Influence of the crystallization rate on the formation of gas hydrates from CH4-C3H8 gas mixtures and extension to other mixtures

Quang-Du Le, Baptiste Bouillot, Jean-Michel Herri

INFLUENCE OF THE CRYSTALLIZATION RATE ON THE FORMATION OF GAS HYDRATES FROM CH_4-C_3H_8 GAS MIXTURES AND EXTENSION TO OTHER MIXTURES

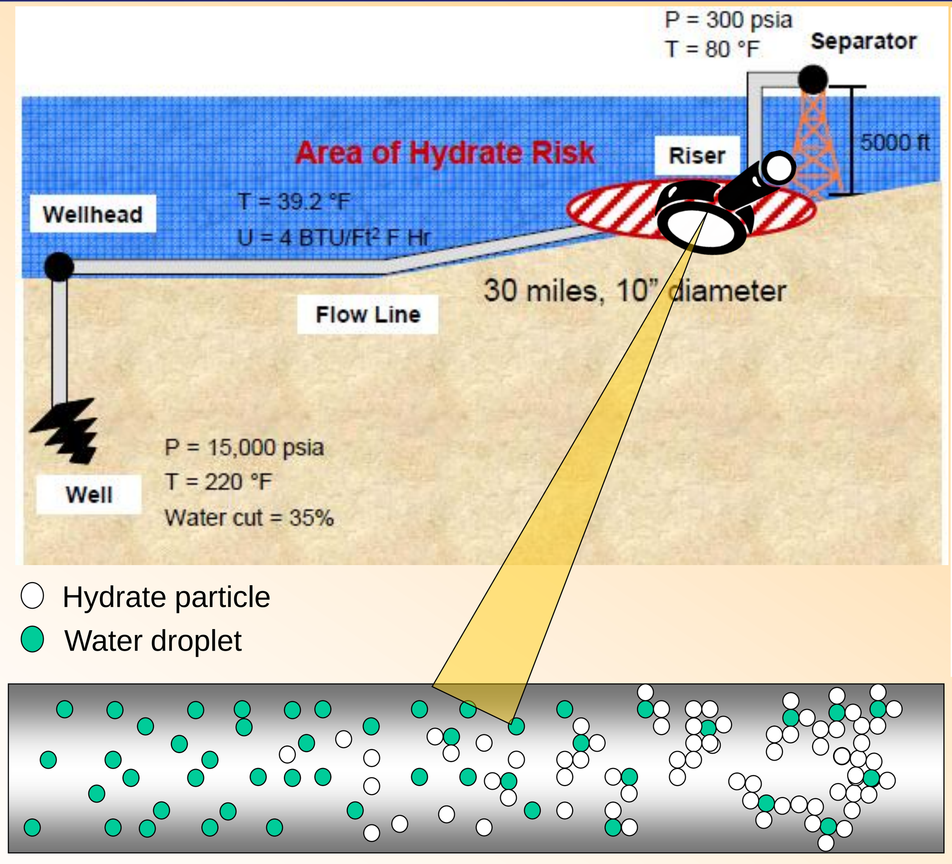
Du LE-QUANG, Baptiste BOUILLOT, **Jean-Michel HERRI***

