A Thermodynamic Model for Structure-H Hydrates

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A statistical thermodynamics model based on the original work of van der Waals and Platteeuw is presented for structure-H hydrates. The model is an extension of the hydrate prediction method generalized by Parrish and Prausnitz for structure-I and -II hydrates. Four structure-H-forming systems, methane + adamantane, methane + neohexane, methane + isopentane, and methane + methylcyclohexane, were considered. Optimized Kihara core parameters are presented for each of the large hydrocarbon guest molecules. The optimized reference chemical potential difference and reference enthalpy difference for structure-H hydrates are also presented. The results show good agreement with the experimentally determined phase-equilibria conditions. A sensitivity analysis is presented for the parameters in the model, and their relative order of influence on the accurate evaluation of the equilibrium pressure is determined.

Introduction

Gas hydrates are inclusion compounds that form when water combines with dissolved gas molecules to produce a crystalline mass which can plug flow channels. Hydrates are nonstoichiometric compounds; the number of gas molecules per water molecule in the hydrate phase is determined by the pressure and temperature conditions at which they form. Generally hydrate formation is favored at low temperatures and high pressures.

The two common forms of hydrates are known as structures I (*s*I) and II (*s*II). These are small (12-17 Å) repeating crystal structures and are composed of two types of cages, one large and one small. The gas molecules occupy these cages and thereby stabilize the hydrate structure. The molecular diameter of the guest molecule relative to the size of the cage determines the type of hydrate structure which forms. Generally small molecules like methane form *s*I hydrates, while larger molecules like propane form *s*II hydrates, with the exception of the smallest hydrate formers like argon and krypton which also form *s*II. A recent monograph (Sloan, 1990) provides a comprehensive summary of these conventional hydrate structures.

Structure H (*s*H) hydrate was discovered by Ripmeester et al. (1987) who showed that *s*H was a double hydrate, that is, it required two kinds of molecules to be stabilized: a small molecule like Xe or H_2S and a larger molecule like methylcyclohexane. Hydrates of *s*H are composed of three different types of cages: the 5^{12} cage has 12 pentagonal faces and is common to all the three known hydrate structures; the $4^3 5^6 6^3$ cage has three square faces, six pentagonal faces, and three hexagonal faces; and the $5^{12} 6^8$ cage has 12 pentagonal faces and eight hexagonal faces. The $4^3 5^6 6^3$ cage is slightly larger than the 5^{12} cage and both these cages accommodate the small guest molecules. The $5^{12} 6^8$ cage can accommodate larger molecules, in the size range of 7.5 to 8.6 Å. Ripmeester and Ratcliffe (1990) have identified 24 *s*H forming large guest molecules. These include substituted methylbutanes and cycloalkanes, many of which constitute a small fraction of crude oil. Adamantane, a *s*H former, is one of the chief constituents of diamondoids which are currently being found *in situ* in offshore pipelines, including Mobile Bay in the Gulf of Mexico. Recently, Ripmeester and coworkers (1991) have formed *s*H from components of a light naptha fraction as well as unleaded gasoline. These indicators demonstrate that *s*H may have a significant impact on both natural gas and petroleum industries as recently reviewed by Mehta and Sloan (1993a).

Initial phase-equilibria measurements for *s*H were made by Lederhos et al. (1992) with methane as the small guest molecule and with adamantane as the large guest molecule. Subsequently, Mehta and Sloan (1993b) have determined the phase equilibria of three other binary systems of *s*H hydrates: methane + neohexane(2,2-dimethylbutane), methane + isopentane-

(2-methylbutane), and methane + methylcyclohexane. The temperature and pressure conditions at which *s*H forms are consistent with those of hydrocarbon processing and transportation.

The basic thermodynamic model for the prediction of hydrate dissociation pressures was developed by van der Waals and Platteeuw (1959) using the Lennard-Jones Devonshire cell theory. Parrish and Prausnitz (1972) developed a generalized method based on the van der Waals-Platteeuw theory, for the prediction of the hydrate dissociation pressures of fifteen different gases and mixtures. Most latter-day hydrate prediction routines are extensions of the simplified method outlined by Parrish and Prausnitz. Various modifications and improvements in the prediction method have been made by Ng and Robinson (1976), Holder et al. (1980), Sloan (1984), John et al. (1985), Anderson and Prausnitz (1986) and others, which extend the method to all regions of the *s*I and *s*II phase diagrams, including inhibitors. This work extends the hydrate prediction technique to include the determination of *s*H phase equilibria. The model employs the Kihara spherical core potential, and optimized core parameters are presented for four *s*H forming binary systems.

