



The next generation of hydrate prediction

I. Hydrate standard states and incorporation of spectroscopy

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Abstract

The van der Waals and Platteeuw hydrate equation of state, coupled with the classical thermodynamic equation for hydrates, has been used in the prediction of hydrate formation for over 40 years. These equations describe a hydrate to liquid water phase change, where the hydrate is always treated as an ideal solid solution. Several limitations of this method have been removed in a new derivation of the model.

In this work, a direct derivation of the standard empty hydrate lattice fugacity has been given. This allows for description of the hydrate phase itself, instead of a specific phase change. The ideal solid solution assumption is removed by defining a specific volume of the standard hydrate lattice. The activity of water in the hydrate is a function of the energy difference between the real and standard lattice. This approach, which allows for distortion of the hydrate from its standard state, is believed to give a more accurate composition of the hydrate. We propose to make the cage radii a linear function of the hydrate lattice parameter. Direct incorporation of spectroscopic data is crucial for parameter optimization in the model.

Preliminary predictions with the new model are presented that show the wider applicability of the approach. H–V and I–H equilibrium can be calculated using this method as well as a correct description of high pressure behavior. This paper is the first in a series of four that the authors believe to be a more complete prescription for hydrate modeling. Therefore, this part only pertains to the theory of the hydrate model. Subsequent papers will discuss: (1) the aqueous phase model; (2) incorporation of the models into a multi-phase flash routine and (3) regressed parameter values and a comparison of our models with four commercial hydrate prediction programs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Model; Hydrate; Standard state; Activity coefficient; Solid–fluid equilibria; Spectroscopy

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1. Introduction

As the demand for oil and natural gas becomes greater, there is a need to go to deeper depths of water to obtain them. Therefore, the pressure and temperature ranges of thermodynamic models that are the basis of flow assurance strategy need to be extended.

The current hydrate fugacity model applies statistical thermodynamics [1] and classical thermodynamics [2]. Predictions from this model are relatively good at moderate pressures and temperatures. However, at high pressures ($P > 200$ bar) and for natural gas hydrates the model predictions deviate from experimental data. This suggests that the hydrate standard state (empty lattice) properties are not well defined. We propose two modifications to the current theory for hydrate fugacity: (1) the first description of the hydrate standard state itself and (2) an activity coefficient based on exact knowledge of the hydrate volume.

2. Current hydrate fugacity model

The current hydrate fugacity model is split into two parts: (1) a statistical part and (2) a classical part. What follows is a brief discussion of both parts.

2.1. Statistical thermodynamic model

The statistical thermodynamic model for the chemical potential of water in the hydrate uses the assumption that, if the standard state hydrate energy is known at T and P , the only accountable energy change is due to the occupation of the hydrate cavities [1]. This assumption requires that the energy of the standard state hydrate be well defined.

In the development of the statistical thermodynamic hydrate model, the free energy of water in the standard hydrate (empty hydrate lattice) is assumed to be known at a given T and v . Since the model was developed at constant volume, the assumption requires that the volume of the empty hydrate lattice, v^β , must be equal to the volume of the equilibrium hydrate, v^H , so that the only energy change is due to occupation of the hydrate cavities, as shown in Fig. 1.

The statistical thermodynamic model relating the free energy change of water for process (1) described in Fig. 1 is given as

$$\frac{\Delta\mu_{w,H}}{RT} = \frac{\mu_{w,H}}{RT} - \frac{g_{w,\beta}}{RT} = \sum_m \nu_m \ln \left(1 - \sum_J \theta_{Jm} \right) \quad (1)$$

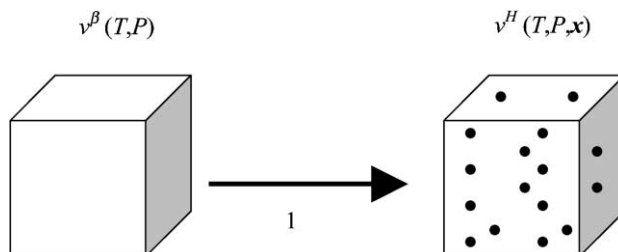


Fig. 1. Current model doesn't allow for distortion of hydrate due to guests ($v^\beta = v^H$).

where $g_{w,\beta}$ is the chemical potential of water in the standard (empty) hydrate lattice at a given volume and θ_{Jm} is the fractional occupancy of guest J in hydrate cage m . The summation term in Eq. (1) is the resulting energy change due to the insertion of the guest molecules into the empty hydrate lattice.