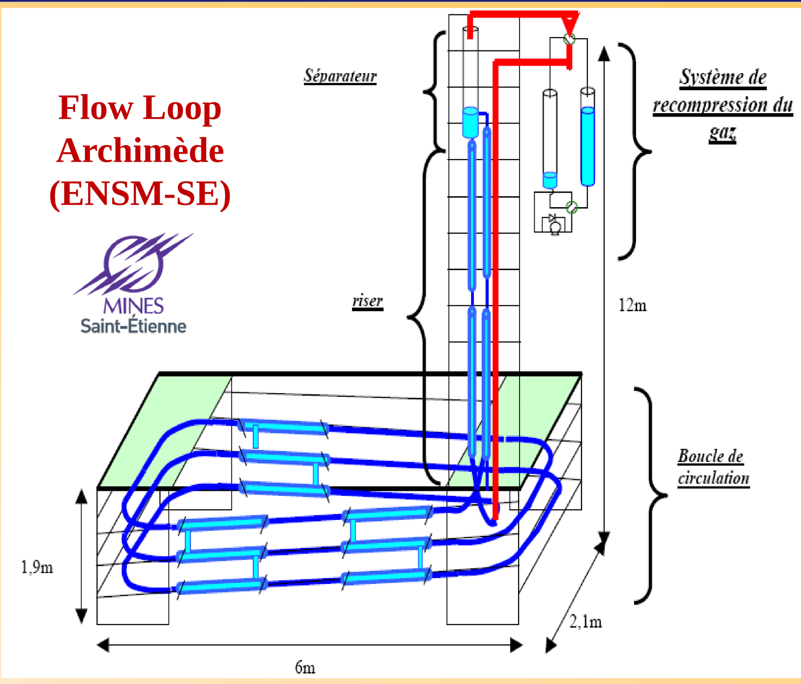
* Corresponding author. Tel.: +33 4 77 42 02 92; fax: +33 4 77 49 96 92. E-mail address: herri@emse.fr (J.-M. Herri).

Centre SPIN, École Nationale Supérieure des Mines de SAINT-ETIENNE, 158 cours Fauriel, 42023 Saint-Etienne Cedex 02, France

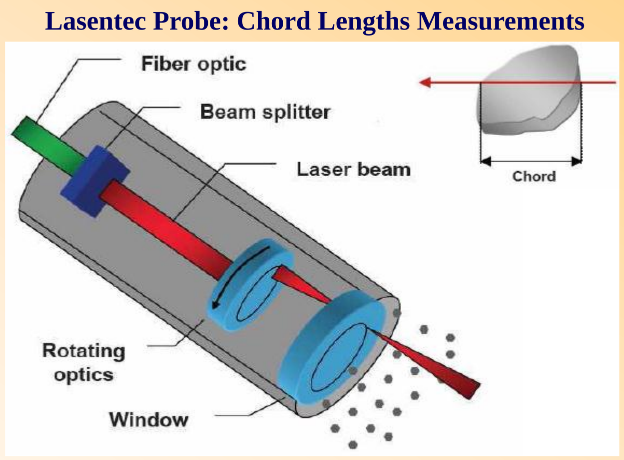
In this study, we present details on two different experimental procedures to form mixed hydrates. They are applied to measure the volume and composition of the crystallized hydrate from CH4-C3H8 gas mixtures at high and low crystallization rate, respectively. The results obtained from both methods reveal a difference in composition, final pressure and volume between the two procedures (quick and slow crystallization). Furthermore, this work aims at contributing to the global understanding of the coupling between kinetics and thermodynamics to provide some insight in the composition of the gas hydrate phase during its crystallization from an aqueous liquid and a mixed gas phase. In addition, we face new experimental facts that open questioning after comparing the modelling of clathrate hydrates following the classical approach (van der Waals and Platteeuw, 1959).