Theoretical Model

The fundamental equations for the prediction of hydrate equilibria were derived by van der Waals and Platteeuw (1959) combining statistical thermodynamics with classical adsorption theory. Their model assumed that each cavity could contain one guest molecule at most and that there were no interactions between adjacent encaged guest molecules. It also assumed that the cages were completely spherical—inside which the guest molecules were free to rotate and that the guest molecule did not distort the hydrate lattice. Many of these assumptions have been recently challenged by Lund (1990) and Sparks (1991) who investigated the effects of guest-guest interactions, Rodger (1990, 1991) to account for lattice relaxation, and Holder and coworkers (Hwang, 1989, 1993) to account for lattice distortion.

The stability of the hydrate phase depends on the occupancy of the cages which constitute the hydrate lattice. If the guest molecules occupy only a small fraction of the hydrate cages, the hydrate lattice would not be stable and it would dissociate. The chemical potential of water in the hydrate phase is used as a measure of the stability of the hydrate structure. At equilibrium the chemical potential of water in the hydrate phase, μ_w^H, is equal to the chemical potential of water in the pure liquid water phase, μ_w^L (or ice, μ_w^α, where α denotes the ice phase):

$$\mu_w^H = \mu_w^L \ (= \mu_w^\alpha) \tag{1}$$

If we denote the chemical potential of water in a hypothetical empty hydrate lattice by μ_w^β, then the condition for equilibrium can be restated as:

$$\Delta\mu_w^H = \Delta\mu_w^L \ (= \Delta\mu_w^\alpha)$$

where

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H;\ \Delta\mu_w^L = \mu_w^\beta - \mu_w^L;\ \Delta\mu_w^\alpha = \mu_w^\beta - \mu_w^\alpha \tag{2}$$

This difference in the chemical potential of water in the empty hydrate lattice and water in one of the other phases (hydrate, pure liquid water, or ice) represents the decrease in the chemical potential of water as a result of the occupation of a hydrate cage by the guest molecule. This difference in the chemical potential was derived by van der Waals and Platteeuw and is given by:

$$\Delta\mu_w^H = -RT\sum_i \nu_i \ln\left(1 - \sum_k \theta_{ki}\right) \tag{3}$$

where ν_i is the number of type *i* cavities per water molecule in the unit hydrate cell. For instance, the unit cell formula for *s*H is $3(5^{12})\cdot 2(4^3 5^6 6^3)\cdot 1(5^{12}6^8)\cdot 34H_2O$; since there is one large cavity, the $5^{12}6^8$ cavity, per 34 water molecules in the unit hydrate cell, $\nu_L = 1/34$. The parameter θ_{ki} is the fractional occupation of a type *i* cavity by a type *k* guest molecule and is expressed as:

$$\theta_{ki} = \frac{C_{ki} f_k}{1 + \sum_k C_{ki} f_k} \tag{4}$$

This expression for the fractional occupation is similar to Langmuir adsorption wherein at most one molecule is allowed to adsorb on one site. Similarly, in hydrates, at most one molecule is allowed to occupy each hydrate cage. Due to the similarity with classical Langmuir adsorption, the constant C_{ki} is known as the Langmuir constant for a type *k* molecule in a type *i* cage. The fugacity of the guest molecule *k*, f_k can be evaluated as:

$$f_k = \Phi_k y_k P \tag{5}$$

where Φ_k and y_k are the fugacity coefficient and the mole fraction of component *k*, respectively, in the gas phase, and *P* is the total pressure.

The fugacity may be calculated using a standard equation of state such as the Soave-Redlich-Kwong (SRK) equation of state, as in the present work. For the methane + liquid hydrocarbon systems, the mole fraction of the liquid hydrocarbon in the vapor phase is not negligible; consequently, a rigorous flash calculation was performed at each given pressure and temperature to determine the fugacity of the liquid hydrocarbon.

