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Framework for Clathrate Hydrate Flash Calculations and Implications on the Crystal Structure and Final Equilibrium of Mixed Hydrates

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Abstract

Clathrate hydrates, usually called gas hydrates, are compounds of great interest in oil industry, as well as in gas separation and storage, water purification etc... Like many other compounds that phase change, in this case from liquid water to non stoichiometric crystalline compound, modeling is required to understand and optimize the processes that involve them.

Therefore, the classic thermodynamic equilibrium model is combined with mass balance calculations during gas hydrate crystallization. Two frameworks for performing clathrate hydrate thermodynamic flash calculations at constant volume are presented and compared to experimental results at low crystallization rate. The inputs are the quantity of mass (water and gas molecules), and the volume. The variable is temperature (three phases thermodynamic flash at a given temperature), while the volume is kept constant.

The first framework suggests that the hydrate phase is growing at local thermodynamic equilibrium, without any reorganization of its content of the occupancy of the cavities. In the second framework, the hydrate phase can reorganize itself during growth (locally or completely). These frameworks are investigated, as well as the impact of the Kihara parameters uncertainties.

These frameworks calculate well the final pressure, hydrate composition. In addition, the hydrate volume and mole amount in each phase is provided with reasonable accuracy. Note: uncertainties on the final pressure and hydrate volume are below 5%. Moreover, the results are quite sensitives to

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the value of the Kihara parameters, demonstrating the importance of their values for a given computer code.

This work provides a more realistic and comprehensive view of gas hydrate crystallization.

Keywords: Thermodynamics, Crystallization, Clathrate hydrates, Flash calculations

1. Introduction

Clathrate hydrates (also called gas hydrates) are crystalline water-based solids that resemble water ice, in which small molecules (typically gases) are trapped inside cavities of hydrogen bonds. They form under high pressure (few to tens Mpa) at low temperature (usually under 20 °C), and cover vast areas of the ocean floor for example. These gas molecules, or guest molecules, are captured in these cavities. These cages are stabilized by van der Waals forces. Thanks to these forces, the clathrate hydrate structure is made possible. Note that recently Falenty et al.[1] managed to form empty SII clathrate hydrates at 145K.

As crystals, different polymorphic forms are known and were studied in the past [2]. There are three main structures: SI, SII and SH, composed of different kind of cavities, surrounded by differing polyhedra sharing faces. Jeffrey [3] suggested the nomenclature e^f to describe the polyhedra (where e is the number of edges, and f the number of faces). The polymorphic forms exhibit different densities with differences in terms of thermodynamic equilibrium. Most important, the kind of guest molecules impacts the polymorphic form to be crystallized. In addition, for a given gas mixture, the occupancy of the cavities is not stoichiometric.

Clathrate hydrates are an crucial issue in many fields, from oil & gas industry [4, 5], to carbon capture and storage [6], air conditioning [7], or even planetary science [8]. They have an enormous potential as an energy resource because of the tremendous quantity of methane trapped within them[9]. Understand that hydrate plugs in deep-sea pipelines probably pushed the worldwide study of clathrate hydrates into being. Hydrate management, or “flow assurance”, in the petroleum industry is a complex technical challenge. Hydrate plugs can have catastrophic consequences, stopping the oil production for days or weeks, with the difficulty of dissociating the hydrate crystals. There are many solutions to this problem, such as kinetic or thermodynamic

additives, or just employing avoidance techniques[10]. In the case of kinetic additives, the aim is to slow down the hydrate nucleation and growth (KHI, for “Kinetic Hydrate Inhibitor”), or to avoid agglomeration (AA, for “Anti-Agglomerant”). In thermodynamic additives (usually alcohols, such as methanol), the objective is to change the thermodynamic equilibrium itself, and avoid the hydrate zone.

To investigate hydrate avoidance, and/or thermodynamic inhibitors, both the understanding of the thermodynamics and the crystallization mechanisms of clathrate hydrates are required. While a thermodynamic model exists to simulate clathrate hydrate liquid-solid equilibrium, there is a major issue in modeling complex situations (such as flow assurance). Moreover, the quantity of kinetic inhibitors to avoid the hydrate formation in a pipe is dependent on the volume of crystal to be formed. So, there is a request to know “when”, and “how many”.

The thermodynamic modeling gives the final state of a system. Usually, this final equilibrium is enough for the modeling of chemical processes, since the thermodynamic path does not matter. In the case of clathrate hydrates, non-stoichiometric compounds are studied, and there is a question about the role of the thermodynamic path. It could matter in this specific case since different mechanisms need to be considered. In our study, many parameters are taken into account: gas consumption that changes the gas composition, and hence the thermodynamic equilibrium; molecules enclathration in the crystal characterized by the occupation of cavities (driven by thermodynamics or kinetics[11]).

Hence, it is crucial to understand clathrate hydrate crystallization to model the local change over time of the hydrate composition during crystal growth. At the end of the crystallization, whatever the topic (flow assurance, carbon capture and storage, planetary science...), the modeling of clathrate hydrate equilibrium and crystallization is key to develop process simulation and sizing. Especially because the volume of the final crystal phase and the amount of gas captured is a essential result to predict. For this purpose, the methodology can be a thermodynamic or kinetic. A kinetic model, incorporating crystal growth, was recently suggested by Herri and Kwaterski[12]. More recently, a kinetic flash algorithm has been suggest by Boesen et al.[13], based on the Skovborg model[14].

In the present approach, a thermodynamic method was chosen, combined with mass balance calculation, that is to say a thermodynamic flash approach for clathrate hydrates. For this endeavor, some assumptions are needed to

68 take into account the molecules' enclathration. Either the hydrate is growing
 69 at local thermodynamic equilibrium, or the whole crystal phase is at thermo-
 70 dynamic equilibrium. So, the two assumptions are considered within a flash
 71 calculation.

72 Our objective is to present two frameworks for the clathrate hydrate ther-
 73 modynamic flash calculations at constant volume. By presenting to differing
 74 frameworks, three kinds of calculations are available: two at local equilib-
 75 rium, and one at overall equilibrium. Then, the resulting simulations are
 76 compared to an experimental reference case from another study[11] that was
 77 performed at slow crystallization rate (to avoid kinetics effects). The aim
 78 is to model the hydrate volume in the end of the crystallization, and final
 79 pressure far from equilibrium. Another objective is to adjust the classic ther-
 80 modynamic parameters (usually Kihara parameters) in the case where the
 81 equilibrium pressure is not sufficient.

82 This paper is organized as follows: section 2 explains further the theory
 83 involved. Section 3 details the modeling approach with the two thermody-
 84 namic frameworks utilized. Section 4 then presents the simulation results
 85 in some details. In addition, a parametric study is suggested. Finally, the
 86 conclusion and some future works are discussed.

87 2. Theory

88 2.1. Calculation of VLE equilibrium

89 2.1.1. Calculating the vapor phase density

90 The vapor phase density and fugacity coefficient are usually calculated
 91 using an equation of state ($f(P, V_m, T) = 0$). Among the numerous equations
 92 of state available, the Soave-Redlich-Kwong (SRK)[15] is known to be a good
 93 choice for density calculation for vaporized small hydrocarbon molecules[16].
 94 This equation was used with the parameters from Danesh[16].

95 Since we consider a constant volume, the knowledge of the vapor phase
 96 density defines the mass (or number of mole) of the initial gas phase ($=$
 97 $PV/Z_{SRK}RT$).

