



HAL
open science

Experimental procedure and results to measure the composition of gas hydrate, during crystallization and at equilibrium, from N₂-CO₂-C₂H₆-C₃H₈-C₄H₁₀ gas mixtures

Baptiste Bouillot, Duyen Le Quang, Quang-Du Le, Jean-Michel Herri, Philippe Glenat, Pierre Duchet-Suchaux

► To cite this version:

Baptiste Bouillot, Duyen Le Quang, Quang-Du Le, Jean-Michel Herri, Philippe Glenat, et al.. Experimental procedure and results to measure the composition of gas hydrate, during crystallization and at equilibrium, from N₂-CO₂-C₂H₆-C₃H₈-C₄H₁₀ gas mixtures. Ziran Zhong. The 8th International Conference on Gas Hydrates, Jul 2014, Pékin, China. P1.081 Paper T1-71, 2014. hal-01069597

HAL Id: hal-01069597

<https://hal.science/hal-01069597v1>

Submitted on 19 Mar 2015

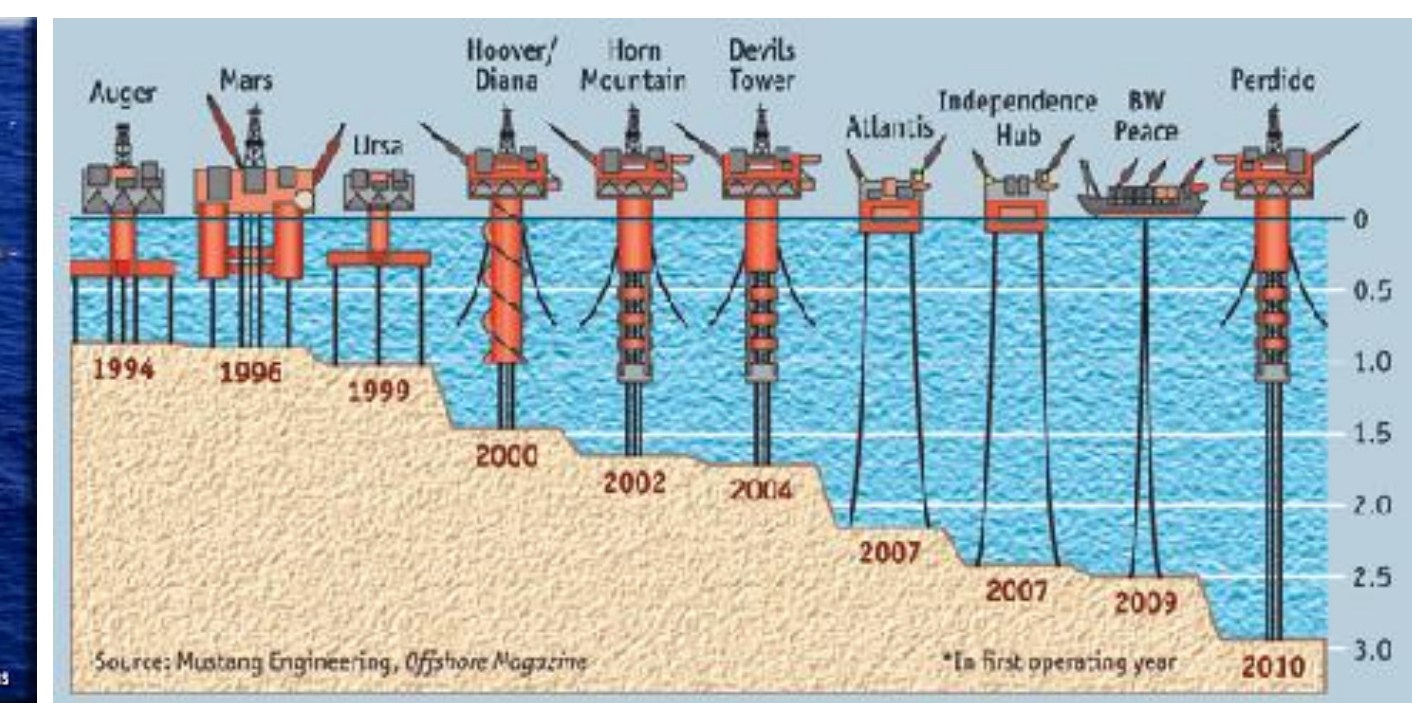
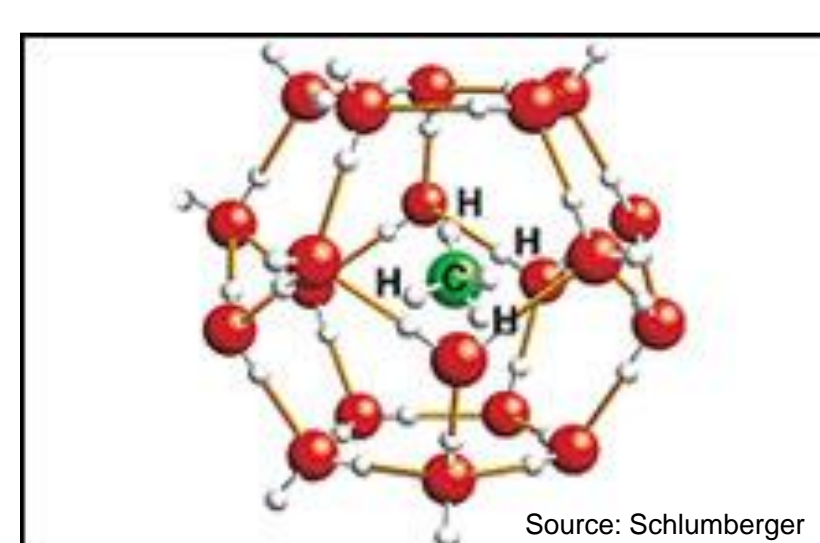
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

