

# Influence of the crystallization rate on the mixed hydrate: experimental and modelling work

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## Abstract

The determination of the volume and precise composition of clathrate hydrates is raising importance with respect to the possible industrial applications of the gas separation and storage and due to lack of data in literature. Therefore, in this work, the volume and composition of hydrate phase during the crystallization and final state, regarding to the rate of crystallization have been investigated. A thermodynamic model, implementing classic van der Waals and Platteeuw model, was also used. The results show that from the same initial conditions, the final pressure, hydrate composition and water conversion are slightly different for two different crystallization processes.

## Introduction

Clathrate hydrates or gas hydrates are crystalline solids composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules. Typical natural gas molecules include methane, ethane, propane, and carbon dioxide. All common natural gas hydrates belong to the three crystal structures, cubic structure I, cubic structure II, or hexagonal structure H [1].

Although clathrate hydrate formation in the oil and gas industry, from extraction to transportation, is a crucial issue, several applications of clathrate hydrates have been recently investigated, like water desalination, carbon capture and storage, air conditioning, or even planetary science [2]–[5]. Moreover, enormous amounts of methane hydrate have been found in the world's oceans and Polar Regions [6]. Hence, it is obvious that studying the thermodynamics and the crystallization mechanisms of clathrate hydrates is really inevitable to investigate gas hydrate phenomena. The determination of the gas composition in hydrate phase, as well as its volume, is also a technical challenge. However gas hydrate from hydrocarbon gas mixtures has been widely studied, but few data involving propane and butane are available. Moreover, these studies do not provide the hydrate volume and water consumption [7].

It is also impractical to perform experiments for each and every composition of gas mixtures, therefore developing reliable modelling is of great importance. In most cases, classical van der Waals and Platteeuw model were used by implementing Kihara parameters. But Kihara parameters depend significantly on the quality of experimental data as well as the reference thermodynamic properties [8].

So in this work, several experiments on a methane-propane mixture were performed to obtain gas composition in hydrate phase and volume of hydrate, as well as classic Pressure-temperature at equilibrium. This document also adds the impact of the crystallization rate on the results, based on two different experimental procedures; quick crystallization process and slow crystallization process. The results then compared to the classical van der Waals and Platteeuw model [9].

## Experimental section

### Experimental set-up

For performing the experiments, two apparatus ACACIA and SECOHYA have been used. They have almost the same characterizations and specification. The SECOHYA reactor consists of a 2.36 liter (ACACIA 2.44 liter) autoclave reactor in which the pressure can reach up to 100 bars. The reactors are equipped with two vertical stirrers with four blades, one in the liquid and one in the gas. The temperature is controlled by a double jacket in which is circulated a fluid at constant temperature from a cryostat HUBERT CC-250. The liquid is injected in the reactor under pressure by using a HPLC pump (JASCO). Temperature is monitored by two Pt100 probes, one in the gas phase and the other one in the liquid phase. A ROLSI sampler is mounted on the reactor. It allows to sampling online the gas and to sending the sample into a gas chromatograph (GC Varian model 38002) equipped with a TCD

detector and two columns PoraBOND Q and CP-Molsieve. The peak integration is possible with software provided by Varian Galaxie. Another sampling system can exit the liquid phase through a mechanical valve and a capillary tube. The liquid is analyzed off-line by ion chromatography. The data acquisition is controlled on the personal computer. The schematic diagram of the apparatus is shown in Figure 1.