98 2.1.2. Calculating gas solubility in water

99 The gas molecule solubility into the water phase can be expressed from
 100 the equality of the chemical potentials (or the fugacities) of each molecules in
 101 the two phases (liquid and vapor). Considering a hydrocarbon gas mixture,
 102 a standard γ^∞/ϕ approach is usual[17]. The γ^∞ account for the activity

coefficient at infinite dilution (Henry's law approach, introducing Henry's constants), while ϕ is the fugacity coefficient (calculated using an equation of state). Since the vapor-liquid equilibrium takes into account the hydrocarbon molecules only, the water molecule in the vapor phase is neglected. This leads to the following equation:

$$f^V = f^{L_w} \leftrightarrow P\phi_i x_i^{L_w} = x_i^{L_w} K_{H,i,w}(T, P_w^\sigma) \exp\left(\frac{PV_{m,i}^{\infty,L_w}}{RT}\right) \quad (1)$$

where $K_{H,i,w}$ is the Henry's constant of molecule i in liquid water L_w , and $V_{m,i}^{\infty,L_w}$ the partial molar volume of the molecule i at infinite dilution. In the same manner as our previous work[18], an average value of $V_{m,i}^{\infty,L_w} = 32\text{cm}^3\text{mol}^{-1}$ was used[19], and the Henry's constant were calculated from an empirical equation[20].

2.2. Thermodynamic equilibrium of clathrate hydrates

Phase equilibria are described by the equality of chemical potentials, μ , in each phase. In the case of clathrate hydrates thermodynamic equilibrium, this is the equality of water in both liquid and hydrate phase :

$$\mu_w^H = \mu_w^L \quad (2)$$

Actually, clathrate hydrate equilibrium is usually described by the van der Waals and platteuw model [21]. This model is based on classic thermodynamics for the water liquid phase (Gibbs-Duhem equation), and on statistical thermodynamics for the hydrate phase, based on the following assumptions:

- Each cavity contain one guest molecule at best,
- the interaction between the guest molecule and the cavity (water molecules) can be described by a pair potential function of the pair gas-molecule,
- the cavities are perfectly spherical,
- The guest molecules do not deform cavities,
- There is no interactions between the guest molecules.

The van der Waals and Platteeuw model also writes the phase equilibrium with an hypothetic reference state (β state) corresponding to the hydrate phase with empty cavities:

$$\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta} \quad (3)$$

where $\Delta\mu_w^{H-\beta}$ and $\Delta\mu_w^{L-\beta}$ are the difference between the chemical potential of the hydrate phase (respectively the liquid phase), and the chemical potential of the hypothetical β phase.

2.2.1. Liquid phase

As previously mentioned, the second part of equation 3 is expressed from classic thermodynamics, while the first part is expressed from statistical thermodynamics. Hence $\Delta\mu_w^{L-\beta}$ is written using Gibbs-Duhem equation as follows:

$$\Delta\mu_w^{L-\beta} = T \frac{\Delta\mu_w^{L-\beta}|_{T^0 P^0}}{T^0} - T \int_{T^0}^T \frac{\Delta h_{w,m}^{L-\beta}|_{P^0}}{T^2} dT + \int_{P^0}^P \Delta\nu_{w,m}^{L-\beta}|_{T^0} dP - RT \ln a_w^L|_{T,P} \quad (4)$$

where (T^0, P^0) are reference temperature and pressure, $\Delta\mu_w^{L-\beta}|_{T^0 P^0}$ is the chemical potential difference of water in the liquid phase and water in the hydrate free cavity phase at the reference state, $\Delta h_{w,m}^{L-\beta}|_{P^0}$ the molar enthalpy difference between the liquid and β phase, $\Delta\nu_{w,m}^{L-\beta}|_T$ the molar volume difference between the liquid and the β phase, and $a_w^L|_{T,P}$ the activity of water in the liquid phase at (T, P) .

Since the water activity is expressed with the activity coefficient $a_w = \gamma_w x_w^L$ and only “pure” water is involved, it is usual to consider the ideal case ($\gamma_w = 1$) (no additives, only gas molecules dissolved into the aqueous phase, showing weak deviation from ideality).

$\Delta\mu_w^{L-\beta}|_{T^0 P^0}$ and $\Delta h_{w,m}^{L-\beta}|_{P^0}$ are thermodynamic properties of the liquid phase compared to reference β phase. As for any thermodynamic model based on activity coefficient formalism, these thermodynamic properties are essential. Many values can be found in the literature according to various authors. Table 1 gives some of these values.

$\Delta\nu_{w,m}^{L-\beta}|_{T^0}$ is a first order parameter that has been measured with high accuracy by von Stackelberg [22] via X-Ray diffraction.

$\Delta h_{w,m}^{L-\beta}|_{P^0}$ is a first order parameter whose expression has been refined by Sloan [20, 2], leading to:

$$\Delta h_{w,m}^{L-\beta}|_{P^0} = \Delta h_{w,m}^{L-\beta}|_{T^0, P^0} + \int_{T^0}^T \Delta C_{p,w,m}^{L-\beta}|_{P^0} dT \quad (5)$$

157 where $\Delta C_{pw,m}^{L-\beta}$ is the molar calorific capacity difference between liquid
 158 water and hydrate β phase, and can be expressed as:

$$\Delta C_{pw,m}^{L-\beta}|_{P^0} = \Delta C_{pw,m}^{L-\beta}|_{T^0,P^0} + b_{p,w}^{L-\beta}(T - T^0) \quad (6)$$

159 Parameters $\Delta C_{pw,m}^{L-\beta}|_{T^0,P^0}$ and $b_{p,w}^{L-\beta}(T - T^0)$ have been calculated by Sloan
 160 et al. [2] (see Table 2).

161 The final equation (from equation 4) is:

$$\begin{aligned} \Delta \mu_w^{L-\beta} = & T \frac{\Delta \mu_w^{L-\beta}|_{T^0,P^0}}{T^0} + \left(b_{p,w}^{L-\beta} T^0 - \Delta C_{pw,m}^{L-\beta}|_{T^0,P^0} \right) - T \ln \frac{T}{T^0} + \frac{1}{2} b_{p,w}^{L-\beta} T (T^0 - T) + \\ & \left(\Delta h_{w,m}^{L-\beta}|_{T^0,P^0} + (b_{p,w}^{L-\beta} T^0 - \Delta C_{pw,m}^{L-\beta}|_{T^0,P^0}) T^0 - \frac{1}{2} b_{p,w}^{L-\beta} T^{02} \right) \left(1 - \frac{T}{T^0} \right) + \\ & \Delta \nu_{w,m}^{L-\beta}|_{T^0} (P - P^0) - RT \ln x_w^L \quad (7) \end{aligned}$$

162 In a previous study [18], the parameters of Handa and Tse [23] were found
 163 to be the best set for the modeling of pure clatrate hydrates. That is why
 164 they were chosen.

165 2.2.2. Hydrate phase

166 The second part of equation 3 deals with statistical thermodynamic de-
 167 velopment of hydrate chemical potential. In the van der Waals and Plat-
 168 teuw model [21], this potential is expressed with the occupancy factor θ_j^i of
 169 molecule j in cavity i of the crystal, therefore:

$$\Delta \mu_w^{H-\beta} = RT \sum_i \nu_i \ln \left(1 - \sum_j \theta_j^i \right) \quad (8)$$

170 where ν_i is the number of type i cavities per mole of water. In this model,
 171 the occupancy factor is expressed from Langmuir kind approach:

$$\theta_j^i = \frac{C_j^i f_j(T, P)}{1 + \sum_j C_j^i f_j(T, P)} \quad (9)$$

172 where C_j^i is the Langmuir constant of molecule j in cavity i , and $f_j(T, P)$
 173 is the fugacity of component j at temperature T and pressure P in the liquid
 174 phase. Usually, this fugacity is to be equal to the fugacity in the gas phase
 175 since there are three phases at equilibrium in hydrates experiments (gas,

176 aqueous and hydrate). In these cases, a standard equation of state can be
 177 used for the calculations.

