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On Estimating the Water Content of Gas in Equilibrium with Gas Hydrate or Ice

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Experimental data for water content of gases and petroleum fluids in equilibrium with gas hydrates/ice are rare and scarce. This is partly due to the fact that water content is very low at these conditions, and, hence, generally very difficult to measure. Furthermore, reaching hydrate/ice equilibrium is a very time-consuming process. Fortunately, estimation of corresponding water content in equilibrium with meta-stable liquid water is easier. Expressions have been developed, based on equality of fugacity in equilibrium phases for relating water content in equilibrium with gas hydrates/ice, to corresponding water content in equilibrium with metastable liquid water. The results of this method are then compared with some experimental data reported in the literature. These results show that using only data on corresponding water content in equilibrium with metastable liquid water can lead to relatively acceptable predictions of water content in equilibrium with gas hydrates/ice. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 1601–1607, 2007

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Introduction

Production, transportation and processing of natural gases in relatively cold regions has renewed interest in determining the water content of the gas, which is necessary to form gas hydrates/ice at a specified temperature and pressure. From a strict thermodynamic standpoint, a gas phase (with dissolved water) can form gas hydrates/ice at the gas hydrates/ice - vapor boundaries without a free water phase. The question of the accumulation of a gas hydrates/ice phase is a question of kinetics, dependent on the time necessary for nuclei to attain a critical size. This time may be in excess of that available for laboratory study, but may occur in processes, which operate over extended periods of days, months or years.[1–8]

Therefore, the determination of water content in gas being in equilibrium with gas hydrates/ice is difficult, because of the low-concentration of water in the gaseous phase. The experimental work done to describe the water content of gas in equilibrium with hydrates/ice in the two-phase region are limited in accuracy due to two factors: the fact that metastable liquid water may extend well into the gas-hydrate/ice region, and the experimental restraint that the existing analysis methods require large amounts of gas in equilibrium with gas hydrates.[1–8] However, measuring corresponding water content in equilibrium with metastable liquid water is easier. Literature survey reveals the availability of few sets of experimental data for water content of gases in equilibrium, with gas hydrates/ice and all other data represent metastable liquid water — gas equilibrium. Therefore, few predictive methods for the water content of gases in equilibrium with gas hydrates/ice have been recommended in the literature as these methods are generally based on experimental data.[1,7,8]

The aim of this work is to develop a method based on equality of water fugacity in equilibrium phases for estimating the water content of gases in equilibrium with gas hydrates or ice by relating it to the corresponding water content in equilibrium with metastable liquid water. The main advantage of this method is the availability of input data and

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the simplicity of the calculations, and no need for tuning parameters. The capability of this method is investigated for methane, the major component of natural gases. The predictions of this method are compared with some experimental data from the literature. It will be shown that the results are in relatively acceptable agreement, demonstrating the capability of the method developed in this work for estimating the water content of gases being in equilibrium with gas hydrates/ice.

Hydrate-gas equilibrium

The gas-hydrate equilibrium of a system is calculated, by equating the fugacities of water in the gas phase f_w^g, and in the hydrate phase f_w^H

$$f_w^g = f_w^H \tag{1}$$

The fugacity of water in the hydrate phase f_w^H is related to the chemical potential difference of water in the filled and empty hydrate by the following expression

$$f_w^H = f_w^{MT} \exp \frac{\mu_w^H - \mu_w^{MT}}{RT} \tag{2}$$

where f_w^{MT} is the fugacity of water in the hypothetical empty hydrate phase, $\mu_w^H - \mu_w^{MT}$ represents the chemical potential difference of water in the filled and empty hydrate, R and T stand for universal gas constant and temperature, respectively.

