Measurement of clathrate hydrate thermodynamic stability in the presence of ammonia

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Introduction

There is a lack of data available for the stability of clathrate hydrates in the presence of ammonia for low-to-moderate pressures in the 0–10 MPa range. Providing such data will allow for a better understanding of natural mass transfer processes on celestial bodies like Titan and Enceladus, on which destabilization of clathrates may be responsible for replenishment of gases in the atmosphere. The experimental process utilizes a custom-built gas handling system (GHS) and a cryogenic calorimeter to allow for the efficient testing of samples under varying pressures and gas species.

Background

Clathrate hydrates are water ice lattice structures which can contain up to 15 mole% gas in cages, those cages stabilizing the outer structure and trapping the gas inside [1]. These clathrate hydrates are able to maintain their structure over a specific range of thermodynamic conditions, outside of which the structure may dissociate, releasing the trapped gas. The phenomenon of clathrate hydrates formation has been observed experimentally since at least the late 1700s, with the first recognized publication of clathrate data coming from Sir Humphrey Davy [2] in 1811. Scientific exploration of clathrates progressed slowly through the first part of the 20th century until approximately 1934 when their formation in transport lines was recognized to be a significant problem for the natural gas industry [1]. Since that time the literature has seen an exponential increase in the number of publications on clathrate hydrates, and most significantly in the mid-1960s an expansion beyond man-made clathrates into natural clathrates occurring in cold and high-pressure terrestrial regions, including deep ocean and permafrost, as well as extraterrestrial regions [1].

Most recently, clathrate hydrates have been of interest to researchers hoping to understand mechanisms leading to the replenishment of atmospheric gases on extraterrestrial bodies. One such body is the Saturn moon Titan. Titan has been shown to hold 1.4–5% methane (CH₄) content in its atmosphere, but the estimated volume of hydrocarbon lakes at the surface cannot account for the required rate of replenishment to sustain the methane content in the atmosphere over the moon’s history. It has been supposed that an internal reservoir of methane contained in
clathrate hydrate structures could provide the source of replenishment of Titan’s atmosphere. The compound ammonia is suspected to be present within Titan’s interior, and is known to affect the phase transition of water and therefore mixed water-gas systems. Ammonia-induced destabilization of clathrate hydrates may be causing outgassing of methane to Titan’s atmosphere in sufficient amounts to sustain the observed gaseous composition. A similar process is suggested to be taking place on the Saturn moon Enceladus.

Recent work by Choukroun et al. [3] has provided the first experimental data for the stability of methane clathrate hydrates in H₂O–NH₃–CH₄ systems over the pressure range 0–800 MPa. The results suggest that outgassing of methane due to the influence of ammonia on methane clathrate hydrates could be a significant contributor of methane to Titan’s atmosphere. These results motivate the continued exploration of ammonia–methane clathrate hydrate interactions, and specifically in the low-temperature, low-to-moderate pressure range where the previous experimental results lack sufficient resolution to conclusively link the process to Titan and other celestial bodies.

Objectives

The primary objective of this work is to observe the effects of ammonia on the stability of methane clathrate hydrates. This is done by comparing the points of dissociation, or melting, of the clathrate hydrate structures for different thermodynamic conditions. The data obtained will aid future work in developing a comprehensive thermodynamic model to characterize the influence of ammonia on methane clathrate hydrates.

Approach

Experimental data is obtained using a custom-built gas handling system, a cryogenic calorimeter, and data logging software. A schematic of the fluid system is provided in Fig. 1.
The sample cell within the calorimeter is loaded with a water–ammonia mixture. The sample is then pressurized to the desired starting pressure using the gas handling system. As the gas is cooled in the calorimeter it becomes less dense and the pressure decreases. The data logging software also sends commands to the calorimeter to heat or cool its contents at intervals and rates specified by the user. The calorimeter reports the amount of heat required to change the temperature of the sample compared to the heat required to change the temperature of a reference cell by the same amount. This quantity rapidly increases or decreases during phase transitions, and the latent heat of transition and saturation temperature and pressure can be interpreted from the recorded data.

Small glass beads are placed in the sample and reference cells. This is done to move the bulk of the fluid in the sample cell closer to the center of the chamber for more accurate temperature measurements. It also forces the clathrates to occupy smaller interstitial spaces for a more homogeneous distribution in the sample. The glass beads are analyzed for size distribution using an Olympus BX51 microscope, equipped with an Olympus SC30 digital camera. All images

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**Fig. 1. Schematic of fluid system showing gas storage and delivery, gas handling system, and cryogenic calorimeter.**

<table>
<thead>
<tr>
<th>Gas cylinders and delivery lines</th>
<th>Cryogenic calorimeter</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 1k N₂, CO₂, CH₄</td>
<td>• LN₂-cooled and temp. regulated</td>
</tr>
<tr>
<td>• HP regulators</td>
<td>• Pressure ONLY in cells (sealed)</td>
</tr>
<tr>
<td>• No back flow</td>
<td>• Relief: 1550 psi</td>
</tr>
<tr>
<td>• Relief pressure: 2000 psi</td>
<td></td>
</tr>
</tbody>
</table>

**Gas handling system**

- Mixing and P monitoring
- Delivery to pressure cells

**Pressure relief and vent**

- Relief pressure: 1800 psi
- System vent

**Vacuum system**

- Cleaning
- Dry pump
- Max. inlet: 15 psi
were obtained using the Extended Focal Imaging mode and processed with the Olympus Stream software. Fig. 2 shows one of the images produced during the process.

![Image of glass beads]

**Fig. 2.** Example of image produced in the process of characterizing glass bead size statistics.

Using this technique, a sample of 422 glass beads is used to determine the size distribution. They are found to have an average diameter of 80.0 μm with a standard deviation of 14.7 μm. A histogram of the bead diameters is given in Fig. 3.

