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A review on hydrate composition and capability of thermodynamic modeling to predict hydrate pressure and composition

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Abstract

Gas hydrates are widely considered to be a crucial topic in oil and gas industries and attracting significant research due to potential applications such as gas storage, separation as well as water desalination. While the guest composition of hydrate phase is vital, due to the experimental difficulties in measuring hydrate composition, very little applicable information is available in the literature. Paradoxically, this is true, in spite of that; completing an experimental database on hydrate composition could have a significant impact on the processes design and modeling. Moreover, this should provide fundamental knowledge of kinetic effects as well as clarifying thermodynamic equilibrium. Hence, this paper was planned with the intent to fill in the gaps, classify and offer an overview of experimentally derived data on hydrate composition for literature. In addition, a thermodynamic model based on the van der Waals and Platteeuw approach and Kihara potential was utilized to simulate the hydrate composition along with equilibrium pressure.

Previous experimental data shows that guest distribution in hydrate phase depends noticeably on the guest composition in vapor phase. In addition, composition of larger molecules, such as propane or butane, in the hydrate phase, is notably higher than in vapor phase. Our simulation results demonstrated that the hydrate composition data from direct measurement (microscopic tools) have been well evaluated by the thermodynamic model. Nevertheless, when structural transition can occur in a system, the thermodynamic model is no longer accurate. In the case of indirect measurements, the thermodynamic model usually predicts well the hydrate composition. Nonetheless, its capability does vary with differing hydrate composition and equilibrium pressure, to the extent that in some cases, it completely fails to predict hydrate composition. This could be due to kinetic effects on the enclathration of guest molecules during the crystallization, errors in experimental techniques to measure the hydrate composition or the model parameters like Kihara potential are not properly applied. Finally, these observations show that more reliable experimental database is needed to study the evolution of guest distribution in hydrate phase and some enhancements are required for the standard thermodynamic model.

1. Introduction

One of the main concerns in flow assurance during oil and gas production is avoiding gas hydrate formation due to the presence of water and light hydrocarbons at high pressure and low temperature conditions, especially true for deep sea drilling or arctic exploration and pipelines. Therefore, the safety and economic costs of removing gas hydrates have been of great interest [1–8]. Plus, the enormous amount of natural gas in the form of oceanic and permafrost gas hydrates are a promising future energy resource [9–12]. Recently, gas hydrates have attracted widespread attention due to diverse applications such as gas separation [13–21], CO₂ capture [22–30], water desalination [31–38], natural gas storage and transportation [39–44] and even planetary science [45–48]. For all above mentioned applications of clathrate hydrates, it is essential to increase our knowledge of thermodynamics, kinetics and the crystallization mechanisms of clathrate hydrates.

Numerous studies have investigated phase equilibria of clathrate hydrates [12,33,49–54]. Nonetheless, there has been little consideration for hydrate composition. Indeed, quantifying hydrate equilibrium composition presents several obstacles such as water occlusion, heterogeneous solid phase and measuring of solid phase concentration [12]. Hence, experimental data on hydrate composition has been rare. However, these publications do include some valuable information about fundamental hydrate phase composition, enclathration process as well as guest distribution in hydrate phase. Thus, we were able to collect invaluable data from the literature about the guest distribution in hydrate phase over a wide range of temperature, pressure and compositions. Furthermore, a thermodynamic model based on van der Waals and Platteeuw approach (vdWP) was used to detect divergences from this standard approach and previous experiments. Differences will be discussed, considering that experimental data may not be at thermodynamic equilibrium.

2. Gas hydrates

Water molecules in presence of gas molecules at high pressure and low temperature can form cavities and guest molecules like CO₂, N₂, CH₄, C₂H₆ etc. can be encased into these cavities. This ice-like structure is called gas hydrate. Based on the type of cavities and also the nature of guest molecules, there are three principal structures, sI, sII and sH. The sI usually forms in presence of small molecules (diameter between 4.2 and 6 Å) like methane and carbon dioxide. Larger molecules (diameter between 6 and 7 Å) like propane, or small molecules (diameter less than 4.2 Å), such as nitrogen, form sII. sH is composed of a combination of small and large molecules (typically between 7 and 9 Å) [1,2]. Table 1 presents the differences between structures.

Table 1. The differences between three structures of gas hydrates [12]

Hydrate structures	sI		sII		sH		
Shape
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 6 ³	5 ¹² 6 ⁸
Number per unit cell (m _i)	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Coordination number ^a	20	24	20	28	20	20	36
(a) The number of oxygen atom per cavity							

72 3. Thermodynamic modeling

73 At thermodynamic equilibrium, the chemical potential of each phase must be the same. In the
 74 case of gas hydrates, based on the classical van der Waals and Platteeuw model [55], liquid-
 75 hydrate equilibrium is expressed by defining a metastable phase β , corresponding to the empty
 76 hydrate:

$$77 \Delta\mu_W^{L-\beta} = \Delta\mu_W^{H-\beta} \quad (1)$$

78 The left hand side of equation 1 is the difference between chemical potential of water in liquid
 79 and β phase and the right hand side is the difference between chemical potential of water in
 80 hydrate and β phase.

81 3.1. Description of $\Delta\mu_W^{L-\beta}$

82 The difference between chemical potential of water in liquid phase and β phase can be described
 83 by classical thermodynamic using Gibbs-Duhem equation. It can be rewritten as follow [14]:

$$84 \Delta\mu_W^{L-\beta} =$$

$$85 T \frac{\Delta\mu_W^{L-\beta}|_{T^0 P^0}}{T^0} + \left(b_{P,W}^{L-\beta} T^0 - \Delta C_{p,w}^{L-\beta} \Big|_{P^0 T^0} \right) - T \ln \frac{T}{T^0} + \frac{1}{2} b_{P,W}^{L-\beta} T (T - T^0) + \left(\Delta h_{W,m}^{L-\beta} \Big|_{P^0 T^0} + \right.$$

$$86 T^0 \left(b_{P,W}^{L-\beta} T^0 - \Delta C_{p,w}^{L-\beta} \Big|_{P^0 T^0} \right) - \frac{1}{2} b_{P,W}^{L-\beta} T^0 \Big)^2 \left(1 - \frac{T}{T^0} \right) + \Delta v_{W,m}^{L-\beta} \Big|_{T^0} (P - P^0) - RT \ln x_W^L \quad (2)$$

87 where $T^0=273.15\text{K}$ and $P^0=0$ are the reference temperature and pressure, respectively. $\Delta v_{W,m}^{L-\beta}$,
 88 $\Delta C_{p,w}^{L-\beta}$ and $b_{P,W}^{L-\beta}$ are thermodynamic properties of water in liquid phase and β phase and they
 89 were calculated by Sloan and Koh [12]. $\Delta h_{W,m}^{L-\beta}$ and $\Delta\mu_W^{L-\beta}$ are microscopic parameters of
 90 hydrates and regrettably there are different values correspond to each author. Based on a previous
 91 study of our team, it was concluded that the values from Handa and Tse are the best set for

modeling gas hydrates equilibrium [14,56]. All parameters are listed in Table 2. More details can be found in the previous works of our group [14,47,57,58].

Table 2. Thermodynamic properties of hydrates

Parameters	Unit	Structure I	Structure II
$\Delta h_{w,m}^{L-\beta}$	J/mol	-5080	-5247
$\Delta v_{w,m}^{L-\beta}$	$10^{-6}\text{m}^3/\text{mol}$	4.5959	4.99644
$\Delta C_{p,w}^{L-\beta}$	J/mol/K	-38.12	-38.12
$b_{p,w}^{L-\beta}$	J/mol/K ²	0.141	0.141
$\Delta\mu_w^{L-\beta}$	J/mol	1287	1068

3.2. Description of $\Delta\mu_w^{H-\beta}$

From van der Waals and Platteeuw approach, statistical thermodynamics is used to express $\Delta\mu_w^{H-\beta}$:

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

where v_i is the number of cavities type i per mole of water. θ_j^i is the occupancy factor of molecule j in the cavity i . The occupancy factor can be described by considering the analogy between gas adsorption in the three dimensional hydrate structures and two-dimensional Langmuir adsorption [12,59].

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

where $f_j(T, P)$ is the fugacity of guest molecule j at desire temperature and pressure. The value of fugacity can be calculated by assuming equilibrium with a gas phase. Therefore, a standard equation of state, such as Soave-Redlich-Kwong (SRK), can be used as fugacities are similar in all phases, including vapor phase. C_j^i is the Langmuir constant of guest molecule j in the cavity type i . The Langmuir constant depends on the interaction potential between the trapped guest molecules and the surrounding water molecules cage, and for spherical guest-cages potentials can be expressed as follows:

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

where $w(r)$ is the potential interaction between the guest molecule and the cavity based on the distance between the gas and water molecule in the structure (r). In our study, the potential interaction was calculated based on the Kihara parameters as following:

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

117 and

$$118 \quad \Delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (7)$$

119 Parameters ε , σ and a are so-called Kihara parameters and they correspond to minimum energy,
 120 collision diameter and hard-core radius, respectively. The Kihara parameters for several gases
 121 were obtained in the previous studies by our group [47,57], and Sloan [60]. They are listed in
 122 Table 3.