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.

EXPERIMENTAL PROCEDURE AND RESULTS TO MEASURE THE COMPOSITION OF GAS HYDRATE, DURING CRYSTALLIZATION AND AT EQUILIBRIUM, FROM N₂-CO₂-C₂H₆-C₃H₈-C₄H₁₀ GAS MIXTURES

Context

The offshore extraction of petroleum in deeper conditions increases day after day and favors the conditions of hydrate formation (low temperature and high pressure), representing a great concern in flow assurance. Actually, another parameter comes into play, because as the oil/gas fields matures, the fraction of water increases.



Objectives

- Study, from an **experimental** point of view, the gas hydrate formation of various **hydrocarbon gas mixtures** in an **instrumented batch reactor**.
- Determine the **equilibrium points (P, T)** and **Composition** of each phase (gas x^G , liquid x^L , hydrate x^H).

Experimental Apparatus and gas mixtures

Gas mixtures	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀
Gas 1	-	-	1	-	-	-
Gas 2	1	-	-	-	-	-
Gas 3	0.24	-	0.76	-	-	-
Gas 4	0.225	-	0.775	-	-	-
Gas 5	0.821	0.179	-	-	-	-
Gas 6	0.057	-	0.915	0.028	-	-
Gas 7	0.053	-	0.919	0.028	-	-
Gas 8	0.052	-	0.919	0.029	-	-
Gas 9	-	-	0.953	0.028	0.019	-
Gas 10	-	-	0.864	0.057	0.053	0.026
Gas 11	-	-	0.848	0.05	0.076	0.026
Gas 12	0.055	-	0.917	0.028	-	-

Table 1. Molar compositions of the studied gas mixtures (std. dev. ≈ 3%)