On the other hand, in the case of the methane + adamantane system, the mole fraction of adamantane in the vapor phase could be determined to be negligible since adamantane is a high melting solid with a very low vapor pressure. Since at equilibrium the fugacities of adamantane in the vapor and solid phase are equal, that is, $f_A^V = f_A^S$, the fugacity of adamantane in the solid phase can be evaluated from:

$$f_A^S = x_A \gamma_A \Phi_A^{sat} P_A^{sat} \exp\left[\frac{v_A(P - P_A^{sat})}{RT}\right] \tag{6}$$

where x_A is the mole fraction of solid adamantane (assumed to be close to unity), γ_A is the activity coefficient of adamantane, and Φ_A^{sat} and P_A^{sat} are the saturation fugacity coefficient and saturation vapor pressures of adamantane. The exponential term is the Poynting correction factor where v_A is the molar volume of adamantane.

Since adamantane has a very low vapor pressure, the saturation fugacity coefficient of adamantane will be close to unity. As a further simplification, adamantane is assumed pure yielding an activity coefficient also close to unity. Thus, in the reduced expression the fugacity of adamantane is equal to the product of the Poynting correction factor and the saturation vapor pressure. The saturation vapor pressure is found from a vapor pressure fit for adamantane by Lee et al. (1975). These simplifications are approximate at best, but are necessary because measurements of methane solubility in adamantane are not currently available.

The Langmuir constant C_{ki} for a guest molecule k in a type i cavity is only a function of temperature; for a fixed value of the fugacity the fractional occupation and consequently the hydrate stability increases with an increase in the Langmuir constant. The Langmuir constant describes the guest-water interactions inside the cage and is given by:

$$C_{ki}=\frac{4\pi}{kT}\int_0^R \exp\left[\frac{-\omega(r)}{kT}\right]r^2dr \tag{7}$$

where T is the absolute temperature, k is the Boltzmann's constant, $\omega(r)$ is the spherically symmetrical cell potential, and r is the radial distance from the center of the cavity.

The Kihara spherical core pair potential energy $\Gamma(x)$ between the guest molecule and any one of the water molecules comprising the cavity is related to the force F, which each exerts on the other by $F=\partial\Gamma(x)/\partial x$, where x is molecular center separation distance between the two. This potential is thus unique to every molecular type and is given as a function of the separation distance by:

$$\Gamma(x)=\infty;\quad x\leq 2a$$

$$\Gamma(x)=4\epsilon\left[\left(\frac{\sigma}{x-2a}\right)^{12}-\left(\frac{\sigma}{x-2a}\right)^{6}\right];\quad x>2a \tag{8}$$

where a is the radius of the spherical core, σ is the distance between the cores at zero potential energy [$\Gamma(x)=0$], and ϵ is the depth of the intermolecular potential well.

McKoy and Sinanoglu (1963) summed up all these guest-water binary interactions $\Gamma(x)$ inside the cell to yield an overall cell potential $\omega(r)$ given by:

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

where

$$\delta^N=\frac{1}{N}\left[\left(1-\frac{r}{R}-\frac{a}{R}\right)^{-N}-\left(1+\frac{r}{R}-\frac{a}{R}\right)^{-N}\right] \tag{9}$$

where N is equal to 4, 5, 10, or 11; z is the coordination number of the cavity, that is, the number of oxygens at the periphery of each cavity and these have been uniquely determined for each cavity type by X-ray diffraction data, and R is the radius of the cavity.