![Histogram of bead diameters]

**Fig. 3.** Histogram of bead diameters calculated through the imaging process.
The general experimental process involves reducing the sample temperature to cryogenic levels, typically between -100 and -150 C, using liquid nitrogen, and then slowly increasing the temperature to record when the exothermic events occur.

Results

The dissociation points are determined from the heating flow curve as recorded by the data logging software. Fig. 4 is a screen capture of one of the experimental runs. The dip shaded in yellow represents an exothermic events, in this case melting.

![Fig. 4. Processed data showing baseline for exothermic event.](image)

The processing software is used to determine the baseline heat flow. Then the tangent at the inflection point of the dip is extrapolated to the baseline. This is defined as the onset temperature. Ideally, the extrapolated tangent line would closely follow the heating curve right to the
intersection with the baseline. However, in the results shown in Fig. 4, as well as from other runs, there is some ambiguity to the position of the onset temperature. Here, the melting appears to begin at a temperature significantly below the calculated onset temperature. It is postulated that this effect is due to a higher concentration of ammonia at the beginning of melting, as much of the water is in ice form. The higher ammonia concentration lowers the melting temperature of the ice. As more ice melts, the ammonia concentration is decreased until it reaches the initial concentration. Unless a secondary curve or some other anomalous shape exists in the dip, it is assumed that the onset temperature calculated by the software is correct and most accurately represents the melting temperature due to the initial ammonia concentration.

The sequence of runs for the water-ammonia experiments is given in Table 1.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample temperature range (K)</th>
<th>Pressure at room temperature (MPa)</th>
<th>Heating rate (K/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-12</td>
<td>108.8–292.2</td>
<td>9.111</td>
<td>0.10</td>
</tr>
<tr>
<td>7-18</td>
<td>123.1–293.2</td>
<td>7.106</td>
<td>0.15</td>
</tr>
<tr>
<td>7-19</td>
<td>141.6–290.2</td>
<td>2.967</td>
<td>0.17</td>
</tr>
<tr>
<td>7-20</td>
<td>147.5–288.8</td>
<td>2.545</td>
<td>0.18</td>
</tr>
<tr>
<td>7-21</td>
<td>136.0–291.9</td>
<td>2.219</td>
<td>0.18</td>
</tr>
<tr>
<td>7-23</td>
<td>119.8–282.0</td>
<td>2.198</td>
<td>0.13</td>
</tr>
<tr>
<td>7-24</td>
<td>125.0–290.3</td>
<td>0.185</td>
<td>0.10</td>
</tr>
<tr>
<td>7-25</td>
<td>140.4–292.2</td>
<td>0.962</td>
<td>0.15</td>
</tr>
<tr>
<td>7-3</td>
<td>159.5–292.6</td>
<td>1.739</td>
<td>0.15</td>
</tr>
<tr>
<td>8-4</td>
<td>140.2–292.1</td>
<td>2.466</td>
<td>0.15</td>
</tr>
<tr>
<td>8-6</td>
<td>155.6–288.9</td>
<td>2.819</td>
<td>0.15</td>
</tr>
<tr>
<td>8-7</td>
<td>154.8–293.1</td>
<td>3.236</td>
<td>0.15</td>
</tr>
<tr>
<td>8-9</td>
<td>169.2–279.9</td>
<td>4.439</td>
<td>0.17</td>
</tr>
<tr>
<td>8-13</td>
<td>178.2–290.2</td>
<td>7.064</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The results of the dissociation analyses are plotted along with reference data for methane hydrates without ammonia. In some cases, a separate dissociation corresponding to the melting of water-ice is recorded. These events are plotted as circles, while the hydrate dissociations are represented as crosses.
The data plotted in Fig. 5 show a general trend of a reduction in the dissociation temperature of methane hydrates in the presence of ammonia. However, the effect is shown to be not as significant as for water for above the quadruple point. The specific ammonia concentration was determined by running a H2O-NH3 test with no pressurizing gas and using the melting temperature with a relation provided by Croft et al. [4], where $X$ is the ammonia concentration and $T_m$ is the melting temperature:

$$T_m = 273.15 - 53.07X - 1651.4X^2 + 11,842X^3 - 46,269X^4 + 56,695X^5$$  \(1\)

The water melting temperature for the set of runs prior to 8-1 was found to be -31.615 °C, corresponding to an ammonia concentration of 17.9 wt-%. For the runs 8-1 and later, a different
water melting temperature of -34.712°C was recorded, corresponding to a higher concentration of 19.0 wt-%. This difference is most likely accounted for by the transfer process of bottle ammonia into the sample cell. For the earlier runs, the sample cell containing the ammonia solution was left uncovered for a longer period of time as it was weighed and sealed. The time between pouring and sealing of the cell for the later set of runs was reduced, leading to potentially fewer losses of ammonia vapor. The results of Fig. 5 are consistent with this hypothesis, as the recorded dissociations occur at lower temperatures for the later runs, which could be the result of a stronger ammonia concentration.

Conclusions

The results of this work show that the presence of ammonia does have a reduction effect on the dissociation temperature of methane clathrate hydrates. However, the effect is not as significant as that recorded for water for the same concentrations. In terms of planetary science applications, this finding suggests that cryovolcanism may not play a significant role in the release of methane into the atmosphere of icy bodies like Titan and Enceladus, as the clathrates appear to be stable at higher temperatures than anticipated. More repetition over the present experimental range is suggested to ensure repeatability, and examining more varied concentrations would assist in the development of a comprehensive thermodynamic model to account for the effects of ammonia on methane hydrate stability.

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Bibliography