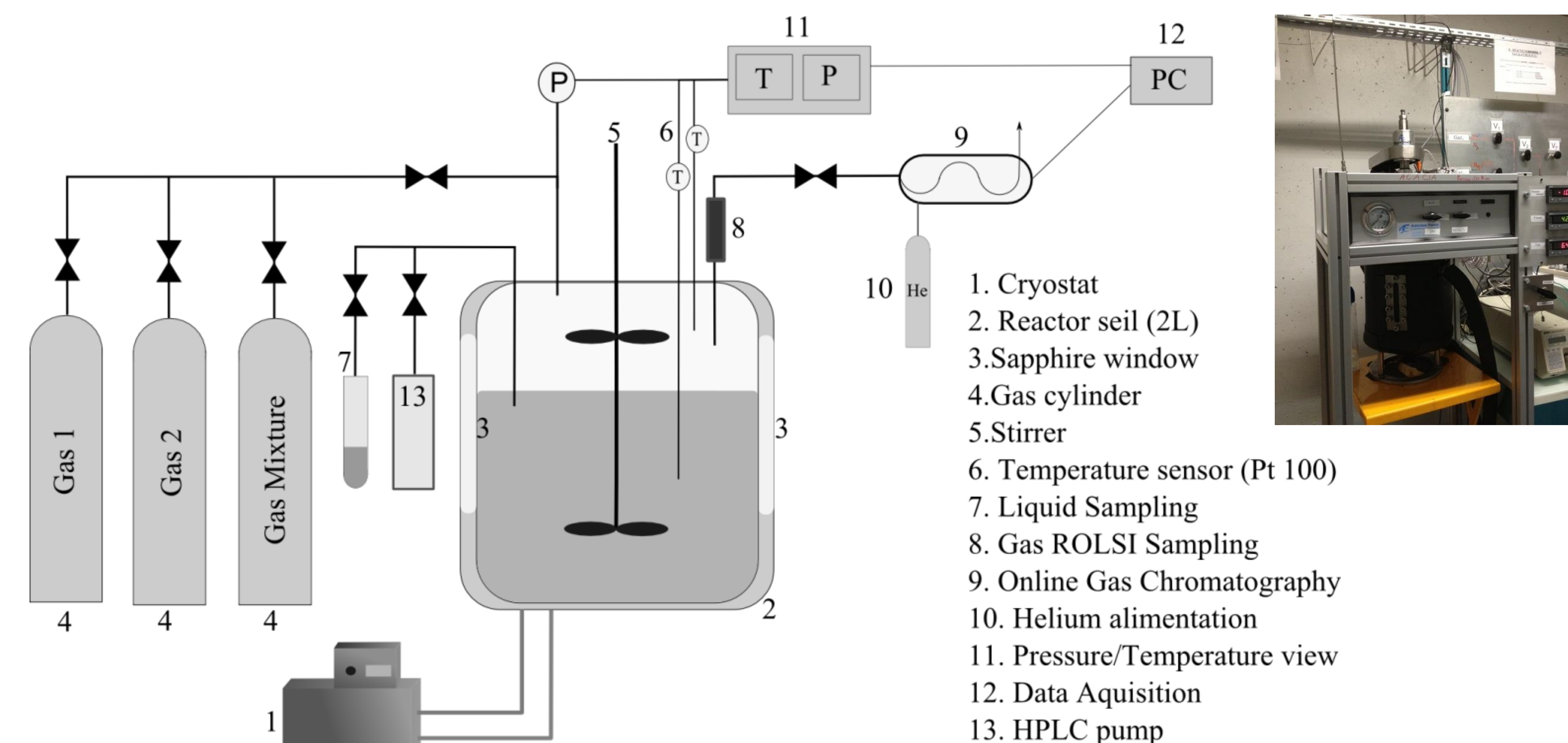


Figure 1. Experimental set-up

Calculation method