123 **Table 3. Kihara parameters for several gases. ε/k , σ for N_2 , CO_2 , CH_4 , C_2H_6 , C_3H_8 and $i-C_4H_{10}$ determined**
 124 **from our earlier studies [47,57,61] and $n-C_4H_{10}$ from Sloan [60]. Hard-core radius for all gases from Sloan**
 125 **[60]**

Gas	ε/k (K)	σ (Å)	a (Å)
N_2	133.13	3.099	0.3526
CO_2	178.21	2.873	0.6805
CH_4	166.36	3.050	0.3834
C_2H_6	177.46	3.205	0.5651
C_3H_8	195.00	3.340	0.6502
$i-C_4H_{10}$	212.50	3.239	0.8706
$n-C_4H_{10}$	209.0	2.9125	0.9379

126
 127 First, for a gas mixture at a desired temperature, the equilibrium pressure which satisfies equation
 128 (1) is calculated. Subsequently, the occupancy factor is determined based on equation (4). Then,
 129 the hydrate composition is calculated as following:

$$130 \quad x_j^H = \frac{\sum_i v_i \theta_j^i}{\sum_i \sum_j v_i \theta_j^i} \quad (8)$$

131 The procedure for calculating hydrate equilibrium pressure and composition of mixed gas
 132 hydrates is shown in Figure 1.

Figure 1. Procedure for calculating gas hydrate equilibrium pressure and composition

The average deviations for pressure and hydrate composition have been calculated based on equations 9 and 10, respectively.

$$AADp\% = \frac{100}{N} \sum_i^N \left(\left| \frac{P_i^{exp} - P_i^{pre}}{P_i^{exp}} \right| \right) \quad (9)$$

$$AADc = \frac{1}{N} \sum_i^N (|x_i^{exp} - x_i^{pre}|) \quad (10)$$

where i is equilibrium point, N total number of equilibrium points, P pressure, x hydrate composition, exp experimental data and pre prediction results. $AADp$ and $AADc$ are average absolute deviation for pressure and composition, respectively.

All the thermodynamic modelling section has been implemented in our in-house software, GasHyDyn. This software has shown a very good capability of liquid-hydrate equilibrium predictions [14,57], and will be used to discuss the experimental results for both pressure and hydrate composition. A photo from GasHyDyn environment with complementary information summarizing the procedure of submitting a calculation has been added to the Supporting Information document (Appendix A).

Nota Bene: the hydrate structure for modeling was chosen based on the statement of each research. Unfortunately, there were some cases that the authors did not provide the structure. Therefore, we simulated their experimental data for both structures I and II. Consequently, the structure which agreed better with the simulation results was chosen.

4. Hydrate composition in literature and model comparison

Despite countless works on equilibrium pressure and temperature of mixed gas hydrates, to the best of our knowledge, there are still few studies on the hydrate composition which depends on the pressure, temperature and gas phase composition. Thanks to gas chromatography, the composition of the gas phase can be easily measured, but solid phase analysis is still challenging, often leading to experimental errors. In addition, some researchers studied the hydrate composition of gas mixtures by different methods making them exceedingly difficult to compare. Hence, in the present work, studies providing hydrate composition in open literature were collected and presented. Moreover, the capability of a thermodynamic model to predict hydrate pressure and composition was evaluated. This should be noted that there were some studies on the hydrate composition of gas mixtures that do not furnish exact values of hydrate composition. Sometimes, only figures were shown and quantitative data were not available. In this section, the collected data from open literature is categorized based on their methods of hydrate composition measurements.

4.1. Dissociation of whole hydrate phase

One of the first systematic reports on the mixed hydrate composition was carried out by Jhaveri and Robinson [62]. They studied the gas hydrate equilibrium curves of methane-nitrogen mixture as well as the guest composition in gas and hydrate phases. They introduced gas mixture and water inside a batch reactor at a pressure 25% more than the equilibrium pressure at a desired temperature. After completion of hydrate formation, the gas phase was analyzed chromatographically. The gas was then removed from the reactor and the hydrate crystals dissociated. The decomposed gas was analyzed to obtain the hydrate composition. They measured hydrate composition at three temperatures 273.2, 277.4 and 279.8K for various ranges of pressure and gas compositions. Their results are illustrated in Figure 2. Clearly, at a constant temperature, by increasing the molar composition of nitrogen in the gas phase, the equilibrium pressure increased. Since the hydrate equilibrium pressure of nitrogen at a desired temperature is

178 higher than of methane. Moreover, the simulation results of equilibrium pressure were in a good
 179 accordance with the experimental data.

Figure 2. P-x diagram of nitrogen-methane mixed hydrate (sI) [62]

Table 4. The experimental results of Jhaveri and Robinson [62] for methane-nitrogen mixture hydrates and simulation results. Uncertainties were not provided.

Texp (K)	Pexp (MPa)	Ppre (MPa)	S	Gas composition (exp)		Hydrate composition (exp)		Hydrate composition (pre)	
				N ₂	CH ₄	N ₂	CH ₄	N ₂	CH ₄
273.2	2.640	2.660	I	0.000	1.000	0.000	1.000	0.000	1.000
273.2	3.620	3.116	I	0.160	0.840	0.065	0.935	0.034	0.966
273.2	4.310	3.708	I	0.310	0.690	0.098	0.902	0.078	0.922
273.2	5.350	5.092	I	0.530	0.470	0.200	0.800	0.176	0.824
273.2	6.550	6.301	I	0.645	0.355	0.350	0.650	0.259	0.741
273.2	7.750	7.517	I	0.725	0.275	0.425	0.575	0.339	0.661
273.2	10.640	9.525	I	0.815	0.185	0.620	0.380	0.466	0.534
273.2	11.650	11.716	I	0.880	0.120	0.710	0.290	0.597	0.403
273.2	12.770	12.577	I	0.900	0.100	0.765	0.235	0.646	0.354
277.4	3.860	4.028	I	0.000	1.000	0.000	1.000	0.000	1.000

277.4	5.200	6.839	I	0.440	0.560	0.180	0.820	0.138	0.862
277.4	8.110	9.575	I	0.630	0.370	0.310	0.690	0.262	0.738
277.4	10.340	12.286	I	0.740	0.260	0.470	0.530	0.378	0.622
277.4	12.060	13.628	I	0.780	0.220	0.560	0.440	0.433	0.567
277.4	13.320	21.582	I	0.925	0.075	0.810	0.190	0.734	0.266
277.4	14.590	22.950	I	0.940	0.060	0.860	0.140	0.779	0.221
277.4	16.210	29.486	I	1.000	0.000	1.000	0.000	1.000	0.000
279.8	5.140	5.161	I	0.000	1.000	0.000	1.000	0.000	1.000
279.8	7.140	7.751	I	0.350	0.650	0.091	0.909	0.102	0.898
279.8	8.370	9.170	I	0.460	0.540	0.224	0.776	0.155	0.845
279.8	15.550	16.516	I	0.750	0.250	0.550	0.450	0.404	0.596
279.8	20.670	21.253	I	0.840	0.160	0.680	0.320	0.549	0.451
279.8	25.230	27.054	I	0.914	0.086	0.802	0.198	0.715	0.285
279.8	32.420	37.997	I	1.000	0.000	1.000	0.000	1.000	0.000
AADp		16.32%	AADc					0.067	

185

186 The results of thermodynamic simulation for hydrate pressure and composition are detailed in
187 Table 4. At 273.2 K and 279.8 K, the equilibrium pressures were successfully predicted.
188 Nonetheless, the equilibrium pressures at 277.4 K for nitrogen compositions more than 90% mole
189 fraction (in gas phase) were poorly simulated (sI). As nitrogen forms sII, we suspected a phase
190 transition in this case. Hence, the experimental data were also simulated by considering sII. The
191 results revealed that sII simulations were also unsuccessful to predict the equilibrium pressures
192 for the 277 K isotherm at high concentrations of nitrogen in the mixture of CH₄/N₂. This might be
193 due to whether the co-existence of sI and sII at this condition (which cannot be predicted by the
194 model as it is implemented in our software) or the experimental measurement uncertainties.

195 The hydrate composition predictions were slightly different. The simulation results at low and
196 high percentages of nitrogen in the hydrate phase agreed satisfactorily with the experimental data.
197 But when there is no significant difference between the compositions of methane and nitrogen,
198 the simulation results deviated from experimental. Still, the average absolute deviation of hydrate
199 composition was less than 0.07 in mole fraction.

200 Kawasaki et al. [63] studied the guest content in hydrate phase for a gas mixture of methane,
201 ethane, propane and iso-butane with initial molar concentrations 0.885, 0.046, 0.054 and 0.015,
202 respectively. They used the same procedure as Jhaveri and Robinson [62] by removing the gas
203 and dissociating the hydrate to measure the hydrate composition at two different temperatures,
204 274.15 and 278.15 K. The experimental and simulation results are presented in Table 5.

205 **Table 5. The gas composition in different phases at 3MPa. Uncertainties were not provided.**

Gas	T=274.15 K	T=278.15 K
	Gas and hydrate phase compositions	Gas and hydrate phase compositions

	Gas (exp)	Hydrate (exp)	Hydrate (Pre)	Gas (exp)	Hydrate (exp)	Hydrate (Pre)
Methane	0.987	0.760	0.827	0.979	0.702	0.784
Ethane	0.011	0.089	0.031	0.017	0.104	0.034
Propane	0.002	0.117	0.141	0.004	0.150	0.181
iso-Butane	0.0	0.034	NA	0.0	0.044	NA

206

207 The authors remarked that all i-butane molecules concentrated in the hydrate phase, irrespective
208 of the temperature. They also considered that the concentration of heavier hydrocarbon in hydrate
209 phase at 278.15 K is higher at 274.15 K. Moreover, the deviation of simulation results for the
210 hydrate composition of methane, ethane and propane were 0.074, 0.064 and 0.027, respectively.
211 The deviations between the experimental and prediction values could be due to uncertainties in
212 the experimental procedure. In fact, Kawasaki et al. removed the gas mixture from the reactor
213 after hydrate formation to measure hydrate composition. Hence, the hydrate phase could be
214 dissociated during the gas removing step due to the pressure drop, leading to the measurement
215 uncertainties.

