Recent improvements in the differential scanning calorimetry methods applied to the study of gas hydrates.

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Thermodynamic properties of gas hydrates (e.g., phase equilibrium data, phase change enthalpies, specific heat, etc.) can be obtained by using high pressure calorimetric techniques. However, in some cases, one of the major drawbacks to existing devices is the absence of in-situ agitation leading to problems such as efficient gas solubilization, long induction times, formation of an hydrate crust covering the gas/liquid interface, low hydrate to water conversion, etc.)

**General views**

- The mechanical agitation in the measuring cell is provided by a removable rotary shaft on which star washers have been welded (N < 200 RPM).
- The link between the wellhead and the measuring cell is provided by two concentric tubes allowing the agitator shaft to rotate freely in the middle of the tubes.
- The space let between the agitator shaft and the first tube is used for the admission of the fluids into the cell, while the annular space between the two concentric tubes allows flowing the fluids to the outlet.
- The direction of the fluid flow is completely reversible and the pressure inside the cell can be dynamic controlled during the experiment.

**Technical details of the prototype**

- The prototype consists of a high pressure calorimeter equipped with a mechanical agitation and a dynamic pressure control.
- The temperature and enthalpy calibrations have been performed; the precision and the sensitivity constant have been determined.
- The prototype has been installed on a SETARAM BT 2.15 calorimeter.

**Experimental results**

- Calibration of the prototype in temperature and enthalpy

<table>
<thead>
<tr>
<th>Reference (°C)</th>
<th>Temp ref (°C)</th>
<th>Temp exp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.00 ± 0.05</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.5 ± 0.1</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>n-C12</td>
<td>-9.9 ± 0.2</td>
<td>-9.9 ± 0.2</td>
</tr>
<tr>
<td>n-C14</td>
<td>5.6 ± 0.9</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td>n-C16</td>
<td>18 ± 1</td>
<td>18 ± 0.2</td>
</tr>
</tbody>
</table>

**Application to CO2 hydrates**

- Calibration of CO2 hydrates

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.05 ± 0.05</td>
<td>330 ± 10</td>
<td>340 ± 20</td>
</tr>
</tbody>
</table>

- The presence of the in-situ agitation triggers the crystalization (rupture of the metastability, reduction of the induction time)
- The stirring process does not create noise/perturbation of the calorimetric signal
- Good reproducibility in the results is obtained

**Comparison of our results to literature data**

- \( \Delta H_{\text{exp}}^{\text{exp}} (P = 3.05 \pm 0.05 \text{MPa}) = 7.6 \pm 0.2 \text{°C} \)

- \( \Delta H_{\text{ref}}^{\text{exp}} (P = 3.05 \pm 0.05 \text{MPa}) = 7.6 \pm 0.2 \text{°C} \)

**References**


**Conclusions**

- A novel high pressure calorimetric cell equipped with a mechanical agitation and a dynamic pressure control has been developed and tested.
- The duration and enthalpy calibrations have been performed; the precision and the sensitivity constant have been determined.
- The cell prototype has been used to obtain equilibrium data and phase change enthalphy of the CO2 hydrate.
- The experimental results obtained are in good agreement with literature data, and demonstrate the potentialities of this novel equipment.

**Development and validation**

- Validation of the prototype in our laboratory (LFCR, France) of a novel type of calorimetric cell for BT 2.15 and C80.
- SETARAM calorimeters: industrialized and commercialized by SETARAM Instrumentation.

- Measurements under pressure (P < 20 MPa)
- In-situ mechanical agitation
- Dynamic control of the pressure inside the cell
- Designed for BT 2.15 and C 80
- SETARAM calorimeters