

Effect of Hydrogen-to-Methane Concentration Ratio on the Phase Equilibria of Quaternary Hydrate Systems

M. Naveed Khan,^{†,§} Laura J. Rovetto,[‡] Cor J. Peters,^{*,§,||} E. Dendy Sloan,[†] Amadeu K. Sum,[†] and Carolyn A. Koh[†]

[†]Center for Hydrate Research, Chemical & Biological Department, Colorado School of Mines, Golden, Colorado 80401, United States

[‡] IDTQ - CONICET. Faculty of Exact, Physical and Natural Sciences, National University of Córdoba Córdoba, Argentina [§]Chemical Engineering Department, Petroleum Institute, Abu Dhabi, United Arab Emirates

^{II}Department of Chemical Engineering and Chemistry, Separation Technology Group, Eindhoven University of Technology, Eindhoven, 5612 AZ, The Netherlands

Supporting Information

ABSTRACT: Clathrate hydrates of hydrogen are of specific interest due to their potential ability to store molecular hydrogen. In particular, structure H (sH) hydrate has a higher theoretical storage capacity in comparison with the other two more common hydrate structures (sI and sII). This paper investigates the effect of hydrogen (H₂) concentration on the phase equilibria of sH hydrate in a quaternary system of water, methane, hydrogen, and methylcyclohexane. Phase equilibria and cage occupancies of the quaternary system were predicted using the van der Waals and Platteeuw (vdWP) model for different hydrogen/methane ratios ranging from 0 to 7. Model predictions for the quaternary systems were found to be in good agreement with measured experimental data. It was evident from the thermodynamic equilibrium conditions of the quaternary system (MCH + H₂O + CH₄ + H₂) that as the H₂ concentration increases (H₂:CH₄ ratio increased from 0 to 7), higher pressures are required to produce sH hydrates at the same temperature. It was also found that the



fractional cage occupancy of CH4 in the small and medium cages of sH hydrate increases with pressure.

INTRODUCTION

Clathrate hydrates of hydrogen have been of interest as a potential means of storing hydrogen.¹⁻³ Clathrate hydrates are the nonstoichiometric inclusion compounds comprising gases of suitable size, which are trapped inside hydrogen-bonded water cages at higher pressures and lower temperatures. Depending upon the hydrate former (e.g., methane, hydrogen) water molecules will arrange themselves into different cages, which are stabilized by the hydrate formers.¹⁻⁴ The three common gas hydrate structures are sI, sII, and sH. Structure I (sI) hydrate has a cubic crystal structure containing 46 water molecules per unit cell, with two 5^{12} and six $5^{12}6^2$ cavities. Structure II (sII) hydrate has a cubic crystal structure containing 136 water molecules per unit cell, with 16 512 cavities and eight 51264 cavities. Structure H (sH) hydrate has a hexagonal crystal structure containing 34 water molecules per unit cell, with 3 small 5^{12} cavities, 2 medium $4^35^66^3$ cavities, and one large $5^{12}6^8$ cavity.^{5–8} Temperature, pressure, and the nature of the guest molecules dictate the thermodynamic stability of the hydrate.^{1,6,9-14} It was also observed that the addition of larger guest molecules results in a decrease in the hydrate formation equilibrium condition, that is, T and P. The guest and water cage molecular interaction dictates the stability of the hydrate formed. It is because of these intermolecular forces that different cavities may not stabilize in the absence of a hydrate former. There are numerous other applications of hydrates, including gas storage, carbon dioxide sequestration, desalination of seawater, energy recovery from naturally occurring methane deposits, flow assurance, and gas separation.^{15–18}

The focus of this paper is to perform phase equilibria predictions including guest occupancy calculation and measurements on hydrates containing molecular hydrogen. Pure hydrogen is capable of forming a sII structure that has one molecule of hydrogen stabilizing the small cavity and up to four molecules of hydrogen stabilizing the large cavity. The importance of incorporating hydrogen into a sH structure is attributed to its enhanced storage capacity in comparison with the other two structures, but the capacity of sH can be limited by most of the promoters.^{19–22} The size of the hydrogen molecule allows it to occupy the small and medium cavities of sH hydrate, with the larger guest (promoter) molecule occupying the large cavity. The main objective of this study