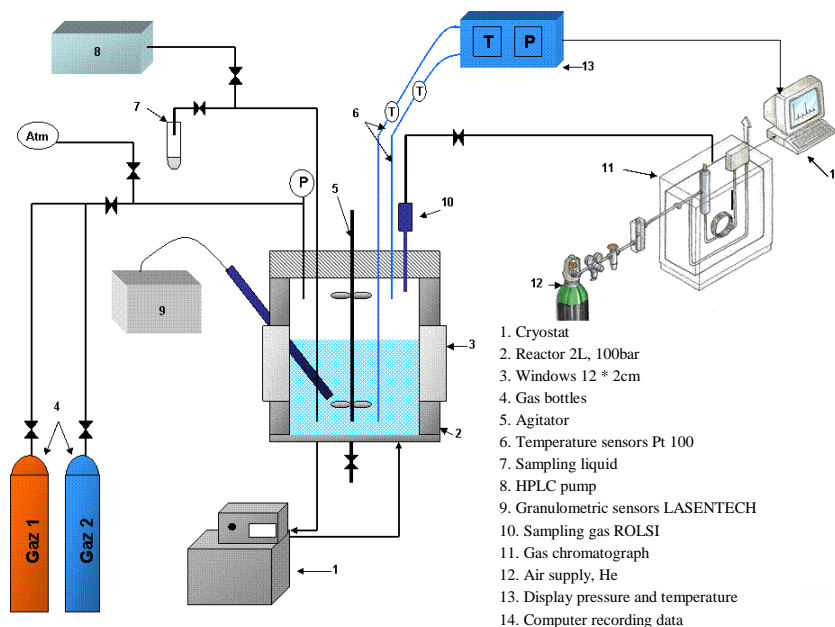


Figure 1: The schematic diagram of the apparatus

### Experimental procedure at quick crystallization process

The first experimental procedure is the same as in our previous studies on gas hydrates equilibria [7], [8]. In this procedure, the crystallization occurs at a “high rate” (or at a high supersaturation).

At first, the reactor is cleaned and vacuumed (for 40-50 minutes). Then, the cell is filled with the gas mixture. 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 800-1000g) into the reactor thanks to the HPLC pump. 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 400 rpm, on the gas upper side, and on the liquid bottom side. The gas is dissolving into the liquid phase, and after some 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 (no more temperature and pressure time evolution). As 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 2-3mg). Then, the dissociation of the hydrate is started. The temperature is increased of about 1-2°C. When the new equilibrium is reached, 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 2a.

### Experimental procedure at slow crystallization process

In this procedure, from the initial state, the temperature is decreased slowly, so the crystallization starts near the first liquid-hydrate equilibrium temperature. The temperature is then decreased very slowly (0.3°C/12hours). At several steps, gas and liquid samples are taken and they are analyzed by gas-chromatograph and ion-chromatograph, respectively. The aim of this procedure is to focus on the thermodynamic equilibrium conditions (ignoring the kinetic effects) which are close to hydrate formation in pipelines. A schematic diagram of this procedure is illustrated in Figure 2b.

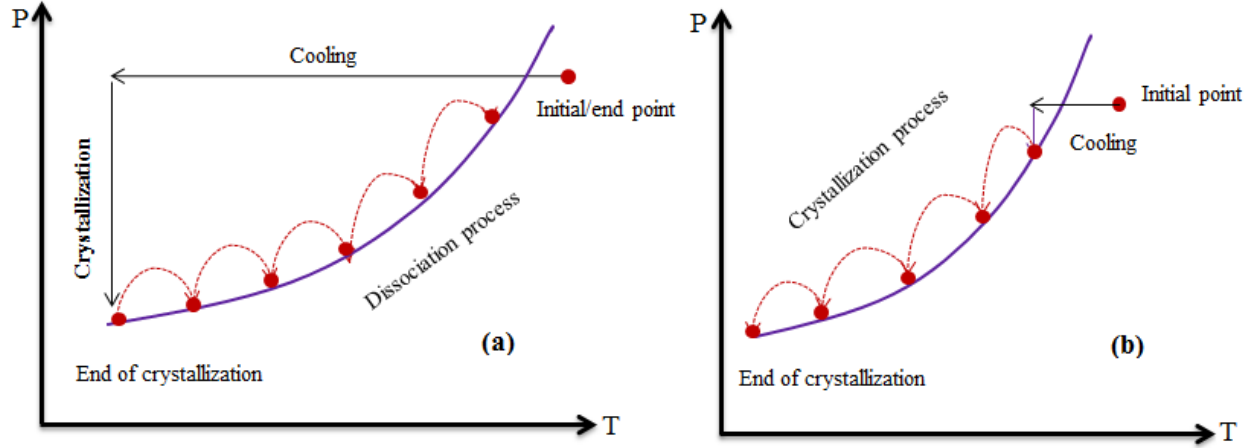


Figure 2: Schematic diagram of the experimental procedures:  
a) Quick crystallization process. b) Slow crystallization process

### Phase compositions

The composition of each phase is calculated based on a mass balance with respect to the experimental measurements including pressure, temperature, gas composition and lithium concentration in the liquid phase. The procedure of the calculations has been reported in detail by our team [8].