FLOW ASSURANCE





Lasentec Probe: Chord Lengths Measurements

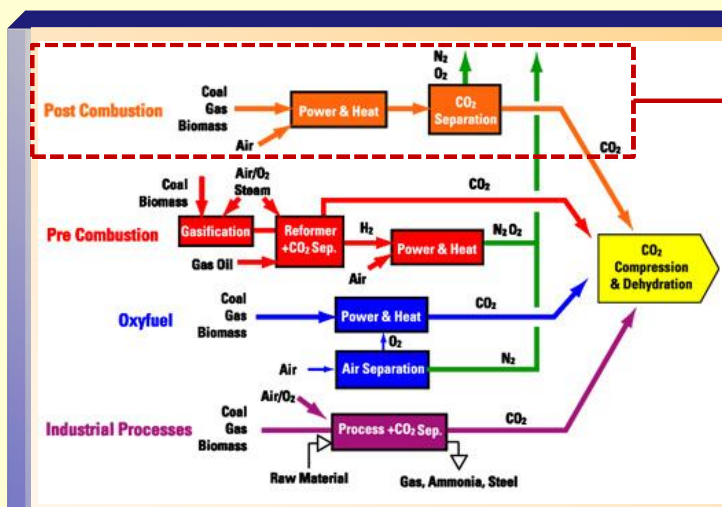


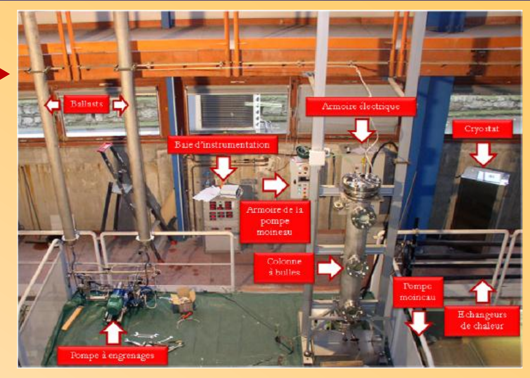
Φ $\quad\Phi_{eff} > \Phi$ $\quad\Phi_{eff} >> \Phi$

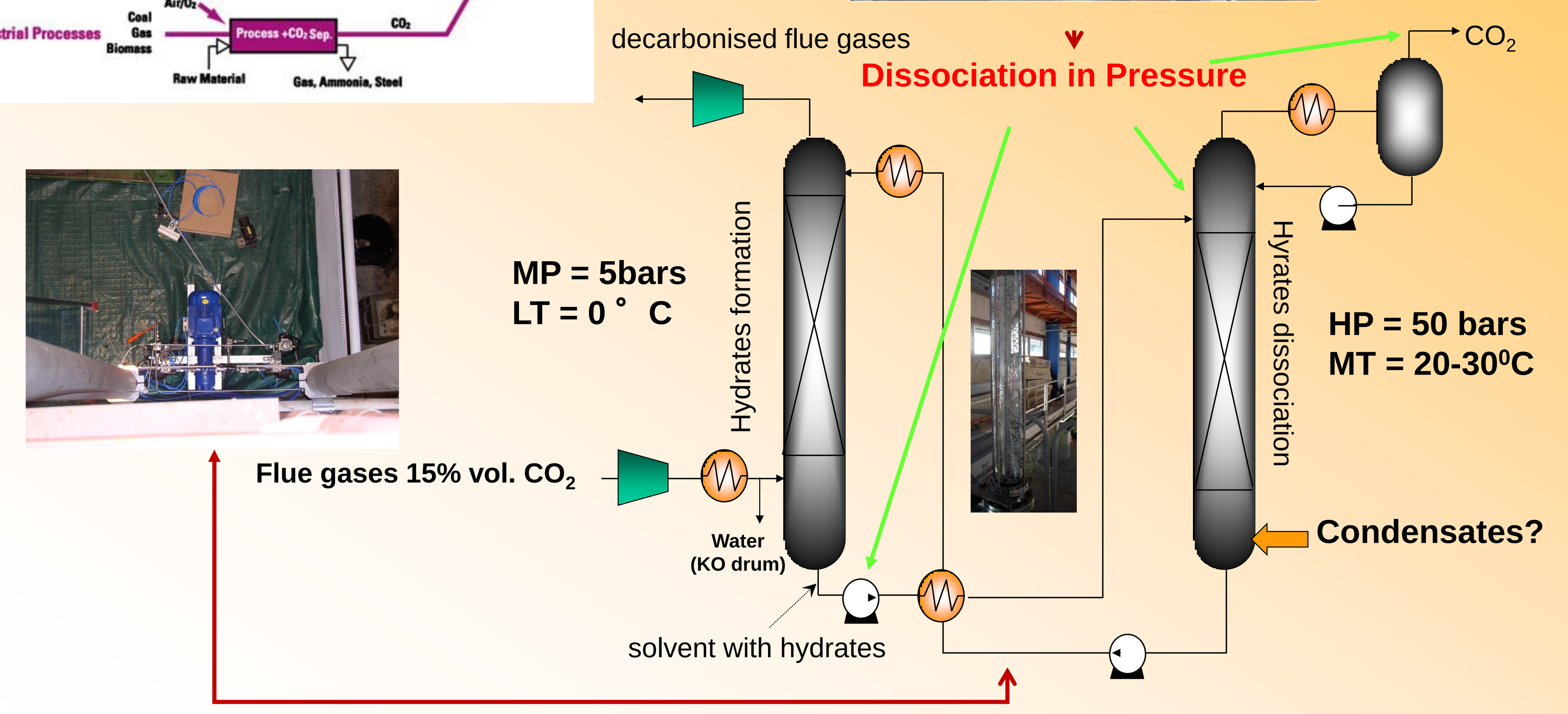
$$\mu_{slurry} = \mu_{oil}\frac{(1-\Phi_{eff})}{(1-\Phi_{eff}/\Phi_{max})^2} \qquad \phi_{eff} = \phi\left(\frac{D_A}{D_p}\right)^{3-f}$$