Received:July 19, 2014Accepted:November 13, 2014Published:December 12, 2014

Special Issue: In Honor of E. Dendy Sloan on the Occasion of His 70th Birthday

Journal of Chemical & Engineering Data

is to investigate the phase equilibria conditions and guest occupancy for a quaternary sH hydrate system formed in the presence of methylcyclohexane as a sH hydrate former (promoter), water, hydrogen, and methane (with varying ratios of hydrogen to methane). The quaternary phase equilibria of the system were predicted including hydrogen as a hydrate former. This work is an extension of the first hydrogen paper published previously²² and is a first step to the extension of a future model.

MATERIALS AND EXPERIMENTAL SETUP

The list of the chemicals with their source and purity is summarized in Table 1. The chemicals are utilized in the experiments as is, with no further purification.

 Table 1. Components Used for the Experiments with Their

 Source and Purity

component	supplier	purity (mol fraction)
water, distilled	in-house DI	> 0.99
methylcyclohexane	Merck	> 0.99
hydrogen	Hoek Loos	0.99999
methane	Hoek Loos	0.99995

A Cailletet apparatus (operating pressures up to about 14 MPa) was used to measure the hydrate phase equilibria data. The thick walled Pyrex glass tube was loaded with the sH hydrate former (methylcyclohexane) and water, followed by the addition of gas. The system was pressurized according to the procedure previously discussed in detail by Rovetto et al.33 The system was agitated with steel balls using a magnetic stirring system. The temperature of the sample was kept constant by circulating thermostat liquid through a glass thermostat jacket surrounding the glass tube. The thermostat bath is able to maintain the coolant fluid at the desired temperature within \pm 0.01 K. A platinum resistance thermometer (Pt-100), located close to the sample-containing part of the Cailletet tube, records the temperature of the coolant fluid with an uncertainty of \pm 0.01 K. The pressure measurement was performed using a dead weight gauge with an uncertainty of \pm 0.05 bar. Measurements were carried out at constant pressure, and the temperature was varied (stepwise increase or decrease) until a visual phase change was observed.

THEORY

The earliest and most successful classical hydrate model is the van der Waals and Platteeuw model, which is based on statistical thermodynamics, and has been further extended for hydrates of more than one component by Parrish and Prausnitz.^{22,23} The van der Waals and Platteeuw model is based on the equality of chemical potential of each species in each phase. The molecules are assumed to be spherically symmetric in the calculations to minimize the complexities of the interaction potential. Later, several researchers determined that the basic assumptions of the van der Waals and Platteeuw

models, such as spherical symmetry of molecules, guest–guest interactions, and lattice distortions caused by the guest molecules introduced several errors in the predicted results. To rectify this, corrections were applied to the basic assumptions of the van der Waals and Platteeuw model. Furthermore, the equality of fugacity of the species in all the phases was utilized as a fundamental criterion for the phase equilibrium calculations.^{23–25}

$$f_i^{\rm H} = f_i^{\rm L} = f_i^{\rm V} \tag{1}$$

In the above eq 1, H represents the hydrate phase that may be sI, sII, or sH, while the superscripts L, V, I represent the liquid, vapor, and ice phases, respectively. Equation 2 is used to calculate the fugacity of water in the hydrate phase.²⁶

$$f_{W}^{k} = f_{W_{o}} \exp\left[\frac{\mu_{W}^{k} - g_{W_{o}}}{RT}\right]$$
(2)

Here f_{W}^{k} is the fugacity of the water in an arbitrary phase k, where k may be hydrate, liquid, vapor, or ice phase, $g_{W_{o}}$ is standard molar Gibbs free energy, and $f_{W_{o}}$ represents the ideal gas fugacity at 1 bar.