178 Then, the Langmuir constant is calculated from the interaction potential:

$$C_j^i = \frac{4\pi}{k_B T} \int_0^{R-a} \exp\left(-\frac{w(r)}{k_B T}\right) r^2 dr \quad (10)$$

179 The integration of potential interaction w is calculated from 0 (surface of
 180 gas molecule) to $R - a$, the distance between the molecule and the cavity. In
 181 clathrate hydrate field, the Kihara potential is used [24], written:

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

182 with

$$\delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} + \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} + \frac{a}{R}\right)^{-N} \right] \quad (12)$$

183 Parameters ϵ , σ and a are the so-called Kihara parameters. ϵ corresponds
 184 to the maximum attractive potential, σ the distance from the cavity center,
 185 and a the hard-core radius. They are fitted for one molecule to experimental
 186 data of pure gas hydrates (except for a that is usually a known geometric
 187 parameter). To do so, a simple root mean square error (RMSE) minimization
 188 of the deviation function is performed from N PT data ($N > 2$):

$$F(\epsilon, \sigma) = \sqrt{\frac{\sum (P_{pred} - P_{exp})^2}{N}} \rightarrow 0 \quad (13)$$

189 where P_{pred} and P_{exp} are the predicted and experimental pressure (respec-
 190 tively) at temperature T .

191 Of course, many Kihara parameters can be found in the literature, de-
 192 pending on authors, thermodynamic properties and experimental data used.
 193 More details on Kihara parameters optimization, and differences between
 194 authors, can be found in a previous study [18].

195 2.2.3. Kihara parameters optimization limits

196 Kihara parameters optimization is a tricky part in the thermodynamic
 197 modeling of clathrate hydrates. As stated previously, there are as many sets
 198 of parameters as there are authors. There are different issues to explain this
 199 observation.

200 First, the quality of the thermodynamic parameters (table 1) can play an
 201 important role[18].

202 Concerning again optimization, the predicted versus experimental equi-
 203 librium pressure is oftenly used. To avoid non-thermodynamic equilibria,
 204 only pure gas hydrates should be considered. But sometimes, this is not
 205 enough to find a global minimum to the deviation function. In these cases,
 206 gas mixtures have to be considered, and the deviation function is based not
 207 only on the pressure, but also on the hydrate composition as follows:

$$F'(\epsilon, \sigma) = \sqrt{\frac{\sum (x_{pred}^H - x_{exp}^H)^2}{N}} \rightarrow 0 \quad (14)$$

208 The first problem with this calculation is that the literature data rarely
 209 gives the mixed hydrate composition, especially at total dissociation point
 210 (hard to obtain and to measure since the hydrate volume is then close to
 211 zero). Then, and this is the main issue, the experimental data obtained and
 212 published in the literature might not be at thermodynamic equilibrium (quick
 213 crystallizations).

214 Indeed, in a previous study, it was observed that the experimentally ob-
 215 tained thermodynamic three phases equilibrium (vapor-liquid-hydrate, or
 216 VLHE) is not systematic [11]. If the equilibrium pressure of pure gas hy-
 217 drates corresponds exactly to the thermodynamic equilibrium, it is not al-
 218 ways the same for mixed hydrates (clathrate hydrate from gas mixtures).
 219 When several gases are involved, kinetics considerations arise. For exam-
 220 ple, the kinetics of gas dissolution in the water phase suggest a different
 221 driving force for the crystallization than the one predicted by pure thermo-
 222 dynamics. Then, the kinetics of gas enclathration into the hydrate structure
 223 could diverge from thermodynamics. Certainly, thermodynamically, various
 224 configurations of the occupancy of the cavities can stabilize the crystalline
 225 structure. In theory, the occupancy factor depends on the langmuir constants
 226 and the gas fugacities in the aqueous phase. All the previous kinetics consid-
 227 erations question the validity of a thermodynamic model when the experiments
 228 are performed at high driving force (far from equilibrium).

229 In our previous work, it appeared that the driving force of the crystal-
 230 lization impacts the “thermodynamic path” during the crystallization. As a
 231 result, in the end of the crystallization, the hydrate phase composition, the fi-
 232 nal pressure and the final hydrate volume, were not the same at low and high
 233 driving forces[11] (severals bars between a slow and a quick crystallization).

234 To take account of kinetics, a novel model was recently suggested by
 235 Herri and Kwaterski [8]. In their model, the rate of enclathration of the
 236 gas molecules into the hydrate crystal is considered in the langmuir constant
 237 (instead of integration an interaction potential , see equation 10).

238 In the next section, a framework to perform flash calculations with the
 239 classic thermodynamic modeling of gas hydrates is presented. The objective
 240 is to take into account the possible non-stoichiometric composition of the
 241 hydrate crystals, and to study more precicely the mechanisms of the hydrate
 242 crystallization process, and the influence of the uncertainties on the Kihara
 243 parameters. Moreover, it can give another criterion for Kihara parameters
 244 optimization from pure gas hydrate: the hydrate volume.

245 **3. Modeling Clathrate hydrate crystallization**

246 *3.1. Flash calculation frameworks*

247 *3.1.1. Classic flash calculations and hydrate approaches*

248 The basic of a thermodynamic flash (or “flash”) is to determine, from an
 249 initial given state, the composition and mass in each phase, by taking care
 250 of the Gibbs phase rule.

251 In a usual flash calculation, all phases are at equilibrium and their com-
 252 position is homogeneous. The flash algorithm is composed of two loops:

- 253 • the thermodynamic equilibrium (equality of chemical potentials/fugacities
 254 by the mean of partition coefficients),
- 255 • mass balance calculation from partition coefficients.

256 So, there is one calculation loop on a thermodynamic intensive property
 257 (usually temperature or pressure), and one loop concerning the mass balance
 258 (an extensive property such as the mass of the components). According to
 259 the Gibbs phase rule, the three phases equilibria allow one less variable than
 260 the simple two phases flash equilibria. In this article, a thermodynamic flash
 261 at constant volume is considererd (the volume of the reactor in a typical
 262 batch experiment).

263 Hydrate flash calculation is a tricky problem since the hydrate phase com-
 264 position is non-stoichiometric. This is due to the gas consumption leading
 265 to pressure variations and the gas/liquid composition change during crystal-
 266 lization (batch experiments).

267 In the case of clathrate hydrates, the composition of the solid phase is, *a*
 268 *priori*, not homogeneous. That is why a partition coefficient cannot be used
 269 to describe the whole solid phase. The thermodynamic calculation can only
 270 describe the composition locally in time. Towards the end, the calculation
 271 has to be performed step by step, by considering successive “classic flash
 272 calculations”, corresponding to the crystal growth. Figure 1 illustrates this
 273 process. In the end, the hydrate crystal shows an occupation gradient of the
 274 cavity by the gas molecules. Hence, this flash calculation can be considered
 275 as a crystal growth at successive equilibria.

276 Of course, this model has as hypothesis that the local composition at the
 277 core of the hydrate crystal is not at equilibrium with the liquid phase. Only
 278 the last layer is. This procedure is then called *Flash calculation framework*
 279 *without hydrate phase reorganization* (see next section).

280 This hypothesis is fundamental, and corresponds to a mass balance for
 281 a given amount of crystallized hydrate. As there is a discretization of the
 282 crystal growth step by step, this hydrate flash is then a succession of usual
 283 thermodynamic flash algorithms instances.

284 There is another approach possible: change the previous hypothesis. It
 285 is conceivable that, at the end of each step during the crystal growth, the
 286 crystal reorganizes itself and reaches thermodynamic equilibrium. Thus, the
 287 last crystal layer is at thermodynamic equilibrium with the surrounding liquid
 288 phase. Furthermore, it is possible to obtain a homogeneous final crystal by
 289 not discretizing the crystal growth. Our second approach is also presented
 290 and discussed after under the name *Flash calculation framework with hydrate*
 291 *phase reorganization* (see also figure 5 further on in the text).