Of the three sH cavities, the 5^{12} cavity is common to all three hydrate structures, and its radius is assumed to be the same value of 3.91 Å as in the other structures (Sloan, 1990). The radius of the $4^35^66^3$ cavity is determined from a correlation by Ripmeester and Ratcliffe (1988), of the ^{129}Xe isotropic NMR chemical shifts vs. free-space radius available to the xenon atom inside the cage. On the basis of this chemical-shift data, the radius of the $4^35^66^3$ cavity is determined to be 4.06 Å, slightly larger than the 5^{12} cavity. There is, however, no chemical-shift data available for the largest $5^{12}6^8$ cavity, and consequently its radius was determined indirectly. Methylcyclohexane is the largest known sH former (Ripmeester et al., 1990) and has a diameter of approximately 8.6 Å. Assuming that the maximum allowable ratio of the diameter of the guest molecule to the free cavity diameter of the $5^{12}6^8$ cage is unity (that is, allowing for no lattice distortion by the large guest molecule), the free cavity diameter for the $5^{12}6^8$ cage is deduced to also equal 8.6 Å. Adding the van der Waals diameter of a water molecule (2.82 Å) which comprises the cage, the final radius of the $5^{12}6^8$ cage is determined to be 5.71 Å. A similar approach was also used on the other hydrate cavities of sI and sII, and it was found to yield cage sizes within 3% of those measured using X-ray diffraction. This assumed value for the $5^{12}6^8$ cavity also agrees well with that obtained by measuring three-dimensional models of the cage. Thus, while the value of the $5^{12}6^8$ cage size is by no means definitive, in the absence of X-ray diffraction data it represents the best working approximation. Cavity dimensions are summarized in Table 1.

The Lennard-Jones Devonshire theory assumes that the positive potential of the water molecules is "smeared" to yield an averaged spherical shell potential and this causes the water parameters to become indistinct. Consequently, the Kihara parameters for the guest molecule within the cavity are fitted to hydrate formation properties for each component. Figure 1 shows a typical potential $\omega(r)$ for the guest-water interactions inside the three different sH cavities. The large attractive potential near the center of the cavity makes the most significant contribution to the Langmuir constant (Eq. 7). The potential becomes highly repulsive at radial distances approaching the wall of the cavity and thus makes a negligible contribution to the Langmuir constant. As the guest molecule approaches the cavity wall, it is both repulsed by one wall and attracted by the opposite wall. These opposing interactions cause the guest molecule to remain close to the center of the cavity.

One of the shortcomings of the smooth-cell assumption is that an appreciable degree of asphericity exists in many of the hydrate forming cavities. For instance, the $5^{12}6^8$ cavity is oblong

Table 1. Structure H Hydrate Unit Cell Characteristics

Cavity Type	5^{12}	$4^35^66^3$	$5^{12}6^8$
Radius of Cavity (Å)	3.91	4.06	5.71
No. of Cavities per Unit Cell	3	2	1
Coordination Number*	20	20	36
Unit Cell Formula	$3(5^{12})\cdot 2(4^35^66^3)\cdot 1(5^{12}6^8)\cdot 34H_2O$		
Space Group	$P6/mmm$		
Lattice Parameters**	$a=12.26$ Å; $c=10.17$ Å		

*Number of oxygens at the periphery of each cavity
**Davidson et al. (1987)

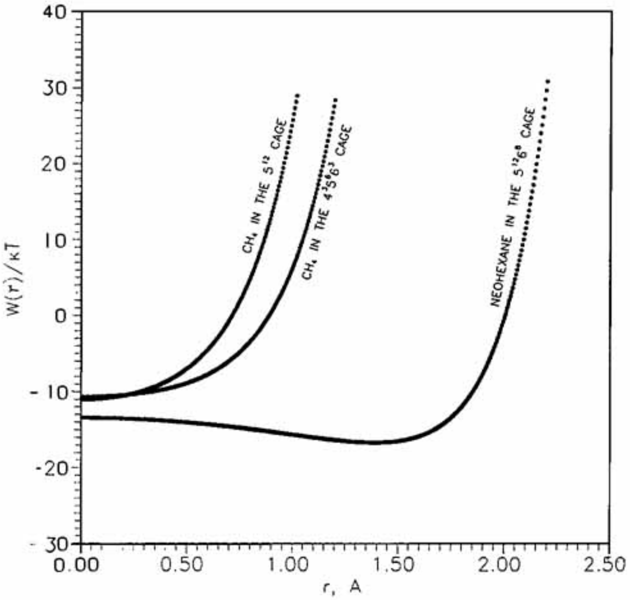

Figure 1. Spherically symmetrical cavity potential function between the guest molecule and cell in each of the *s*H cages.

and ellipsoidal rather than spherical; therefore, to rigorously determine the true Langmuir constant, the potential energy of the guest-water interaction should be found as a function of angular as well as radial coordinates as demonstrated by John and Holder (1981, 1982). In the absence of definitive crystallographic data on *s*H hydrate, the exact location of the water molecules in the cage is unknown and consequently for the present model the asphericity effects are ignored.