The standard molar Gibbs free energy, g_{W_o} , of water at standard conditions is corrected to temperature, *T*, in order to calculate the Gibbs free energy of water at the ideal state, which is given by eq 3.

$$\frac{g_{W_o}}{RT} = \frac{g_{W_o^0}}{RT_0} - \int_{T_0}^T \frac{h_{W_o}}{RT^2} \, \mathrm{d}T$$
(3)

The μ_W^H (chemical potential of the water in the hydrate phase) is calculated by eq 4, where g_W^β is the Gibbs free energy of the standard empty hydrate phase under given conditions of temperature and pressure.

$$\mu_{wH} = g_{w\beta} + RT \sum_{m} v_m \ln(1 - \sum_{i} \theta_{im}) + RT \ln \gamma_{wH}$$
(4)

Where *T* is the temperature, *R* is the gas constant, and v_m is the number of cavities of type *i* in a hydrate unit cell. The cage occupancy, θ_{im} , of component *i* in cavity *m* is found to be a function of the fugacity of component *i* and the Langmuir constant,²⁸ while the activity of water in the hydrate phase is calculated by eq 5

$$\ln \gamma_{wH} = \frac{\Delta g_{w_0\beta}}{RT_0} + \frac{\Delta h_{w_0\beta}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \int_{P_0}^{P} \frac{\Delta \nu_H}{RT} dP$$
(5)

where

$$\Delta g_{w_0\beta} = a\Delta v_{H_0}$$
$$\Delta h_{w_0\beta} = b\Delta v_{H_0}$$

Table	2.	Properties	of Pure	Hvdrate	Phases ²⁷
1 abic	2.	roperties	of 1 uic	ilyulate	1 mases

phase	$v_0/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	α_1/K^{-1}	α_2/K^{-2}	α_3/K^{-3}	κ/bar^{-1}
sΙ-β	22.7712	3.384960.10-4	5.400990·10 ⁻⁷	$-4.769460 \cdot 10^{-11}$	$3.0000 \cdot 10^{-5}$
sII- β	22.9456	$2.029776 \cdot 10^{-4}$	$1.851168 \cdot 10^{-7}$	$-1.879455 \cdot 10^{-10}$	$3.0000 \cdot 10^{-6}$
sH- β	24.2126	$3.575490 \cdot 10^{-4}$	6.294390·10 ⁻⁷	0	$3.0000 \cdot 10^{-7}$

Journal of Chemical & Engineering Data

The activity coefficient of the hydrate phase accounts for the nonideality of the real hydrate in terms of disturbance to the empty lattice caused by guest occupancy. The Gibbs free energy in the hydrate state is given by eq 6, whereas the formation properties and parameters for the calculation of molar volume of hydrate are listed in Table 2.¹

$$\frac{g_{w\beta}}{RT} = \frac{g_{w\beta}}{RT_0} - \int_{T_0}^T \frac{h_{w\beta}}{RT^2} \,\mathrm{d}T + \int_{P_0}^P \frac{v_{w\beta}}{RT} \,\mathrm{d}P \tag{6}$$

$$v_{\omega\beta} = (a_0)^3 \exp[\alpha_1(T - T_0) + \alpha_2(T - T_0)^2 + \alpha_3(T - T_0)^3 - \kappa_{\rm H}(P - P_0)]$$
(7)

The cage occupancy of the hydrate is given by eq 8

$$\theta_{im} = \frac{C_{im}f_i}{1 + \sum_j C_{jm}f_j} \tag{8}$$

Here C_{ii} is the Langmuir constant of component *j* in cavity *i*, and f_i is the fugacity of component *i*. Equation 9 is used to calculate the overall Langmuir constant of the system. The Langmuir constant is a function of temperature, which is calculated by assuming a spherically symmetric potential. It was assumed that the size of the empty hydrate is equal to the size of the actual hydrate, and the lattice size is not found to be a function of composition. The numerical value of the Langmuir constant is defined by the guest-cavity interactions.^{23,24,2}

$$C_{im} = \frac{4\pi}{kT} \int_0^{R_1 - a_i} \exp\left[\frac{-\sum_n \omega_{in}(r)}{kT}\right] r^2 dr$$
(9)

