

**EXPERIMENTAL PROCEDURE AND RESULTS TO MEASURE THE COMPOSITION  
OF GAS HYDRATE, DURING CRYSTALLIZATION AND AT EQUILIBRIUM, FROM  
N<sub>2</sub>-CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub>-C<sub>3</sub>H<sub>8</sub>-C<sub>4</sub>H<sub>10</sub> GAS MIXTURES**

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**ABSTRACT**

Gas hydrates are of great interest in petroleum industry. They are especially a flow assurance issue in deep offshore oilfields. In this study, an experimental work concerning the equilibrium of gas hydrates of light hydrocarbon molecules is proposed. 12 experiments from N<sub>2</sub>-CO<sub>2</sub>-CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub>-C<sub>3</sub>H<sub>8</sub>-C<sub>4</sub>H<sub>10</sub> gas mixtures in temperature range of [0.8-19°C] and pressure range of [1.4 – 66bars] have been carried out. 78 equilibrium points have been measured following two procedures. The first and main procedure (71 equilibrium data) corresponds to a procedure at high crystallization rate (high supersaturation, or high  $\Delta P$ ). The objective of this first procedure is to study the gas hydrates formation in usual dynamic conditions (start-up or reboot of an exploitation). The second procedure corresponds to a procedure at very low crystallization rate (7 data). The objective of this second procedure is to anticipate a further study about the thermodynamic or kinetic involvement in hydrate formation. It might also be closer to the conditions along a pipe-line at steady state. In this article, for all the points and procedures, the P-T data are given. Also, the hydrate phase molar compositions are given for most of the measured equilibria.

*Keywords:* gas hydrates, Experimental study, Thermodynamics, Hydrocarbon mixtures, Hydrate composition.

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## NOMENCLATURE

- $j$  Molecule index (as subscript)  
 $K_{H,j}^{\infty}$  Henry constant at solvent vapor pressure [Pa]  
 $M_w$  water molecular weight [g/mol.]  
 $n_j^0$  Initial number of moles of molecule  $j$  [mol.]  
 $n_j^G$  Number of moles of  $j$  in the gas phase [mol.]  
 $n_j^L$  Number of moles of  $j$  in the liquid phase [mol.]  
 $n_j^H$  Number of moles of  $j$  in the hydrate [mol.]  
 $N_{\text{hyd}}$  Hydration number  
 $P$  Pressure [bar]  
 $T$  Temperature [°C]  
 $x_j$  Mole fraction of  $j$  in the hydrate phase  
 $y_j$  Mole fraction of  $j$  in the liquid phase  
 $v_j^{\infty}$  Molar volume [ $\text{cm}^3 \cdot \text{mol}^{-1}$ ]  
 $V$  Volume [ $\text{m}^3$ ]  
 $V_R$  Volume of the reactor [ $\text{m}^3$ ]  
 $w$  Water (as subscript)  
 $z_j$  Mole fraction of  $j$  in the vapor phase  
 $\rho_H^{\beta}$  Pure clathrate (gas free) density [ $\text{kg} \cdot \text{m}^{-3}$ ]  
 $\rho_w$  Water density [ $\text{kg} \cdot \text{m}^{-3}$ ]  
 $\varphi$  Fugacity coefficient  
 $0$  initial situation (as subscript or superscript)

## INTRODUCTION

Gas hydrates are component of great interest in different fields. They are crystalline compounds that can be formed at low temperature and high pressure in presence of water and small molecules (methane, ethane, carbon dioxide...). They can be a problem, especially in the oil industry, the gas hydrates being formed in deep offshore pipes [1], or wanted (carbon dioxide capture and storage [2], air conditioning [3], etc...).

In this present study, we are focusing on gas hydrate problems in flow assurance ( $\text{CO}_2$ - $\text{CH}_4$ - $\text{C}_2\text{H}_6$ - $\text{C}_3\text{H}_8$ - $\text{C}_4\text{H}_{10}$  gas mixtures), and also on  $\text{CO}_2$  capture and storage ( $\text{N}_2$ - $\text{CO}_2$  gas mixture). For these kinds of applications, an important issue is the determination of the thermodynamic equilibrium: pressure as function of the temperature for a given global composition at fixed volume. Especially in the oil industry, there is up to now a zero tolerance policy about hydrate formation in the deep-sea pipelines. But in the near future, it will be required to operate pipe-lines inside the hydrates region at steady-state conditions. The determination of the hydrate formation area for some given gas mixtures is the start of the present study.

## GAS HYDRATES

Gas hydrates, or clathrate hydrates, are ice-like compounds composed of molecules of water and small molecules (usually small molecules of "gases", like carbon dioxide or small alkanes). They are crystalline compounds, like ice, but presenting different polymorphic structures (more like cubic packing rather than hexagonal packing). These structures may exist because of the presence of small molecules into the cavities. Three main structures are well known: SI, SII and SH (see also [4]).