According to Camargo & Palermo (2002)

CO_2 CAPTURE

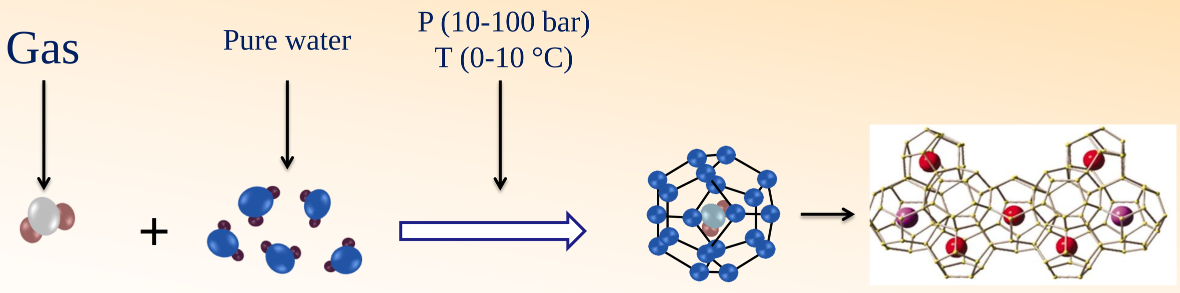






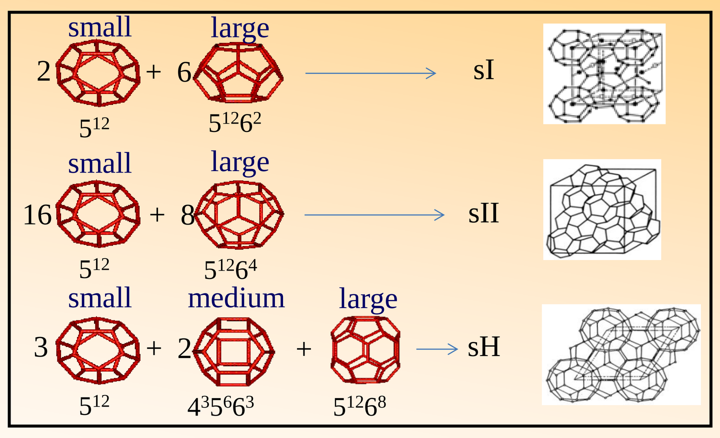
GAS HYDRATES FORMATION

1 – Conditions needed for the gas hydrate to form



- **The cavity** formed by water molecules linked by hydrogen bonds
- **The cavities** contain gas molecules
- **The cavities** are stabilized by Van der Waals forces