Where ω_{in} is the potential function, which is obtained as a result of interaction between a guest molecule and the entire cage, the summation is taken over all the shells n in a cage m. During development of eq 9, it was assumed that binary interactions between the guest and the water molecules are important. In the original work of van der Waals and Platteeuw it was assumed that hydrate lattice size is independent of the guest molecule. This is why the value of chemical potential of the empty hydrate is independent of the guest component. The summed guest-host interactions over all the guest-host interactions in the cage is given by eq 10.29,30 The interaction potential between guest i and shell n is given by the spherically symmetric Kihara potential.

$$\omega_{in}(r) = 2\varepsilon_{i}z_{n} \left[\frac{\sigma_{i}^{12}}{R_{n}^{11}r} \left(\delta_{in}^{10} + \frac{a_{i}}{R_{n}} \delta_{in}^{11} \right) - \frac{\sigma_{i}^{6}}{R_{n}^{5}r} \left(\delta_{in}^{4} + \frac{a_{i}}{R_{n}} \delta_{in}^{5} \right) \right]$$
(10)

-

where

$$\delta_{in}^{N} = \frac{1}{N} \left[\left(1 - \frac{r}{R_{n}} - \frac{a_{i}}{R_{n}} \right)^{-N} - \left(1 + \frac{r}{R_{n}} - \frac{a_{i}}{R_{n}} \right)^{-N} \right]$$

 R_n and Z are the cavity cell radius and the coordination number, respectively (listed in Table 3), while the parameters a, σ , and ε are the spherical core of the hydrate guest, distance between the core surfaces corresponding to zero potential energy, and depth of intermolecular potential well for water-guest interactions, respectively, as shown in Table 4. The fugacity of water in the liquid phase is calculated using the Helgeson equation that is given in eq $2.^{31,32}$

Article

Table 3. Gas Hydrates Structural Parameters and Formation Properties

Structure H			
number of cavities perwater molecule (v)	3/34	2/34	1/34
radius of the firstcell (R_n/nm)	0.391	0.406	0.571
number of water molecules surrounding a cavity in the first shell (Z)	20	20	36
number of cavities	3	2	1
$g_{W^0}/\mathrm{J}~\mathrm{mol}^{-1}$	-	-235491.0	2
$h_{W^0_o}/\mathrm{J} \mathrm{mol}^{-1}$	-	-291979.2	6

Table 4. Kihara Potential Parameters

component	$\sigma/{ m nm}$	a/nm	$\varepsilon/k/K$
methane	0.314	0.0383	155.593
hydrogen	0.307	0.0197	80.424
MCH	0.358	0.106	237.98

RESULTS AND DISCUSSION

Experimental (Table 5) and predicted hydrate phase equilibria data for the CH₄-MCH-water system were compared with

Table 5. Experimental Data for Clathrate H	Hydrates	of
Methane + Methylcyclohexane + Hydrogen	1	

$T/K (\pm 0.01)$	$p/MPa~(\pm~0.05)$		
Methylcyclohexane + Methane + Water			
284.82	5.052		
287.87	7.552		
289.53	10.05		
291.04	12.549		
Methylcyclohexane + Methane + Hydrogen + Water (1:1 H ₂ /CH ₄)			
278.20	4.951		
281.39	7.548		
283.40	10.048		
284.85	12.5		
Methylcyclohexane + Methane + Hydrogen + Water (3:1 H ₂ /CH ₄)			
272.87	5.051		
275.68	7.550		
277.82	10.049		
279.21	12.549		
Methylcyclohexane + Methane + Hydrogen + Water (7:1 H ₂ /CH ₄)			
272.79	10.048		
274.72	13.049		

the system containing CH4-MCH-H2-water (where hydrogen-to-methane concentration ratios were varied from 0 to 7). The results show that increasing the H_2/CH_4 ratio raises the equilibrium pressure of the system. This shift in phase equilibria behavior with increasing hydrogen concentration occurs because hydrates of hydrogen are found to be more stable at higher pressures and lower temperatures.³³

Figure 1 shows the phase behavior of the methylcylohexane +water+methane (MCH+H₂O+CH₄) system, where predicted results are in good agreement with the experimental measurements.