216 Kang et al. [64] measured the hydrate composition of CO₂-N₂ mixture at three isotherms of
217 vapor-hydrate equilibrium condition. After hydrate formation, they purged the gas outside the
218 cell and dissociated the hydrate by increasing temperature. Figure 3 presents the equilibrium
219 pressure versus nitrogen composition in the gas phase at H-V equilibrium condition for three
220 isotherms. Our simulation results are also shown by dash lines in the figure. The simulation of
221 hydrate composition is detailed in Table 6 as well as the experimental results.

Figure 3. Experimental H-V equilibrium data for N₂/CO₂ mixture by Kang et al. [64] and the simulation results (sI)

Table 6. Experimental results of Kang et al. [64] and simulation. Composition uncertainties were not provided.

T _{exp} (K) (±0.1)	P _{exp} (MPa) (±0.01)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp)		Hydrate composition (pre)	
				CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
274.0	1.36	1.42	I	1.00	0.00	1.00	0.00	1.00	0.00
274.0	1.73	1.74	I	0.82	0.18	0.99	0.02	0.98	0.02
274.0	2.30	2.39	I	0.60	0.40	0.95	0.05	0.94	0.06
274.0	2.77	2.84	I	0.50	0.50	0.93	0.07	0.92	0.08
274.0	3.48	3.57	I	0.40	0.60	0.90	0.10	0.87	0.13
274.0	7.07	6.55	I	0.21	0.79	0.58	0.42	0.71	0.29
274.0	10.95	10.03	I	0.12	0.88	0.34	0.66	0.53	0.47
274.0	14.59	14.91	I	0.05	0.95	0.18	0.82	0.28	0.72
274.0	17.52	20.81	I	0.00	1.00	0.00	1.00	0.00	1.00
277.0	1.91	1.99	I	1.00	0.00	1.00	0.00	1.00	0.00
277.0	2.54	2.38	I	0.85	0.15	0.98	0.02	0.98	0.02
277.0	3.30	3.65	I	0.57	0.43	0.95	0.05	0.93	0.07

277.0	5.12	5.40	I	0.39	0.61	0.89	0.11	0.85	0.15
277.0	11.71	11.30	I	0.18	0.82	0.54	0.46	0.62	0.38
277.0	15.15	14.81	I	0.12	0.88	0.35	0.65	0.49	0.51
277.0	18.74	19.56	I	0.07	0.93	0.19	0.81	0.31	0.69
277.0	23.50	28.37	I	0.00	1.00	0.00	1.00	0.00	1.00
277.0	1.91	1.99	I	1.00	0.00	1.00	0.00	1.00	0.00
277.0	2.54	2.38	I	0.85	0.15	0.98	0.02	0.98	0.02
280.0	2.74	2.86	I	1.00	0.00	1.00	0.00	1.00	0.00
280.0	3.52	3.57	I	0.83	0.17	0.98	0.02	0.98	0.02
280.0	4.14	4.35	I	0.70	0.30	0.96	0.04	0.95	0.05
280.0	4.95	5.29	I	0.59	0.41	0.94	0.06	0.92	0.08
280.0	8.09	8.50	I	0.39	0.61	0.86	0.14	0.83	0.17
280.0	14.64	13.50	I	0.25	0.75	0.64	0.36	0.68	0.32
280.0	20.29	18.39	I	0.17	0.83	0.45	0.55	0.55	0.45
280.0	26.09	25.74	I	0.09	0.91	0.22	0.78	0.35	0.65
280.0	31.58	38.81	I	0.00	1.00	0.00	1.00	0.00	1.00
AADp		6.5%	AADc					0.04	

As Figure 3 and Table 6 indicate, the thermodynamic model acceptably predicted the equilibrium pressure (average deviation 6.5%). The hydrate composition simulation could be categorized in two parts. The first part is when carbon dioxide was dominant in the hydrate phase. In this case, the simulation results were well predicated (average absolute deviation for 13 equilibrium points was 0.016 mole fraction). While nitrogen was dominant in the hydrate phase, the average absolute deviation was 0.071 in mole fraction.

4.2. Material balance and volumetric properties evaluated from equation of state

Ohgaki et al. investigated the phase equilibrium of carbon dioxide-methane hydrate at 280.3 K [65]. They obtained the guest composition in gas, liquid and hydrate phases at isothermal conditions in a batch reactor. Their experimental procedure is briefly described as follows: They injected separately carbon dioxide and methane to the reactor. Pure water was then introduced to the reactor. The amount of each material was weighed. Thanks to a gas chromatograph, they determined the gas composition of carbon dioxide and methane at equilibrium temperature and pressure. The solubility of carbon dioxide and methane in water was calculated based on Henry constants. They assumed that the general formula for mixed carbon dioxide-methane hydrate is as follows:

$$zCO_2 \cdot (1 - z) \cdot qH_2O \quad (11)$$

where z is the mole fraction of carbon dioxide in hydrate phase and q is the hydration number at ideal condition. They also hypothesized that the molar volume of hydrate is $130.1 \text{ cm}^3/\text{mol}$ [65]. They calculated the volumetric properties from Soave-Redlich-Kwong equation of state or

IUPAC recommended equation of state for carbon dioxide and methane [60,65–67]. The hydrate compositions were then calculated by the material balance.

Figure 4 shows their experimental results for hydrate phase composition and our simulation results. Furthermore, Table 7 summarizes the experimental and modeling results by details for carbon dioxide-methane hydrate at 280.3 K.

Figure 4. Carbon dioxide-methane hydrates phase equilibria at 280.3 K. Experimental [65] and simulation results (sI). Error bars correspond to the standard uncertainty of experimental hydrate composition.

Table 7. Experimental results of Ohgaki et al. [65] for methane-carbon dioxide mixture hydrates at 280.3 K and simulation results.

P _{exp} (MPa) (±0.005)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp) (±5%)		Hydrate composition (pre)	
			CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
3.04	2.98	I	1.00	0.00	1.00	0.00	1.00	0.00
3.24	3.46	I	0.68	0.32	0.84	0.16	0.79	0.21
3.38	3.55	I	0.59	0.42	0.80	0.20	0.72	0.28
3.60	3.85	I	0.49	0.51	0.67	0.33	0.63	0.37
3.64	3.93	I	0.45	0.55	0.69	0.31	0.60	0.40
3.67	3.93	I	0.45	0.55	0.68	0.32	0.60	0.40
3.71	3.98	I	0.43	0.57	0.61	0.39	0.58	0.42

3.77	4.09	I	0.38	0.62	0.60	0.40	0.53	0.47
3.86	4.16	I	0.36	0.64	0.59	0.41	0.50	0.50
4.22	4.49	I	0.24	0.76	0.44	0.56	0.37	0.63
4.31	4.57	I	0.22	0.79	0.39	0.61	0.34	0.66
4.32	4.57	I	0.22	0.78	0.36	0.64	0.34	0.66
4.34	4.61	I	0.20	0.80	0.37	0.63	0.32	0.68
4.37	4.61	I	0.20	0.80	0.35	0.65	0.32	0.68
4.37	4.68	I	0.18	0.82	0.36	0.64	0.30	0.70
4.44	4.70	I	0.18	0.82	0.36	0.64	0.29	0.71
4.50	4.73	I	0.17	0.83	0.35	0.65	0.28	0.72
4.57	4.82	I	0.14	0.86	0.32	0.68	0.24	0.76
3.98	4.31	I	0.30	0.70	0.53	0.47	0.44	0.56
4.00	4.29	I	0.31	0.69	0.52	0.48	0.45	0.55
4.01	4.28	I	0.31	0.69	0.55	0.45	0.45	0.55
4.06	4.35	I	0.29	0.71	0.51	0.49	0.43	0.57
4.07	4.33	I	0.29	0.71	0.52	0.48	0.43	0.57
4.15	4.41	I	0.27	0.73	0.47	0.53	0.41	0.59
4.20	4.48	I	0.25	0.76	0.45	0.55	0.38	0.62
4.58	4.83	I	0.14	0.86	0.32	0.68	0.24	0.76
4.63	4.83	I	0.14	0.86	0.29	0.71	0.24	0.76
4.75	4.96	I	0.10	0.90	0.24	0.76	0.18	0.82
4.85	5.03	I	0.09	0.91	0.23	0.77	0.16	0.84
4.99	5.14	I	0.07	0.94	0.16	0.84	0.12	0.88
5.46	5.44	I	0.00	1.00	0.00	1.00	0.00	1.00
AADp	5.8%	AADc					0.06	

259

260 They observed that at each equilibrium condition, the mole fraction of carbon dioxide in hydrate
261 phase is significantly larger than in gas phase. Hence, based on the idea of methane exploration
262 by carbon dioxide injection and by defining the average distribution coefficient of methane, they
263 concluded that methane in hydrate phase can be replaced by carbon dioxide; as a result, methane
264 concentration in the gas phase will be increased.

265 The simulation results agreed well with the experimental data for hydrate equilibrium pressure
266 (AADp 5.8%). Additionally, the mole fraction deviation of hydrate composition calculations was
267 about 0.06.