Traditionally, the chemical potential of the standard hydrate is assumed to be at a given volume. However, X-ray diffraction (XRD) measurements of several different hydrates show that the volume of the equilibrium hydrate is dependent on the hydrate guest(s) [3,4]. That is, different sizes and compositions of hydrate guest(s) correspond to different volumes of the hydrate. If the standard hydrate volume is not the volume of the equilibrium hydrate, there should be an energy change proportional to the difference in volume ($\Delta v^H = v^H - v^\beta$). Note that, in the development of Eq. (1), Δv^H is assumed to be equal to zero. However, we account for this distortion via an activity coefficient as shown below.

2.2. Classical thermodynamic model

The classical thermodynamic hydrate model uses the following two equations, which can be derived using pure component thermodynamics

$$\frac{\mu_{w,L_w}}{RT} = \frac{g_{w_0,L_{\text{pure}}}}{RT_0} - \int_{T_0}^T \frac{h_{w,L_{\text{pure}}}}{RT^2} dT + \int_{P_0}^P \frac{v_{w,L_{\text{pure}}}}{RT} dP + \ln a_{w,L_w} \quad (2)$$

and

$$\frac{g_{w,\beta}}{RT} = \frac{g_{w_0,\beta}}{RT_0} - \int_{T_0}^T \frac{h_{w,\beta}}{RT^2} dT + \int_{P_0}^P \frac{v_{w,\beta}}{RT} dP \quad (3)$$

where g_w , h_w and v_w are the molar Gibbs energy, enthalpy, and volume of water, respectively, and the superscripts L_w , L_{pure} , and β correspond to the aqueous, pure liquid water, and standard hydrate phases, respectively. Subtracting Eq. (3) from Eq. (2), we get the needed expression to describe the phase change from a standard hydrate lattice to an aqueous phase [2]

$$\frac{\Delta\mu_{w,L_w}}{RT} = \frac{\mu_{w,L_w}}{RT} - \frac{g_{w,\beta}}{RT} = \frac{\Delta g_{w_0}}{RT_0} - \int_{T_0}^T \frac{\Delta h_w}{RT^2} dT + \int_{P_0}^P \frac{\Delta v_w}{RT} dP + \ln a_{w,L_w} \quad (4)$$

Using Eqs. (1) and (4), the following equation for the fugacity of water in hydrates can be derived

$$f_{w,H} = f_{w,L_w} \exp \left[\frac{\Delta\mu_{w,H} - \Delta\mu_{w,L_w}}{RT} \right] \quad (5)$$

Note that, since the fugacity of water in the aqueous phase must be known in Eq. (5), an aqueous phase must be present to correctly calculate the fugacity of water in the hydrate. We have eliminated this constraint.

3. Accounting for non-ideality

Note that Eq. (1) is considered to be an ideal solid solution model. That is, upon rearrangement, Eq. (1) can be expressed as

$$\mu_{w,H} - g_{w,\beta} = RT \ln \prod_m \left(1 - \sum_J \theta_{Jm} \right)^{v_m} \quad (6)$$

which is quite similar to the well known thermodynamic expression

$$\mu_i - g_{i,o} = RT \ln a_i \quad (7)$$

where $g_{i,o}$ is the Gibbs energy of species i in its pure state. With Eqs. (6) and (7) in mind, the activity of water in the hydrate can be expressed as

$$a_{w,H} = \prod_m \left(1 - \sum_J \theta_{Jm} \right)^{v_m} \quad (8)$$

which is simply a function of the composition of water in the hydrate. Expanding the product term in Eq. (8) leads to

$$a_{w,H} = \left(1 - \sum_J \theta_{JS} \right)^{v_S} \left(1 - \sum_J \theta_{JL} \right)^{v_L} = a_{w,S} a_{w,L} \quad (9)$$

where we can see that the activity of water in the hydrate can be expressed in terms of its activity in each of the cavities. Upon further inspection of Eq. (9), we can see that the activity of water in a given hydrate cavity is an effective composition of water in that cavity. That is, Eq. (9) gives the decrease in energy of water in the hydrate due to the inclusion of the guest(s) in the hydrate cavities. Note that, in the derivation of Eq. (1), it was assumed that there were no energy changes due to other effects (i.e. the water and guest(s) in the hydrate act as an ideal solution).