292 3.1.2. *Flash calculation framework without hydrate phase reorganization*

293 Our first approach concerns the model with no solid phase reorganization.
 294 Figure 1 illustrates this method. The first crystals appear in the bulk at
 295 thermodynamic equilibrium with the liquid phase at the beginning of the
 296 nucleation. The occupancy of the cavities of this new hydrate phase (hydrate
 297 nuclei) is controlled by thermodynamics and can be calculated from van der
 298 Waals and Platteuw model.

299 Figure 1 also shows a discretization of the crystal growth. The more itera-
 300 tions there are, the more the growth is continuous. The main objective of this
 301 hydrate growth modeling is to follow the thermodynamic equilibrium curves,
 302 as shown on figure 2, and later in figure 7. On the former figure, there is
 303 not only one thermodynamic equilibrium curve since the gas is consumed.

304 As the gas is consumed, the pressure decreases, and the gas compositions
 305 in fluid phases change along the crystallization. Since the gas hydrate equi-
 306 librium curve (PT) depends on the gas composition, the crystal growth goes
 307 through many steps until the final composition is reached. The number of
 308 iterations (discretization) is important since it fixes the amount of gas in the
 309 hydrate phase at each step. It is a growth model locally at thermodynamic
 310 equilibrium (on the crystal surfaces).

311 The figures 2 and 3 illustrate the whole framework for the hydrate flash.
 312 The framework is define by the starting conditions:

- 313 • initial temperature T_i ,
- 314 • initial pressure P_i ,
- 315 • initial gas composition z_i ,
- 316 • the total fixed volume (= initial gas volume, single phase before liquid
 317 injection, or “reactor volume”) V^R ,
- 318 • initial mass of water m_i ,

319 These inputs allow for the calculation of the mass of each compound
 320 in each phase (liquid-gas). The total mass of the gas phase is calculated
 321 with the SRK equation of state. This corresponds to point *A* on figure 2,
 322 which is also an initial liquid-vapor thermodynamic flash calculation (VLE
 323 thermodynamic flash).

324 This initial VLE thermodynamic flash is at constant temperature and
 325 volume (flash TV). The SRK equation of state is used to model the vapor
 326 phase, while a Henry’s law approach for the gas solubility is considered (VLE,
 327 see section 2.1). More information about thermodynamic flash calculations
 328 can be found in the literature[25].

329 Then, another two inputs of the framework are essential:

- 330 • the final temperature T_f (= final state),
- 331 • the number of iterations n to reach the final state.

332 Gibbs phase law for three phases equilibria gives one degree of freedom less
 333 than for simple VLE flash. Here, the temperature T_f is the variable. The final
 334 temperature imposes the final state of the calculation (the temperature is the

only variable). The number of iterations corresponds to the discretization of the hydrate flash, via decreasing increments of temperature (ΔT).

The second step of the flash framework is to determine the temperature at which the liquid-hydrate thermodynamic equilibrium (LHE) is reached (point B). It is a VLE flash that also satisfy the LHE equation. The equilibrium temperature T_B is determined from the predicted pressure of the VLE equilibrium and LHE equilibrium ($P^{VLE} = P^{LHE}$)

From this point, the temperature step is calculated from the number of iterations: $\Delta T = (T_B - T_f) / n$. The higher n is, the more continuous the growth is. The lower n is, the more the driving force is significant in the model.

Then, the crystal growth begins. The temperature is decreased step by step (ΔT) until the final temperature T_f . Both thermodynamic equilibria (VLE and LHE) have to be checked before going any further. The VLE is checked flash calculation prior to the LHE calculation. This VLE flash provides an equilibrium pressure P^{VLE} . Then, the LHE is calculated, providing another equilibrium pressure P^H . The error between P^{VLE} and P^H is the criterion of the algorithm. The variable that is used to minimize this error is the mass (volume) of water that has crystallized into the hydrate phase. This mass has consequences on the fluid volume (and also the VLE flash) and the LHE since the amount of gas molecules in each phase is affected (through the occupancy factor θ_j^i).

At each step, a given mass of liquid water is transferred to the hydrate phase (dm_w^i). As a consequence, the total volume of the hydrate phase (V^H) is increased. This volume is calculated from the density of the empty clathrate. These densities (790 kg/m^3 for structure I, and 785 kg/m^3 for structure II) can be obtained from lattice parameters of each structure, neglecting temperature dependency. Sloan and Koh[2] also suggested a formula to calculate hydrate density. In the end, the hydrate volume crystallized is:

$$V^H = \frac{\sum_i dm_w^i}{\rho^{H-\beta}} \quad (15)$$

In order to determine the gas consumption toward the hydrate phase, the occupancy of the cavities (θ_j^i) is calculated from van der Waals and Platteeuw model.

At this point, the amount of matter taken from the fluid phase, and added to the solid phase, is known. A new VLE flash is performed on the fluid phases. This provides P^{VLE} . The new gas composition in the liquid phase

370 is also known, and the LHE can be checked by determining the equilibrium
 371 pressure P^H . If $P^{VLE} \neq P^H$, the quantity dm_w^i is not right (wrong mass
 372 balance), and needs to be fine tuned in order to obtain the “same” pressures.
 373 The criterion used is the following:

$$F_{obj}(dm_i) = \frac{P^{VLE} - P^{LHE}}{P^{VLE}} \rightarrow 0 \quad (< 10^{-3}) \quad (16)$$

374 In order to simplify the calculations, an hypothesis is added: the amount
 375 of gas molecules into the liquid phase is considered constant in the calculation
 376 of each iterations. This hypothesis is not very strong since the gas solubility
 377 of hydrocarbon is generally low, or is slightly impacted by the evolution of
 378 gas phase composition at each iterations. Notice also that the liquid water
 379 density is considered constant at $1000\text{kg}/\text{m}^3$ in our simulations (due to low
 380 variations within the range of temperature $0 - 10^\circ\text{C}$).

381 By performing the n calculations, the final state (point D) is reached,
 382 and the hydrate flash calculation is over.

383 The number n affects the length of the calculations, but also the results.
 384 This is investigated later in section 4.4.

385 3.1.3. Flash calculation framework with hydrate phase reorganization

386 Two situations are considered: a reorganization of the last layer to ob-
 387 tain a thermodynamic equilibrium (Gas-Liquid-Last layer of hydrate crystal),
 388 or a completely homogeneous hydrate phase. Earlier, the last layer being
 389 crystallized was at thermodynamic equilibrium with the previous iteration
 390 (“begining” of the crystallization). Indeed, cavities occupancy is calculated
 391 from iteration i to compute iteration $i + 1$. So, the layer $i + 1$ of the hydrate
 392 crystal has an occupancy at equilibrium with the gas phase composition at
 393 iteration i .

394 To have a different situation than this, two solutions are conceivable.
 395 First, use as many iterations as possible. This will be investigated in sec-
 396 tion 4.4. Secondly, the last layer can be reorganized in order to compute a
 397 hydrate layer completely at equilibrium with the gas and liquid composition
 398 at each step of the process. This implies another loop on the occupancy
 399 factor used at the begining of the hydrate phase calculations (i.e. calculate
 400 the amount of molecules in the hydrate phase).

401 In the end, a complete homogeneous hydrate phase is possible to compute.
 402 To do so, the method reorganizing the hydrate can be performed with only
 403 one iteration (crystal growth in single step).

404
405

406 *Phase reorganization of last layer.*

407

408 This second framework (framework II) presents the same hydrate flash
409 calculation than before with the last crystal layers at equilibrium with the
410 liquid phase. The previous framework had to be changed to take into account
411 this reorganization at the end of each step. As the hydrate composition is
412 slightly different with this new model, the final state is also different in
413 terms of mass balance, final pressure and hydrate volume. Though, these
414 two frameworks (I and II) are equivalent when $n \rightarrow \infty$.