## EXPERIMENTAL PROCEDURE AND SET-UP

### Experimental set-up

The target of this experimental campaign is to measure at different temperatures the composition of the hydrate phase, knowing the composition of the mixture in the cell as well as its mass.

The apparatus used for this study is drawn on figure 1. This experimental set-up is mainly composed of an instrumented batch reactor (Autoclave, 2.36 L). This reactor is fed with pure gas, or prepared gas mixture. A HPLC pump (JASCO-PU-1587) allows the liquid injection (water +  $\text{LiNO}_3$  as tracer for determining by mass balance the amount of aqueous phase in the cell at each step). A cryostat (HUBERT CC-505) allows the temperature control with  $0.02^\circ\text{C}$  accuracy, and two sapphire windows (12cm x 2cm) are placed on each sides of the reactor to survey the inside. The reactor is stirred on the upper side (vapor phase) and lower side (liquid/hydrate phase). The pressure, as well as the temperature on the upper/lower side, is monitored online with a data acquisition system (Pt 100, accuracy  $0.02^\circ\text{C}$  for the temperature, 0.1 bar accuracy for the pressure). To be able to determine the composition of each phase at the equilibrium, the gas phase composition is monitored online using a gas chromatograph (VARIAN model CP-3800 GC with a 50m PORA BOND Q column). A ROLSI<sup>TM</sup> injector is used for the sampling (a few  $\mu\text{m}^3$  each sample), and Helium is used a carrier gas. The liquid phase can be analyzed offline by ionic chromatography (DIONEX ionic exchange chromatograph). A valve allows the sampling of the liquid phase (water +  $\text{LiNO}_3$ ) with the help of the inner pressure of the reactor.

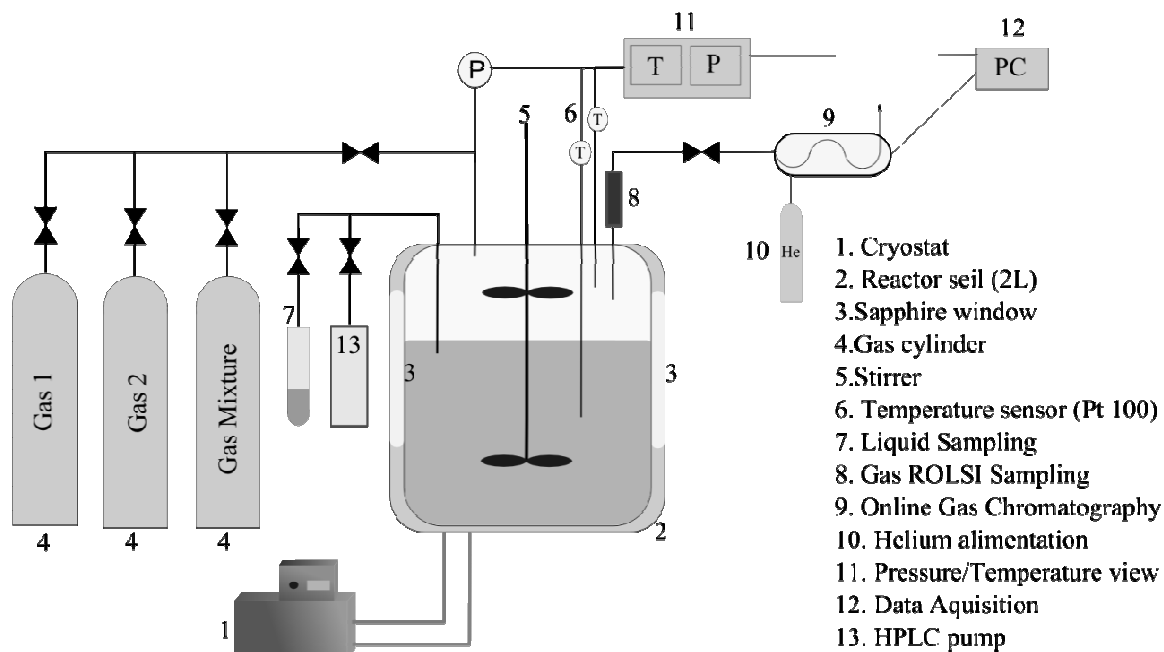


Figure 1. Experimental set-up

### Experimental procedure at high crystallization rate

The first experimental procedure is the same as in our previous studies on gas hydrates equilibrium (see [5]). In this procedure, the crystallization occurs at a “high rate” (or at a high supersaturation). At first, the reactor is cleaned and vacuum is made (for 40 minutes). Then, the cell is filled with the desired composition (see table 1) either by direct injection of the various components or from a bottle where the mixture has been prepared.