The solid-solution theory of van der Waals - Platteeuw[9] can be employed for calculating $\frac{\mu_w^H - \mu_w^{MT}}{RT}$

$$\frac{\mu_w^H - \mu_w^{MT}}{RT} = -\sum_i v_i' \ln(1 + C_i f_{CH_4}) = \sum_i \ln(1 + C_i f_{CH_4})^{-v_i'} \tag{3}$$

where v_i' is the number of cavities of type i per water molecule in a unit hydrate cell (the values of v_i' have been reported by Sloan[1]), C_i stands for the Langmuir constant for methane's interaction with each type cavity, and f_{CH_4} is the fugacity of methane in the gas phase. In the earlier equation, f_{CH_4} can be set to P (pressure), with a good approximation for simple gas hydrate up to relatively intermediate pressures,[1,8] where nonideality of the system is not very important. Therefore,

$$\exp\left(\frac{\mu_w^H - \mu_w^{MT}}{RT}\right) = \prod_i (1 + C_i P)^{-v_i'} \tag{4}$$

The Langmuir constants accounting for the interaction between the gas and water molecules in the cavities were reported by Parrish and Prausnitz[10] for a range of temperatures. The integration procedure was followed in obtaining the Langmuir constants for lower-temperatures using the Kihara potential function, with a spherical core according to the study by McKoy and Sinanoğlu.[11] The Langmuir constants are consistent with initial hydrate data. However, since the experimental conditions go far below the initial hydrate formation conditions, the assumptions that are evidently valid at the initial hydrate formation conditions may be invalid elsewhere.[1] Nevertheless, until experimental occupation numbers as a function of temperature, pressure, composition, and so on, are obtained, there can be no independent check of this assumption as discussed by Davidson.[1,12] In this work, the Langmuir constants for methane's interaction with each type cavity, have been determined as a function of temperature, which are expressed from statistical mechanics, as well as from data at the three-phase line by Parrish and Prausnitz:[10]

for pentagonal dodecahedra (Small cavity)

$$C_{small} = \frac{3.7237 \times 10^{-2}}{T} \exp\left(\frac{2.7088 \times 10^3}{T}\right) \tag{5}$$

for tetrakaidecahedra (Large cavity)

$$C_{large} = \frac{1.8373 \times 10^{-1}}{T} \exp\left(\frac{2.7379 \times 10^3}{T}\right) \tag{6}$$

where T is in K, and C has units of reciprocal MPa.

The fugacity of water in the empty lattice can be expressed as

$$f_w^{MT} = P_w^{MT} \varphi_w^{MT} \exp \int_{P_w^{MT}}^{P} \frac{v_w^{MT} dP}{RT} \tag{7}$$

where P_w^{MT}, φ_w^{MT}, v_w^{MT}, and P are the vapor pressure of the empty hydrate lattice, the correction for the deviation of the saturated vapor of the pure (hypothetical) lattice from ideal behavior, the partial molar volume of water in the empty hydrate, given by von Stackelberg and Müller[13] (Quoted by Sloan[1]), and pressure, respectively, and the exponential term is a Poynting type correction. The concept in the earlier equation of universal empty hydrate vapor pressure for each structure, prompted Dharmawardhana et al.[14] to calculate the P_w^{MT} from a number of simple hydrate three-phase ice-vapor-hydrate equilibrium, which represent the upper concentration limit of the method.[1] By equating the fugacity of water in the hydrate phase to that of pure ice at the three-phase line, Dharmawardhana et al.[14] obtained the following equation for the vapor pressure of the empty hydrate structure I[1]

$$P_w^{MT} = 0.1 \times \exp\left(17.440 - \frac{6003.9}{T}\right) \tag{8}$$

where P_w^{MT} is in MPa, and T in K. The nonideality of water vapor pressure of the empty hydrate at saturation seems to be negligible, due to the small quantity (typically, 10^{-3} to 10^{-5} MPa).[1] However, they have been corrected for pressure by Poynting effect. Again, the vapor pressures of the empty hydrate lattice are consistent with initial hydrate data. However, since the experimental conditions go far below the initial hydrate formation conditions, the assumptions that are evidently valid at the initial hydrate formation conditions may be invalid elsewhere.