268 Belandria et al. investigated the compositional analysis of carbon dioxide-methane hydrate by the
269 same method as Ohgaki et al. [65,68]. Our simulation results based on the experimental data of
270 Belandria et al. are presented in Table 8 and Figure 5. As it is clear on the table, the
271 thermodynamic model predicted hydrate equilibrium pressure with an acceptable error (7.8%).
272 Although the hydrate composition simulation had mostly an adequate agreement with the data

obtained, several experimental equilibrium points were poorly simulated (for instance 280 K and 3.54MPa). Additionally, they reported that CSMGem model was not capable to converge three phase flash calculations in some cases, in comparison, the thermodynamic model had no problem with three phase flash calculations [68].

Table 8. Experimental results of Belandria et al. [68] for methane-carbon dioxide hydrates and simulation results.

T (K) (± 0.02)	P _{exp} (MPa) (± 0.002)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp) ($\pm 1\%$)		Hydrate composition (pre)	
				CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
273.6	2.44	2.55	I	0.08	0.92	0.10	0.90	0.16	0.84
273.6	1.84	2.03	I	0.35	0.66	0.55	0.45	0.52	0.48
273.6	1.94	2.12	I	0.29	0.71	0.39	0.61	0.46	0.54
273.6	2.05	2.24	I	0.22	0.78	0.29	0.71	0.37	0.63
273.6	1.51	1.67	I	0.63	0.37	0.88	0.12	0.77	0.23
273.6	1.61	1.77	I	0.55	0.46	0.80	0.20	0.71	0.29
275.2	2.58	2.77	I	0.17	0.83	0.34	0.66	0.29	0.71
275.2	2.77	2.98	I	0.09	0.91	0.18	0.82	0.16	0.84
275.2	2.12	2.33	I	0.38	0.62	0.65	0.35	0.56	0.44
275.2	2.22	2.48	I	0.30	0.70	0.59	0.41	0.47	0.53
275.2	2.40	2.63	I	0.23	0.77	0.37	0.63	0.38	0.62
275.2	1.79	1.96	I	0.66	0.34	0.83	0.17	0.79	0.21
275.2	1.87	2.07	I	0.57	0.44	0.75	0.25	0.72	0.28
276.1	2.81	3.00	I	0.18	0.82	0.26	0.74	0.31	0.69
276.1	3.03	3.12	I	0.13	0.87	0.24	0.76	0.24	0.76
276.1	3.03	3.23	I	0.10	0.90	0.24	0.76	0.18	0.82
276.1	2.32	2.43	I	0.41	0.60	0.64	0.36	0.57	0.43
276.1	2.50	2.70	I	0.32	0.69	0.40	0.60	0.48	0.52
276.1	2.69	2.88	I	0.23	0.77	0.31	0.69	0.38	0.62
276.1	1.99	2.14	I	0.67	0.33	0.88	0.12	0.80	0.20
276.1	2.17	2.26	I	0.58	0.42	0.78	0.22	0.73	0.27
278.1	3.42	3.64	I	0.20	0.80	0.23	0.77	0.33	0.67
278.1	3.63	3.83	I	0.14	0.86	0.23	0.78	0.24	0.76
278.1	3.80	3.95	I	0.10	0.90	0.15	0.85	0.19	0.81
278.1	3.04	3.33	I	0.32	0.68	0.46	0.54	0.48	0.52
278.1	3.32	3.55	I	0.23	0.77	0.27	0.73	0.37	0.63
278.1	2.58	2.77	I	0.61	0.39	0.79	0.21	0.74	0.26
279.2	3.57	4.09	I	0.20	0.80	0.27	0.73	0.33	0.67
280.2	4.49	4.76	I	0.15	0.85	0.31	0.69	0.25	0.75
280.2	4.66	4.90	I	0.11	0.89	0.25	0.76	0.19	0.81
280.2	3.54	4.14	I	0.34	0.66	0.73	0.27	0.49	0.51
280.2	4.11	4.46	I	0.24	0.77	0.34	0.66	0.37	0.63

280.2	3.14	3.53	I	0.62	0.38	0.86	0.14	0.74	0.26
280.2	3.48	3.75	I	0.49	0.51	0.79	0.21	0.64	0.36
282.2	5.77	6.08	I	0.11	0.89	0.28	0.72	0.19	0.81
284.2	7.19	7.65	I	0.12	0.89	0.11	0.89	0.18	0.82
AADp		7.8%	AADc					0.07

Figure 5. Hydrate composition for methane-carbon dioxide hydrates. Experimental data [68] and simulation results (sI).

Belandria et al. also studied the hydrate composition of carbon dioxide-nitrogen mixture using the same method [65,69]. They calculated the guest composition in gas, liquid and hydrate phases based on the material balance and volumetric properties evaluated from equation of state. Table 9 details their experimental data and our simulation results. Moreover, Figure 6 illustrates the experimental [69] and simulation results for two isotherms of N_2/CO_2 binary hydrates.

Table 9. Experimental results of Belandria et al. [69] for nitrogen-carbon dioxide mixture hydrates and simulation results.

T (K) (± 0.02)	P _{exp} (MPa) (± 0.002)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp) ($\pm 1\%$)		Hydrate composition (pre)	
				CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
273.6	2.03	2.22	I	0.62	0.38	0.97	0.03	0.95	0.05

273.6	8.15	7.22	I	0.17	0.83	0.66	0.34	0.66	0.34
273.6	11.94	6.94	I	0.18	0.82	0.37	0.63	0.67	0.33
273.6	2.96	3.17	I	0.43	0.57	0.90	0.10	0.89	0.11
274.6	2.54	2.10	I	0.73	0.27	0.74	0.26	0.97	0.03
274.9	5.20	2.21	I	0.72	0.28	0.79	0.21	0.96	0.04
275.2	2.29	2.51	I	0.66	0.34	0.90	0.10	0.95	0.05
275.2	2.64	2.25	I	0.73	0.27	0.89	0.11	0.97	0.03
275.2	3.26	3.69	I	0.45	0.55	0.88	0.12	0.89	0.11
275.2	7.45	8.83	I	0.17	0.83	0.82	0.18	0.64	0.36
275.2	8.25	8.74	I	0.18	0.82	0.80	0.20	0.65	0.35
275.2	12.75	9.32	I	0.16	0.84	0.38	0.62	0.62	0.38
275.6	2.71	2.36	I	0.73	0.27	0.76	0.24	0.97	0.03
275.8	5.38	2.45	I	0.72	0.28	0.80	0.20	0.96	0.04
276.1	2.50	2.69	I	0.68	0.32	0.98	0.02	0.96	0.04
276.1	2.87	2.50	I	0.73	0.27	0.79	0.21	0.97	0.03
276.1	3.70	3.80	I	0.49	0.51	0.70	0.30	0.90	0.10
276.1	4.40	4.70	I	0.40	0.60	0.69	0.31	0.86	0.14
276.1	8.58	9.07	I	0.20	0.80	0.57	0.43	0.67	0.33
276.7	3.70	4.11	I	0.49	0.51	0.70	0.30	0.90	0.10
277.1	2.71	2.94	I	0.71	0.30	0.84	0.16	0.96	0.04
277.3	3.13	2.89	I	0.73	0.27	0.83	0.17	0.96	0.04
277.8	6.16	3.01	I	0.75	0.25	0.86	0.14	0.97	0.03
278.1	2.97	3.21	I	0.73	0.27	0.89	0.11	0.96	0.04
278.1	3.41	3.19	I	0.73	0.27	0.75	0.25	0.96	0.04
278.1	4.19	4.63	I	0.52	0.48	0.66	0.35	0.91	0.09
278.1	9.15	10.69	I	0.23	0.77	0.54	0.46	0.69	0.31
278.1	14.26	16.69	I	0.13	0.87	0.51	0.49	0.49	0.51
279.7	4.82	5.42	I	0.56	0.44	0.70	0.30	0.91	0.09
279.7	10.02	12.26	I	0.26	0.74	0.61	0.39	0.71	0.29
279.7	15.82	19.25	I	0.15	0.85	0.55	0.45	0.50	0.50
281.2	17.63	21.78	I	0.18	0.82	0.58	0.42	0.53	0.47
281.7	6.33	5.22	I	0.75	0.25	0.81	0.19	0.96	0.04
AADp		17.4%	AADc					0.13	

290

291 From Table 9 and Figure 6, notice that neither equilibrium pressure nor hydrate composition were

292 well simulated. Nevertheless, at equilibrium pressures below 7MPa, the simulation results were

293 satisfactory. In contrast, equilibrium pressures more than 7MPa were poorly simulated. In the

294 case of hydrate composition, the average deviation was large (0.13) compared to the simulation

295 of experimental data of Kang et al. (0.04) for the same mixture. This divergence might be due to

296 different experimental procedures.

Figure 6. Hydrate composition for nitrogen-carbon dioxide hydrates at two isotherms. Experimental data [69] and simulation results (sI).

