation rates are increased significantly by impurities present in natural systems. The effect of sea water may be extreme in our experiments because of the high sample porosity and the high thermal conductivity of sea water relative to CH4. A detailed study of the effects of impurities is in progress.
A key question arises: what causes the thermal buffering near 272.5 K? An apparent buffering effect could occur if the reaction rate and hence heat consumption rate were balanced by the heat flux rate from the surroundings, holding the sample temperature within a narrow band. However, the heat flux and buffering temperature should vary with $T_{th}$, and we observe a narrow range of temperatures. It is more likely a thermal property of a reaction, like that for a phase change, but what that reaction might be is unclear. No methane hydrate phase boundary, including the metastable extension of hydrate $\rightarrow$ CH$_4$ + H$_2$O, corresponds to the buffering temperature at 0.1 MPa. The temperature is close to the melting point of H$_2$O, a correspondence that is probably not coincidental. Buffering is not observed in the isostructural portions of the rapid depressurization experiments below 272 K, where experimental conditions are further from the H$_2$O melting curve. However, we are not observing a simple case of H$_2$O melting or fusion: the buffering temperature is markedly lower than the ice point (Fig. 5), which is recorded after dissociation ceases at the thermocouples. Clearly, the source of the narrow buffering near 272.5 K is an interesting question, but one that cannot be resolved with the data from this study.

Although the values of the isothermal $T_{th}$ span 16 K, all of the reactions proceed at the same temperature after a few minutes of dissociation. However, the rate of dissociation increases monotonically with $T_{th}$. We infer that the rate is a function of the heat flow supplied from the surroundings (bath) into the sample through the vessel. This influx supplies heat for the endothermic hydrate dissociation reaction. In the next section, we compare the cumulative heat budget for dissociation and the calculated heat flow into the system.

**Heat Budget**

Using the measured extent of reaction and the system temperature evolution over time, we calculate the cumulative heat budget for the dissociation reaction and the expected heat flow from the bath into the vessel interior. We considered the simplest case of steady-state heat flow, $\Delta Q/\Delta t$, across a material (304 stainless steel) with thermal conductivity $k$ (0.3 J/sec-K-cm$^{-1}$), across section A (area of vessel surface), thickness $\Delta x$, and temperature difference $\Delta T$ (sample temperature $- T_{th}$), where $\Delta Q/\Delta t = kA(\Delta T/\Delta x)$. We assumed that the vessel wall is continuous and that the indium jacket lining the sample has no significant effect. We ignored vessel wall curvature, using the inner and outer wall surface areas as boundary conditions. We considered only radial heat flow through the vessel sides or axial heat flow through the vessel bottom (the top is insulated by a layer of CH$_4$). The heat budget for methane hydrate dissociation was calculated using the starting amount of hydrate, the enthalpy of dissociation (18.13 kJ/mol for CH$_4$ dehydrate), and the reaction progress with time (Fig. 3).

The calculated total radial heat flow (vessel sides) by the end of hydrate dissociation exceeds that needed to dissociate the hydrate by more than 50-fold (see Fig. 6). There would be ample heat to also melt 100% of the ice product by the end of dissociation, but this is not observed experimentally. Axial heat flow (vessel bottom) is comparable to that needed to dissociate hydrate on the reaction time scale (Fig. 6). At 273.8 K, the calculated heat flow is insufficient for complete dissociation. In higher temperature experiments, heat flow lags behind heat consumption for
about 50% of the reaction. At the end of dissociation, however, the available excess heat is sufficient to melt 10–30% of the ice product, consistent with observed vessel contents.

Of course, both radial and axial heat flow occurred in the experiments. The calculations can be reconciled by using the thermal evolution data (see Figure 7). In warmer tests, sample temperatures near the cylinder surface exceeded 273 K in minutes. Thus, this zone was hydrate- and ice-free, leaving only CH₄ and H₂O (f) (Fig. 7c). The water segregated by gravity, leaving CH₄ along the sides. Methane gas has a thermal conductivity of 0.1% that of stainless steel,⁹ as the gap between the steel and sample exceeds 13 μm, CH₄ becomes an insulating layer and greatly reduces the radial heat transfer. The pooling water is a better conductor (2% that of stainless steel⁹), although heat transfer will be affected when the water depth exceeds 0.5 mm. In the 273 K experiment, radial heat flow occurred over a longer time interval, since the side and bottom thermocouples indicated that hydrate and/or ice was present along the sample perimeter throughout the reaction (Fig. 7b). These observations are broadly consistent with the independent results of Peters et al.⁵

![Figure 6. Comparison of the cumulative heat needed to dissociate hydrate near 273.5 K and the extended heat flow through the vessel from the surroundings (exothermic baths) into the samples. Radial heat flow moves too quickly into the sample; dissociation should be finished in minutes and all ice should be melted at the end of the experiments, both predictions inconsistent with observations (see text). Axial heat flow in core consistent with observed dissociation rates (see text). Note that curves were placed at the lower bound (heat flow based on the inner stainless steel surface area) for the radial heat flow results; heat flow would be slightly higher for a true cylindrical conduction model. The samples are believed to be largely insulated from radial heat flow by a gas layer (see text and Fig. 7c).](image)
FIGURE 7. Schematic diagram of sample assembly, phases, and their distribution in dissociation experiments: natural and synthetic/crystalline vessels (dark gray), sample ( ), CH₄ ( ), hydrate ( ), H₂O (s→l), H₂O (l), and thermocouples (positions shown). Diagrams are approximately to scale. (a) Prior to depressurization: $T_{	ext{end last}} = T_{	ext{pres}}$ porous hydrate = CH₄. (b) After depressurization: $T < 233$ K; hydrate = CH₄ + H₂O (s→l). Dissociation is greater along sample sides and bottom, and ice product may begin to melt. (c) Several minutes after depressurization: $T_{	ext{gas}} > 273$ K; $T_{	ext{water}}$ > 273 K; H₂O = CH₄ + H₂O (s→l). An insulating CH₄ gap has formed and H₂O (l) pools at the vessel bottom (see text). A similar configuration is observed after dissociation ceases, when only melting ice remains around the center thermocouple (see text).

Their vessel axis was horizontal, and they observed preferential ice melting and water pooling along the bottom surface, clearly indicating that the direction of maximum heat flow was perpendicular to the vessel axis over a narrow, lower sector of the vessel circumference for the latter part of the experiment.

CONCLUSIONS

Temperature depression below 273 K has been observed in hydrate-bearing ocean drilling cores, suggesting that the process observed in our experiments is similar to that occurring in the field. A significant finding of our study is that at temperatures relative to natural settings, hydrate dissociation is a thermal process that is largely
dependent on the heat flow into the system. Our results may help improve procedures for natural hydrate sample recovery. For instance, core retrieval systems could reduce heat flow into the drill core by using insulating gas gaps or by segregating the more thermally conductive fluid phases (open water and/or the water dissociation product) from the hydrate. These issues will be pursued in a future paper.

ACKNOWLEDGMENTS

We gratefully acknowledge support by a grant from the LDRD Program, Lawrence Livermore National Laboratory, Livermore, CA. Work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

REFERENCES