415 In framework II, a new loop is introduced. In the end of each step the oc-
416 cupancy factor before crystallization is compared with the occupancy factor
417 after. This means that the occupancy factor of the last layer is in agreement
418 with equation 9 according to the liquid state. If there is a difference, the
419 iteration calculation starts again with the previous θ_j^i as the starting point
420 (another weighted calculation of the new θ_j^i can be utilized to improve the
421 algorithm speed). The calculation of the amount of water crystallized (dm_w^i)
422 is repeated with a new gas consumption until $(\theta_i^j)_{initial} = (\theta_i^j)_{final}$. Figure 4
423 describes framework II.

424
425

426 *Homogeneous hydrate phase.*

427

428 In this approach (framework II*) the whole hydrate phase is at equilib-
429 rium with the liquid phase, both from local and global points of view. The
430 first possibility to obtain this is to use the second framework, and use only
431 one iteration from framework II. This can cause a problem of convergence
432 since only one iteration implies an initial state far from the final equilibrium
433 (hard to reach). Another solution is to use the total mass of the hydrate
434 phase (m_w^H) instead of the new amount dm_w^H . This divides the calculations
435 into successive m_w^H crystallized, and avoids convergence issues. As a conse-
436 quence (many loops), the computing time of this approach is slightly higher.
437 More work on the algorithm would optimize the calculations.

438 Figure 5 shows the path of framework II*.

439 4. Simulation results

440 The two frameworks are tested and compared to reference results. These
 441 results are from a previous experimental work [11] (from CO₂, CH₄, C₂H₆
 442 gas mixture).

443 The thermodynamic frameworks were computed through a MATLAB
 444 code. Since it is a “new code”, Kihara parameters optimization was neces-
 445 sary. Indeed, the Kihara parameters are very author (and code)-dependents.

446 Then, the frameworks were compared to experimental results. A great
 447 deal of attention was paid to the number of iterations n .

448 Afterwards, a parametric study of kihara parameters is suggested to de-
 449 termine the consequences of the uncertainty of kihara parameters on the
 450 equilibrium pressure and hydrate volume.

451 Finally, the results are analysed looking at the experimental results, both
 452 at quick and slow crystallization, to discuss the hydrate crystallization pro-
 453 cess.

454 4.1. Kihara parameters

455 A set of experimental pure hydrates equilibria was considered (8 data
 456 from [26, 27] for CO₂, 14 data from [26, 11, 28, 29, 30] for CH₄, and 18 data
 457 from [30, 31, 32, 33] for C₂H₆).

458 Table 3 summarizes the parameters optimized from the above experimen-
 459 tal results on pure gas hydrates (temperature range from 273K to 300K).
 460 The objective is simply to have a starting set of parameters to work with.
 461 A MATLAB code of LHE calculation was performed presented, as presented
 462 in section 2. The parameters regression was executed with the use of the
 463 *lsqnonlin* function of Matlab, by considering local minima. The root mean
 464 square errors (RMSE) obtained are quite satisfying here (from 0.02 to 2.43).

465 4.2. Reference case

466 The first reference case is a ternary gas mixture + water. The mixture is
 467 CO₂-CH₄-C₂H₆ at molar compositions of 5%/92%/3% (± 0.1) respectively.
 468 The initial temperature of the gas mixture is 285.75K and pressure was
 469 30.5bars. The total volume (V^R) is 2.36L. The amount of water added to
 470 the mixture is 801.3g. The reference case is taken from Duyen et al.[11].

4.3. Test of thermodynamic model on benchmark

Table 4 and figure 6 present the results of the thermodynamic model only (without the mass balance component of the flash calculation) compared to the reference baselines. The table shows well that the thermodynamic model (LHE) with our parameters is pretty accurate (RMSE of 0.31 on the pressure). It also demonstrates that a slow crystallization is closer to a thermodynamic equilibrium. Duyen et al.[11] on this same mixture, obtained thermodynamic modeling results closer to this experiment at slow crystallization than at quick crystallization. Although another code was used, our results are in accordance with the afore-mentioned study.

4.4. Frameworks results, and influence of the number of iterations

Table 5 shows the results for the first reference results ($\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$). By cooling this mixture, all the frameworks give a three phases equilibrium (nucleation point) at 280.14K and 42.63bars . This means that when we cool the reference case down to 280.14K , this causes the system to crystallize.

Then, there is a cooling, step by step as a function of the iterations number (n). The number of iterations corresponds to the number of cooling steps from the last temperature (here 280.14K , or T_B on figure 2) to the final fixed temperature (274.5K , or T_f , or T_D). This also corresponds to the discretization of the crystal growth modeling.

Figure 7 illustrates the experimental and predicted thermodynamic paths for the crystallization process (PT digrams) assuming a SI structure. The first figure (7(a)) shows, for framework I ($n = 7$), the first point of crystallization. The successive evolution of the solid phase and the PT equilibrium curves corresponds to each temperature step. The second figure (7(b)) shows the experimental path compared to predicted (all frameworks). Like the theoretical example (figure 2), as the gas is consumed, the most stabilizing molecules are removed from the fluid phases. That is why the system reaches successive equilibrium with a narrower hydrate zone (the PT curves are higher in pressure at a given temperature).

A quick investigation of the iteration number influence shows that frameworks I and II converge when $n \rightarrow \infty$, as expected. Since n impacts the calculation time, it is of utmost importance in process simulations. A number of 20 iterations to model a continuous crystallization is a satisfying compromise. Keep in mind that there is an experimental uncertainty on pressure and mass measurements. When using 20 iterations for frameworks I and II,

507 there is a difference of 0.01bar in pressure and 0.1g in hydrate mass compared
 508 to $n \rightarrow \infty$. Logically, framework II* is not affected by n .

509 Concerning final pressure and water mass in the hydrate phase, both
 510 frameworks provide solid results (errors under 5% for pressure and mass). If a
 511 few iterations are used ($n = 3$), the accuracy deteriorates. This can also cause
 512 the calculation of negative compositions (too many gas molecules into the
 513 hydrate phase, and a negative number in the gas phase). Above 10 iterations,
 514 frameworks I and II are pretty similar. Framework II* (total hydrate phase
 515 reorganization) predicts very well the final pressure, but not as well the
 516 hydrate volume (or the water mass in hydrate). So, reorganizing the crystal,
 517 by comparison to the reference case, improves the accuracy of the pressure
 518 but decreases the accuracy of water conversion. In framework II, the gas
 519 consumption is higher, leading to more gas molecules in the crystal, a higher
 520 hydrate volume, and a lower pressure. Indeed, since the final pressure is lower
 521 than initially, the final occupancy of the cavity of the whole homogeneous
 522 crystal is lower than the occupancy factor of the first layer of frameworks I
 523 and II. In detail, the hydration number is 7.02 (II*) against 7.06 (I and II).

524 The gas and hydrate phase compositions are also well predicted, although
 525 the deviation is higher than the experimental uncertainty.

526 4.5. Kihara parameters influence on hydrate volume

527 As the volume of hydrate formed is crucial for many applications (pipe
 528 plugs, CO₂ capture...), knowing the Kihara parameters influence of the model
 529 is essential. Since these parameters are very author dependent, an evaluation
 530 of their uncertainties on the simulation results is presented here.

531 The Kihara parameters are the characteristics of the guest molecules,
 532 but various values exist. Usually, they need to be determined for each code,
 533 hence the authors dependency. But, it is not always an easy task since the
 534 experimental data can be missing or inaccurate (see discussion section 2.2.3).