In traditional thermodynamics, the activity of a component in a phase is defined as the ratio of the fugacity of that component in the phase to the fugacity of that component in its pure state. Hence, the idea of an empty hydrate lattice. Note, however, that the Gibbs energy of the component in its pure state is usually known quite well. That is, the activity is simply a perturbation in the fugacity of the component from its pure state. For fluid phases, the following expression for the activity of a component is familiar

$$a_{i,f} = x_{i,f} \gamma_{i,f} \quad (10)$$

where $x_{i,f}$ is the composition and $\gamma_{i,f}$ is the activity coefficient of component i in the fluid phase. Note that the activity coefficient accounts for non-idealities between component i and other components in the fluid. We can extend this principle to water in the hydrate phase.

Using the statistical thermodynamic model for effective composition and introducing an activity coefficient, which accounts for non-ideal interactions, we can define the activity of water in a hydrate cavity as

$$a_{w,m} = \left(1 - \sum_J \theta_{Jm} \right)^{v_m} \gamma_{w,m} \quad (11)$$

Substituting Eq. (11) into Eq. (8), the activity of water in the hydrate becomes

$$a_{w,H} = \prod_m \left(1 - \sum_J \theta_{Jm} \right)^{v_m} \gamma_{w,m} \quad (12)$$

where $\gamma_{w,m}$ is the activity coefficient of water in cavity m , accounting for perturbations of cavity m from the standard hydrate lattice. However, since non-idealities will most likely not be known for each

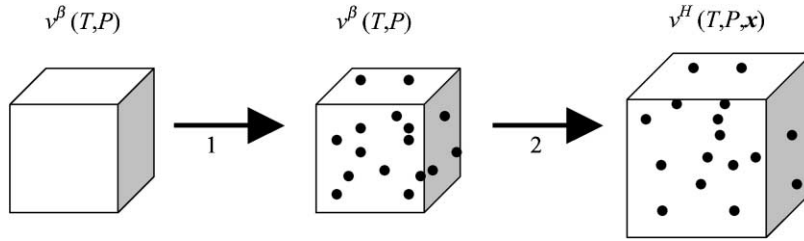


Fig. 2. Corrected model which allows for distortion of hydrate due to guests ($v^\beta \neq v^H$).

hydrate cavity, we assume that they can be gathered into a structural activity coefficient which accounts for non-ideality from the standard hydrate. Therefore, Eq. (12) can be expressed as

$$a_{w,H} = \gamma_{w,H} \prod_m \left(1 - \sum_J \theta_{Jm} \right)^{\nu_m} \tag{13}$$

where $\gamma_{w,H}$ is the effective activity coefficient. Substitution of Eq. (13) into Eq. (1) gives

$$\mu_{w,H} = g_{w,\beta} + RT \sum_m \nu_m \ln \left(1 - \sum_J \theta_{Jm} \right) + RT \ln \gamma_{w,H} \tag{14}$$

Note that Eq. (14) can be visualized in a similar manner as in Fig. 1. Fig. 2 illustrates the processes needed to determine the chemical potential of water in the hydrate (as given by Eq. (14)). Process (1) in Fig. 2 is done at constant volume and therefore, the van der Waals and Platteeuw statistical model can be used. Process (2) in Fig. 2, the volume change of the hydrate from its standard state volume, is done at constant composition and is described by the activity coefficient in Eq. (14).