Equation 7 may be simplified by two assumptions: (1) that the hydrate partial molar volume equals to the molar volume, and is independent of pressure, and (2) that P_w^{MT} is relatively small (on the order of 10^{-3} MPa), so that $\varphi_w^{MT} = 1$. Therefore,

$$f_W^{MT} = P_w^{MT} \exp \frac{v_w^{MT}(P - P_w^{MT})}{RT} \tag{9}$$

The fugacity of water in the gas phase is expressed by:

$$f_w^g = y_w^H \varphi_w{}^g P \tag{10}$$

where y_w^H is the water content of the gas phase in equilibrium with gas hydrates, and φ_w^g is the fugacity coefficient of water in the gas phase.

Using the earlier equations, the following expression is obtained for estimating the water content of methane in equilibrium with gas hydrates

$$y_w^H = \frac{P_w^{MT}}{\phi_w^g P} \times \exp\left[\frac{v_w^{MT}(P - P_w^{MT})}{RT}\right] \times [(1 + C_{small}P)^{-v'_{small}} \times (1 + C_{large}P)^{-v'_{large}}] \tag{11}$$

In the earlier equation, the following values can be used

$$v_w^{MT} = 0.022655 \text{ m}^3/\text{kgmol}$$

(von Stackelberg and Müller[13])

$$v'_{small} = \frac{1}{23}$$

(Sloan[1])

$$v'_{large} = \frac{3}{23}$$

(Sloan[1])

Using an appropriate expression for the fugacity coefficient of water in the gas phase, Eq. 11 can be applied directly to estimate water content of pure gas in equilibrium with gas hydrate.

Metastable liquid water/ice-gas equilibria

The metastable liquid water-gas equilibrium of a system is calculated, using the following equation

$$f_i^g = f_i^L \quad i = 1, N \tag{12}$$

where f is the fugacity, superscripts g and L represent gas and liquid phases, and N is the number of components. The equality of fugacities can be calculated using the following relationship

$$y_i \phi_i P = x_i \gamma_i P_i^{sat} \exp \int_{P_i^{sat}}^{P} \frac{v_i^L dP}{RT} \tag{13}$$

where y, ϕ, P, x, γ, v, R and T represent mole fraction in the gas phase, fugacity coefficient, pressure, mole fraction in the liquid phase, activity coefficient, molar volume, universal gas constant and temperature, respectively. Superscript *sat* stands for saturation condition. In the intermediate pressure range, liquid water is an incompressible fluid and gas solubility is very small comparing to unity for hydrocarbons and some gases like nitrogen (solubility of hydrocarbons in water are, in general, considerably less than water in hydrocarbons), and to an approximation activity coefficient of water can be taken unity. However, the nonideality of the liquid phase and gas solubility become important at high-pressure conditions. Therefore, the mole fraction of water in the gas phase can be estimated using the following equation[15]

$$y_w^{L_w} = \frac{P_w^{sat}}{\varphi_w P} \exp\left(\frac{v_w^L (P - P_w^{sat})}{RT}\right) \tag{14}$$

where subscript w stands for water, and superscript L_w represents liquid water. As can be seen, water content is determined primarily by the fugacity coefficient of water (ϕ_w) in the gas phase, temperature and pressure. In other word, the nonideality of the gas phase is the critical factor determining water content in the intermediate pressure range.

To estimate vapor pressure and molar volume of water in Eq. 14, the relations reported by Daubert and Danner[16] and McCain[17,18] can be used, respectively

$$P_w^{sat} = 10^{-6}\exp(73.649 - 7258.2/T - 7.3037\ln(T) + 4.1653 \times 10^{-6}T^2) \tag{15}$$

$$v_w{}^L = 18.015/\rho_w \tag{16}$$

$$\rho_w = 1000/D_w \tag{17}$$

$$D_w = (1 + \Delta V_w) \tag{18}$$

$$\Delta V_w = -1.0001 \times 10^{-2} + 1.33391 \times 10^{-4} \times [1.8(T - 273.15) + 32] + 5.50654 \times 10^{-7} \times [1.8(T - 273.15) + 32]^2 \tag{19}$$

where T, P_w^{sat}, v_w^L are, respectively, in K, MPa and m^3/kgmol, and ρ_w, D_w and ΔV_w, are water density in kg/m^3, formation volume factor, volume change due to temperature, respectively. Equations 18 and 19 are valid at $T < 400$ K, and $P <$ 34.5 Mpa, even over a wide range of salt concentration.[18]