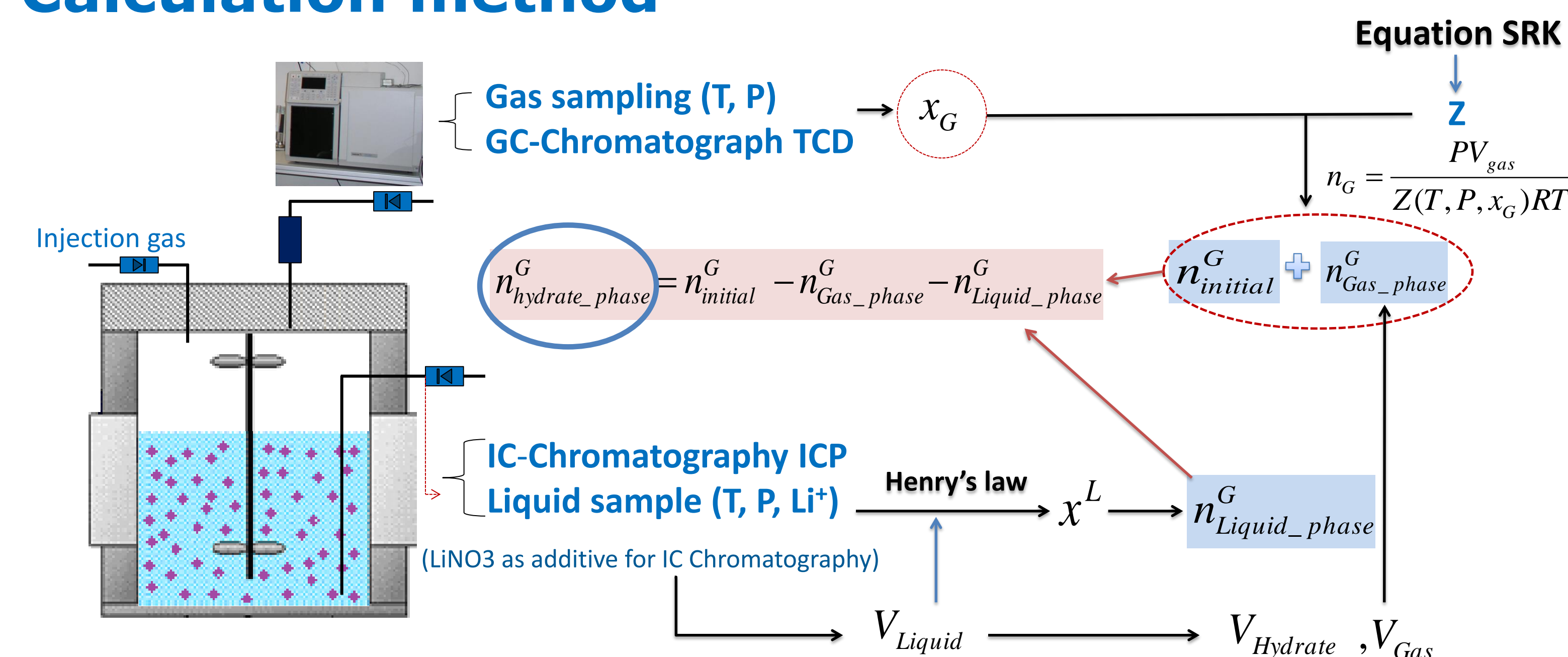


Figure 2. Calculation procedure (see also [1])