### Modelling section

Classic van der Waals and Platteuw model was used for the description of the hydrate phase, leading to the standard liquid hydrate equilibrium (LHE) equation [9];

$$\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta} \quad (1)$$

where  $\Delta\mu_w^{H-\beta}$ ,  $\Delta\mu_w^{L-\beta}$  are the differences of the chemical potentials between water in hydrate or liquid phase and water in the reference phase, and they can be described by statistical thermodynamics and means of relations from classical thermodynamics, respectively.  $\beta$  is a hypothetical phase that corresponds to the empty cavities.

where  $\beta$  is a hypothetical phase that corresponds to the empty cavities.  $\Delta\mu_w^{L-\beta}$  is the difference of chemical potentials between water in liquid phase and water in the reference phase and it can be described by means of relations from classical thermodynamics as following:

$$\Delta\mu_w^{L-\beta} = T \frac{\Delta\mu_w^{L-\beta}|T^0, P^0}{T^0} - T \int_{T^0}^T \frac{\Delta h_w^{L-\beta}|P^0}{T^2} dT + \int_{P^0}^P \Delta v_w^{L-\beta}|T^0 dp - RT \ln a_w^L|T, P \quad (2)$$

$\Delta\mu_w^{L-\beta}|T^0, P^0$  and  $\Delta h_w^{L-\beta}|P^0$  are thermodynamic properties of the liquid phase compared to reference b phase.  $a_w^L$  is also the activity of water in the liquid phase.

$\Delta\mu_w^{H-\beta}$  is the difference of chemical potentials between water in hydrate phase and water in the reference phase and it can be described by statistical thermodynamics as following:

$$\Delta\mu_w^{H-\beta} = RT \sum_i v_i \ln \left( 1 - \sum_j \theta_j^i \right) \quad (3)$$

$v_i$  is the number of cavities and  $\theta_j^i$  is the occupancy factor. The occupancy factor can be described based on Langmuir adsorption theory [10]:

$$\theta_j^i = \frac{C_{ji} f_j(T, P)}{1 + \sum_j C_{ji} f_j(T, P)} \quad (4)$$

$C_{ji}$  is the Langmuir constant and can be expressed from a symmetrical potential:

$$C_j^i = \frac{4\pi}{kT} \int_0^\infty \exp\left(-\frac{w(r)}{kT}\right) r^2 dr \quad (5)$$

$w(r)$  is the potential interaction between the cavity and gas according to the distance  $r$ . It can be calculated from different method, but Kihara potential has been mostly used:

$$w(r) = 2z\epsilon \left[ \frac{\sigma^{12}}{R^{11}r} \left( \delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left( \delta^4 + \frac{a}{R} \delta^5 \right) \right] \text{ with } \delta^N = \frac{1}{N} \left[ \left( 1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left( 1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (6)$$

$a$  is a spherical hard-core radius, representing the guest molecule as a spherical hard-sphere. Its value is calculated from results of viscosity measurement [11], and also from values of the second virial coefficient [12].  $a$  is considered as a reliable parameter of general validity that does not need to be fitted again.  $\sigma$  represents the distance from the cavity center at which the interaction potential  $w$  is zero, whereas  $\epsilon$  stands for the maximum attractive potential and they are considered as fitting parameters. In case of gas hydrate equilibria involving a single gas component only the fitting has to be performed at least against equilibrium data of pressure and temperature. If the parameter adjustment is to be carried out on hydrate equilibrium data involving binary gas mixtures, ideally both the gas as well as the hydrate stoichiometry has to be taken into account [8], [13].

## Results and discussion

As it was mentioned, two sets of experiments based on different crystallization rates (Quick and slow) were performed. The initial conditions were almost the same to compare better the results and they are presented in Table 1.