535 In this work, the influence of the Kihara parameters uncertainties on the
 536 final pressure and hydrate volume is suggested. To do this investigation,
 537 a statistical approach was employed using Monte Carlo simulations. 1000
 538 random (ϵ/k and σ) parameters were computed according to a normal dis-
 539 tribution around the mean values given in table 3). The standard deviations
 540 in the normal distribution were taken from 1% to 5%. These Monte Carlo
 541 simulations were performed using the framework I with 8 iterations (to lower
 542 time consumption and good approximation of the final state).

543 Table 6 presents the effect of kihara parameters uncertainty on the final
 544 equilibrium pressure and hydrate volume. This demonstrates a small differ-
 545 ence in the Kihara parameter value (5%) can have a significant consequence
 546 on the final pressure and hydrate volume of standard deviations of 42% and
 547 125% respectively.

548 Since the models deviations from experimental results are usually under
 549 5%, it can be concluded that the frameworks are in good accordance with
 550 the experiments.

551 4.6. *Understanding hydrate crystallization*

552 Initially, an experimental reference case at low crystallization rate was
 553 chosen. The objective was to compare a thermodynamic based model to an
 554 experiment which was as close as possible to a transformation at thermody-
 555 namic equilibrium (no kinetic effects).

556 Towards the better understanding of the clathrate hydrate crystallization,
 557 firstly framework I is compared to more usual experimental measurements
 558 at quick crystallization rates. These data come from the previous study [11]
 559 on CO₂-CH₄ and CO₂-CH₄-C₂H₆ gas mixtures.

560 Table 7 gives the results on the final pressures and masses of water in
 561 hydrate phase. Surprisingly, the results are in pretty good accordance with
 562 the final equilibrium pressure (deviation < 5%). Since we suspect a kinetic
 563 effect on the hydrate crystallization, a higher difference was expected. Con-
 564 cerning the final volume of hydrate (or final mass of water in hydrate phase),
 565 the deviation from the experimental results is higher, but within the 3% un-
 566 certainty ($\pm$ standard deviation σ) on the kihara parameters (or within 1%
 567 uncertainty at $\pm$ variance/ 2σ).

568 In conclusion, it seems that the CO₂/CH₄ gas mixtures are not very much
 569 affected by kinetics. Also, framework I with 5 iterations gives slightly better
 570 results. This framework, combined with this number of iterations, was not
 571 the best as compared to the reference case at slow driving force. This could
 572 validate that a higher driving force is closer to framework I with no hydrate
 573 reorganization. Nevertheless, the results are more than adequate, and it
 574 would probaly not be the same for other mixtures where kinetics could be
 575 predominating.

5. Conclusion

Two main thermodynamic frameworks for the clathrate hydrate crystallization have been suggested. They are thermodynamic flash calculations of three phases equilibria (aqueous, gas and hydrate) at constant volume. The temperature is the variable imposed. Two thermodynamic paths have been modelled and investigated.

In frameworks I and II, the crystallization is discretized in mass of hydrate (equivalent to subcooling degree). Crystal growth is supposed to occur at local thermodynamic equilibrium with the surrounding liquid (itself at thermodynamic equilibrium with the surrounding gas phase). In the case of framework I, the equilibrium is considered before crystallization, and after for framework II. The discretization corresponds to successive layers of the hydrate crystal. As a consequence, the final clathrate is non-stoichiometric (local composition different than whole composition).

In a slightly different physical approach with a single iteration (framework II*), the local composition of the hydrate phase is the same as the overall composition (homogeneous solid phase in composition). To accomplish this, the crystal composition is homogenized during crystallization.

The simulation results, compared to a reference case (experiment at low crystallization rate from $\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$ gas mixture), are fairly accurate. All the frameworks show a deviation on the final pressure and mass of crystallized water under 5%. Frameworks I and II provide better results in terms of crystallized mass of water while framework II* seems to be better at predicting the final pressure. Also, a study on the uncertainties due to Kihara parameters uncertainties showed that the experimental results are within the margin of error for the models.

Concerning the discretization of the crystallization, a number above 20 iterations for the crystal growth is enough (frameworks I and II). As suspected, frameworks I and II converge when the iteration number is infinite.

The influence of the uncertainties on Kihara parameters has been studied on framework I. It has shown that the results are very sensitive to these kind of errors (errors of 1% $\Rightarrow$ 15% on Pressure and 35% on hydrate volume).

It is important to notice and underline that these flash calculations are only based on thermodynamic equilibria. If different paths are investigated, then no kinetic considerations exist such as mass transfer limitation at gas/liquid interface[34], or possible diffusion effects at the liquid/hydrate interface[12]. These considerations might be necessary to model hydrate crystallization at

613 high driving force, where the final pressure could to be significantly affected.

614 These frameworks provide a usefull tool for industry and academia to
615 predict with a more reallistic accuracy the final pressure, as well as give a
616 good order of magnitude of the hydrate volume. For gas mixtures that do
617 not show important kinetic effects (such as CO_2/CH_4 , as investigated in this
618 study), predictions are still accurate and within the same uncertainties.

619 Future works might include further elaboration of the principles discov-
620 ered while at the same time simplifying the process so that it can be clearly
621 implicated in industrial situations.

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Symbol	description	dimension
a	hard core radius	nm
a_w^L	liquid water activity	-
C	Langmuir constant	nm^3/J
c_p	Molar calorific capacity	$J/mol/K$
f	Fugacity	Pa
$K_{H,i,w}$	Henry's constant	Pa
k_B	Boltzmann constant	J/K
h	molar enthalpy	J/mol
m	total mass of water	g
m_i	initial mass of water	g
n	number of iterations in frameworks (growth discretization)	-
N	number of experimental data	-
P	Pressure	bars
T	Temperature	$^{\circ}C$ or K
$V_{m,i}^{\infty,L_w}$	Partial molar volume of i at infinite dillution	cm^3/mol
w	interaction potential	J
x	Molar composition of compound in hydrate phase	mol.frac.
Z	Compressibility factor	
ϵ	maximum attractive potential	J
ν_w	Water molar volume	m^3/mol
ν_i	number of cavity i per mole of water	mol/mol
μ	Chemical potential	J/mol
ρ	Density	kg/m^3
σ	distance from cavity center	nm
θ_j^i	Occupancy factor of molecule j in cavity i	-
ϕ	Fugacity coefficient	
Superscript	description	
0	reference state	
β	Empty hydrate reference state	
H	Hydrate phase	
j	molecule index	
L	Liquid phase	
L_w	Aqueous liquid phase	
V	Vapor phase	
Subscript	description	
exp	experimental result	
i	iteration number, or intial state, or index of cavity (1,2,3)	
m	molar quantity	
$pred$	predicted result	
w	water molecule	

Table 1: Thermodynamic properties of liquid water compared to β structure

Structure I		Structure II		
$\Delta\mu_w^{L-\beta,0}$	$\Delta h_w^{I-\beta,0}$	$\Delta\mu_w^{L-\beta,0}$	$\Delta h_w^{I-\beta,0}$	
699	0	820	0	van der Waals and Platteuw [21]
1255.2	753	795	837	Child [35]
1297	1389	937	1025	Dharmawardhana et al. [36]
1120	931	1714	1400	John et al. [37]
1287	934	1068	764	Handa and Tse [23]
$\Delta h_w^{L-\beta,0} = \Delta h_w^{I-\beta,0} - 6011$, where 6011 is the enthalpy of fusion of ice (J/mol).				