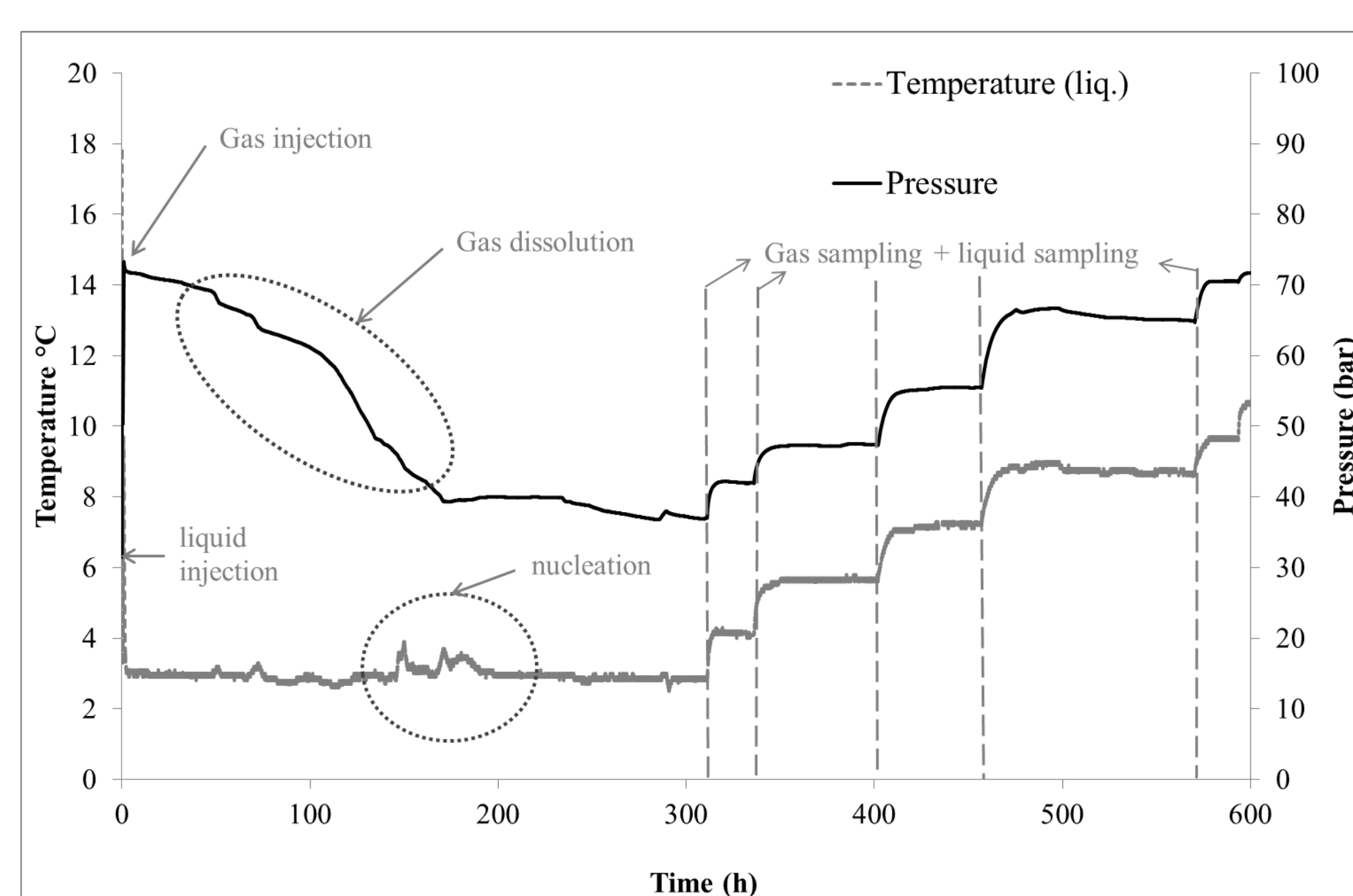


Figure 3. Experimental procedure

- Assumptions:**
- $\Delta x_i/x_i = 3\%$ (mol. Frac.),
 - $\Delta T = 0.2^\circ\text{C}$,
 - $\Delta P = 0.1$ bar,
 - $\Delta m_w = 0.1\text{g}$ (of mass of injected water),
 - Δm_w (liq. sample) = 0.1g,
 - $\Delta V_R = 3\%$ (Reactor Volume),
 - $\Delta \rho_w = 10 \text{ kg}\cdot\text{m}^{-3}$,
 - $\Delta \rho_H^\beta = 40 \text{ kg}\cdot\text{m}^{-3}$.
 - $P_w = 1000 \text{ kg}/\text{m}^3$.
 - $\rho_H^\beta = 790 \text{ kg}/\text{m}^3$.

Experimental results

Validation on others experimental results Pure CO₂ and Pure CH₄:

