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Frédéric Plantier, Jean-Philippe Torre, Laurent Marlin, Rémi André, Pierre Le Parlouer. Recent improvements in the differential scanning calorimetry methods applied to the study of gas hydrates.. 20th European Conference on Thermophysical Properties (ECTP 2014), Aug 2014, Porto, Portugal. . hal-02009661

HAL Id: hal-02009661

<https://hal.science/hal-02009661>

Submitted on 6 Feb 2019

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Plantier, Frédéric and Torr , Jean-Philippe  and Marlin, Laurent and Andr , R mi and Le parlouer, Pierre *Recent improvements in the differential scanning calorimetry methods applied to the study of gas hydrates*. (2014) In: 20th European Conference on Thermophysical Properties, 31 August 2014 - 4 September 2014 (Porto, Portugal). (Unpublished)

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RECENT IMPROVEMENTS IN THE HIGH PRESSURE DIFFERENTIAL SCANNING CALORIMETRY METHOD APPLIED TO THE STUDY OF GAS HYDRATES

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Outline

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 drawback 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.)

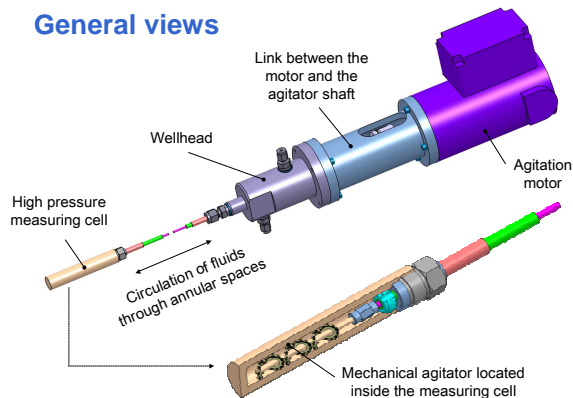
Development, tests and validation in our laboratory (LFCR, France) of a novel type of calorimetric cell for BT 2.15 and C80 SETARAM calorimeters :

Patent number
WO2014016414 (A1)
Patent Cooperation Treaty application

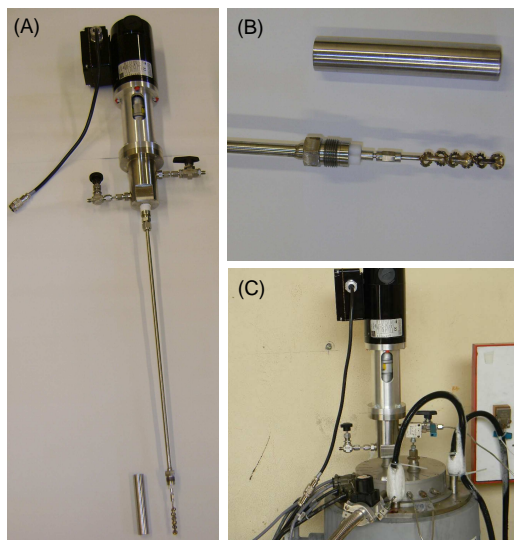
industrialized and commercialized by SETARAM Instrumentation

Technical details of the prototype

General views

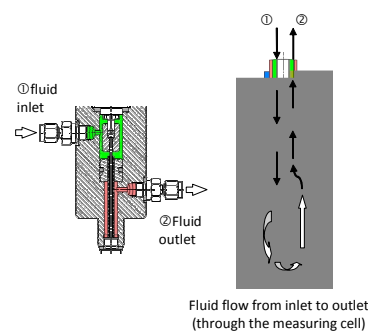


- ◆ The mechanical agitation in the measuring cell is provided by a removable rotary shaft on which star washers have been welded (N < 200 RPM).
- ◆ The link between the wellhead and the measuring cell is provided by two concentric tubes allowing the agitator shaft to rotate freely in the middle of the 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.