Table 1: Initial condition for the experiments

Gas composition (%)		Reactor volume (L)	Water injected (g)	Initial pressure (bar)	Initial temperature (°C)
CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>				
86.14	13.86	2.36	801.37	16.8	10.9

First of all, pressure-temperature experimental results for two different methods are presented in Figure 3. As it is clear on the figure, the final pressure is not the same and it is slightly different. And also for a given temperature, the equilibrium pressure at slow crystallization process is higher than quick crystallization process (For example at 7.9°C and 10.3°C).

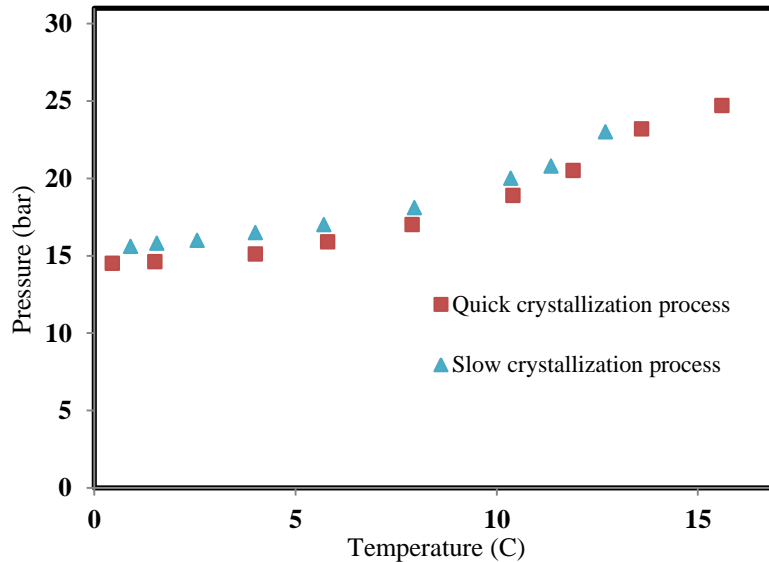


Figure 3: The comparison between the results of equilibrium points for a mixture of methane-propane and two different crystallization rates.

Table 2 shows the gas composition in gas and hydrate phase, water conversion and hydrate volume with respect to each equilibrium points for two different crystallization methods.

Table 2: Experimental data for two different crystallization methods

Method	P (bar)	T (°C)	Molar gas fraction		Molar hydrate fraction		Water conversion (%)	Hydrate volume (cc)
			CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>		
Quick crystallization rate	14.5	0.45	0.9928	0.0072	0.6906	0.3094	20.4919	207.8688
	14.6	1.5	0.9911	0.0089	0.6877	0.3123	16.1130	162.6757
	15.1	4	0.9842	0.0158	0.6851	0.3149	15.6439	157.0567
	15.9	5.8	0.9746	0.0254	0.6754	0.3246	13.9910	139.7892
	17	7.9	0.9624	0.0376	0.6608	0.3392	12.6964	126.2632
	18.9	10.4	0.9388	0.0612	0.6375	0.3625	11.1793	110.5444
	20.5	11.9	0.9192	0.0808	0.6112	0.3888	9.8015	96.3486
	23.2	13.6	0.8900	0.1100	0.4377	0.5623	7.3016	71.3477
Slow crystallization rate	20.8	11.35	0.9264	0.0736	0.5588	0.4412	5.3229	53.6249
	20	10.35	0.9364	0.0636	0.5744	0.4256	6.0342	60.4158
	18.1	7.95	0.9641	0.0359	0.6016	0.3984	8.2310	81.9044
	17	5.7	0.9795	0.0205	0.6136	0.3864	8.5663	84.7816
	16.5	4	0.9860	0.0140	0.6218	0.3782	- <sup>a</sup>	- <sup>a</sup>
	16	2.55	0.9907	0.0093	0.6271	0.3729	11.0690	108.2102
	15.8	1.55	0.9927	0.0073	0.6292	0.3708	12.6918	123.3355
	15.6	0.9	0.9938	0.0062	0.6289	0.3711	- <sup>a</sup>	- <sup>a</sup>

<sup>a</sup> Analyses error

One of the most interesting observations in Table 2, is the enclathration of propane. As the table presents, at the final state, the composition of propane in hydrate phase at slow crystallization process is larger than quick crystallization process. It shows that in a hydrocarbon mixture at slow crystallization rate, enclathration of heavier hydrocarbon is more important. The second observation is that the water conversion in slow crystallization is lower than quick crystallization. It means that less crystals of hydrate formed (Last column is Table 2), and more occupation of cavities occurred. Based on these observations, it can be concluded that the driving force for hydrate crystallization has a significant impact on the enclathration of guest molecules and their selectivity.