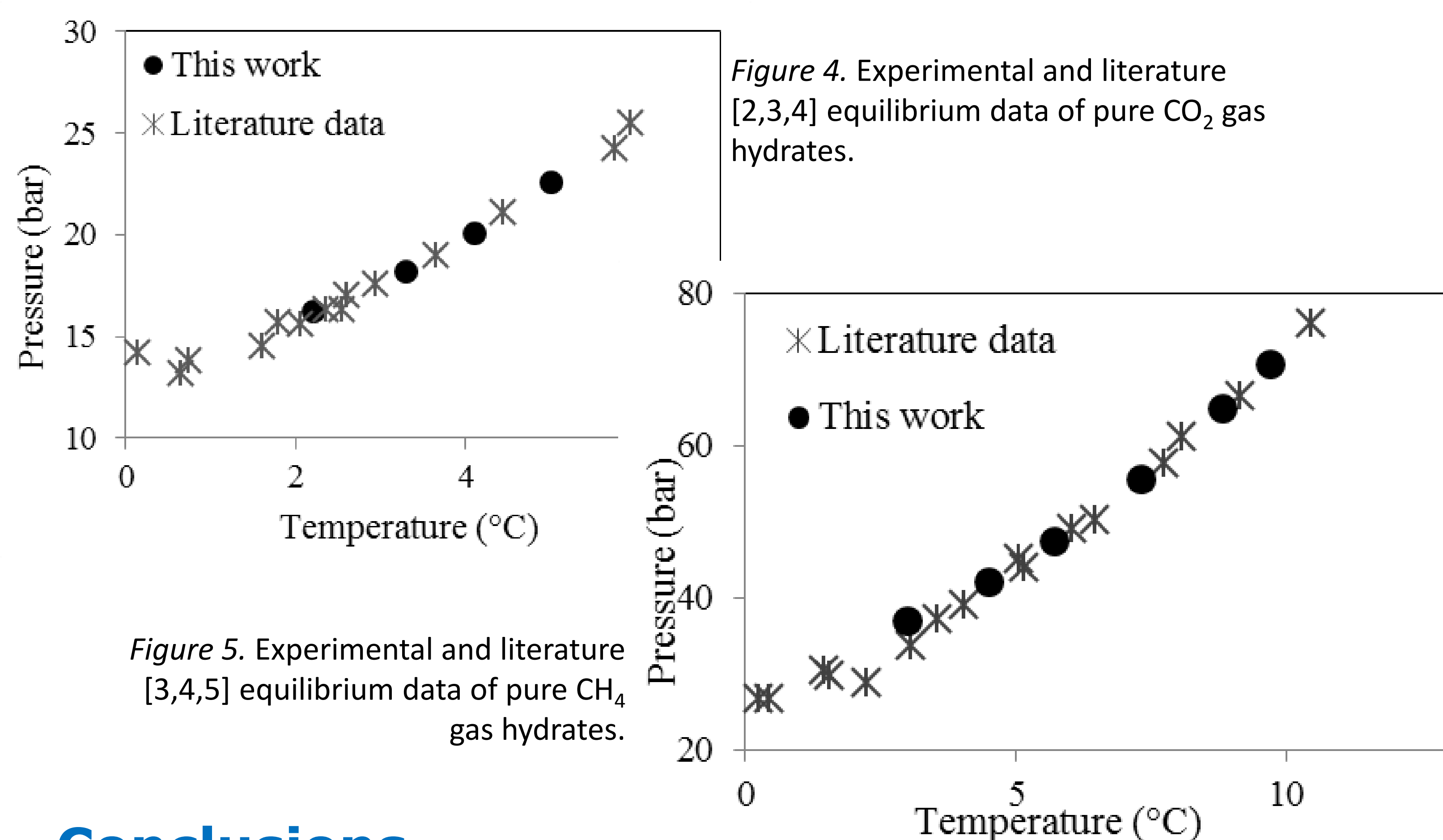


Figure 4. Experimental and literature [2,3,4] equilibrium data of pure CO₂ gas hydrates.

Figure 5. Experimental and literature [3,4,5] equilibrium data of pure CH₄ gas hydrates.

Others experimental results on gas mixtures (example)

