

RECENT IMPROVEMENTS IN THE HIGH PRESSURE DSC METHOD APPLIED TO THE STUDY OF GAS HYDRATES

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BACKGROUND

High Pressure Differential Scanning Calorimetry (HP-DSC)

- Able to accurately detect phase transitions
- Allows follow up the kinetics of a thermal event
- Allows the determination of materials specific heat capacity

Gas hydrates common applications up to date

- Oil and gas production and flow assurance [1]
- Oil-water-gas systems [2]
- Gas storage / sequestration [3]

BUT: gas hydrate formation at the gas-liquids interface [4]

- Inefficient gas dissolution
- Long induction times
- Formation of a hydrate crust covering the gas/liquid interface
- Low hydrate to water conversion, etc.



↳ Design of a **new calorimetric setup**: high pressure, mechanically stirred calorimetric cell (**patent #FR/2012/57319 UPPA-CNRS**)

EXPERIMENTAL SET-UP

Development based on a **Calvet-type low temperature** (-196°C to +200°C) BT2.15 calorimeter manufactured by SETARAM Instrumentation, France.

The whole setup (Fig. 1) is able to work **under pressures as high as 200 bar**. Pressure inside the cell can be dynamically controlled during the experiment.

Cell body

- 17mm outer diameter stainless steel cylinder, **sample volume of approx. 7mL**
- Connection of the cell body: 316L stainless steel part compressed by a stainless steel 303 nut

Stirring mechanism

- Rotates freely in two concentric tubes
- The actual agitation part is screwed on the rotating rod: **Adaptable design**
- The maximum stirring rate is **200 rotations per minute**
- **Magnetic stirring** version under development (Fig. 3)

Fluid

- Between the stirring rod and the smaller diameter tube: fluid injection into the cell
- Annular space between the two concentric tubes : fluids out of the cell

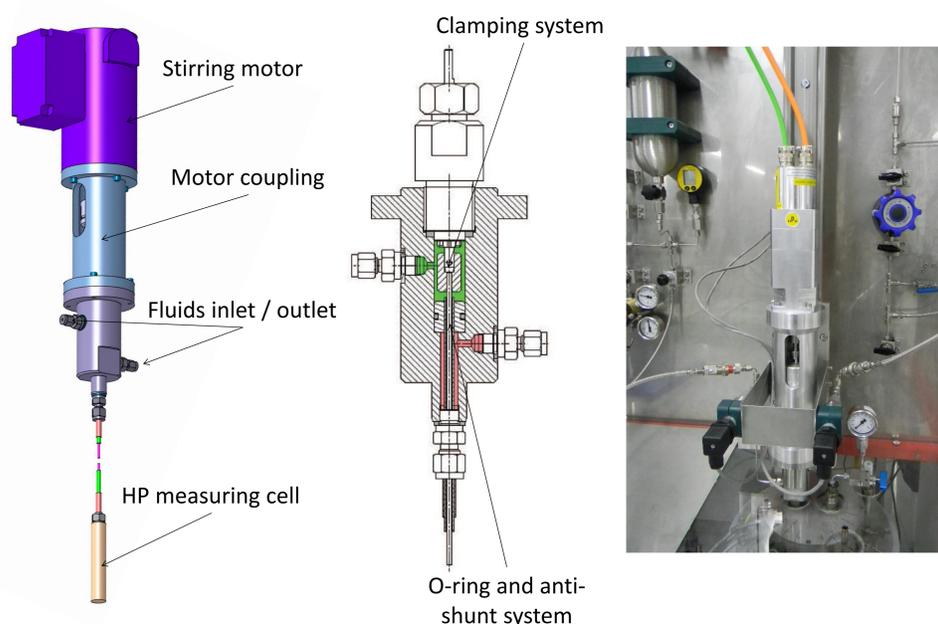


Fig 1. HP stirred calorimetric cell Fig 2. Detail of upper part

Fig 3. Magnetic stirring version inserted in the calorimeter

CO₂ HYDRATE FORMATION / DISSOCIATION

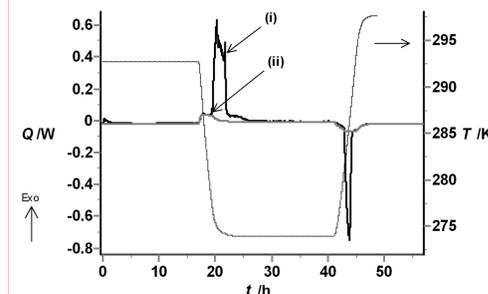


Fig 4. Q with and without stirring

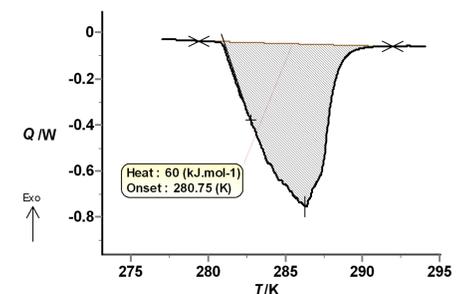


Fig 5. Dissociation endotherm

Run	T_{diss} / °C	ΔH_{diss} / kJ.mol ⁻¹
1	7.5	62
2	7.6	60
3	7.7	61
Average	7.6	61
Std Dev	0.1	1

Table 1. Repeated dissociation tests

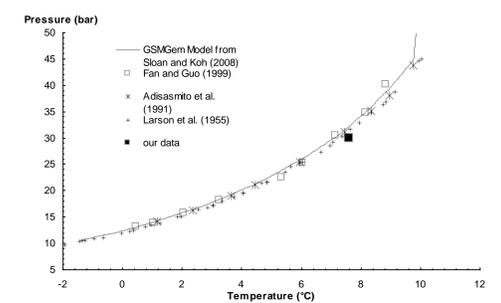


Fig 6. Comparison with literature

Test conditions

- Pressurized at **30.5 bar** with CO₂ maintained stable in a ± 0.5 bar range
- Temperature profile as depicted on Fig. 4 with:
 - Cooling and heating rates of **0.1°C/min**
 - Temperature maintained constant at **0.9°C**
- When under stirring conditions: **150 RPM**

Results

- With the absence of stirring (Fig. 4): **only poorly energetic effects**
 - Formation (exo) and dissociation (endo) of CO₂ hydrates **at the interface**
- Under stirred condition: **strong endo/exo thermic peaks**
 - **Dissociation temperature**: onset temperature of the peak (Fig. 5)
 - **Heat of dissociation** area between the integration baseline and the curve (Fig. 5)
- **Comparison** between obtained data (Table 1) and those from other authors (Fig. 6) **shows a very good agreement**
- **Enthalpy measurements** (Table 1) **agree with the available literature**
 - Anderson [6]: enthalpy varying between 63.6 ± 1.8 kJ.mol⁻¹ and 57.7 ± 1.8 kJ.mol⁻¹ between the two quadruple points
 - Sabil et al. [7]: a value of 62.48 kJ.mol⁻¹ in very similar conditions of pressure (P = 30 bar instead of 30.5 bar)

CONCLUSION

Because it allows reaching the complete conversion of the water, **this system will allow more into depth studies of gas hydrates like:**

- **Isothermal kinetics** of formation and dissociation
- **Heat capacity** measurements
- Potentially **viscosity measurements** by treating the torque data of the motor

Improvement on the system design being conducted: **magnetic coupling** (Fig. 3)

- **To limit the risks of leakage** at the level of the upper part
- **To allow faster stirring rates** (potentially up to 1500 rpm)

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