Liquid-hydrate calculations have been implemented in our in-house software, “GasHyDyn”. The results of simulations of gas composition in hydrate phase compared to experimental results and presented in Table 3.

The results show that the simulation of gas composition in hydrate phase has the better accordance for slow crystallization process. For example the mean deviation of methane composition in hydrate phase for slow and quick crystallization processes is 4.97% and 9.70%, respectively. It should be noticed that experimental results of hydrate composition is an average value. Also, for the mixture including heavier hydrocarbon like propane and n-butane, it is more difficult to implement the liquid-hydrate equilibrium since their Kihara parameters could not be fitted.

Based on the results, it can be supposed that in slow crystallization process the hydrate crystal are more homogenous, but at quick crystallization process which the driving force is high, kinetic could be dominant more than thermodynamic. During hydrate crystallization, the mass transfer could be significant in most of steps. Due to driving force, contact surface and mass transfer coefficients, gas dissolution in the liquid phase is a limiting step. It leads to the change the gas concentration in liquid phase and as a result, different driving force for the crystallization [14]. Herri et al. suggested that the kinetic consideration have significant effect on the enclathration of guest molecules. Depending on the rate of enclathration, and the crystal growth speed, the final composition of the mixed hydrate could be different [15].

Table 3: Gas composition in hydrate phase, experimental and predicted results

Method	P (bar)	T (°C)	Exp. hydrate compositions		Predicted hydrate compositions	
			CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>
Quick crystallization rate	14.5	0.45	0.6906	0.3094	0.6476	0.3524
	14.6	1.5	0.6877	0.3123	0.6441	0.3559
	15.1	4	0.6851	0.3149	0.6354	0.3646
	15.9	5.8	0.6754	0.3246	0.6290	0.3710
	17	7.9	0.6608	0.3392	0.6262	0.3738
	18.9	10.4	0.6375	0.3625	0.6231	0.3769
	20.5	11.9	0.6112	0.3888	0.6217	0.3783
	23.2	13.6	0.4377	0.5623	0.6203	0.3797
				Dev %	9.70%	13.41%
Slow crystallization rate	20.8	11.35	0.5588	0.4412	0.6219	0.3781
	20	10.35	0.5744	0.4256	0.6221	0.3779
	18.1	7.95	0.6016	0.3984	0.6274	0.3726
	17	5.7	0.6136	0.3864	0.6328	0.3672
	16.5	4	0.6218	0.3782	0.6387	0.3613
	16	2.55	0.6271	0.3729	0.6462	0.3538
	15.8	1.55	0.6292	0.3708	0.6509	0.3491
	15.6	0.9	0.6289	0.3711	0.6544	0.3456
				Dev.	4.97%	7.34%

## Conclusion

During the last decade, our “GasHyDyn” team has measured equilibrium data for many gas mixtures, and this document adds new data involving propane based on two different experimental procedures; quick crystallization process and slow crystallization process. The gas composition in hydrate phase is a new challenge and there is few experimental data available in literature. Hence, based on a new approach in our laboratory, the molar composition of each phase (Gas, liquid and hydrate phases) as well as hydrate volume and water conversion has been also investigated. To evaluate the importance of kinetic effects on hydrate formation, a thermodynamic model, implementing classic van der Waals and Platteuw model, were used. The results show that the equilibrium pressure for a given temperature is slightly different. The Volume of hydrate and also water conversion in quick crystallization process is larger than slow crystallization rate. Moreover, in a hydrocarbon mixture at slow crystallization rate, enclathration of heavier hydrocarbon is more important. Furthermore, the thermodynamic simulation of hydrate phase has a better accordance with the results of slow crystallization rate. On the other hand, it can be concluded that mixed hydrate equilibrium could not be at thermodynamic equilibrium.

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