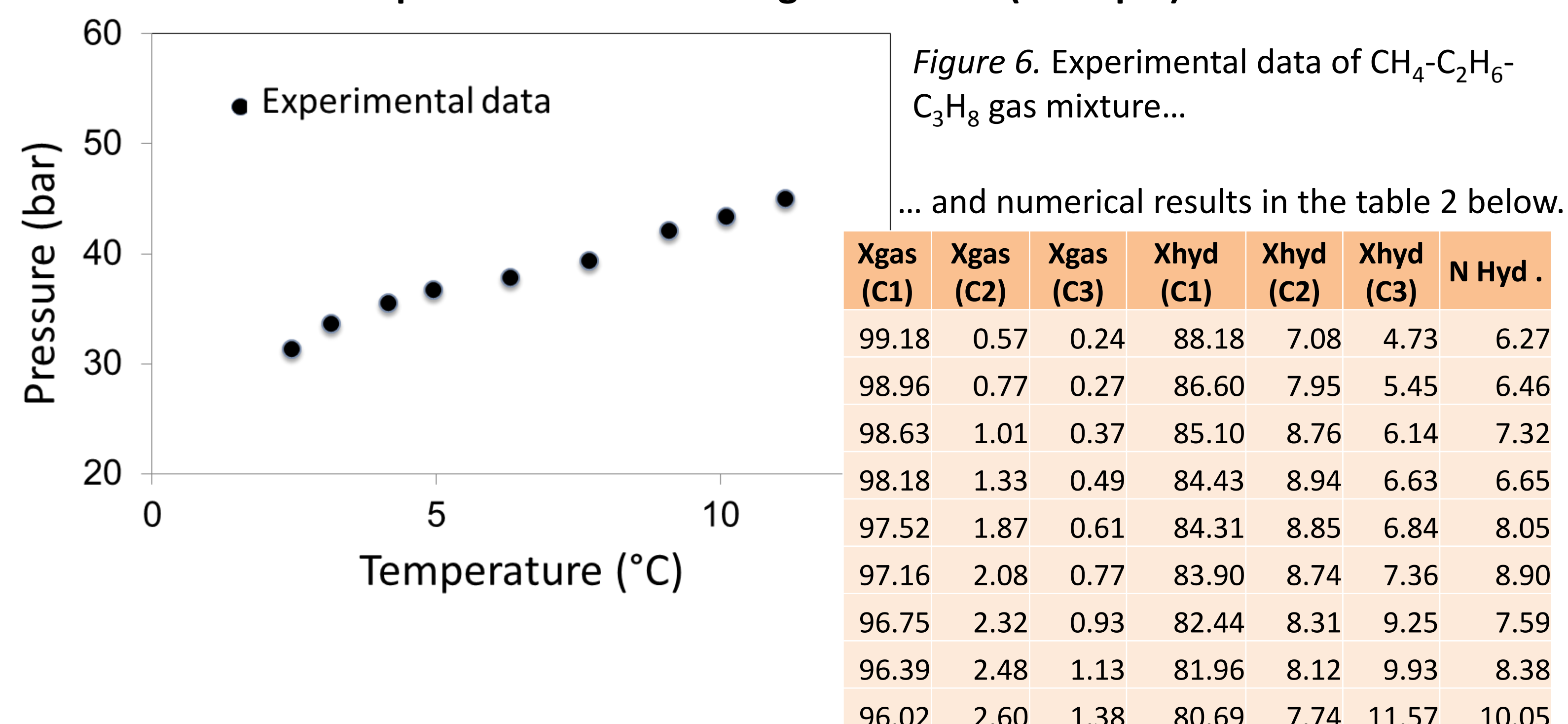


Figure 6. Experimental data of CH₄-C₂H₆-C₃H₈ gas mixture...

... and numerical results in the table 2 below.

- Other data available in the **full text**.
- Most of the experimental data were obtain from **quick crystallization process**
- One experiment from **slow crystallization** to detect a possible **kinetic effect** (see [6])

Conclusions

- Gas hydrates equilibrium experiments of **hydrocarbon gas mixtures** (N₂-CO₂-CH₄-C₂H₆-C₃H₈-C₄H₁₀) were performed in an **instrumented batch reactor**.
- **Pressure** and **Temperature** of equilibrium for **quick crystallization** (high crystallization rate) are given and are **in accordance** with literature data.
- The **molar composition** at equilibrium for gas mixtures are given and present uncertainties inferior to 4% (for both gas phase and hydrate phase).
- The **modeling** part is presented in [6] and discuss the relevancy of thermodynamics in this case

References:

- [1] Herri JM., Bouchemoua A., Kwaterski M., Fezoua A., Ouabbas Y., Cameirao A, *Fluid Phase Equilibria* 2011;301:171-190.
- [2] Robinson. DB, Mehta BR., *J.Can.Pet.Tech.* 1971(10):33.
- [3] Adisasmito S., Frank RK., Sloan ED., *Journal of Chemical and Engineering Data* 1991(36):68.
- [4] Yasuda K., Ohmura R., *Journal of Chemical and Engineering Data* 2008(53):2182-2188.
- [5] Thakore, J.L., Holder G.D., *Industrial & Engineering Chemistry Research* 1987(26):462.
- [6] Herri JM, Le Quang D, Kwaterski M, Bouillot B, Glenat P, Duchet-Suchaux P., In: *Proceedings of the 8th International Conference on Gas Hydrates (SN460)*. 2014.