Table 2: Reference properties of hydrates from Sloan[2]

	unit	Structure I	Structure II
$\Delta h_w^{L-\beta,0}$	J/mol	$\Delta h_w^{I-\beta} _{T^0,P^0,SI} - 6011$	$\Delta h_w^{II-\beta} _{T^0,P^0,SII} - 6011$
$\Delta v_w^{L-\beta} _{T^0,P^0}$	$10^{-6}m^3/mol$	4.5959	4.99644
$\Delta C_{pw,m}^{L-\beta} _{T^0,P^0}$	$J/mol/K$	-38.12	-38.12
$b_{p,w}^{L-\beta}$	$J/mol/K^2$	0.141	0.141

Table 3: Quick Kihara parameters optimization of CO₂, CH₄, and C₂H₆ on a few experimental data[27, 26, 11, 28, 29, 30, 31, 32, 33] (* data from Sloan et al. [2])

	ϵ/k	σ	a^*	RMSE	nb. of data
CO ₂	171.78	2.978	0.6805	0.02	8
CH ₄	160.70	3.101	0.3834	2.43	14
C ₂ H ₆	176.83	3.22	0.5651	0.062	18

Table 4: Experimental versus predicted results for the reference case ($\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$) from classic thermodynamic calculations assuming a SI structure

T (K)	P exp (bars)	$x^V(\text{CO}_2)$	Exp. Gas composition $x^V(\text{CH}_4)$	Exp. Gas composition (%mol) $x^V(\text{C}_2\text{H}_6)$	Exp. hydrate composition $x^H(\text{CO}_2)$	Exp. hydrate composition (%mol) $x^H(\text{C}_2\text{H}_6)$	P pred (bars)	Pred. hydrate composition $x^H(\text{CO}_2)$	Pred. hydrate composition (%mol) $x^H(\text{C}_2\text{H}_6)$
279.35	41.7	0.037	0.943	0.020	0.117	0.669	41.10	0.0569	0.8598
277.75	37.75	0.035	0.951	0.014	0.081	0.799	36.39	0.0579	0.8801
277.35	35.6	0.034	0.952	0.014	0.081	0.828	35.09	0.0566	0.8828
276.4	31.8	0.033	0.957	0.010	0.075	0.849	32.79	0.0567	0.8977
275.6	30.4	0.031	0.959	0.010	0.076*	0.854*	30.35	0.0546	0.8996
274.45	27.6	0.030	0.963	0.007	0.075	0.862	27.54	0.0534	0.9093
RMSE:								0.0129	0.0383
								0.0256	

Table 5: Influence of the number of iteration n on the flash hydrate results: example of $\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$ mixture (reference case) assuming SII structure (dev. is mean deviation on P_f and m_w^H)

	n	Pf (bars)	m_w^H (g)	conv. %mass	n^G (mol)	$x^V(\text{CO}_2)$	gas composition $x^V(\text{CH}_4)$ (%mol)	$x^V(\text{C}_2\text{H}_6)$	n^H (mol)	hydrate composition $x^H(\text{CO}_2)$	hydrate composition $x^H(\text{CH}_4)$ (%mol)	$x^H(\text{C}_2\text{H}_6)$	dev. (%)
I	3*	30.03	111.43	13.91%	2.166	0.031	0.972	-0.004	1.045	0.073	0.831	0.096	0.106
I	5	29.18	119.38	14.99%	2.098	0.031	0.969	0.000	1.117	0.073	0.845	0.082	0.059
I	10	28.9	122.05	15.34%	2.076	0.031	0.968	0.001	1.140	0.072	0.849	0.079	0.043
I	20	28.79	123.05	15.47%	2.067	0.031	0.968	0.002	1.149	0.072	0.851	0.077	0.037
I	50	28.74	123.51	15.49%	2.063	0.031	0.967	0.002	1.153	0.072	0.852	0.077	0.035
I	100	28.74	123.51	15.53%	2.064	0.031	0.967	0.002	1.153	0.072	0.852	0.076	0.035
II	8	28.47	125.98	15.86%	2.042	0.031	0.966	0.003	1.175	0.071	0.856	0.073	0.020
II	20	28.62	124.55	15.67%	2.055	0.031	0.967	0.002	1.162	0.071	0.854	0.075	0.029
II	100	28.68	124.05	15.48%	2.059	0.031	0.967	0.002	1.158	0.072	0.853	0.076	0.032
II*	5	27.39	135.94	17.11%	1.958	0.031	0.961	0.008	1.263	0.069	0.871	0.061	0.039
II*	20	27.39	135.93	17.10%	1.958	0.031	0.961	0.008	1.263	0.069	0.871	0.061	0.039
exp.		27.6	127.1	15.99%	2.009	0.030	0.963	0.007	1.210	0.075	0.862	0.062	3.4

Table 6: Influence of the Kihara parameters uncertainties on the flash hydrate results (framework I, reference case)

uncert.	$\bar{P}_f$ (bars)	$\text{std}(P_f)$ (bars)	$\text{std}(P_f)$ %	$\bar{V}^H$ (mL)	$\text{std}(V^H)$ (mL)	$\text{std}(V^H)$ %
1%	30.6	4.7	15.36%	162	56	34.57%
2%	31.204	8.06	25.83%	152.3	98	64.35%
3%	31.55	10.4	32.96%	145.7	128.5	88.19%
5%	32.05	13.4	41.81%	138.6	172.9	124.75%

Table 7: Framework I predictions ($n = 20$) compared to experimental results[11] at quick crystallization (gas 3-4 from $\text{CO}_2\text{-CH}_4$ mixtures and 6-7-8 from $\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$ mixtures) and slow crystallization (reference case of the present study)

Gas mixtures	T_f (± 0.1 °C)	P_f (± 0.1 bars)	V^H ($mL \pm 4\%$)	m^H ($g \pm 4\%$)	Framework I, $n = 20$			
					$P_{f_{pred}}$ (bars)	m^H_{pred} (g)	dev P (%)	dev m^H (%)
Gas 3	3.4	33.3	268.4	212.0	31.6	256	5	21
Gas 4	2.2	29.1	217.8	172.1	28.19	186.11	3.1	8.2
Gas 6	2.2	30.7	-	-	31.59	139.9	2.9	-
Gas 7	1	27.1	-	-	26.21	43.1	3.3	-
Gas 8	2.75	35.4	345.3	272.8	33.87	333.5	4.3	22
Gas 12	1.3	27.6	160.9	127.1	28.79	123.1	4.3	3.2
Gas mixtures	Framework I, $n = 5$				Framework II*			
	$P_{f_{pred}}$ (bars)	m^H_{pred} (g)	dev P (%)	dev m^H (%)	$P_{f_{pred}}$ (bars)	m^H_{pred} (g)	dev P (%)	dev m^H (%)
Gas 3	31.7	255.5	5	21	31.3	259	5.9	22
Gas 4	28.26	185.4	2.9	7.8	28.1	187.9	3.4	9.2
Gas 6	32	135.9	4.2	-	29.95	155	2.4	-
Gas 7	26.2	43	3.3	-	25.53	49.3	5.8	-
Gas 8	33.88	333.1	4.3	22	32.3	349.5	8.8	28
Gas 12	29.2	119.4	5.8	6.1	27.39	135.9	0.08	6.9

Figure 1: Non-stoichiometric clathrate hydrate growth model (layer by layer growth at different successive equilibrium)

Figure 2: PT evolution during crystal growth of non-stoichiometric hydrate from the initial state (A point), to the 1st three phases equilibrium (B point) and the successive equilibrium during crystallization (C_i and D points).