2 – Hydrate structure



3 –Clathrate hydrate

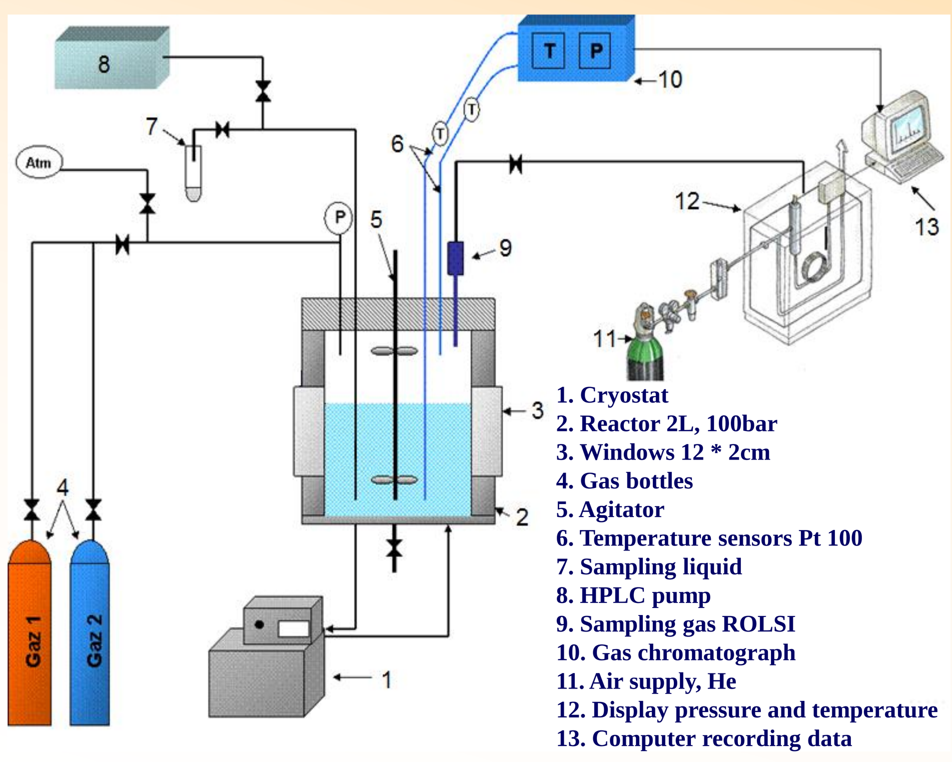
Clathrate hydrate structures	S_I		S_{II}		S_H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number per unit cell (m_i)	2	6	16	8	3	2	1
Average cavity radius (Å)	3,95	4,33	3,91	4,73	3,91[c]	4,06[c]	5,71[c]
Coordination number[a]	20	24	20	28	20	20	36