The pressure is measured, and the temperature is set to 1°C (internal regulation of the cryostat). The gas composition in the cell is checked with GC analysis before any measurement.

A 10 mg/L water mixture of LiNO<sub>3</sub> is prepared and injected (about 800g) into the reactor thanks to the HPLC pump (n°13). The water is ultrapure water (first category, 18.2 MΩ.cm). A raise of the pressure, due to the added volume of liquid, is observed. Then, the reactor is stirred at the rate of 450 rpm, on the upper side, and on the bottom. The gas is dissolving into the liquid phase, and after some time (induction time), the crystallization begins. Due to the exothermicity of the reaction, a brief raise of temperature is observed. At this point, we wait for the equilibrium to happen (no more temperature/pressure evolution). This takes about 2 to 4 days in function of the mixture and initial pressure. When the equilibrium is reached, a

sample of the gas phase is taken and injected into the gas chromatograph to determine the molar composition. A liquid sample is also taken to be analyzed *offline* by ionic chromatography (about 4.5mg). Then, the dissociation of the hydrate is started. The temperature is increased of about 1.5°C. When the new equilibrium is reached (24h), new samples of the fluid phases are taken. Then, the process is repeated until there is no longer a hydrate phase into the reactor. The whole procedure is summarized on figure 2. This procedure concerns gas mixtures n°1 to n°11.

### Experimental procedure at low crystallization rate

In this second procedure, the objective is to focus on thermodynamic equilibrium avoiding as much as possible any kinetic effect. In this procedure, the crystallization rate should be closer to the hydrate formation process in pipelines at steady state (constant evolution of the pressure and of the temperature along the pipes). The objective is to stay as close as possible to the thermodynamic equilibrium curve, in order to decrease kinetic effects on crystallization.

The pressure/temperature evolution in function of the time for the only experiment with this procedure is shown on figure 3. Instead of decreasing very quickly the temperature to the final point (between 0 and 2°C), the crystallization occurs close to the initial point in the hydrate free area. Then, the temperature is decreased very

slowly (about 0.1 to 0.2 °C per day). Every 1°C decreased samples of the gas and liquid phases are taken and analyzed. This procedure concerns only gas mixture n°12.

On the next section is explained which are the studied mixtures, and how they have been prepared.

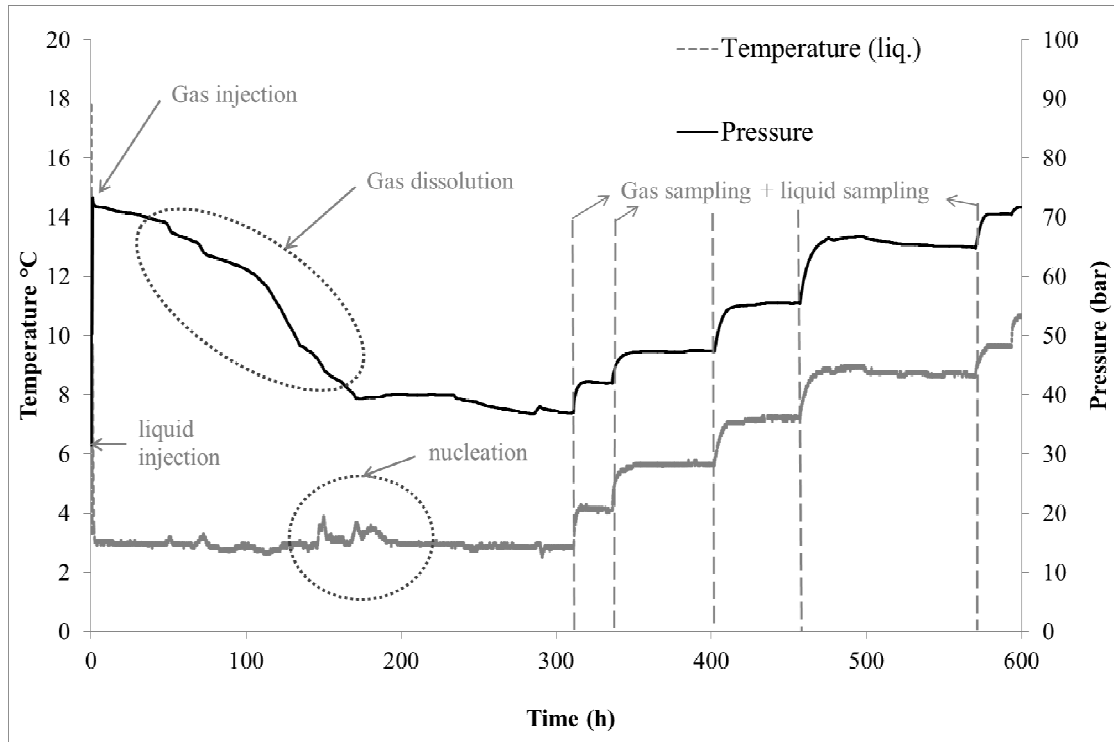


Figure 2. Pressure – Temperature evolution during equilibria experiments at high crystallization rate.

