Hydrate Phase Equilibria of Natural Gas Mixture plus Carbon Dioxide in the Presence of Thermodynamic Inhibitors: Experimental Measurements and Modelling
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Hydrate Phase Equilibria of Natural Gas Mixtures Plus CO\textsubscript{2} in the Presence of Thermodynamic Inhibitors

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About 40% of natural gas fields are sour, producing these reservoirs involves also low temperatures combined with high pressures working conditions, presence of water and transport times, leading to the possibility of gas hydrate formations in pipelines.

Hydrate dissociation points were measured for two systems natural gas + CO\textsubscript{2}. These measurements were conducted in the presence of 25\%wt and 50\%wt of thermodynamic inhibitors (methanol, ethanol and ethylene glycol or MEG).

Thermodynamic Modelling
To predict hydrate phase equilibria, the following models are used:
- **Hydrate Phase**: Van der Waals and Platteeuw model (1959) as implemented by Parrish and Prausnitz (1979)
- **Fluid phase**: 
  - SRK-CPA (Kontogeorgis et al., 1994) with adjusted binary interaction parameters (used for systems with MEG)
  - GC-PR-CPA (Hajiw et al., 2014): the PR-CPA equation of state is coupled with a group contribution method (modified PPR78 EoS), which calculates (in a predictive way) binary interaction parameters.

### Device for hydrate dissociation point measurements

A mixed autoclave rig has been used for hydrate dissociation point measurements. The cell volume is about 500 mL and can operate up to 400 bar and between -35°C and 50°C.

### Schematic illustration of the autoclave cell used for hydrate equilibrium studies

**Composition of the natural gas**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>7.00</td>
</tr>
<tr>
<td>Methane</td>
<td>84.13</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.68</td>
</tr>
<tr>
<td>Propane</td>
<td>2.33</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.93</td>
</tr>
<tr>
<td>n-Propane</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Effect of the presence of carbon dioxide on the hydrate dissociation curve

The presence of CO\textsubscript{2} slightly shifts the hydrate stability curve of the natural gas systems to lower temperatures (about 1°C for 10% of CO\textsubscript{2}).