(a)The number of oxygen atom per cavity

Experimental procedure and set-up

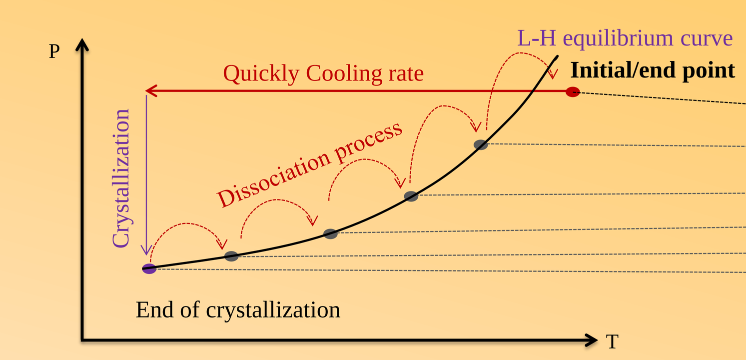
✓ Experimental apparatus and laboratory

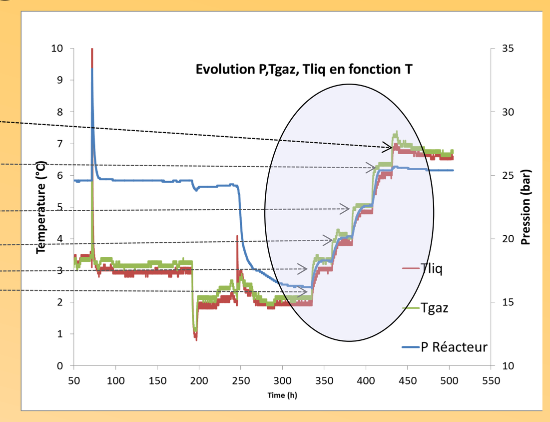
Experimental apparatus



Laboratory

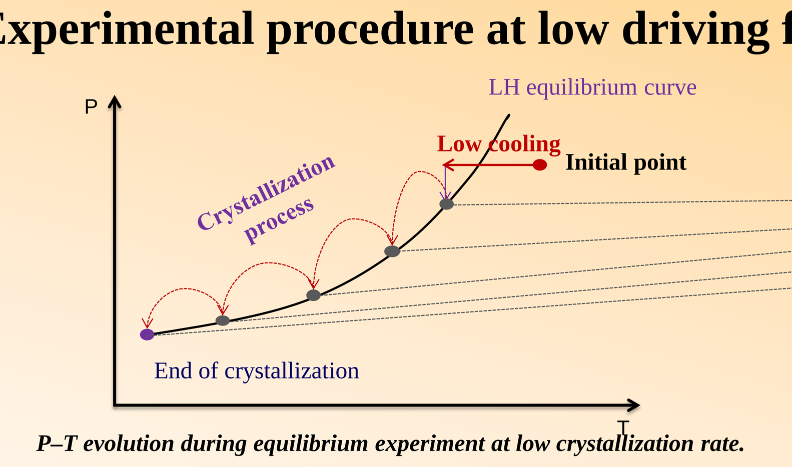
✓ Experimental procedure at high driving force

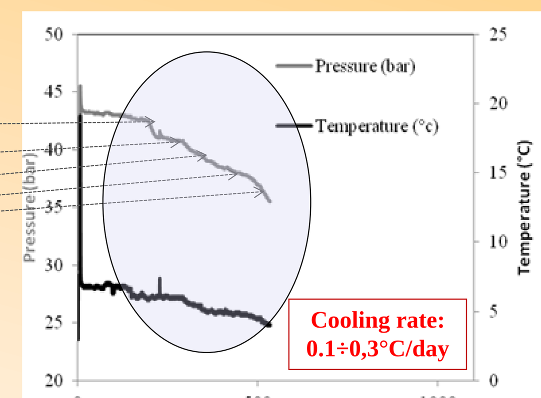




P–T evolution during equilibrium experiment at high crystallization rate.

✓ Experimental procedure at low driving force



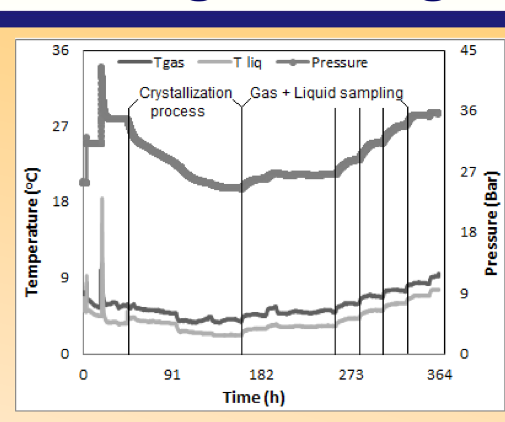


P–T evolution during equilibrium experiment at low crystallization rate.

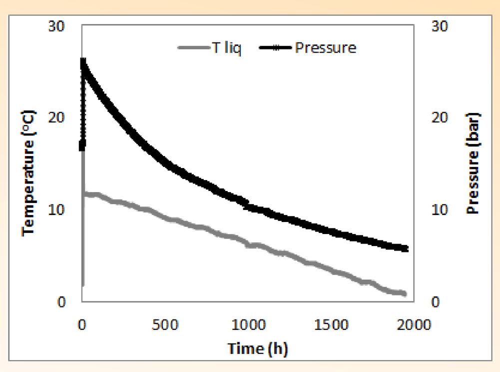
COMPARING: Results from procedure at high driving force AND procedure at low driving force