Phase equilibria predictions for a quaternary system containing $CH_4 + MCH + H_2O + H_2$ as a function of $H_2/$ CH₄ ratio were calculated and compared with experimental data (Figure 2). The calculations were performed by keeping the MCH composition constant, while the ratio of hydrogen to methane was varied from 0 to 7. Figure 2 shows that the



Figure 1. Hydrate phase equilibrium diagram for ternary system of CH_4 +MCH +water:^{33,35} +, •, experimental data; —, model predictions.



Figure 2. Hydrate phase equilibria plots for the quaternary system of $CH_4 + MCH + water + H_2$ as a function of H_2/CH_4 ratio. Lines are predictions. Points are experimental data measured by Peters and Rovetto;^{33,35} H_2/CH_4 ratios = +, 7; $\mathbf{\nabla}$, 3; $\mathbf{\Delta}$, 1; O,*, 0; —, model predictions.

hydrate conditions for the methylcyclohexane (MCH) + water + CH_4 system are at more moderate *P* and *T* than those for the (MCH) + water + CH_4 + H_2 systems.

The phase equilibria data for the 1:1 hydrogen-methane system are at relatively higher pressures and lower temperatures compared with the $CH_4 + MCH + H_2O$ system without H_2 . This shift in the phase equilibrium curve toward higher pressures is because of the increase in hydrogen concentration, which is directly indicative of the equilibrium pressure being dependent on hydrogen concentration. Further increases in the hydrogen to methane mole ratio results in a pronounced pressure increment; this increase in hydrogen results in more hydrogen trapped in the hydrate cages, but at relatively higher

pressures and lower temperatures. The calculated data were found to be in good agreement with the experimental measurements (Figure 2).

The thermodynamic model can be also used to estimate the cage occupancies of the small, medium, and large cavities of structure H hydrate. The calculated results are shown in Figures 3 and 4. Figure 3 shows the change in occupancy in the small



Figure 3. Cage occupancies of methane in the small cavity of sH at different H_2/CH_4 ratios.



Figure 4. Cage occupancies of methane in the medium cavity of sH at different $\rm H_2/CH_4$ ratios.

cavity as a function of the pressure at different ratios of hydrogen-to-methane (for the feed gas mixture). As the pressure increases, the occupancy of methane molecules in small hydrate cages increases, while an increase in hydrogen concentration displaces the methane molecules from the cavities. The guest/cage size ratio is a measure of the interactive forces between a cage and an entrapped molecule. Increasing the pressure above 50 MPa results in smaller increases in the

421

Journal of Chemical & Engineering Data

cage occupancy. However, the mechanism of replacement of methane with hydrogen molecules at higher pressure is still not well understood.³⁴

Similarly, increasing the hydrogen/methane ratio of the feed gas mixture results in a lower fractional cage occupancy of methane in the medium sized cage of sH, since more hydrogen molecules can compete with methane molecules and enter the hydrate lattice (Figure 4).

CONCLUSIONS

Hydrate phase equilibria predictions for ternary and quaternary systems were performed and found to be in good agreement with experimental measurements. Increasing the hydrogen to methane (feed gas) ratio shifts the phase equilibria curves toward lower temperatures and higher pressures. The cage occupancies of methane and hydrogen in sH (methane + hydrogen + MCH) hydrate were found to increase with increasing pressure.

ASSOCIATED CONTENT

Supporting Information

Composition data from sources cited here. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +971 26075492. Fax: +971 26075200. E-mail: cpeters@ pi.ac.ae.

Funding

This work is funded by the Petroleum Institute in Abu Dhabi. Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge Patrick Lafond and Giovanny Grasso for their help.