An expression must be developed which describes the differences between the hydrate and the standard state. XRD data show that the volume of the hydrate is a strong function of the guest(s) present in the hydrate [3,4]. Therefore, we suggest that the activity coefficient be a function of the difference in volume between the hydrate and the standard hydrate, Δv^H . We note, however, that the activity coefficient must have the following property $\gamma_{w,H} \rightarrow 1$ as $\Delta v^H \rightarrow 0$. Implementing the above constraint reduces Eq. (14) to Eq. (1) when $\Delta v^H = 0$ (i.e. $\gamma_{w,H} = 1$). In the strictest sense, the activity coefficient accounts for the energy change involved in taking the volume of the standard lattice to the volume of the real hydrate. That is, it will perturb the Gibbs energy of the standard lattice such as

$$\mu_{w,H} = g_{w,\beta} + \Delta g_{w,\beta} + RT \sum_m \nu_m \ln \left(1 - \sum_J \theta_{Jm} \right) \tag{15}$$

where the perturbation can be described in a manner similar to Eq. (3) as

$$\Delta g_{w,\beta} = \frac{\Delta g_{w_0,\beta}}{RT_0} - \int_{T_0}^T \frac{\Delta h_{w,\beta}}{RT^2} dT + \int_{P_0}^P \frac{\Delta v^H}{RT} dP \tag{16}$$

Evaluating Eqs. (14)–(16) and assuming that the heat capacity of the hydrate is not affected in the process, we propose that the activity coefficient of water in the hydrate be expressed as

$$\ln \gamma_{w,H} = \frac{\Delta g_{w_0,\beta}}{RT_0} + \frac{\Delta h_{w_0,\beta}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \int_{P_0}^P \frac{\Delta v^H}{RT} dP \quad (17)$$

where $h_{w_0,\beta}$ is the enthalpy of formation at reference conditions. In this work, we arbitrarily define the perturbed Gibbs energy and enthalpy of formation be linear in Δv^H , satisfying the above constraint on the activity coefficient.

It is important to note that the molar volume difference between the standard hydrate and the real hydrate, Δv^H , is a strong function of composition of the real hydrate and small function of pressure. Therefore, the activity coefficient will be a strong function of composition and a small function of pressure, as is the normal case for liquids. There will also be a temperature dependence in the activity coefficient due to the temperature dependent term introduced by the integration of the enthalpy (Eq. (17)).

4. Defining the standard hydrate

The best choice for the standard hydrate would be one that is well characterized and not too different from the real state of the system. If the standard state is well defined, small perturbations from this standard state can be accounted for correctly. With this in mind, we turn to the two most well-known hydrates of sI and sII: methane and propane hydrate, respectively. Note that the standard states for sI and sII are the empty hydrate lattices of these and not the actual hydrates. Therefore, the activity coefficients for methane and propane hydrates will be close to unity.

The Gibbs energy of water in the standard state can be expressed using classical thermodynamics and is given in Eq. (3). Note that $g_{w_0,\beta}$ is the molar Gibbs energy of formation of the standard hydrate at the reference conditions (T_0 and P_0), $h_{w,\beta}$ is the molar enthalpy, and $v_{w,\beta}$ is the molar volume. These three properties are the unknowns that need to be determined in order to specify the standard state hydrate.

We define the molar volume of the standard hydrates of sI and sII as the molar volumes of methane and propane hydrate, respectively. The molar volume of these hydrates, and therefore of the standard states, is well characterized via XRD data [3,4]. The following is the derived expression for the molar volume of water in hydrates:

$$v_{w,\beta} = v_0 \exp[\alpha_1(T - T_0) + \alpha_2(T - T_0)^2 + \alpha_3(T - T_0)^3 - \kappa(P - P_0)] \quad (18)$$

The compressibility coefficient, κ , and reference volume, v_0 , are solely dependent on the composition of the guest(s) in the hydrate lattice while the thermal expansion coefficients, α_1 , α_2 , and α_3 are solely dependent on the hydrate structure. The values of these parameters will appear in the fourth part of this series.

The molar enthalpy of water in the standard hydrate can be expressed as

$$h_{w,\beta} = h_{w_0,\beta} + \int_{T_0}^T c_{P_{w,\beta}} dT \quad (19)$$

where $h_{w_0,\beta}$ is the molar enthalpy of formation of the standard hydrate at the reference conditions (T_0 and P_0) and $c_{P_{w,\beta}}$ is the heat capacity. The heat capacity of the standard hydrates for both sI and sII is well

approximated by that of ice [5]. However, the molar enthalpy of formation is not known and needs to be regressed to experimental data.