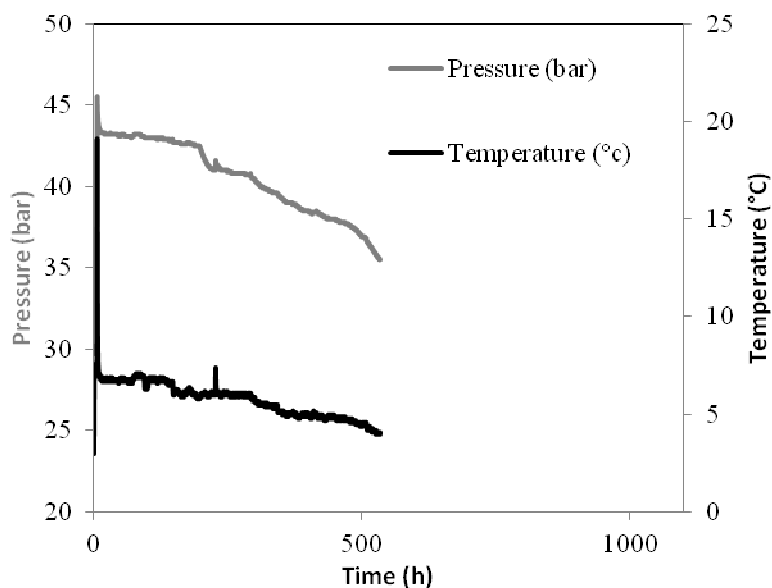


Figure 3. Pressure – Temperature evolution during equilibrium experiment at low crystallization rate.

### Gas compositions

The studied gas compositions are given in table 1. There are 12 gas mixtures from N<sub>2</sub>/CO<sub>2</sub>/C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub>/n-C<sub>4</sub>. The gases were provided by Air Liquid and Air Product (CO<sub>2</sub> premium, impurities < 60ppm, nitrogen premium impurities < 6ppm, methane 3.5, ethane 2.5, propane 3.5 and n-butane 3.5). These initial compositions were determined by GC (n°9 on figure 1).

To prepare these initial gas mixtures, two methods were applied.

For binary mixtures (gas 3 to 5), the mixtures were prepared from pure gas directly connected to the reactor. The less volatile gas (CO<sub>2</sub>) was first injected into the reactor. Then, the second one (N<sub>2</sub> or CH<sub>4</sub>) was injected. The knowledge of the

pressure after each injection, and the use of the SRK equation of state allow the calculation of the gas composition.

The second method used was a prior prepared bottle of gas directly connected to the reactor. This bottle was prepared by injecting the different gases, from the less volatile to the most volatile, and by weighting the bottle after each injection. From the injected mass of each gas, the mole composition was then calculated. In order to have a quite homogeneous mixture, the bottle is not used before a few days after the preparation.

A 20% margin from the vapor pressure was chosen in order to avoid any condensation.

Gas mixtures	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>
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 composition of the studied gas mixtures (standard deviation about 3%).

### Calculation of the three phases compositions

The calculation of the composition of each phase is a basic mass balance based on the measurements (the Li concentration in the aqueous phase, the pressure, the temperature and the gas composition):

$$n_j^g = n_j^L + n_j^H + n_j^S \quad (1)$$

### Gas phase calculation

The gas phase density (initial case and at equilibrium) is calculated by the Soave-Redlich-Kwong equation of state (SRK EoS) in the following equation:

$$PV = Z(P, T, z)n^G RT \quad (2)$$

The compressibility factor is calculated using SRK. The SRK parameters used are given in table 2.

The composition  $z$  in the SRK equation is obtained each time by GC. The initial volume of the gas is the volume of the reactor (2.36 L). The gas volume at the equilibrium is the reactor volume minus the liquid volume minus the hydrate volume. These two last volumes are calculated thanks to the ionic chromatography (see liquid phase calculation section).

In the end, the SRK EoS allows the calculation of  $n_j^g$  and  $n_j^L$ .

$j$	$T_c(K)$	$P_c(bar)$	$\omega$	$k_{(N_2/i)}$	$k_{(CO_2/i)}$	$k_{(CH_4/i)}$	$k_{(C_2H_6/i)}$	$k_{(C_3H_8/i)}$	$k_{(C_4H_{10}/i)}$
N <sub>2</sub>	126.20	34.00	0.03772	0	-0.03	0.03	0.06	0.09	0.1130
CO <sub>2</sub>	304.21	73.83	0.22362	-0.03	0	0,0933	0,1363	0,1289	0,1430
CH <sub>4</sub>	190.56	45.99	0.01155	0.03	0,0933	0	-0,0078	0,009	0,0056
C <sub>2</sub> H <sub>6</sub>	305.32	48.72	0.09949	0.06	0,1363	-0,0078	0	-0,0022	0,067
C <sub>3</sub> H <sub>8</sub>	369.83	42.48	0.15229	0.09	0,1289	0,009	-0,0022	0	-0,01
n-C <sub>4</sub> H <sub>10</sub>	425.15	37.99	0.2013	0.1130	0,1430	0,0056	0,067	-0,01	0

Table 2. SRK parameters used.