4.3. Gas uptake at isobaric equilibrium condition

Seo et al. studied the vapor-liquid-hydrate equilibrium conditions of nitrogen-carbon dioxide and methane-carbon dioxide mixtures at isobaric condition [70]. They performed their experiments in a batch reactor by injecting gas mixtures and water by a syringe pump at a desired pressure. Then they decreased the temperature to 5 degrees Kelvin below the hydrate formation temperature. Hydrate formation led to a decrease in hydrate pressure. In order to keep constant the pressure, they recharged reactor by the gas mixtures. Then, they increased the temperature by the rate of 1-2 K per hour. The pressure increased due to hydrate dissociation. Then, the dissociated gases were vented. When only a small amount of hydrate crystals remained in the cell and the pressure was constant, this was considered as the three phase equilibrium [70]. Both their experimental and our simulation results for nitrogen-carbon dioxide mixture are listed and presented in Table 10 and Figure 7. Moreover, the results of methane-carbon dioxide mixture are presented in Table 11.

Figure 7. Pressure-gas composition diagram for nitrogen-carbon dioxide at three isotherms (sI). Experimental data from Seo et al. [70] and our prediction results

Table 10. Experimental results of carbon dioxide-nitrogen hydrate equilibrium pressure and composition from Seo et al. [70] and our simulation results. Composition uncertainties were not provided.

T (K) (± 0.1)	P _{exp} (MPa) (± 0.01)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp)		Hydrate composition (pre)	
				CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
274	1.39	1.42	I	1.00	0.00	1.00	0.00	1.00	0.00
274	1.77	1.74	I	0.82	0.18	0.99	0.02	0.98	0.02
274	2.35	2.39	I	0.60	0.40	0.95	0.05	0.94	0.06
274	2.84	2.84	I	0.50	0.50	0.93	0.07	0.92	0.08
274	3.46	3.57	I	0.40	0.60	0.90	0.10	0.87	0.13
274	7.24	6.55	I	0.21	0.79	0.58	0.42	0.71	0.29
274	11.20	10.03	I	0.12	0.88	0.34	0.66	0.53	0.47
274	14.93	14.91	I	0.05	0.95	0.18	0.82	0.28	0.72
274	17.93	20.81	I	0.00	1.00	0.00	1.00	0.00	1.00
277	1.95	1.99	I	1.00	0.00	1.00	0.00	1.00	0.00
277	2.60	2.38	I	0.85	0.15	0.98	0.02	0.98	0.02
277	3.38	3.52	I	0.59	0.41	0.95	0.05	0.93	0.07
277	5.23	5.40	I	0.39	0.61	0.89	0.11	0.85	0.15
277	11.98	11.30	I	0.18	0.82	0.54	0.46	0.62	0.38

277	15.50	15.07	I	0.12	0.88	0.35	0.65	0.48	0.52
277	19.17	19.56	I	0.07	0.93	0.19	0.81	0.31	0.69
277	24.04	28.37	I	0.00	1.00	0.00	1.00	0.00	1.00
280	2.80	2.86	I	1.00	0.00	1.00	0.00	1.00	0.00
280	3.60	3.59	I	0.83	0.18	0.98	0.02	0.98	0.02
280	4.23	4.35	I	0.70	0.30	0.96	0.04	0.95	0.05
280	5.07	5.29	I	0.59	0.41	0.94	0.06	0.92	0.08
280	8.28	8.50	I	0.39	0.61	0.86	0.14	0.83	0.17
280	14.97	13.50	I	0.25	0.75	0.64	0.36	0.68	0.32
280	20.75	18.39	I	0.17	0.83	0.45	0.55	0.55	0.45
280	26.69	25.74	I	0.09	0.91	0.22	0.78	0.35	0.65
280	32.31	38.81	I	0.00	1.00	0.00	1.00	0.00	1.00
AADp		5.7%	AADc					0.04	

Table 11. Experimental results of carbon dioxide-methane hydrate equilibrium pressure and composition from Seo et al. [70] and our simulation results. Composition uncertainties were not provided.

T (K) (±0.1)	Pexp (MPa) (±0.01)	Ppre (MPa)	S	Gas composition (exp)		Hydrate composition (exp)		Hydrate composition (pre)	
				CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
273.1	2.00	1.92	I	0.28	0.72	0.92	0.09	0.45	0.55
274.1	2.00	2.03	I	0.40	0.60	0.94	0.06	0.58	0.42
275.4	2.00	2.06	I	0.61	0.39	0.98	0.02	0.75	0.25
276.3	2.00	2.04	I	0.79	0.21	1.00	0.00	0.88	0.12
273.8	2.60	2.48	I	0.13	0.87	0.66	0.34	0.24	0.76
274.9	2.60	2.54	I	0.23	0.77	0.85	0.15	0.38	0.62
276.3	2.60	2.56	I	0.42	0.59	0.93	0.07	0.58	0.42
277.5	2.60	2.55	I	0.64	0.36	0.98	0.02	0.77	0.23
278.1	2.60	2.46	I	0.83	0.17	0.99	0.01	0.90	0.10
276.6	3.50	3.29	I	0.13	0.87	0.65	0.35	0.24	0.76
277.6	3.50	3.32	I	0.25	0.75	0.73	0.27	0.40	0.60
279.0	3.50	3.45	I	0.42	0.58	0.89	0.11	0.57	0.43
279.9	3.50	3.43	I	0.61	0.39	0.95	0.05	0.74	0.26
280.5	3.50	3.30	I	0.83	0.17	0.99	0.01	0.90	0.10
AAD		3.3%						0.29	

As it is clear in Table 10, Table 11 and Figure 7, the thermodynamic model predicts the equilibrium pressure with adequate deviations (average deviations for methane-carbon dioxide and nitrogen-carbon dioxide hydrate pressure were 3.3 and 5.7%, respectively).

As seen in Table 10, at low concentrations of nitrogen, the hydrate phase compositions were acceptably simulated (sI). Nevertheless, when nitrogen was the dominate component in hydrate

phase, the simulation results deviated from the experimental data. Hence, the hydrate phase compositions were again simulated by taking into account both structures, sI and sII. Prediction results for two isotherms of N_2/CO_2 binary hydrate are presented in Figure 8. This figure shows that, at higher pressures, the hydrate preferentially encapsulates nitrogen from the N_2/CO_2 mixture. Consequently, the nitrogen composition in hydrate phase increases. As clear on the figure, at high concentrations of nitrogen in hydrate phase, sII simulation results are in better agreement with experimental data compared to sI results. This can be explained by the fact that pure nitrogen forms sII hydrates. Thus, when nitrogen is the major component in the mixture, there might be a structural transition from sI to sII.

Figure 8. P-x diagram of N_2 - CO_2 hydrate based on the experimental results of Seo et al. (sI) [70] and our simulation results

For the methane-carbon dioxide mixture, although the equilibrium pressure were satisfactorily simulated (average absolute deviation 3.3%), the thermodynamic model failed to evaluate the hydrate composition (average absolute deviation 0.29 mole fraction).

4.4. Using a tracer

Using a tracer in gas or liquid phase could help to measure hydrate composition. A tracer must not be able to form hydrates and only a small amount should be utilized. This section presents a short report of publications which have used a tracer in their experiment to measure hydrate

composition. Of course, based on the experimental results of these papers, the capability of the thermodynamic model to simulate hydrate composition is evaluated.

Ng determined the hydrate composition for six gas mixture including methane, ethane, propane, iso-butane, n-butane and carbon dioxide. He used n-pentane as a tracer in gas phase. Thanks to a gasometer and composition of n-pentane at the end of experiments, he successfully determined the amount of original gas mixture and overall gas dissociation [71]. Table 12 shows the different gas mixtures in the study. Ng's experimental data and our simulation results are presented in Table 13.

Table 12. Feed composition of different mixtures [71]

Gas	Mixtures (Concentration mole %) (± 0.003)					
	a	b	c	d	e	f
Carbon dioxide	0	0	0	2	0	2
Methane	90	99	84	88	80	86.5
Ethane	0	0	10	0	10	0
Propane	10	1	4	8	5	4
iso-Butane	0	0	2	2	2	0.5
n-Butane	0	0	0	0	3	1

Table 13. Experimental results of Ng [71] and our modeling results

T (C) (± 0.05)	P (MPa) (± 0.007)	Feed	Experimental hydrate composition (± 0.003)						Hydrate composition simulation					
			C ₁	C ₂	C ₃	iC ₄	nC ₄	CO ₂	C ₁	C ₂	C ₃	iC ₄	nC ₄	CO ₂
11.4	2.07	a	0.586	-	0.414	-	-	-	0.61	-	0.39	-	-	-
20.1	6.89	a	0.657	-	0.343	-	-	-	0.64	-	0.36	-	-	-
3.7	2.07	b	0.726	-	0.274	-	-	-	0.65	-	0.35	-	-	-
13.2	6.89	b	0.771	-	0.229	-	-	-	0.67	-	0.33	-	-	-
AADc									0.05					
10.9	2.07	c	0.606	0.087	0.182	0.124	-	-	0.62	0.01	0.2	0.17	-	-
19.4	6.89	c	0.59	0.087	0.2	0.123	-	-	0.64	0.01	0.2	0.15	-	-
AADc									0.03	0.07	0.009	0.02		
12.9	2.07	d	0.6	-	0.297	0.092	-	0.0102	0.6	-	0.28	0.1	-	0.02
21.6	6.89	d	0.63	-	0.289	0.078	-	0.0104	0.62	-	0.27	0.09	-	0.02
AADc									0.005	-	0.018	0.01	-	0.01
11.3	2.07	e	0.581	0.074	0.206	0.107	0.031	-	0.62	0.01	0.22	0.14	0.01	-
19.6	6.89	e	0.617	0.089	0.181	0.087	0.027	-	0.64	0.01	0.23	0.11	0.01	-
AADc									0.031	0.07	0.03	0.02	0.02	
9.8	2.07	f	0.584	0.076	0.265	0.044	0.018	0.011	0.6	0.006	0.31	0.06	0.007	0.017
18.7	6.89	f	0.621	0.077	0.238	0.039	0.011	0.01	0.63	0.007	0.29	0.05	0.006	0.017
AADc									0.01	0.07	0.05	0.01	0.008	0.006

Obviously, in Table 13, there is a wide range of average absolute deviation according to the number and type of components in the feed gas, between 0.006 and 0.07. This variation could be

explained by the fact that for the ternary or quaternary mixtures, kinetic considerations might affect experimental results. Note: the largest deviation belongs to ethane in all the mixtures.