Ice-gas equilibrium normally reaches at low pressures, and, therefore, the ealier method can be used for estimating water content of gases in equilibrium with ice. For this purpose, the following relations for molar volume of ice and ice vapor pressure can be used[15,19]

$$v_w^I = (19.655 + 0.0022364 \times (T - 273.15))/10^3 \tag{20}$$

$$P_I^{sat} = [10^{(-1032.558/T + 51.056 \times \log(T) - 0.0977 \times T + 7.0357 \times 10^{-5} \times T^2 - 98.512)}]/7600 \tag{21}$$

where superscript I and *sat* refer to ice and saturation, respectively, and subscript I stands for ice. In the ealier equations T, v_w^I and P_I^{sat} are in K, $m^3/kgmol$ and MPa, respectively.

Again, the earlier equation can be applied directly to estimate the water content of a gas in equilibrium with liquid water or ice by using an appropriate expression for the fugacity coefficient of water in the gas phase. The ice-gas equilibrium normally reaches at relatively low-pressures as mentioned earlier, and, therefore, the fugacity coefficient of water in the gas phase can be set to unity with a good approximation. In other words, the *Ideal* model (Raoult's law) or ideal model *Poynting* correction can be used to estimate water content of a gas in equilibrium with ice.[15]

Relationship between water content of gas in equilibrium with gas hydrates and metastable liquid water

From Eqs. 11 and 14, it is possible to drive an equation to relate the water content of a pure gas in equilibrium with gas hydrates to corresponding water content in equilibrium with metastable liquid water. By dividing Eqs. 11 and 14, the following relation is obtained

$$\frac{y_w^H}{y_w^{L_w}} = \frac{P_w^{MT}}{P_w^{sat}} \times \left[(1 + C_{small}P)^{-\nu'_{small}} \times (1 + C_{l\,\mathrm{arg}\,e}P)^{-\nu'_{l\,\mathrm{arg}\,e}}\right] \quad (22)$$

where $y_w^{L_w} > y_w^H$. It should be noted that the Poynting corrections in Eqs. 11 and 14 were ignored for developing Eq. 22. Furthermore, since the water content of gas is very low, it can be assumed that the fugacity coefficients of water in the gas phase in Eqs. 11 and 14 are approximately in the same order of magnitude.[3] As can be seen, ratio $\frac{y_w^H}{y_w^{L_w}}$ is a function of temperature, pressure and gas nature.

Equation 22 can be written as

$$y_w^H = y_w^{L_w} \times F_H \quad (23)$$

where F_H is a correction factor and can be expressed using the following equation:

$$F_H = \frac{P_w^{MT}}{P_w^{sat}} \times \left[(1 + C_{small}P)^{-\nu'_{small}} \times (1 + C_{large}P)^{-\nu'_{large}}\right] \quad (24)$$

where, $F_H = 1$ on liquid water- vapor-hydrate (L_W-V-H) phase boundary.

Relationship between water content of gas in equilibrium with ice and meta-stable liquid water

A similar method can be used to derive an equation to relate the water content of a gas (pure gas or gas mixture) in equilibrium with ice, to corresponding water content in equilibrium with metastable liquid water from Eq. 14, as indicated in the following equation

$$\frac{y_w^I}{y_w^{L_w}} = \frac{P_I^{sat}}{P_w^{sat}} \quad (25)$$

Again, the Poynting correction was ignored for developing Eq. 25.[8] As can be seen, Eq. 25 shows that the ratio of $\frac{y_w^I}{y_w^{L_w}}$ for all gases is approximately equal to the ratio of ice vapor pressure to vapor pressure of metastable liquid water. In other words, the ratio $\frac{y_w^I}{y_w^{L_w}}$, for all gases is approximately function of temperature.

Equation 25 can be written as follows

$$y_w^I = y_w^{L_w} \times F_I \quad (26)$$

where F_I is a correction factor that can be expressed using the following equation

$$F_I = \frac{P_I^{sat}}{P_w^{sat}} \quad (27)$$

At ice point $P_I^{sat} = P_w^{sat}$, and, therefore, $F_I = 1$.