### Liquid phase calculation

The liquid phase calculation is a two steps calculation:

- The liquid volume calculation,
- The vapor-liquid equilibrium calculation.

To calculate the liquid volume, a tracer is used (LiNO<sub>3</sub>). From the Li<sup>+</sup> concentration (obtained by ionic chromatography), the liquid volume is deduced:

$$V^L = \frac{V_0^L [Li^+]_0}{[Li^+]} \quad (3)$$

Then, the number of moles in the liquid phase is calculated from the vapor-liquid equilibrium equation from Henry's law like equation:

$$n_j^L = \frac{V^L \rho_w^0 z_j \phi_j^G P}{M_w K_{H,j}^0 \exp\left(\frac{(P - P^{sat}) v_j^{G0}}{RT}\right)} \quad (4)$$

Some assumptions are made. The fugacity coefficient  $\phi$  is taken equal to the unity. The molar volume of the gases in water ( $v_j^{G0}$ ) is supposed to be 32 cm<sup>3</sup> mol<sup>-1</sup>. The Henry's constant is calculated using Holder correlation [6]:

$$K_{H,j}^0(T) = \exp\left(A + \frac{B}{T}\right) \quad (5)$$

The A and B constants are given in table 3.

Gas	A	B (K)
CO <sub>2</sub>	14.283146	-2050.3269
N <sub>2</sub>	17.934347	-1933.381
CH <sub>4</sub>	15.826277	-1559.0631
C <sub>2</sub> H <sub>6</sub>	18.400368	-2410.4807
C <sub>3</sub> H <sub>8</sub>	20.958631	-3109.3918
n-C <sub>4</sub> H <sub>10</sub>	22.150557	-2739.7313

Table 3. Constants in equation (5) [6].

The water vapor pressure in the Poynting correction is calculated using classic Duperray equation:

$$P^{sat} = \left(\frac{T}{100}\right)^4 \times P^{atm} \quad (6)$$

In the end, equation (4) allows the calculation of  $n_j^L$ .

### Hydrate phase calculation

The hydrate phase calculation comes from a mass balance (equation 1). The hydration number is also calculated.

### A few words about experimental errors

Evaluation of errors of the calculations was made and written previously (see [5]). This last evaluation led to an uncertainty on the gas phase equals to  $\Delta x/x < 3\%$  (determined from GC errors), and to an uncertainty of the hydrate phase of  $\Delta z/z < 6\%$ . In the present work, another evaluation was performed using Monte Carlo simulations. To compute these simulations, the following standard deviations of the input data were used:

- $\Delta[Li^+]/[Li^+] = 0.1\%$ ,
- $\Delta x_i/x_i = 3\%$ ,
- $\Delta T = 0.2^\circ C$ ,
- $\Delta P = 0.1$  bar,
- $\Delta m_w = 0.1$  g,
- $\Delta m_w$  (sampled) = 0.1 g,
- $\Delta V_R = 3\%$ ,
- $\Delta \rho_w = 10$  kg.m<sup>-3</sup>,
- $\Delta \rho_H^\beta = 40$  kg.m<sup>-3</sup>.

Also, the following assumptions were done:

- $P_w = 1000$  kg/m<sup>3</sup>.
- $\rho_H^\beta = 790$  kg/m<sup>3</sup>.

The simulations were done 1000 times each point, and the molar fraction errors on the hydrate composition were found to be usually inferior to 4%. The standard deviation close to the total dissociation point was calculated to be between 20% and 100%. Indeed, the initial and final  $\text{Li}^+$  concentrations for these points are very close.

## EXPERIMENTAL RESULTS

### Main results

The experimental results are presented in tables 4, 5 and 6. Tables 4 and 5 correspond to the first procedure (high crystallization rate). Table 6 corresponds to the second procedure (low crystallization rate).

All these tables give the equilibrium pressure and temperature. They also give the gas molecules compositions in the gas phase and in the hydrate phase (except for Gas 6 and 7 that suffered from analysis problems).

Concerning the Pressure/Temperature results, all the experimental data could not be compared to the data in the literature (difficulty to find the same gas composition). However, the obtained results for pure gases ( $\text{CO}_2$  and  $\text{CH}_4$ ) are in accordance with the literature (see figures 4 and 5). This validates the procedure for PT data.