In the 21st century, researchers at Ecole National Supérieur des Mines de Saint-Etienne (Mines Saint-Etienne) developed a new method to determine the hydrate composition not only at equilibrium condition, but also during the crystallization under non-equilibrium conditions. Their new procedure was based on tracing the concentration of lithium salt in liquid phase and material balance. The protocol is as follows: after gas injection inside the reactor, water solution with 10 ppm concentration of lithium salt was inserted in the reactor. By decreasing the temperature at a desire value, hydrate formation started. After several days, the system reached at equilibrium. At this point a gas and liquid sample was taken. The gas sample was analyzed by gas chromatography to determine the gas composition in vapor phase. The liquid sample was analyzed by ion chromatograph to measure the concentration of lithium salt in liquid phase. As lithium does not participate in hydrate formation, it is possible to calculate the amount of water at equilibrium according to the lithium concentration. Then, the system temperature increased stepwise and gas and liquid samples were taken [14,57]. A diagram of their experiments is shown in Figure 9.

Figure 9. The diagram of experimental procedure

Based on this procedure, Herri et al. [14] studied the equilibrium conditions of carbon dioxide-nitrogen and carbon dioxide-methane hydrates. Table 14 and Table 15 present their experimental

results and our corresponding simulation results for carbon dioxide-nitrogen and carbon dioxide-methane mixtures, respectively.

Table 14. Experimental results from Herri et al. [14] and simulation results for carbon dioxide-nitrogen mixture

T (K) (± 0.1)	P _{exp} (MPa) (± 0.01)	P _{pre} (MPa)	S	Gas composition (exp) (± 0.001)		Hydrate composition (exp) (± 0.003)		Hydrate composition (pre)	
				CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
273.4	6.10	7.51	I	0.16	0.84	0.66	0.34	0.63	0.37
274.5	6.20	8.31	I	0.16	0.84	0.66	0.34	0.63	0.37
275.4	6.40	8.64	I	0.19	0.82	0.66	0.34	0.66	0.34
276.5	6.60	9.42	I	0.20	0.80	0.58	0.42	0.67	0.33
273.9	5.90	5.40	I	0.25	0.75	0.75	0.25	0.77	0.23
274.7	5.90	5.93	I	0.26	0.75	0.73	0.27	0.76	0.24
276.0	5.90	6.90	I	0.26	0.74	0.70	0.30	0.76	0.24
276.9	6.00	7.70	I	0.27	0.74	0.70	0.30	0.75	0.25
277.8	6.30	8.14	I	0.29	0.71	0.67	0.33	0.77	0.23
278.1	6.40	8.41	I	0.30	0.71	0.69	0.31	0.77	0.23
278.4	6.40	8.82	I	0.30	0.71	0.72	0.29	0.76	0.24
278.6	6.50	8.93	I	0.30	0.70	0.70	0.31	0.77	0.23
275.4	6.10	7.99	I	0.20	0.80	0.67	0.33	0.69	0.31
276.0	6.20	8.14	I	0.22	0.78	0.65	0.35	0.70	0.30
280.1	5.30	5.75	I	0.56	0.44	0.85	0.16	0.91	0.09
281.1	5.60	6.42	I	0.59	0.42	0.82	0.18	0.91	0.09
AADp		25.6%	AADc					0.05	

Table 15. Experimental results from Herri et al. [14] and simulation results for carbon dioxide-methane mixture

T (K) (± 0.1)	P _{exp} (MPa) (± 0.01)	P _{pre} (MPa)	S	Gas composition (exp) (± 0.001)		Hydrate composition (exp) (± 0.003)		Hydrate composition (pre)	
				CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
277.15	2.04	2.03	I	1.00	0.00	1.00	0.00	1.00	0.00
277.15	2.36	2.45	I	0.64	0.36	0.77	0.23	0.77	0.23
277.15	2.55	2.63	I	0.52	0.48	0.68	0.32	0.68	0.32
277.15	2.80	2.92	I	0.36	0.64	0.54	0.47	0.53	0.47
277.15	3.55	3.55	I	0.11	0.89	0.21	0.79	0.20	0.80
277.15	3.90	3.94	I	0.00	1.00	0.00	1.00	0.00	1.00
AADp		2.10%	AADc					0.004	

In the case of carbon dioxide-nitrogen, the simulation results for hydrate equilibrium pressure are not very reliable. Nonetheless, the average absolute deviation for prediction of hydrate

composition is small (0.05). For carbon dioxide-methane mixture, the simulation results are in respectable agreement with the experimental results. As it can be seen in Table 15, the average deviation of equilibrium pressure was about 2%. The thermodynamic model better predicts the hydrate composition. The average deviation for carbon dioxide and methane compositions in hydrate phase was 0.004. Figure 10 presents clearly the excellent match between the experimental and simulation results for carbon dioxide-methane hydrate mixture.

Figure 10. Experimental data from Herri et al. [14] for methane-carbon dioxide hydrate (sI) and simulation results

Le Quang et al. studied the equilibrium conditions of several gas mixtures from $\text{N}_2\text{-CO}_2\text{-CH}_4\text{-C}_2\text{H}_6\text{-C}_3\text{H}_8\text{-nC}_4\text{H}_{10}$. They also determined the guest composition in vapor and hydrate phases [57]. They used the same method as Herri et al [14] to analyze guest composition in different phases. In addition, they studied the influence of crystallization rate on the final equilibrium pressure and composition during the crystallization of $\text{CO}_2\text{-CH}_4\text{-C}_2\text{H}_6$ mixed hydrate. All the experimental data and our equivalent simulation results are listed in Table 16, Table 17 and Table 18. They reported that, for the equilibrium points near total dissociation, hydrate composition was suspected to have large errors. Thus, they were not used for our purposes. As Table 16 shows, the thermodynamic model realistically predicts the equilibrium pressures of binary mixtures including carbon dioxide. The average deviation of the equilibrium pressure predictions for $\text{CO}_2\text{-}$

CH₄ and CO₂-N₂ are about 2 and 3%, respectively. For hydrate composition extrapolation, the average absolute deviations are 0.05 and 0.04 for CO₂-CH₄ and CO₂-N₂, respectively.

Table 16. Carbon dioxide-methane and carbon dioxide-nitrogen hydrate mixtures, experimental data [57] and simulation results

Gas	T _{exp} (°C) (±0.1)	P _{exp} (MPa) (±0.01)	P _{pre} (MPa)	S	Gas composition (exp) (±0.001)			Hydrate composition (exp) (±0.003)			Hydrate composition (Pre)		
					N ₂	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂	CO ₂	CH ₄
CO ₂ -CH ₄	3.4	3.33	3.29	I	-	0.13	0.87	-	0.32	0.68	-	0.23	0.77
	4.4	3.53	3.62	I	-	0.13	0.87	-	0.32	0.68	-	0.24	0.76
	4.9	3.71	3.80	I	-	0.14	0.86	-	0.32	0.68	-	0.24	0.76
	5.8	4.03	4.14	I	-	0.15	0.85	-	0.32	0.68	-	0.26	0.74
	6.8	4.45	4.57	I	-	0.16	0.84	-	0.32	0.68	-	0.27	0.73
	7.8	4.93	5.06	I	-	0.18	0.83	-	0.30	0.70	-	0.28	0.72
	2.2	2.91	2.93	I	-	0.12	0.88	-	0.29	0.71	-	0.22	0.78
	2.5	2.97	3.00	I	-	0.13	0.87	-	0.28	0.72	-	0.23	0.77
	3.6	3.18	3.33	I	-	0.14	0.87	-	0.28	0.72	-	0.24	0.76
	4.5	3.47	3.63	I	-	0.15	0.85	-	0.27	0.73	-	0.25	0.75
	5.2	3.80	3.85	I	-	0.16	0.84	-	0.23	0.77	-	0.27	0.73
	AADp		2.4%	AADc							0.05		
CO ₂ -N ₂	2.3	2.46	2.53	I	0.33	0.67	-	0.06	0.94	-	0.05	0.95	-
	3.1	2.60	2.69	I	0.31	0.69	-	0.07	0.93	-	0.04	0.96	-
	3.3	2.66	2.73	I	0.30	0.70	-	0.07	0.93	-	0.04	0.96	-
	4.3	2.87	2.99	I	0.28	0.72	-	0.09	0.91	-	0.04	0.96	-
	5.2	3.13	3.22	I	0.25	0.75	-	0.12	0.88	-	0.03	0.97	-
	AADp		3.16%	AADc							0.04

Figure 11. P-T diagram of mixed CO₂/CH₄ and CO₂/N₂ hydrates, experimental data [57] and simulation results (sI). The vapor and hydrate compositions were listed in Table 16.