Results and discussion

Figure 1 shows the typical pressure-temperature for a water (limiting reactant)-single (pure) hydrocarbon system. As mentioned earlier, there is a paucity of accurate equilibrium data in the gas-hydrate and gas-ice regions, due to the difficulty in analyzing low-water concentrations in the gas, and due to the unusual metastability of liquid water in the gas-hydrate and gas-ice regions. Most of the available experimental data inside the hydrate and ice regions do not warrant thermodynamic equilibrium, that is, these data are not in equilibrium with gas hydrates or ice. The establishment of gas-hydrate or gas-ice equilibrium constitutes the principle problems associated with properly conducting the tests. Another serious problem is the sampling and analysis of the gas phase for the small equilibrium or concentrations of water. Furthermore, it is necessary to decompose and recrystallize the hydrate phase to ensure that the hydrate crystal is indeed in equilibrium with the gas phase.[1–8,15]

Among the data reported for gaseous systems in the literature, those reported by Aoyagi et al.[4] and Song et al.[5] for water content of methane seem to correspond to gas-hydrate equilibrium points. These data are reported in Tables 1 and 2, respectively. As can be seen, the temperature range is from 196 K to 270 K, and the pressures are up to 10.34 MPa, respectively. Furthermore, there is some deviation between the data reported by Aoyagi et al.[4] and Song et al.[5] at 3.45 Mpa and 240 K, 3.45 MPa and 270 K, and 6.9 MPa and 260 K.

In order to use Eqs. 22 and 25 and estimate water content of gas in equilibrium with gas hydrate or ice, it is necessary to calculate water content of methane in equilibrium with metastable liquid water. For this purpose, the results coming from a previously reported thermodynamic model is used.[19,20] Briefly, this thermodynamic model is based on uniformity of the fugacity of each component throughout all the phases, which uses the Valderrama modification of the Patel-

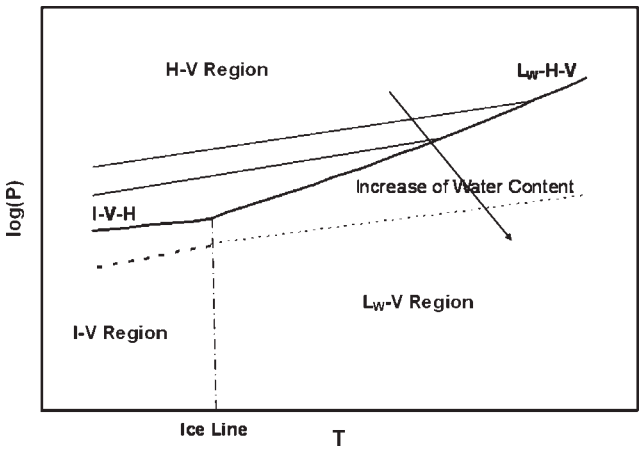

Figure 1. Hydrate (H) — vapor (V), ice (I) — vapor and liquid water (L_W) — vapor equilibria regions.

Bold solid lines: L_W-V-H and I-V-H equilibria; solid lines: hydrate phase boundaries in low water content gases representing water content of gas in equilibrium with gas hydrate; dashed line: condensate phase boundary in low water content gases representing water content of gas in equilibrium with liquid water (In L_W-V region); bold dashed line: ice phase boundary in low water content gases representing water content of gas in equilibrium with ice; solid-dashed line: ice line representing L_W-V-I equilibrium.