Concerning the gas mixtures results, the errors are usually inferior to 4%. This last calculation tends to validate the results. Another study of this last issue from a theoretical point of view is suggested in another article in the same issue (see [11]).

Comparing the two procedures (gas 8 and 12, "same" initial global composition), the PT data are a bit different (about  $1.5^\circ\text{C}$  at same equilibrium pressure). The equilibrium temperature is higher at low crystallization rate (see at 35.6 bars and 37.75 bars). Also, the enclathration of  $\text{C}_2\text{H}_6$  is also more important (mole fractions two times higher) while the molar fraction of  $\text{CH}_4$  is lower. These

observations highlight the kinetic effects on hydrate formation. This observation led to an analysis from a theoretical point of view, using thermodynamic and kinetic modeling. This last work is presented in another article (see [11]).

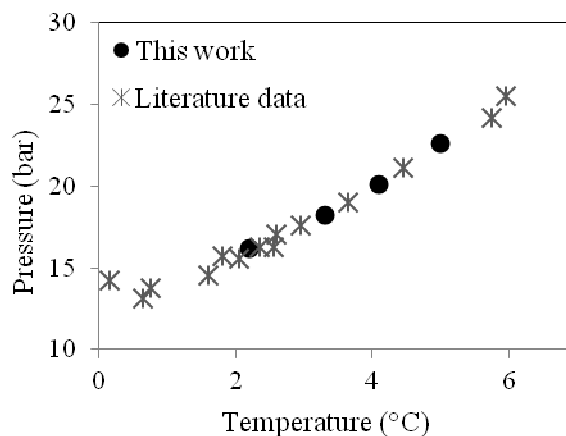


Figure 4. Experimental and literature [7,8,9] equilibrium data of pure  $\text{CO}_2$  gas hydrates.

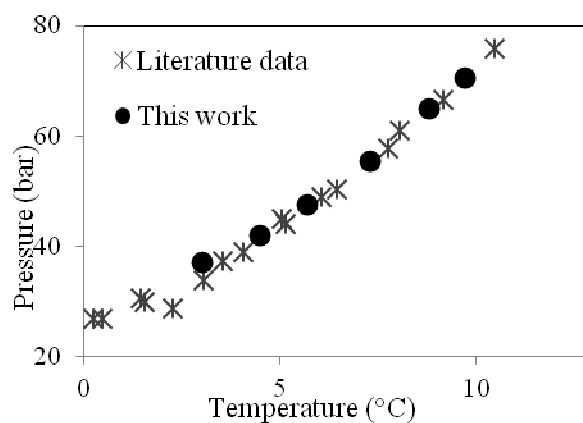


Figure 5. Experimental and literature [8,9,10] equilibrium data of pure  $\text{CH}_4$  gas hydrates.

Gas	P ( $\pm 0.1$ bar)	T ( $\pm 0.2$ °C)	Molar gas fraction (Std. Dev. $\approx 3\%$ )					Molar hydrate fraction (Std. Dev. $< 4\%$ )				Nhyd	
			N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>		C <sub>3</sub> H <sub>8</sub>
1	16.2	2.2	-	1	-	-	-	-	1	-	-	-	5.58
	18.2	3.3	-	1	-	-	-	-	1	-	-	-	6.42
	20.1	4.1	-	1	-	-	-	-	1	-	-	-	7.28
	22.6	5	-	1	-	-	-	-	1	-	-	-	7.03
2	37	3	-	-	1	-	-	-	-	1	-	-	3.34
	42	4.5	-	-	1	-	-	-	-	1	-	-	3.57
	47.4	5.7	-	-	1	-	-	-	-	1	-	-	3.40
	55.4	7.3	-	-	1	-	-	-	-	1	-	-	3.22
	64.9	8.8	-	-	1	-	-	-	-	1	-	-	2.88
	70.5	9.7	-	-	1	-	-	-	-	1	-	-	1.96
3	33.3	3.4	-	0.127	0.874	-	-	-	0.290	0.710	-	-	5.51
	35.3	4.4	-	0.134	0.866	-	-	-	0.289	0.711	-	-	6.10
	37.1	4.9	-	0.141	0.859	-	-	-	0.288	0.712	-	-	6.07
	40.3	5.8	-	0.151	0.849	-	-	-	0.284	0.716	-	-	6.24
	44.5	6.8	-	0.163	0.837	-	-	-	0.277	0.723	-	-	6.49
	49.3	7.8	-	0.175	0.825	-	-	-	0.258	0.742	-	-	6.08
	56	9	-	0.184*	0.817*	-	-	-	0.230*	0.770*	-	-	-*
4	29.1	2.2	-	0.120	0.880	-	-	-	0.292	0.708	-	-	5.69
	29.7	2.5	-	0.129	0.871	-	-	-	0.282	0.718	-	-	6.53
	31.8	3.6	-	0.135	0.865	-	-	-	0.283	0.717	-	-	6.53
	34.7	4.5	-	0.147	0.853	-	-	-	0.270	0.730	-	-	6.95
	38	5.2	-	0.162	0.838	-	-	-	0.226	0.774	-	-	7.36
	41.6	6.4	-	0.177	0.823	-	-	-	0.097	0.903	-	-	8.84
	56.3	9.5	-	0.225*	0.775*	-	-	-	-*	-*	-	-	-*
5	24.6	2.46	0.333	0.667	-	-	-	0.026	0.974	-	-	-	5.05
	26	2.6	0.311	0.689	-	-	-	0.029	0.971	-	-	-	4.85
	26.6	2.66	0.301	0.699	-	-	-	0.032	0.968	-	-	-	4.80
	28.7	2.87	0.277	0.723	-	-	-	0.034	0.966	-	-	-	3.39
	31.3	3.13	0.253*	0.747*	-	-	-	0.034*	0.966*	-	-	-	2.84*
6**	30.7	2.2	-	-	-	-	-	-	-	-	-	-	
7**	27.1	1	-	0.034	0.955	0.012	-	-	-	-	-	-	-
	27.6	1.4	-	0.035	0.953	0.013	-	-	-	-	-	-	-
	28.3	2	-	0.035	0.951	0.014	-	-	-	-	-	-	-
	28.8	2.5	-	0.035	0.948	0.017	-	-	-	-	-	-	-
	28.9	2.8	-	0.036	0.946	0.019	-	-	-	-	-	-	-
	29.3	3.3	-	0.035	0.944	0.021	-	-	-	-	-	-	-
	30.2	4	-	0.035	0.939	0.026	-	-	-	-	-	-	-
	30.6	5	-	0.036	0.936	0.028	-	-	-	-	-	-	-
	30.6	5.8	-	0.036*	0.936*	0.029*	-	-	-	-	-	-	-