As aforementioned, Le Quang et al. investigated the effect of crystallization rate on hydrate equilibrium pressure and composition of CO₂-CH₄-C₂H₆ ternary mixture. They reported that the hydrate equilibrium pressure and composition at final state differed according to the rate of crystallization. They concluded that at quick crystallization rate, mixed gas hydrate could not be at thermodynamic equilibrium [57]. Table 17 reveals that the results of thermodynamic model is closer to the slow crystallization data. The average deviations of equilibrium pressure prediction for slow and quick crystallization are about 2 and 8%, respectively. The average deviations for carbon dioxide in hydrate phase for slow and quick crystallization are similar (0.01). This is not the case for methane and ethane compositions in hydrate phase, where the deviation of simulation for slow crystallization are much better compared to quick rate (e.g. ethane, 0.009 for slow compared to 0.05 for quick).

Table 17. Experimental results of Carbon dioxide-methane-ethane hydrate from Le Quang et al. [57] and simulation results

Gas	Texp (°C) (±0.1)	Pexp (MPa) (±0.01)	Ppre (MPa)	S	Gas composition (exp) (±0.001)			Hydrate composition (exp) (±0.003)			Hydrate composition (Pre)		
					CO ₂	CH ₄	C ₂ H ₆	CO ₂	CH ₄	C ₂ H ₆	CO ₂	CH ₄	C ₂ H ₆
CO ₂ -CH ₄ -C ₂ H ₆ Quick crys.	2.75	3.54	3.11	I	0.03	0.96	0.01	0.07	0.89	0.04	0.05	0.87	0.08
	3.65	3.81	3.35	I	0.03	0.96	0.01	0.07	0.89	0.04	0.05	0.86	0.09
	5.15	4.23	3.79	I	0.03	0.95	0.02	0.07	0.89	0.04	0.05	0.83	0.11
	6.55	4.56	4.33	I	0.03	0.95	0.02	0.07	0.89	0.04	0.06	0.83	0.12
	7.80	5.12	4.76	I	0.04	0.94	0.02	0.07	0.89	0.04	0.06	0.81	0.13
	9.25	5.99	5.67	I	0.04	0.94	0.02	0.04	0.90	0.07	0.07	0.82	0.12
	AADp		8.6%	AADc							0.01	0.05	0.05
CO ₂ -CH ₄ -C ₂ H ₆ Slow crys.	4.60	3.78	3.64	I	0.04	0.95	0.01	0.08	0.80	0.12	0.06	0.84	0.09
	4.20	3.56	3.50	I	0.03	0.95	0.01	0.08	0.83	0.09	0.06	0.84	0.10
	3.25	3.18	3.27	I	0.03	0.96	0.01	0.08	0.85	0.08	0.06	0.87	0.07
	1.30	2.76	2.76	I	0.03	0.96	0.01	0.08	0.86	0.06	0.06	0.89	0.05
	4.20	3.57	3.46	I	0.04	0.95	0.02	0.06	0.84	0.09	0.07	0.83	0.10
	AADp		2.2%	AADc							0.01	0.02	0.01

As seen in Table 18, the average deviation of the equilibrium pressures calculated for the quaternary mixture of methane-ethane-propane-butane is about 13% which is expected due to more significant kinetic effects in quaternary mixtures.

Hydrate composition for the methane and butane is well simulated (AADc=0.01), while for ethane and propane, the average deviation of hydrate composition are 0.06 and 0.07, respectively.

Table 18. Experimental data of methane-ethane-propane-butane hydrate from Le Quang et al. [57] and simulation results

Texp (°C) (±0.1)	Pexp (MPa) (±0.01)	Ppre (MPa)	S	Gas composition (exp) (±0.001)				Hydrate composition (exp) (±0.003)				Hydrate composition (Pre)			
				C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄	C ₁	C ₂	C ₃	C ₄
2.40	2.28	1.70	II	0.97	0.02	0.00	0.01	0.73	0.11	0.11	0.05	0.75	0.03	0.16	0.06
3.45	2.31	1.82	II	0.97	0.02	0.01	0.01	0.73	0.11	0.11	0.05	0.74	0.03	0.18	0.06
7.60	2.75	2.50	II	0.94	0.04	0.01	0.02	0.71	0.10	0.14	0.05	0.72	0.04	0.18	0.07
9.15	2.97	2.70	II	0.93	0.04	0.01	0.02	0.68	0.10	0.17	0.05	0.70	0.03	0.20	0.06
9.90	3.05	2.78	II	0.92	0.04	0.02	0.02	0.68	0.10	0.17	0.05	0.70	0.03	0.22	0.05
10.80	3.12	2.86	II	0.92	0.05	0.02	0.02	0.69	0.10	0.17	0.05	0.69	0.03	0.24	0.04
11.70	3.22	2.94	II	0.91	0.05	0.03	0.02	0.69	0.10	0.16	0.05	0.68	0.02	0.25	0.04
12.65	3.34	3.09	II	0.90	0.05	0.03	0.02	0.70	0.09	0.16	0.05	0.68	0.02	0.26	0.04
13.65	3.46	3.32	II	0.89	0.05	0.04	0.02	0.70	0.09	0.16	0.05	0.68	0.02	0.27	0.03
14.70	3.48	3.75	II	0.89	0.05	0.04	0.02	0.70	0.09	0.16	0.05	0.68	0.02	0.27	0.03
15.65	3.52	4.20	II	0.89	0.05	0.04	0.02	0.70	0.09	0.16	0.05	0.68	0.02	0.27	0.03

16.60	3.61	4.61	II	0.88	0.05	0.04	0.02	0.71	0.09	0.16	0.05	0.68	0.02	0.27	0.03
2.75	2.14	1.52	II	0.96	0.02	0.01	0.01	0.73	0.08	0.15	0.04	0.71	0.03	0.19	0.07
4.30	2.16	1.80	II	0.96	0.02	0.01	0.01	0.73	0.08	0.15	0.04	0.72	0.03	0.18	0.07
4.85	2.18	1.82	II	0.95	0.03	0.01	0.01	0.73	0.08	0.15	0.04	0.71	0.02	0.21	0.06
5.90	2.21	1.98	II	0.95	0.03	0.01	0.01	0.72	0.08	0.16	0.04	0.71	0.02	0.21	0.06
6.80	2.26	2.14	II	0.95	0.03	0.01	0.01	0.72	0.08	0.16	0.04	0.71	0.02	0.22	0.05
7.45	2.36	2.12	II	0.94	0.03	0.02	0.02	0.72	0.08	0.16	0.04	0.69	0.02	0.24	0.05
9.20	2.53	2.31	II	0.93	0.04	0.02	0.02	0.71	0.08	0.17	0.04	0.68	0.02	0.26	0.04
11.05	2.82	2.55	II	0.91	0.04	0.03	0.02	0.71	0.07	0.18	0.04	0.67	0.02	0.27	0.04
AADp		13%	AADc									0.01	0.06	0.07	0.01

4.5. Microscopic measurements tools

In the previous sections, various indirect methods of determining hydrate composition have been reviewed. All approaches were based on measuring fluid and system properties like pressure, temperature, gas phase composition etc. and then calculating the hydrate composition according to the material balance and hydrate properties. Recently, innovative microscopic instruments helped researchers to measure directly the properties and molecular aspects of clathrate hydrates such as hydrate structure, cage occupancy, hydrate composition and guest molecule position.

4.5.1. Experimental data and simulation results

One of the first studies using Raman spectroscopy was performed by Sum et al [72] to explore the properties of clathrate hydrates for pure guest molecules such as CH₄, CO₂, C₃H₈ and binary mixtures CH₄-CO₂, CD₄-C₃H₈, CH₄-N₂, CH₄-THF_{d8} and CH₄-C₇D₁₄. As to hydrate composition, they only reported the guest composition in hydrate phase for CH₄-CO₂ binary mixture. Their procedure included several steps; preparation of hydrate sample in cell and setting the cell into the sample chamber of the Raman. Then, the pressure was adjusted to a value which was within 5% of the predicted pressure at a desired temperature. They predicted hydrate equilibrium pressure by CSMHYD [60,72]. Spectra were then collected at the equilibrium conditions for hydrate composition analyses. Table 19 presents their experimental data and reciprocal simulation results by the thermodynamic model.

Table 19. Experimental data from Sum et al. [72] and simulation results

T (K)	Gas composition (exp)		S	Hydrate composition (exp) (±1%)		Hydrate composition (pre)	
	CO ₂	CH ₄		CO ₂	CH ₄	CO ₂	CH ₄
273.15	0.57	0.43	I	0.75	0.25	0.73	0.27
274.15	0.57	0.43	I	0.73	0.27	0.73	0.27
277.15	0.57	0.43	I	0.71	0.29	0.72	0.28
278.15	0.57	0.43	I	0.71	0.29	0.72	0.28
273.15	0.34	0.66	I	0.55	0.45	0.52	0.48

274.15	0.34	0.66	I	0.55	0.45	0.51	0.49
275.15	0.34	0.66	I	0.53	0.47	0.51	0.49
278.15	0.34	0.66	I	0.52	0.48	0.50	0.50
					AADc	0.02	

Table 19 illustrates that the thermodynamic model satisfactorily simulated the hydrate composition. The average absolute deviation for hydrate composition was 0.02.

Subramanian et al. studied the structural transition of methane-ethane hydrate mixture based on Raman spectroscopy and ^{13}C NMR measurements [73,74]. According to the Raman spectra, they reported that for methane-ethane hydrate mixture at 274.2 K, there was a structural transition from structure I to II, when the methane composition in gas phase was between 0.722 and 0.750 (mole fraction). Moreover, they observed that the structure changed from sII to sI, once the methane composition in vapor phase was between 0.992 and 0.994 (mole fraction). Furthermore, Raman spectra showed that structural transition leads to a 20% variation in hydrate composition. They also measured the hydrate composition by ^{13}C NMR at six different vapor compositions. Their results are listed in Table 20.