REFERENCES

(1) Sloan, E. D. and Koh, C. A. Clathrate Hydrates of Natural Gases; CRC Press, Boca Raton, FL, 2007.

(2) Carroll, J. Natural Gas Hydrates: A Guide For Engineers; Gulf Professional Publishing: Houston, TX, 2009.

(3) Englezos, P.; Ngan, Y. T. Incipient Equilibrium Data For Propane Hydrate Formation in Aqueous Solutions of NaCl, KCl, and CaCl₂. *J. Chem. Eng. Data* **1993**, *38*, 250–253.

(4) Ballard, A. L.; Sloan, E. D. The Next Generation of Hydrate Prediction: I. Hydrate Standard States and Incorporation of Spectroscopy. *Fluid Phase Equilib.* **2002**, *194*, 371–383.

(5) Davidson, D. W.; Ripmeester, J. A.; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D. Inclusion Compounds. *Phys. Prop. Appl.* **1984**, *3*, 69– 128.

(6) Ripmeester, J. A.; John, S. T.; Ratcliffe, C. I.; Powell, B. M. A New Clathrate Hydrate Structure. *Nature* 1987, 325, 135–136.

(7) Hütz, U.; Englezos, P. Measurement of Structure H Hydrate Phase Equilibrium and the Effect of Electrolytes. *Fluid Phase Equilib.* **1996**, *117*, 178–185.

(8) Claussen, W. F. A Second Water Structure for Inert Gas Hydrates. J. Chem. Phys. 1951, 19, 1425.

(9) Jager, M. D.; et al. Experimental Determination and Modeling of Structure II Hydrates in Mixtures of Methane + Water + 1,4-Dioxane. *Fluid Phase Equilib.* **1999**, *165*, 209–223.

(10) Patchkovskii, S.; Tse, J. S. Thermodynamic Stability of Hydrogen Clathrates. Proc. Natl. Acad. Sci. U.S.A. 2003, 100, 14645.

(11) Tanaka, H. On the Thermodynamic Stability of Clathrate Hydrates. *Can. J. Phys.* **2003**, *81*, 55–60.

(12) Østergaard, K. K.; Tohidi, B.; Danesh, A.; Todd, A. C.; Burgass, R. W. Gas Hydrate Equilibria of 2,3-Dimethylbutane and Benzene with Methane and Nitrogen. *Chem. Eng. Res. Des.* 2000, *78*, 731–737.
(13) Ripmeester, J. A.; Ratcliffe, C. I. ¹²⁹Xe NMR Studies of Clathrate

(13) Ripmeester, J. A.; Ratcliffe, C. I.¹²⁹Xe NMR Studies of Clathrate Hydrates: New Guests for Structure II and Structure H. *J. Phys. Chem.* **1990**, *94*, 25.

(14) Khokhar, A. A.; Gudmundsson, J. S.; Sloan, E. D. Gas Storage in Structure H Hydrates. *Fluid Phase Equilib.* **1998**, *150*, 383–392.

(15) Barduhn, A. J.; Roux, G. M.; Richard, H. A.; Giuliano, G. B.; Alexander Stern, S. The Rate of Formation of the Hydrates of F-31 (CH₂ClF) and F-142b (CH₃CClF₂) in a Stirred Tank Reactor. *Desalination* **1976**, *18*, 59–69.

(16) Max, M. and Cruickshank, M. Extraction of Methane from Oceanic Hydrate System Deposits., Proceedings of the Offshore Technology Conference, Houston Texas, 3–6 May 1999; pp 1–8.

(17) Hammerschmidt, E. G. Formation of Gas Hydrates in Natural Gas Transmission Lines. *Ind. Eng. Chem.* **1934**, *26*, 851–855.

(18) Brewer, P. G.; Friederich, G.; Peltzer, E. T.; Orr, F. M. Direct Experiments on the Ocean Disposal of Fossil Fuel CO₂. *Science* **1999**, 284, 943.