Figure 3: Non-stoichiometric flash hydrate framework: discretization of the cooling in ΔT steps, assumption of the mass of hydrate, validation of the VLH equilibrium

Figure 4: Flash hydrate framework II with reorganization of hydrate last layer, or “stoichiometric” flash hydrate framework II* (homogeneous phase at final gas composition = unique occupancy factor) if $n = 1$

Figure 5: Clathrate hydrate growth approach with hydrate phase reorganization (framework II*) for 4 iterations

Figure 6: PT diagram of experimental and predicted results of the reference case ($\text{CO}_2 - \text{CH}_4 - \text{C}_2\text{H}_6$) at different temperatures from the same initial state (see section 4.2)

(a) Experimental and framework I (n=7)

(b) Experimental and all frameworks during crystallization (PT)

628 References

- 629 [1] H. T. Falenty, A., W. Kuhs, Formation and properties of ice xvi obtained
630 by emptying a type sii clathrate hydrate, *NATURE* 516 (2014) 231.
- 631 [2] E. Sloan, C. Koh, *Clathrate Hydrates of Natural Gases*, 3rd ed., CRC
632 Press, Boca Raton, 2007.
- 633 [3] G. Jeffrey, “Hydrate inclusion compounds”: in Atwood, J. L.; Davies,
634 J. E. D.; MacNicol, D. D.; eds., “Inclusion compounds”, I, Vol. I, Aca-
635 demic Press, New York, 1984.
- 636 [4] F. E. Deaton, W.M., Gas hydrates and their relation to operation of
637 natural-gas pipelines, U.S., Bur. Mines Monogr. 8 (1946) 1–101.
- 638 [5] L. K. Mokhatab S., Wilkens R.J., A review of strategies for solving gas-
639 hydrate problems in subsea pipelines, *Energy Sources. Part A: Recovery.*
640 *Utilization. and Environmental Effects* 29.
- 641 [6] C. F. Duc, N.H., J. Herri, Co2 capture by hydrate crystallization a
642 potential solution for gas emission of steelmaking industry, *Energy Con-*
643 *version Management* 8 (2007) 1313–1322.
- 644 [7] K. M. L. A. C. F. F. D. Douzet, J., J. Herri, Prototyping of a real size
645 air-conditioning system using a tetra-n-butylammonium bromide semi-
646 clathrate hydrate slurry as secondary two-phase refrigerant - experimen-
647 tal investigations and modelling, *International Journal of Refrigeration-*
648 *Revue Internationale du Froid* 36.
- 649 [8] J. Herri, C. E., Carbon dioxide, argon, nitrogen and methane clathrate
650 hydrates: thermodynamic modeling, investigation of their stability in
651 martian atmospheric conditions and variability of methane trapping,
652 *Planetary and Space Science* 73 (2012) 376–386.
- 653 [9] K. kvenvolden, A review of the geochemistry of methane in natural gas
654 hydrate, *Organic Geochemistry* 23.
- 655 [10] E. Sloan, A changing hydrate paradigm-from apprehension to avoidance
656 to risk management, *Fluid Phase Equilibria* 228-229 (2005) 67–74.

- 657 [11] L. Q. D. B. B. H. J. G. P. Le Quang, D., P. Duchet-Suchaux, Exper-
 658 imental procedure and results to measure the composition of clathrate
 659 hydrates, during crystallization and at quilibrium, from n_2 - co_2 - ch_4 - c_2h_6 -
 660 c_3h_8 - c_4h_{10} gas mixtures, Submitted to Fluid Phase Equilibria.
- 661 [12] J. Herri, M. Kwaterski, Derivation of a langmuir type model to describe
 662 the intrinsic growth rate of gas hydrates during crystallization from gas
 663 mixtures, Chemical Engineering Science 81 (2012) 28–37.
- 664 [13] S. r. H. Boesen, R.R., K. Perdersen, New approach for hydrate flash
 665 calculations, Proceedings of the 8th International Conference on Gas
 666 Hydrates.
- 667 [14] P. Skovborg, P. Rasmussen, A mass transport limited model for the
 668 growth of methane and ethane gas hydrates, Chemical Engineering Sci-
 669 ence 49 (1994) 1131–1143.
- 670 [15] G. Soave, Equilibrium constants from a modified redlich-kwong equation
 671 of state, Chemical Engineering Science 27 (1972) 1197–1203.
- 672 [16] A. Danesh, PVT and Phase Behavior of Petroleum Reservoir Fluids,
 673 Elsevier, 1998.
- 674 [17] J. Prausnitz, R. Lichtenthaler, E. de Azevedo, Molecular thermodynam-
 675 ics of fluid-phase equilibria, Prentice Hall PTR, 1998.
- 676 [18] B. A. K. M. F. A. O. Y. Herri, J.M., C. A., Gas hydrate equilibria from
 677 co_2 - n_2 and co_2 - ch_4 gas mixtures, - experimental studies and thermody-
 678 namic modeling, Fluid Phase Equilibria 301 (2011) 171–190.
- 679 [19] G. Holder, S. Zetts, N. Pradhan, Phase behavior in systems containing
 680 clathrate hydrates: A review, Reviews in Chemical Engineering 5.
- 681 [20] E. Sloan, Clathrate Hydrates of Natural Gases, 2nd ed., Marcel Dekker,
 682 New York., 1998.
- 683 [21] P. J. van der Waals, J.H., Clathrate solutions, Adv. Chem. Phys. 2
 684 (1959) 1–57.
- 685 [22] M. H. von Stackelberg, M., On the structure of gas hydrates, J. Chem.
 686 Phys. 2 (1951) 1319–1320.

- 687 [23] T. J. Handa, Y.P., J. Phys. Chem. 23 (1986) 5917.
- 688 [24] V. McKoy, O. J. Sinanoğlu, Theory of dissociation pressures of some
689 gas hydrates, J Chem. Phys 38 (1963) 2946–2956.
- 690 [25] L. Michelsen, J. Mollerup, Thermodynamic models: Fundamentals &
691 Computational Aspects, 2nd edition, Tie-Line Publications, 2007.
- 692 [26] F. R. Adisasmito, S., E. Sloan, Hydrate of carbon dioxide and methane
693 mixtures, J. Chem. Eng. Data 36 (1991) 68–71.
- 694 [27] S. Larson, Phase studies of the two component carbon dioxide-water
695 system involving the carbon dioxide hydrate,, Ph.D. thesis, University
696 of Illinois, Urbana, IL (1955).
- 697 [28] Y. Dyadin, E. Aladko, Proceedings of the 2nd Int.Conf.on Natural Gas
698 Hydrates, Toulouse.
- 699 [29] H. G. Thakore, J.L., Solid vapor azeotropes in hydrate-forming systems,
700 Ind. Eng. Chem. Res. 26 (1987) 462–469.
- 701 [30] O. R. Yasuda, K., Phase equilibrium of clathrate hydrates formed with
702 methane, ethane, propane or carbon dioxide at temperatures below the
703 freezing point of water, J. Chem. Eng. Data 53 (2008) 2182–2188.
- 704 [31] D. A. Avlonitis, D., A. Todd, Measurement and prediction of hydrate
705 dissociation pressure of oil-gas systems, Ph.D. thesis, Heriot-Watt Uni-
706 versity, Edinburgh (1988).
- 707 [32] B. P. R. Englezos, P., Experimental study on the equilibrium ethane
708 hydrate formation conditions in aqueous electrolyte solutions, Ind. Eng.
709 Chem. (30) 1655–1659.
- 710 [33] O. L. Nixdorf, J., Experimental determination of hydrate equilibrium
711 conditions for pure gases, binary and ternary mixtures and natural gases,
712 Fluid Phase Equilib. 139.
- 713 [34] P. J.-S. G. F. Herri, J.M., M. Cournil, Interest of in situ particle size dis-
714 tribution for the characterization of methane hydrate formation: Iden-
715 tification of the mechanisms of crystallization, AIChE Journal 45 (1999)
716 590–602.

- 717 [35] W. J. Child, Thermodynamic functions for metastable ice structures i
718 and ii, J. Phys. Chem. 68 (1964) 1834–1838.
- 719 [36] P. Dharmawandhana, The measurement of the thermodynamic param-
720 eters of the hydrate structure and application of them in the prediction
721 of natural gas hydrates, Ph.D. thesis, Colorado School of Mines (1980).
- 722 [37] P. K. John, V.T., G. Holder, AIChE. J. 31 (1985) 252–259.