



HAL
open science

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

Frédéric Plantier, Jean-Philippe Torre, Laurent Marlin, Rémi André, Pierre Le Parlouer

► To cite this version:

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

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/21951>

To cite this version:

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 (Unpublished)

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

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

Frédéric Plantier^{a,*}, Jean-Philippe Torrè^a, Laurent Marlin^a, André Rémi^b, Le Parlouer Pierre^b

^a Laboratoire des Fluides Complexes et leurs Réservoirs UPPA - TOTAL - CNRS Pau (France)

^b SETARAM Instrumentation Caluire, France

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.)

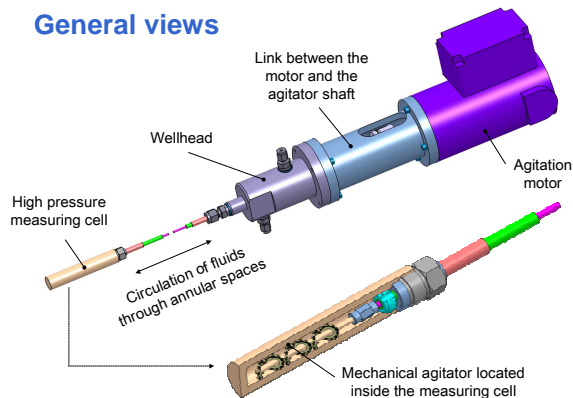
Development, tests and validation in our laboratory (LFCR, France) of a novel type of calorimetric cell for BT 2.15 and C80 SETARAM calorimeters :

Patent number
WO2014016414 (A1)
Patent Cooperation Treaty application

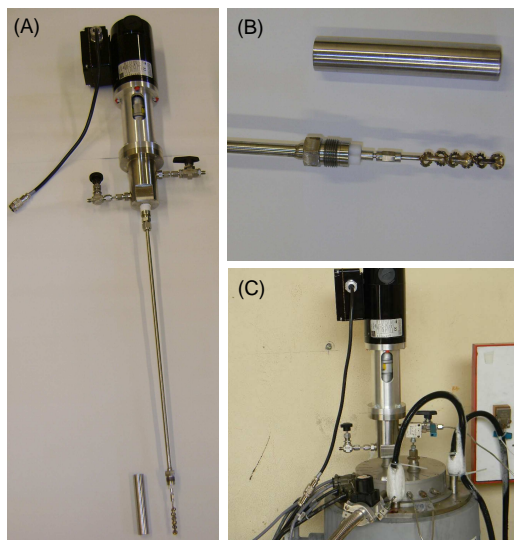
industrialized and commercialized by
SETARAM Instrumentation

Technical details of the prototype

General views

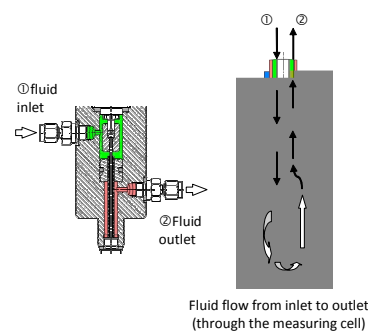


- ◆ The mechanical agitation in the measuring cell is provided by a removable rotary shaft on which star washers have been welded ($N < 200$ RPM).
- ◆ The link between the wellhead and the measuring cell is provided by two concentric tubes allowing the agitator shaft to rotate freely in the middle of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

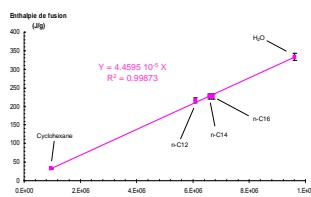
- measurements under pressure ($P < 20$ Mpa)
- in-situ mechanical agitation
- dynamic control of the pressure inside the cell
- designed for BT 2.15 and C 80 SETARAM calorimeters

Experimental results

Calibration of the prototype in temperature and enthalpy

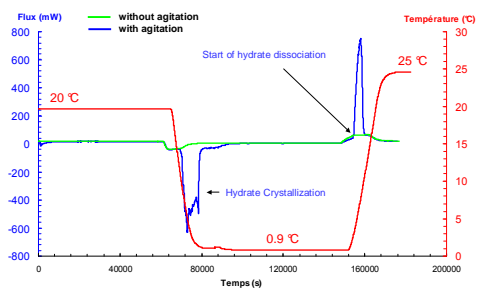
reference (NIST)	$T_{\text{fusion_ref}} (^\circ\text{C})$	$T_{\text{fusion_exp}} (^\circ\text{C})$
Water	$0,00 \pm 0,05$	$0,1 \pm 0,1$
Cyclohexane	$6,5 \pm 0,3$	$6,7 \pm 0,2$
n-C ₁₂	$-9,7 \pm 0,3$	$-9,9 \pm 0,2$
n-C ₁₄	$5,6 \pm 0,9$	$5,3 \pm 0,2$
n-C ₁₆	18 ± 1	$18,1 \pm 0,2$

Precision in temperature : $\pm 0,2$ °C ($-10 < T (^\circ\text{C}) < 18$)



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 $P = 3.05 \pm 0.05$ MPa

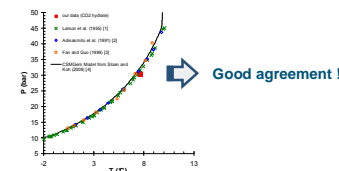


	$T_{\text{diss}} (^\circ\text{C})$	$\Delta H_{\text{diss}} (\text{J/g}_{\text{eau}})$
Test 1	$7,5 \pm 0,2$	480 ± 10
Test 2	$7,6 \pm 0,2$	480 ± 10
Test 3	$7,7 \pm 0,2$	460 ± 10

- 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

$T_{\text{eq}}^{\text{EXP}} (P_{\text{CO}_2} = 3.05 \pm 0.05 \text{ MPa}) = 7.6 \pm 0.2$ °C



$\Delta H_{\text{diss}}^{\text{EXP}} (P_{\text{CO}_2} = 3.05 \pm 0.05 \text{ MPa}) :$

- Assumptions:
 - $N_h = \text{hydration number } (\text{CO}_2 - N_h \cdot \text{H}_2\text{O})$ equal to 7.3 ± 0.13 [5]
 - the water to hydrate conversion is total ($\eta = 100$ %)

References [6]	T (°C)	$\Delta H_{\text{diss}} (\text{J/g}_{\text{eau}})$
Vishalakshi 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
Dalhayeh et al. (2006)	7.1	65.22
Sabli et al. (2010)	7.6 (P = 3.0 MPa)	62.46

$\Delta H_{\text{diss}}^{\text{EXP}} = 62 \pm 3 (\text{kJ/mol}_{\text{CO}_2})$

OK!

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

References

- [1] Larson, D., 1995, PhD Thesis, University of Illinois, Urbana, Illinois, USA.
- [2] Adisasmito S. et al. (1991), J. Chem. Eng. Data 36(1), 66-71
- [3] Fan S. and Guo T.M. (1998), J. Am. Chem. Soc. 44, 829-832
- [4] Sloan, E.D and Koh, C.A., 2008, Clathrate hydrates of natural gases, 3rd edition, CRC Press, New York.
- [5] Uchida et al. (1995), Direct Ocean Disposal of Carbon Dioxide, Terra Sci. Publish., 45-61
- [6] Sabli et al. (2010), Fluid Phase Equilibria 290 (2010) 109-114