(A) Picture of the prototype
(B) High pressure cell and its agitation system
(C) Prototype installed on a SETARAM BT 2.15 calorimeter

Dynamic control of the pressure



Benefits:

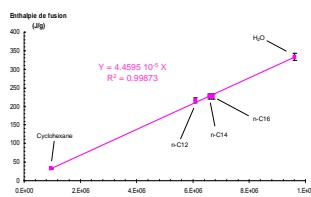
- measurements under pressure (P < 20 Mpa)
- in-situ mechanical agitation
- dynamic control of the pressure inside the cell
- designed for BT 2.15 and C 80 SETARAM calorimeters

Experimental results

Calibration of the prototype in temperature and enthalpy

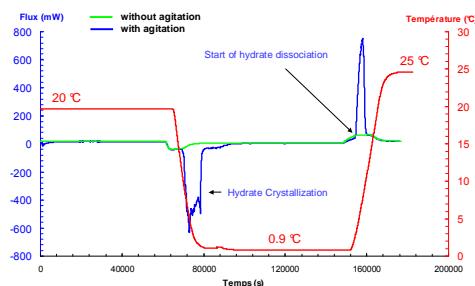
reference (NIST)	T _{fusion_ref} (°C)	T _{fusion_exp} (°C)
Water	0,00 ± 0,05	0,1 ± 0,1
Cyclohexane	6,5 ± 0,3	6,7 ± 0,2
n-C ₁₂	-9,7 ± 0,3	-9,9 ± 0,2
n-C ₁₄	5,6 ± 0,9	5,3 ± 0,2
n-C ₁₆	18 ± 1	18,1 ± 0,2

Precision in temperature : ± 0.2 °C (-10 < T (°C) < 18)



Sensitivity constant: $K = (3,46 \pm 0,05) \cdot 10^{-5} \text{ J} \cdot \mu\text{V}^{-1} \cdot \text{s}^{-1}$

Application to CO₂ hydrates P = 3.05 ± 0.05 MPa

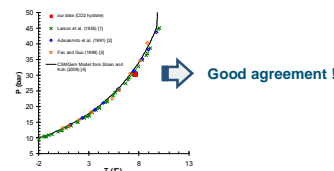


Test	T _{diss} (°C)	ΔH _{diss} (J/g _{eau})
Test 1	7,5 ± 0,2	480 ± 10
Test 2	7,6 ± 0,2	480 ± 10
Test 3	7,7 ± 0,2	460 ± 10

- the presence of the in-situ agitation triggers the crystallization (rupture of the metastability, reduction of the induction time)
- the stirring process no creates noise/perturbation of the calorimetric signal
- a good reproducibility in the results is obtained

Comparison of our results to literature data

T_{eq,EXP} (P_{CO2} = 3.05 ± 0.05 MPa) = 7.6 ± 0.2 °C



ΔH_{diss,EXP} (P_{CO2} = 3.05 ± 0.05 MPa) :

- Assumptions:
 - N_h = hydration number (CO₂ - N_h · H₂O) equal to 7.3 ± 0.13 [5]
 - the water to hydrate conversion is total (η = 100 %)

References [6]	T (°C)	ΔH (kJ/mol _{CO2})
Yoshida et al. (1972)	0	59.9
Kamath (1984)	-	80.1
Long (1994)	-	73
Skjovborg and Rasmussen (1994)	0.5	68.71
Uchida et al. (1996)	0.5	65.22
Yoon et al. (2003)	quadruple point Q1	57.66
Anderson (1983)	0.0 - 1.0	58.2 - 62.5
Dalrymple et al. (2006)	7.1	65.22
Sabli et al. (2010)	7.6 (P = 3.0 MPa)	62.46

→ ΔH_{diss,EXP} = 62 ± 3 (kJ / mol_{CO2})

Conclusions

- A novel high pressure calorimetric cell equipped with a mechanical agitation and a dynamic pressure control has been developed and tested.
- The temperature 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 enthalpy of the CO₂ hydrate
- The experimental results obtained are in good agreement with literature data, and demonstrate the potentialities of this novel equipment

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