5. Developing the fugacity

In order to solve for thermodynamic equilibrium, the fugacity of water in the hydrate must be known. Recall that the current approach to this is to relate the chemical potential of water in the hydrate to that in the aqueous phase. This approach can be burdensome in that, as shown above, if an aqueous phase is not present, comparing chemical potentials will not be consistent with thermodynamic equilibrium. Therefore, we suggest the following approach.

It is common when solving for fugacity, with equations of state, to use the standard state of the ideal gas of the pure component at 1 bar. To be consistent, we follow the same approach in this work. Therefore, the fugacity of water in the hydrate is defined as

$$f_{w,H} = f_{w,o} \exp \left[\frac{\mu_{w,H} - g_{w,o}}{RT} \right] \quad (20)$$

where $f_{w,o}$ is 1 bar, $g_{w,o}$ the Gibbs energy of pure water in the ideal gas state at 1 bar, and $\mu_{w,H}$ is given by Eqs. (3) and (14). Note that the fugacity of water in the hydrate, as determined by Eq. (20), does not require that an aqueous phase be present.

6. Calculation of cage occupancy

The calculation of the cage occupancies of the guest(s) in the hydrate is given by the following equation:

$$\theta_{J,m} = \frac{C_{J,m} f_{J,m}}{1 + \sum_k C_{k,m} f_{k,m}} \quad (21)$$

where $f_{J,m}$ is the fugacity of component J in cage m and $C_{J,m}$ is the Langmuir constant of component J in cavity m . The Langmuir constants describe the potential interaction between the encaged guest molecule and the water molecules surrounding it. They are evaluated by assuming a spherically symmetrical cage and can be described by a spherically symmetrical potential as

$$C_{J,m} = \frac{4\pi}{kT} \int_0^{R_m - a_J} \exp \left[-\frac{\omega_{J,m}(r)}{kT} \right] r^2 dr \quad (22)$$

where R_m is the radius of cage m and $\omega_{J,m}(r)$ is the potential function. The Kihara spherical core potential is used to calculate the Langmuir constants. McKoy and Sinanoglu [6] summed all the guest–water binary interactions to yield an overall cell potential $\omega_{J,m}(r)$ given by

$$\omega_{J,m}(r) = 2\varepsilon_J z_m \left[\frac{\sigma_J^{12}}{R_m^{11} r} \left(\delta_{J,m}^{10} + \frac{a_J}{R_m} \delta_{J,m}^{11} \right) - \frac{\sigma_J^6}{R_m^5 r} \left(\delta_{J,m}^4 + \frac{a_J}{R_m} \delta_{J,m}^5 \right) \right] \quad (23a)$$

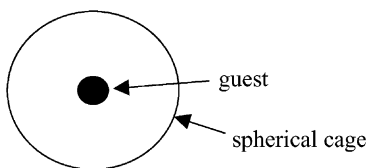


Fig. 3. Illustration of guest–cage interaction.

where

$$\delta_{J,m}^N = \frac{1}{N} \left[\left(1 - \frac{r}{R_m} - \frac{a_J}{R_m} \right)^{-N} - \left(1 + \frac{r}{R_m} - \frac{a_J}{R_m} \right)^{-N} \right] \quad (23b)$$

where z_m is the number of water molecules at the periphery of each cage (coordination number), a_J the spherical core of the hydrate guest, and σ_J and ε_J are the distance between core surfaces corresponding to zero potential energy and depth of the intermolecular potential well for the water–guest interaction, respectively. The cell potential model essentially calculates each water–guest interaction as a summed spherical field around the enclathrated molecule.

In the development of Eq. (22), it was assumed that the interaction between the guest and the water molecules in cage m could be approximated using an average cage radius. Fig. 3 illustrates this. In this work, we suggest another approach. We propose that the interactions between the guest and water molecules can be better approximated using a “multi-layered” cage (Fig. 4). We use direct single crystal XRD data for the radii of each water molecule in the hydrate cages [7,8]. Table 1 lists these radii for sI and sII hydrates. Note that the cubic lattice parameter, which corresponds to these cage radii, is given for each hydrate structure. Eq. (24) is the proposed expression for the Langmuir constant

$$C_{J,m} = \frac{4\pi}{kT} \int_0^{R_1 - a_J} \exp \left[- \frac{\sum_n \omega_{J,n}(r)}{kT} \right] r^2 dr \quad (24)$$

where the summation is over all shells (n) in cage m . Note that the upper limit of the integral is evaluated at R_1 , which is the smallest shell in cage m . Eq. (23) can still be used to evaluate the potential for a given layer. In the development of Eq. (24), it is assumed that binary interactions between the guest and the water molecules (shells) are of most importance.