Table 1. Water Content of Methane in Equilibrium with Gas Hydrates

		Water Content of Methane (Mole Fraction)			
P/MPa	T/K	Experimental	Prediction, *H-V* Equilibrium	Prediction,† Meta-stable L_W-*V* Equilibrium	AD%**
3.45*	240	1.23E-05	1.09E-05	1.38E-05	11.4
3.45	250	3.22E-05	2.87E-05	3.42E-05	10.9
3.45	260	7.82E-05	6.96E-05	7.82E-05***	11.0
3.45*	270	1.78E-04	1.57E-04	1.67E-04***	11.8
6.9	240	5.60E-06	6.27E-06	8.94E-06	12.0
6.9	250	1.55E-05	1.60E-05	2.14E-05	3.2
6.9*	260	3.96E-05	3.77E-05	4.77E-05	4.8
6.9	270	9.44E-05	8.34E-05	1.00E-04	11.7
10.34	**240**	2.72E-06	3.41E-06	5.22E-06	25.4
10.34	**250**	8.46E-06	10.4E-06	15.0E-06	22.9
10.34	**260**	2.42E-05	2.87E-05	3.89E-05	18.6
10.34	270	6.42E-05	6.21E-05	7.97E-05	3.3

(Experimental data from Aoyagi *et al.*[4]).
[a]There is some deviation between this data and the data generated by Song *et al.*[5] and reported in Table 2.
**For *H-V* equilibrium.
***Equal or less than experimental water content of gas in equilibrium with gas hydrates, indicating inaccurate predicted water content of gas in equilibrium with meta-stable liquid water.
†Using the previously reported thermodynamic model.[19,20,23]

Teja equation of state,[21] with the nondensity dependent mixing rules [22] for calculating fugacities in all fluid phases. This combination has proved to be a strong tool in estimating water content of gases, especially in equilibrium with liquid water near the hydrate region.[23] However, it is expected that the existing models, including this model, show some deviations for estimating the water content of gases in equilibrium with metastable liquid water, and inside the hydrate region, as the interaction parameters in these models were tuned using data at higher-temperature conditions.

Tables 1 and 2 show predictions of the model[19,20] for water content of methane in equilibrium with metastable liquid water. Corresponding water content of methane in equilibrium with gas hydrate using Eq. 22, is also shown in these tables. As can be seen, the water content of a gas in equilibrium with gas hydrates is lower than that of the same gas in equilibrium with metastable liquid water. Equation 22 with no adjustable parameter shows encouraging results. Except the bold points shown in these tables, other points show less than 15% absolute deviation (AD). The average absolute deviation (AAD) among all the experimental and predicted data is 17.1%.

As mentioned earlier, and as can be observed from Eq. 22, these deviations may be attributed to different factors: the results of the thermodynamic model[19,20] for water content of gas in equilibrium with metastable liquid water, and also Eq. 15 for water vapor pressure at low-temperatures can be a source of error. Furthermore, the Langmuir constants and the vapor pressures of the empty hydrate lattice are consistent with initial liquid water- vapor-hydrate (L_W-*V*-*H*) data, and may be invalid elsewhere, as the conditions go far from the initial hydrate formation conditions.[1] The assumption in

Table 2. Water Content of Methane in Equilibrium with Gas Hydrates

		Water Content of Methane (Mole Fraction)			
P/MPa	T/K	Experimental	Prediction, *H-V* Equilibrium	Prediction,† Meta-stable L_W-*V* Equilibrium	AD%**
3.45*	270	1.73E-04	1.57E-04	1.67E-04***	9.2
3.45	254	4.24E-05	4.13E-05	4.80E-05	2.6
3.45*	240	1.17E-05	1.09E-05	1.38E-05	6.8
3.45	224	2.17E-06	1.93E-06	2.72E-06	11.1
3.45	**213**	5.48E-07	6.57E-07	1.00E-06	19.9
3.45	**196**	6.32E-08	7.74E-08	1.35E-07	22.5
6.9	260	4.16E-05	3.77E-05	4.77E-05	9.4
6.9	254	2.07E-05	2.27E-05	2.97E-05	9.7
6.9	246	9.48E-06	1.11E-05	1.52E-05	17.1
6.9	230	2.08E-06	2.28E-06	3.47E-06	9.6
6.9	**213**	2.32E-07	2.91E-07	5.00E-07	25.4
6.9	**204**	6.95E-08	8.69E-08	1.60E-07	25.0
6.9	**202**	5.26E-08	6.57E-08	1.23E-07	24.9