Molar composition of the studied gas mixtures (standard deviation about 3%)

Gas mixtures	Methods	CH_4	C_3H_8	Pint	Tint	Reactor volume	Mass water injected
		%	%	MPa	oK	lite	gram
Gas 1	Slow	84.61	15.39	1.73	279.95	2.36	801.10
Gas 2	Slow	84.61	15.39	1.73	279.95	2.36	801.10
Gas 3	Slow	86.86	13.14	1.83	284.95	2.36	800.94
Gas 4	Quick	85.77	14.23	1.81	281.00	2.36	801.15
Gas 5	Quick	85.81	14.19	1.71	280.45	2.36	801.05
Gas 6	Quick	86.89	13.11	1.77	285.05	2.44	800.94
Gas 7	Quick	86.89	13.11	1.77	285.05	2.44	800.94



P–T evolution during experiment at high crystallization rate.



P–T evolution during experiment at low crystallization rate.

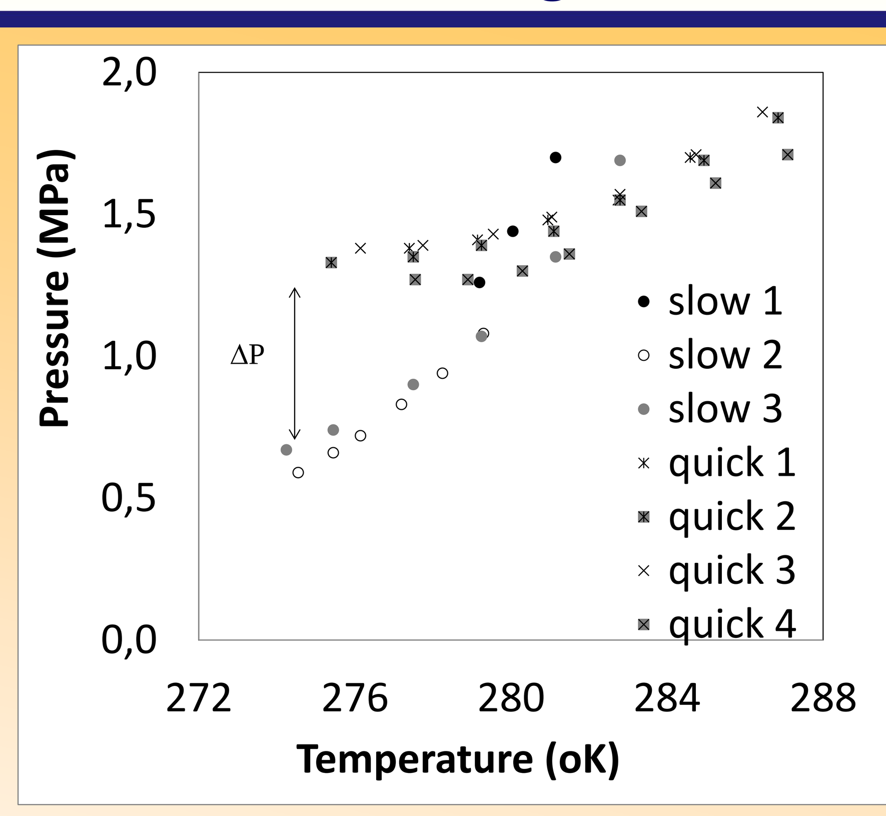


Figure 1. Experimental equilibrium data of CH_4-C_3H_8 gas hydrate at high and low driving force.

Conclusions

- ✓ Hydrate equilibria are given (T, P, gas and hydrate compositions) following two procedures.
- ✓ The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation.
- ✓ The most interesting observation is the comparison between the two procedures from the same initial conditions (same pressure, temperature, mass of water and gas mixture). The Pressures are different at each equilibrium point (temperature uncertainty ±0.5 °C, pressure uncertainty ± 0.1 bar). Figure 1 illustrates these observations.