The crucial change introduced in this work is to make the radii of each shell functions of temperature, pressure, and composition. As the lattice expands or compresses, the cages also expand or compress. The

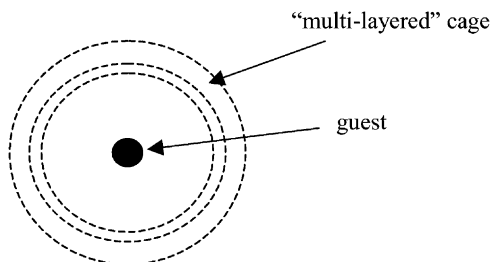


Fig. 4. Illustration of multiple shell with “multi-layered” first shell.

Table 1
Types of oxygen atoms at the periphery of both sI and sII hydrate cages and distance of each to the center of the cages

	Small cage (5^{12})		Large cage ($5^{12}6^2$)			
Number of waters in cage	20		24			
Average radius	3.908		4.326			
Layer type	(i)	(k)	(i)	(k)	(k)	(c)
(a) sI ethylene oxide hydrate ($a = 12.03 \text{ \AA}$) [7]						
Number of waters in layer	8	12	8	8	4	4
Radius (\AA)	3.83	3.96	4.47	4.06	4.645	4.25
Large cage ($5^{12}6^4$)						
Number of waters in cage	20		28			
Average radius	3.902		4.683			
Layer type	(a)	(e)	(g)	(e)	(g)	(g)
(b) sII tetrahydrofuran and hydrogen sulfide hydrate ($a = 17.1 \text{ \AA}$) [8]						
Number of waters in layer	2	6	12	4	12	12
Radius (\AA)	3.748	3.845	3.956	4.729	4.715	4.635

radii of the shells are assumed to be a linear function of the cubic hydrate lattice parameter. For example, if the lattice parameter expands by 1% of its original value, each shell radius, R_n , also expands by 1% of its original value.

7. Regression of unknown parameters

The unknown parameters in the given hydrate model are the molar Gibbs energy of formation of the standard hydrate at the reference conditions (T_0 and P_0), $g_{w_0,\beta}$, the molar enthalpy of formation of the standard hydrate at the reference conditions (T_0 and P_0), $h_{w_0,\beta}$, the distance between core surfaces corresponding to zero potential energy, σ_J , and the depth of the intermolecular potential well, ε_J . The formation properties only need to be regressed for the standard hydrates, however, the potential parameters need to be regressed for all hydrate formers. The regression procedure was multi-dimensional because the formation properties and the potential parameters are dependent on one another. Because of this, it was important that there were several sets of hydrate data to regress the parameters.

The traditional approach in optimizing these parameters is to use pressure–temperature (PT) hydrate dissociation data only. In this work, we use various hydrate phase measurements to optimize parameters: occupancy ratio, hydration number, hydrate lattice parameters, sI–sII transitions in the methane + ethane + water and ethane + propane + water systems, and PT hydrate dissociation data. The occupancy ratio data for methane hydrates and the sI–sII transitions in the methane + ethane + water system were determined using Raman and NMR spectroscopy [9,10], the hydrate lattice parameters for all former hydrates are from XRD [3,4,7,8], and the sI–sII transitions in the ethane + propane + water system were determined qualitatively by Holder and Hand [11].

With a given set of formation properties, an infinite line of potential parameters can be found from PT hydrate dissociation data, as shown by Ballard and Sloan [12]. Therefore, for all possible combinations

of formation properties, there is an infinite set of potential parameters in the potential parameter space (ϵ_j versus σ_j). To reduce this number, hydration number and occupancy ratio data at 273.15 K were used. Since the prediction of hydration number and occupancy ratio are independent of the formation properties, the infinite set of potential parameters was reduced. High pressure methane occupancy ratio data [13] was used to reduce the set even more.