Table 4. Experimental data (Gas 1 to 7)

\* equilibrium points near total dissociation, hydrate composition errors close to 100%

\*\* some composition data unavailable



Gas	P ( $\pm 0.1$ bar)	T ( $\pm 0.2$ °C)	Molar gas fraction (Std. Dev. $\approx 3\%$ )					Molar hydrate fraction (Std. Dev. $< 4\%$ )					N <sub>hyd</sub>
			CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	
8	35.4	2.75	0.025	0.964	0.011	-	-	0.070	0.888	0.042	-	-	5.44
	38.1	3.65	0.028	0.959	0.013	-	-	0.070	0.888	0.042	-	-	6.50
	42.3	5.15	0.031	0.952	0.017	-	-	0.069	0.891	0.041	-	-	6.69
	45.6	6.55	0.033	0.948	0.020	-	-	0.070	0.891	0.040	-	-	6.51
	51.2	7.8	0.035	0.943	0.021	-	-	0.068	0.890	0.043	-	-	6.52
	59.9	9.25	0.042	0.937	0.021	-	-	0.035	0.898	0.067	-	-	7.57
	64.3	10.7	0.044	0.933	0.023	-	-	-0.04*	0.95*	0.09*	-	-	3.66*
	65.7	12.05	0.044	0.928	0.028	-	-	-0.10*	1.08*	0.01*	-	-	0.11*
9**	31.3	2.5	-	0.994	0.004	0.002	-	-	0.888	0.067	0.045	-	5.95
	33.6	3.3	-	0.993	0.005	0.002	-	-	0.873	0.076	0.052	-	6.09
	35.5	4.15	-	0.992	0.006	0.002	-	-	0.859	0.083	0.058	-	6.84
	36.7	4.95	-	0.990	0.008	0.003	-	-	0.850	0.086	0.064	-	6.28
	37.8	6.3	-	0.986	0.010	0.004	-	-	0.849	0.085	0.066	-	7.53
	39.4	7.7	-	0.982	0.013	0.005	-	-	0.844	0.085	0.071	-	8.34
	42.1	9.1	-	0.975	0.019	0.006	-	-	0.821	0.085	0.095	-	7.48
	43.4	10.1	-	0.972	0.021	0.008	-	-	0.809	0.085	0.105	-	8.54
	45	11.15	-	0.968	0.023	0.009	-	-	0.781*	0.086*	0.133*	-	11.09*
10	22.8	2.4	-	0.971	0.017	0.004	0.008	-	0.731	0.107	0.113	0.049	6.56
	23.1	3.45	-	0.968	0.019	0.005	0.008	-	0.734	0.105	0.113	0.049	8.01
	27.5	7.6	-	0.942	0.035	0.008	0.015	-	0.706	0.102	0.143	0.049	6.96
	29.7	9.15	-	0.930	0.041	0.012	0.017	-	0.681	0.102	0.166	0.051	5.31
	30.5	9.9	-	0.923	0.044	0.015	0.018	-	0.682	0.099	0.170	0.050	5.85
	31.2	10.8	-	0.915	0.046	0.020	0.019	-	0.688	0.096	0.166	0.050	7.23
	32.2	11.7	-	0.906	0.048	0.026	0.021	-	0.692	0.096	0.163	0.049	8.27
	33.4	12.65	-	0.896	0.050	0.032	0.022	-	0.699	0.094	0.158	0.049	9.63
	34.6	13.65	-	0.888	0.052	0.037	0.023	-	0.699	0.094	0.158	0.050	10.29
	34.8	14.7	-	0.887	0.052	0.038	0.023	-	0.700	0.092	0.158	0.050	10.06
	35.2	15.65	-	0.885	0.053	0.039	0.023	-	0.702	0.090	0.160	0.048	12.66
	36.1	16.6	-	0.879	0.054	0.042	0.024	-	0.705	0.086	0.160	0.049	14.87
	38.1	17.7	-	0.863	0.057	0.054	0.026	-	0.91*	0.05*	0.01*	0.03*	49.86*
38.2	18.6	-	0.863	0.057	0.054	0.026	-	0.91*	0.05*	0.01*	0.03*	41.99*	
11	21.4	2.75	-	0.955	0.024	0.007	0.014	-	0.728	0.079	0.153	0.040	7.23
	21.6	4.3	-	0.955	0.024	0.007	0.014	-	0.726	0.080	0.154	0.040	7.21
	21.8	4.85	-	0.953	0.025	0.009	0.014	-	0.726	0.080	0.154	0.040	7.28
	22.1	5.9	-	0.951	0.025	0.010	0.014	-	0.724	0.080	0.155	0.041	7.22
	22.6	6.8	-	0.948	0.027	0.011	0.014	-	0.721	0.080	0.157	0.041	7.05
	23.6	7.45	-	0.939	0.031	0.015	0.016	-	0.718	0.078	0.163	0.041	7.31
	25.3	9.2	-	0.926	0.035	0.022	0.017	-	0.714	0.076	0.169	0.041	7.48
	28.2	11.05	-	0.905	0.042	0.032	0.021	-	0.706	0.070	0.185	0.040	8.10
	37.2	18.15	-	0.845	0.050	0.078	0.027	-	0.98*	0.04*	-0.02*	-0.01	28.64*