(Experimental data from Song *et al.*[5]).
*There is some deviation between this data and the data generated by Aoyagi *et al.*[4] and reported in Table 1.
**For *H-V* equilibrium.
***Less than experimental water content of gas in equilibrium with gas hydrates, indicating inaccurate predicted water content of gas in equilibrium with meta-stable liquid water.
†Using the previously reported thermodynamic model.[19,20,23]

Table 3. Water Content of Methane in Equilibrium with Ice

T/K	P/MPa	Water Content of Methane (Mole fraction) Experimental	Prediction, I-V Equilibrium	Prediction, Meta-stable L_W-V Equilibrium	AD%*
Experimental data from Althaus[24]					
253.15	0.5	2.10E-04	2.15E-04	2.59E-04	2.2
258.15	1.5	1.10E-04	1.21E-04	1.39E-04	9.7
258.15	0.5	3.10E-04	3.42E-04	3.94E-04	10.4
263.15	1.5	1.90E-04	1.89E-04	2.07E-04	0.8
263.15	0.5	5.20E-04	5.36E-04	5.88E-04	3.1
268.15	1.5	2.80E-04	2.90E-04	3.04E-04	3.5
268.15	0.5	8.30E-04	8.26E-04	8.65E-04	0.5
Experimental data from Kosyakov *et al.*[25]					
263.15	1.013	2.80E-04	2.72E-04	2.99E-04	2.9
253.15	1.013	1.10E-04	1.09E-04	1.32E-04	0.8
243.15	1.013	4.00E-05	4.07E-05	5.38E-05	1.7

*For *H-V* equilibrium.

Eq. 4 that f_{CH_4} can be set to P, for simple gas hydrates is also conservative at high-pressures.

Limited information is available for ice-gas equilibrium. We use the data reported by Althaus[24] and Kosyakov et al.[25] as shown in Table 3. Furthermore, we assume that these data represent water content of methane in equilibrium with ice, as further information is not available in the original manuscripts. Predictions of Eq. 25 for water content of methane in equilibrium with ice, and corresponding water content of methane in equilibrium, with metastable liquid water predicted by the previously reported thermodynamic model, [19,20] as well as ADs are also shown in this table. As can be seen, water content of gas in equilibrium with ice is always less than water content of the same gas in equilibrium, with corresponding metastable liquid water. The difference becomes of importance at very low-temperature conditions. Furthermore, good agreement is observed between predictions of Eq. 25 and experimental data. Maximum AD is 10.4%, and the AAD between all experimental and predicted data is 3.5%.

It is clear that using more accurate data on water content of gas in equilibrium with metastable liquid water can lead to more accurate predictions of the water content of the gas in equilibrium with gas hydrate or ice. This is a useful remark to reduce experimental information required to evaluate hydrate-gas or ice-gas equilibrium of the gas-water system, where estimating water content of gas in equilibrium with metastable liquid water is a much easier and less time-consuming process, than measuring the water content in equilibrium with gas hydrate or ice. The results can provide better understanding and evaluation of water content of gases in equilibrium with gas hydrates/ice associated with production, transportation and processing of gases.[26]

Conclusions

Predictive methods based on equality of fugacity concept were developed for estimating the water content of gases in equilibrium with gas hydrates or ice using data on corresponding water content in equilibrium with metastable liquid water. The method with no adjustable parameter showed encouraging results. Acceptable agreement was achieved between the results of these methods and experimental data reported in the literature.

Acknowledgment

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Notation

AAD = average absolute deviation
AD = absolute deviation
C = Langmuir constant
D = formation volume factor
F = correction factor
H = hydrate
I = ice
L = liquid
N = number of components
P = pressure
R = universal gas constant
T = temperature
V = vapor
f = fugacity
v = molar volume
v_i' = number of cavities of type i per water molecule in a unit hydrate cell
x = mol fraction in the liquid phase
y = mol fraction in the gas phase

Greek letters

ΔV = volume change
γ = activity coefficient
ρ = density
φ = fugacity coefficient
μ = chemical potential

Superscripts

MT = hypothetical empty hydrate
I = ice state
L = liquid state
sat = property at saturation
H = hydrate
g = gas
w = water

Subscripts

H = hydrate
I = ice
g = gas
w = water

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