Influence of the crystallization rate on the formation of gas hydrates from CH4-C3H8 gas mixtures and extension to other mixtures
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In this study, we present details on two different experimental procedures to form mixed hydrates. They are applied to measure the volume and composition of the crystallized hydrate from CH4-C2H6 gas mixtures at high and low crystallization rates, respectively. The results obtained from both methods reveal a difference in composition, final pressure and volume between the two procedures (quick and slow crystallization). Furthermore, this work aims at contributing to the global understanding of the coupling between kinetics and thermodynamics to provide some insight in the composition of the gas hydrate phase during its crystallization from an aqueous liquid and a mixed gas phase. In addition, we face new experimental facts that open questioning after comparing the modelling of clathrate hydrates following the classical approach (van der Waals and Platteeuw, 1959).

**FLOW ASSURANCE**

**CO2 CAPTURE**

**GAS HYDRATES FORMATION**

1 – Conditions needed for the gas hydrate to form

- Pressure and temperature
- Water concentration
- Gas concentration

2 – Hydrate structure

- Cavity formation
- Hydrate structure
- Crystal structure

3 – Clathrate hydrate

- Cavity structure
- Clathrate hydrate formation
- Hydrate dissociation

**Experimental procedure and set-up**

- **Experimental apparatus and laboratory**
- **Experimental apparatus**
- **Laboratory**

**COMPARING:** Results from procedure at high driving force AND procedure at low driving force

**Molar composition of the studied gas mixtures (standard deviation about 3%)**

<table>
<thead>
<tr>
<th>Gas mixtures</th>
<th>Methods</th>
<th>CH4</th>
<th>C2H6</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Mass water injected (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas 1</td>
<td>Skirt</td>
<td>94.61</td>
<td>15.39</td>
<td>278.95</td>
<td>2.36</td>
<td>881.10</td>
</tr>
<tr>
<td>Gas 2</td>
<td>Skirt</td>
<td>94.61</td>
<td>15.39</td>
<td>278.95</td>
<td>2.36</td>
<td>881.10</td>
</tr>
<tr>
<td>Gas 3</td>
<td>Skirt</td>
<td>88.06</td>
<td>11.44</td>
<td>284.95</td>
<td>2.36</td>
<td>881.04</td>
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<tr>
<td>Gas 4</td>
<td>Quick</td>
<td>85.77</td>
<td>12.23</td>
<td>283.00</td>
<td>2.36</td>
<td>881.13</td>
</tr>
<tr>
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<td>Quick</td>
<td>85.71</td>
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<td>280.45</td>
<td>2.36</td>
<td>881.05</td>
</tr>
<tr>
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<td>13.10</td>
<td>285.05</td>
<td>2.44</td>
<td>880.94</td>
</tr>
<tr>
<td>Gas 7</td>
<td>Quick</td>
<td>86.09</td>
<td>13.10</td>
<td>285.05</td>
<td>2.44</td>
<td>880.94</td>
</tr>
</tbody>
</table>

**Conclusions**

- **Hydrous equilibrium:** the gas and hydrate compositions following two procedures.
- **The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation.**
- **The most interesting observation is the comparison between the two procedures from the same initial conditions (same pressure, temperature, mass of water and gas mixture). The Pressures are different at each equilibrium (T evolution during equilibrium experiment at high driving force).**

**Figure 1. Experimental equilibrium data of CH4-C2H6 gas hydrate at high and low driving force.**