Table 5. Experimental data (Gas 8 to 11)

\* equilibrium points near total dissociation, hydrate composition errors close to 100%

\*\* hydrate composition uncertainties  $\approx 10\%$  for  $C_2H_6$  and  $C_3H_8$

Gas	P ( $\pm 0.1$ bar)	T ( $\pm 0.2$ °C)	Molar gas fraction (Std. Dev. $\approx 3\%$ )			Molar hydrate fraction (Std. Dev. $< 4\%$ )			Nhyd
			CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	
12	41.7	6.2	0.037	0.943	0.021	0.117*	0.669*	0.214*	35.50*
	37.75	4.6	0.035	0.951	0.014	0.081	0.799	0.121	10.27
	35.6	4.2	0.034	0.952	0.014	0.081	0.828	0.091	9.52
	31.8	3.25	0.033	0.957	0.010	0.075	0.850	0.076	6.65
	30.4	2.45	0.031	0.959	0.009	0.077	0.854	0.070	5.60
	27.6	1.3	0.030	0.963	0.007	0.075	0.862	0.063	5.71
	35.7	4.2	0.037	0.948	0.015	0.061	0.843	0.096	6.50

Table 6. Experimental data (Gas 12, low crystallization rate).

\* equilibrium points near total dissociation, hydrate composition errors close to 100%

## CONCLUSION

Gas hydrates equilibrium experiments of hydrocarbon gas mixtures ( $N_2$ - $CO_2$ - $CH_4$ - $C_2H_6$ - $C_3H_8$ - $C_4H_{10}$ ) were performed in an instrumented batch reactor. In this study, both classic pressure/temperature equilibrium data but also molar compositions (gas phase and hydrate phase) are given. The results for pure gases are in accordance with literature data, which comfort the use of the present procedure. The molar composition results for gas mixtures present uncertainties inferior to 4% (for both gas phase and hydrate phase).

The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation. For example, the enclathration of the bigger molecule (ethane) is more important at low crystallization rate. The equilibrium temperature seems to be also different.

In the end, in this work, a modeling part was not added since it is the subject of another work. In this other work, based on a kinetic consideration (see [12]), there is a questioning about the validity of these measurements as thermodynamic measurements (but as kinetic measurements). This is why the presents data were analyzed using a thermodynamic model in an in-house software to discuss the possibility to crystallize gas hydrate at thermodynamic equilibrium at a high crystallization rate (see [11]).

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