At this point, the potential parameters and formation properties were regressed simultaneously using a Newton–Raphson procedure. The PT hydrate dissociation data and sI–sII transition data were used for the regression. Derivatives of the fugacity of water in the hydrate with respect to each unknown parameter were developed for the regression. Due to their complexity and length, they are not listed here. It should be noted that range of values for the potential parameters was constrained within the possible sets found using hydration number and cage occupancy ratio data. The regressed values for formation properties and potential parameters will be given in Section 4 of this series.

8. Predictions with new model

Fig. 5 is a plot of the sI methane hydrate dissociation line (L_w –sI–V). The dashed line is a prediction with the current hydrate fugacity model (Eq. (5)) and the solid line is a preliminary prediction with the proposed model (Eq. (22)). Both models fit the data well at lower pressures. However, note that the proposed model predicts the maximum temperature at which sI hydrates can form (~ 320 K), whereas the current model fails to do this. This is a direct result of treating the shell radii as functions of temperature

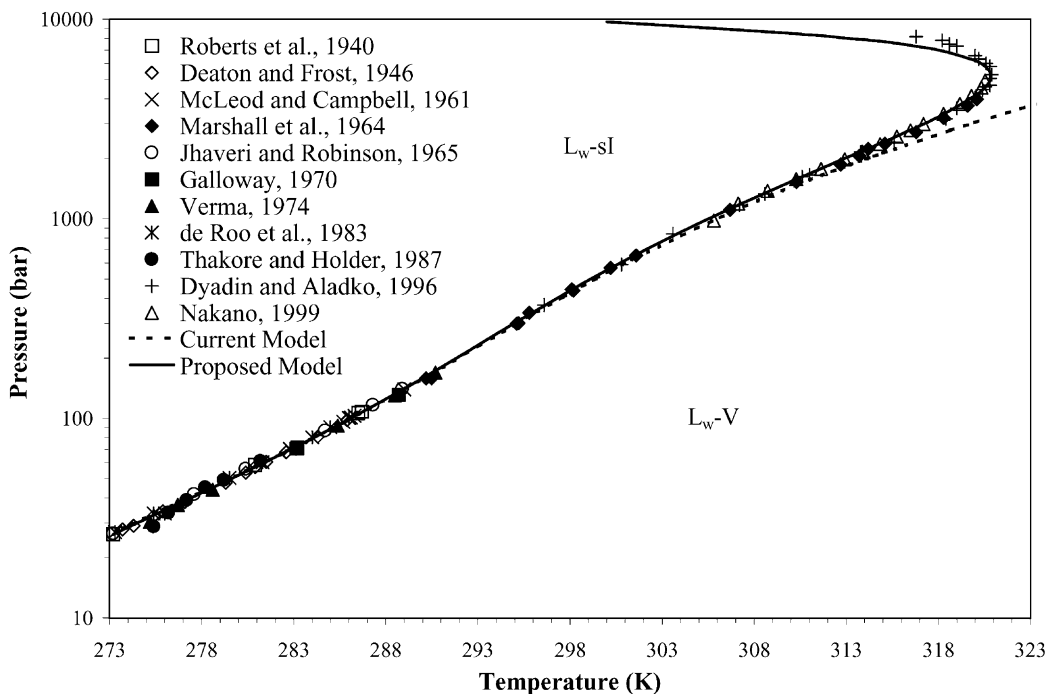


Fig. 5. Pressure vs. temperature plot for sI methane hydrates (L_w –sI–V).