(19) Lee, H.; Lee, J. W.; Do Youn Kim, J. P.; Seo, Y. T.; Zeng, H.; Moudrakovski, I. L.; Ratcliff, C. I.; Ripmeester, J. A. Tuning Clathrate Hydrates for Hydrogen Storage. *Nature* **2005**, *434*, 743–746.

(20) Martin, A.; Peters, C. J. Hydrogen Storage in sH Clathrate Hydrates: Thermodynamic Model. *J. Phys. Chem. B* 2009, *113*, 7558–7563.

(21) Duarte, A. R. C.; Shariati, A.; Peters, C. J. Phase Equilibrium Measurements of Structure sH Hydrogen Clathrate Hydrates with Various Promoters. *J. Chem. Eng. Data* **2009**, *54*, 1628–1632.

(22) Strobel, T. A.; Koh, C. A.; Sloan, E. D. Thermodynamic Predictions of Various Tetrahydrofuran and Hydrogen Clathrate Hydrates. *Fluid Phase Equilib.* **2009**, *280*, 61–67.

(23) Klauda, B. Phase Behavior of Clathrate Hydrates: A Model for Single and Multiple Gas Component Hydrates. *Chem. Eng. Sci.* 2003, 58, 27–41.

(24) Klauda, J. B.; Sandler, S. I. A Fugacity Model for Gas Hydrate Phase Equilibria. *Ind. Eng. Chem. Res.* 2000, 39, 3377–3386.

(25) Martin, A.; Peters, C. J. New Thermodynamic Model of Equilibrium States of Gas Hydrates Considering Lattice Distortion. *J. Phys. Chem. C* 2008, *113*, 422–430.

(26) Strobel, T. A.; Koh, C. A.; Sloan, E. D. Thermodynamic Predictions of Various Tetrahydrofuran and Hydrogen Clathrate Hydrates. *Fluid Phase Equilib.* **2009**, *280*, 61–67.

(27) Ballard, A. L. A Non-ideal Hydrate Solid Solution Model for a Multi-phase Equilibria Program. Ph.D. Thesis, Colorado School of Mines, Golden, CO, 2002.

(28) van der Waals, J. H.; Platteeuw, J. C. Clathrate Solutions. In *Advances in Chemical Physics*; Prigogine, I., Ed.; Interscience: London, 1959; p 1–57.

(29) Ballard, A. L.; Sloan, E. D. The Next Generation of Hydrate Prediction: An Overview. *J. Supramol. Chem.* **2002**, *2*, 385–392.

(30) Barkan, E. S.; Sheinin, D. A. A General Technique for the Calculation of Formation Conditions of Natural Gas Hydrates. *Fluid Phase Equilib.* **1993**, *86*, 111–136.

(31) Prausnitz, J. M., Lichtenthaler, R. N., de Azevedo, E. D. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1986.

(32) John, V. T.; Holder, G. D. Contribution of Second and Subsequent Water Shells to the Potential Energy of Guest-Host Interactions in Clathrate Hydrates. J. Phys. Chem. **1982**, *86*, 455-459.

(33) Rovetto, L. J., Peters. C. J. Storage of hydrogen as gas hydrates and it's near-future impact on the oil, gas; chemical and automotive industry. 2nd Mercosur Conference on Chemical Engineering; Rio de Janeiro, Brazil, 14–18 August 2005.

(34) Matsumoto, Y.; Grim, R. G.; Khan, M. N.; Sugahara, T.; Ohgaki, K.; Sloan, E. D.; Koh, C. A.; Sum, A. K. Investigating the

Thermodynamic Stabilities of Hydrogen and Methane Binary Gas Hydrates. J. Phys. Chem. C 2014, 118, 3783–3788. (35) Mooijer-van den Heuvel, M. M. Phase behavior and structural

(35) Mooijer-van den Heuvel, M. M. Phase behavior and structural aspects of ternary clathrate hydrate systems: The role of additives. Ph.D. Thesis, Delft University of Technology, Delf, The Netherlands, 2004.