Table 20. Experimental data from Subramanian et al. [74] for methane-ethane mixture and simulation results

T (K)	P _{exp} (MPa) (±0.014)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp) (±0.1%)		Hydrate composition (Pre)	
				CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆
274.2	0.88	0.82	I	0.63	0.37	0.28	0.72	0.30	0.70
274.2	0.96	0.88	I	0.68	0.32	0.36	0.64	0.32	0.68
274.2	0.97	0.96	I	0.72	0.28	0.37	0.63	0.35	0.65
AADp		5.3%	I	AADc				0.02	
274.2	0.99	1.02	II	0.75	0.25	0.57	0.43	0.37	0.63
274.2	1.17	1.34	II	0.85	0.15	0.65	0.35	0.47	0.53
274.2	1.45	1.76	II	0.92	0.08	0.70	0.30	0.61	0.39
AADp		41.6%	II	AADc				0.09	

Clearly, in Table 20, the thermodynamic simulation concurs with the experimental results for structure I. While for the structure II, the simulations fail. This reveals that the thermodynamic model cannot be proficient to well evaluate the hydrate equilibrium conditions when the structure transition occurs in the system.

Seo and Lee [75] analyzed the structure and gas distribution of nitrogen-carbon dioxide hydrate at different vapor compositions. They revealed from X-ray diffraction patterns that when carbon dioxide composition in gas phase was between 3 and 20 mole percent, structure sI formed. While for CO₂ composition under 1%, the hydrate structure seemed to be sII. Additionally, they measured the hydrate composition by NMR spectroscopic analyses. They noticed that the CO₂

molecules were mostly localized in the large sI cages. Also, the hydrate composition was significantly augmented by a small increase of CO₂ in the vapor phase. Table 21 and Figure 12 present their experimental and our simulation results for hydrate guest distribution. This is clear from the figure that the results of thermodynamic model for hydrate composition prediction corresponds well with the experimental data (average deviation of hydrate phase prediction is 0.02).

Table 21. Experimental results from Seo and Lee [75] and our simulation results

T (K)	P _{exp} (MPa)	P _{pre} (MPa)	S	Gas composition (exp)		Hydrate composition (exp) ($\pm 0.1\%$)		Hydrate composition (Pre)	
				CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
272.1	14.50	13.57	I	0.01	0.99	0.09	0.91	0.07	0.93
272.1	13.00	12.11	I	0.03	0.97	0.15	0.85	0.17	0.83
272.1	10.50	8.79	I	0.10	0.90	0.47	0.54	0.41	0.59
272.1	7.70	6.24	I	0.18	0.82	0.59	0.41	0.61	0.39
272.1	5.00	3.99	I	0.33	0.67	0.74	0.26	0.79	0.21
272.1	4.10	2.80	I	0.50	0.50	0.86	0.14	0.88	0.12
272.1	3.50	2.14	I	0.67	0.34	0.94	0.06	0.94	0.06
272.1	3.20	1.69	I	0.85	0.15	0.97	0.04	0.98	0.02
AADp		23.3%		AADc				0.02

Figure 12. CO₂ composition in gas and hydrate phase versus pressure for CO₂-N₂ system at 272.1 K (sI). Experimental [75] and our simulation results

Uchida et al. [76] investigated cage occupancy, hydrate composition and structure of methane-ethane mixture by Raman spectroscopy and XRD analyses [76]. They prepared the mixed methane-ethane hydrates from ice powder at different feed guest compositions. In the case of hydrate structure by Raman spectroscopy, they reported that, when the composition of ethane in the gas phase was below 2% or over 22% mole fraction, only structure I exists. However, there was a coexistence of both structures I and II at ethane concentrations between 12 and 22% mole fraction. Results of XRD analyses confirmed these investigations. They also observed that ethane molecules were only encapsulated in large cavities, while the methane molecules occupied both small and large cavities. Interestingly, their results revealed that the vapor composition had a significant influence on the cage occupancy in large cavities [76].

Uchida et al. [77] expanded their experiments for C₂H₆-C₃H₈, CH₄-C₂H₆-C₃H₈ and CH₄-C₂H₆-C₃H₈-iC₄H₁₀ mixed hydrates. Based on the Raman spectra and confirmation of X-ray diffraction, they reported that for C₂H₆-C₃H₈ mixed hydrates, only structure II existed when the vapor composition of ethane ranged from 28 to 73% mole fraction. They also stated that both molecules occupied the 5¹²6⁴ cages (sII large cages). Moreover, they concluded that the preferential occupancy of 5¹²6⁴ cages is C₃H₈>C₂H₆>CH₄. For CH₄-C₂H₆-C₃H₈ hydrates, the initial methane composition in gas phase was between 90 and 98% mole fraction. Their work showed that, at

final state, the composition of methane in gas phase increased, whereas the ethane and propane composition decreased. In hydrate phase, propane enriched more than other guest molecules. Furthermore, if the cage occupancy of ethane and propane was less than 33%, the methane molecules can occupy some $5^{12}6^4$ cages. For the quaternary hydrate mixture, they reported the existence of structure II. In addition, all the molecules except methane, occupied the $5^{12}6^4$ cages and the ratio is $C_2H_6-C_3H_8-iC_4H_{10} = 2:3:5$. They concluded that at a desired temperature, the larger molecules with lower dissociation pressure, enriched more in hydrate phase [77].

Schicks et al. [78] studied the phase behavior of methane-propane and methane-ethane-propane hydrates in a temperature range between 260 and 290 K and a pressure range from 1 to 6MPa. They investigated the phase transition, hydrate structure and composition by Raman spectroscopy and x-ray diffraction. They observed two different types of crystals after hydrate formation; light and dark. They reported the presence of occluded gas in the structure of light hydrate crystals. However, there was no evidence of the occluded gas in the dark crystals which was supposed to be structure II. Their approach demonstrated that there was a transformation process near the decomposition line. During the transformation, the crystal formation and decomposition was quick. They suggested that this is due to the occluded of free gas or water. Below this, they observed both structure I and II [78].

4.5.2. Issues of hydrate composition calculation from cage occupancy

Although there are a lot of studies on the pure hydrate formers or kinetic investigation of mixed hydrates by microscopic measurements tools [79–86], there is still little research based on these tools to measure mixed hydrates composition at equilibrium. Furthermore, even in these pertinent studies, they sometimes did not mention clearly their experimental data on hydrate composition (reporting experimental results only on figures, for instance). Therefore, it was impossible to compare their experimental results with the thermodynamic model. In some studies, researchers measured the relative ratios of cage occupancy for mixtures based on Raman spectroscopy. Then, based on the statistical thermodynamics, they calculated absolute cage occupancy. Hydrate composition could be calculated based on the absolute cage occupancy [74]. Since this information was retrieved from statistical thermodynamics, they are of less interest for this review.

5. Conclusion

While equilibrium conditions of clathrate hydrates, such as temperature, pressure and gas phase composition have been widely studied, the hydrate composition is usually ignored due to the experimental difficulties, like the non-homogenous hydrate phase, water and free gas occlusion, etc. [12]. However, vital data for hydrate composition can be compiled from literature. This information provides comprehensive, representative, and additional knowledge about hydrate composition according to the different equilibrium conditions. Hence, this was the motivation to assemble the relevant research on the hydrate composition by different experimental procedures

and compare these methods via simulation based on the van der Waals and Platteeuw approach and Kihara potential for hydrate equilibrium pressure and composition.

Hydrate composition of binary mixtures of carbon dioxide, methane and nitrogen were usually studied since the idea of methane exploration from the hydrate resources by carbon dioxide isolation and gas separation was presented. Experimental data indicated that hydrate composition strongly depends on guest composition in gas phase. A small change in gas composition could lead to a substantial change in hydrate composition. Furthermore, the composition of heavier hydrocarbons (propane and butane) in the hydrate phase was significantly higher than in the gas phase.

Our simulations showed that generally, the thermodynamic model predicted adequately the hydrate equilibrium composition. In fact, the thermodynamic model had the best accordance with the experimental data obtained by the microscopic tools like Raman spectroscopy. This suggests that using these direct measurement techniques might help researchers to get closer to reality. Nevertheless, the existence of structural transition led to a significant deviation. Failure to predict structure change could be one of the main challenges for applying effectively the thermodynamic models.

Furthermore, at pressures higher than 7 MPa or when CO₂ was the minor component in hydrate phase, the deviation of the thermodynamic model from the experimental data was considerable.

Unfortunately, there were some cases which the agreement between the results of thermodynamic model and experimental data were not satisfactory. This might be explained by kinetic effects during the crystallization as well as the experimental methodology which could have a significant influence on the experiment. Furthermore, Bouillot and Herri reported that a small change of Kihara parameters had a considerable effect on the hydrate pressure and composition calculations [58]. Hence, it is essential to extend the experimental database in order to well optimize the Kihara parameters. Interestingly, there is still a lack of data concerning storage capacity of hydrates. This information could be used to re-design and develop chemical processes which the volume of gas stored in hydrate phase has been taken into account. Finally, consistent, reliable and extensive experimental data is still needed to examine the ability of thermodynamic modeling to predict hydrate composition as well as its developments.

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