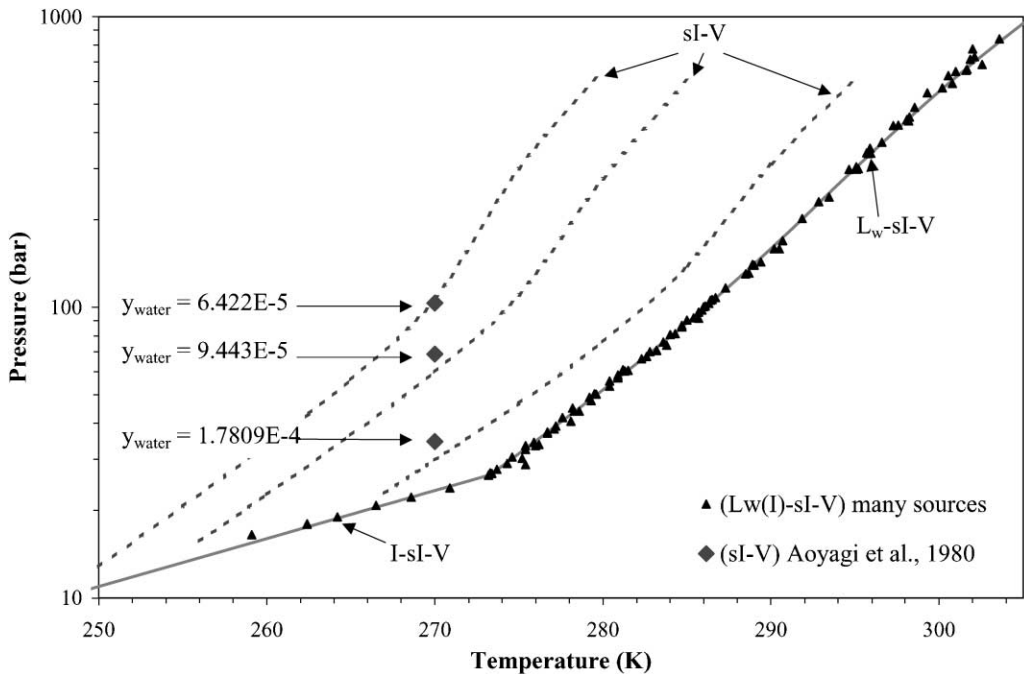


Fig. 6. Pressure vs. temperature plot for sI methane hydrates (sI-V and I-sI-V).

and pressure. That is, at high pressure the hydrate cages compress such that methane can no longer fit into the small cages.

Fig. 6 is a plot of the sI methane hydrate dissociation in the absence of an aqueous phase. Note that the three-phase line, I-sI-V, and the two-phase lines, sI-V, are predicted well. This is one of the main advantages of the new hydrate model: the ability to predict hydrate equilibria with any phase.

9. Conclusions

We have proposed a new hydrate fugacity model that accounts for non-idealities from the standard state hydrate, introducing an activity coefficient for water in the hydrate phase. The proposed model reduces to the ideal solid solution theory, developed by van der Waals and Platteeuw, when the activity coefficient equals unity. A new approach for the calculation of the Langmuir constants has also been proposed, treating the hydrate cavity radii as a function of hydrate volume. Table 2 is a listing of the major differences between the current and proposed hydrate models. A method for the regression of unknown model parameters is given, allowing for the incorporation of spectroscopic data.

The proposed hydrate fugacity model gives a direct description of the hydrate phase, and is thus not limited to calculations with an aqueous phase. This constraint with the previous hydrate model was inherent in choosing to describe the hydrate as a phase change instead of describing the hydrate phase itself. Predictions with the new model for I-H-V, H-V, and high pressure L_w-H-V equilibria show its wider applicability.

Table 2

Listing of the major differences between the current and proposed hydrate models

Hydrate property	Current model	Proposed model
Volume	Constant	$f(T, P, x)$
Formation properties (T_0, P_0)	Constant	$f(x)$
	Constant	$f(v)$
Cage size	Single shell	Multi-layered shell

List of symbols

a	guest core radius, activity
C	Langmuir constant
f	fugacity
g	Gibbs energy (J/mol)
h	molar enthalpy (J/mol K)
k	Boltzmann's constant (J/K)
P	pressure
r	integration variable
R	universal gas constant and hydrate shell radius (Å)
T	temperature (K)
v	molar volume (cm ³ /mol)

Greek letters

α	volumetric thermal expansion coefficients
Δ	properties difference between liquid water and empty hydrate lattice
κ	volumetric compressibility coefficient
μ	chemical potential (J/mol)
θ	fractional occupancy of guests in the hydrate cages, stability variable
ν	number of hydrate cavities per water molecule
ω	cell potential function

Subscripts and superscript

0	property at reference conditions
f	arbitrary fluid phase
H	hydrate phase
i	arbitrary component
J	hydrate guest component
L_{pure}	pure liquid water
L_{w}	aqueous phase
m	hydrate cavity
o	ideal gas at 1 bar
w	water (as a component)
β	standard empty hydrate lattice

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