All the above equations are derived from statistical mechanics; with the right set of core parameters for the guest molecules, it is possible to determine the chemical potential difference between water in the empty hydrate lattice and water in the pure liquid water phase, using Eq. 3. However, for this value of the chemical potential difference to be meaningful, it should be equal to the chemical potential difference determined from classical thermodynamics, as will be discussed in the next section.

$\Delta\mu_w^L$ from Classical Thermodynamics

The expresison for the difference in chemical potential of water between the empty hydrate lattice and pure liquid water phase was derived by Marshall et al. (1964):

$$\frac{\Delta\mu_w^L}{RT}=\frac{\Delta\mu_w^o}{RT_o}-\int_{T_o}^{T}\left(\frac{\Delta h_w}{RT^2}\right)dT+\int_{T_o}^{T}\left(\frac{\Delta v_w}{RT}\right)\left(\frac{dP}{dT}\right)dT \quad (10)$$

where Δh_w and Δv_w are the molar enthalpy and the reference volume differences, respectively, between the empty hydrate lattice and pure ice (if $T \leq 273.15$ K) or liquid water (if $T > 273.15$ K). $\Delta\mu_w^o$ is the reference chemical potential difference between water in the empty hydrate lattice and pure water in the ice (α) phase, at an arbitrary reference temperature T_o (usually 273.15 K) and absolute zero pressure. The term (dP/dT) is the slope of the experimentally determined equilibrium *P-T* curve.

The above equation applies for a pure condensed water phase such as ice or liquid water without solute. If the condensed water phase were not pure, the above equation should be modified to include a final term for the activity of water $\gamma_w x_w$, where γ_w is the activity coefficient of water and x_w is the mole fraction of water. To maintain $\Delta\mu_w^L$ as the difference between pure phases, the relation $\mu_w=\mu_w^{\text{pure}}+RT\ln\gamma_w x_w$ is used to obtain an additional term on the right of Eq. 10 to give:

$$\frac{\Delta\mu_w^L}{RT}=\frac{\Delta\mu_w^o}{RT_o}-\int_{T_o}^{T}\left(\frac{\Delta h_w}{RT^2}\right)dT$$
$$+\int_{T_o}^{T}\left(\frac{\Delta v_w}{RT}\right)\left(\frac{dP}{dT}\right)dT-\ln\gamma_w x_w \quad (11)$$

where the activity coefficient of water γ_w may normally be assumed as unity without appreciable error, unless inhibitors are used.

Parrish and Prausnitz (1972) and most subsequent workers modified Eq. 11 to include a reference gas for which the derivative dP/dT was obtained. A second pressure correction $\Delta v_w[P-P_{\text{ref}}]/RT$ was required to translate from the reference pressure to the pressure of interest. A third pressure term corrected the empty hydrate chemical potential difference from zero pressure to the dissociation pressure of the reference hydrate at T_o.

Holder et al. (1980) considerably simplified the method of finding $\Delta\mu_w^H$ by directly integrating over P and T to give:

$$\frac{\Delta\mu_w^L}{RT}=\frac{\Delta\mu_w^o}{RT_o}-\int_{T_o}^{T}\left(\frac{\Delta h_w}{RT^2}\right)dT+\int_{0}^{P}\left(\frac{\Delta v_w}{RT}\right)dP-\ln\gamma_w x_w \quad (12)$$

where the second term gives the temperature dependence of the chemical potential difference at zero pressure, and the third term corrects the pressure to the final equilibrium value. The molar volume difference Δv_w is assumed to be temperature-independent. However, the temperature dependence of the molar enthalpy is given by:

$$\Delta h_w=\Delta h_w^o+\int_{T_o}^{T}\Delta C_{pw}dT \quad (13)$$

where the heat capacity difference between the empty hydrate lattice and the pure liquid water phase is also temperature dependent and is given by:

$$\Delta C_{pw}=\Delta C_{pw}^o+b(T-T_o) \quad (14)$$

where values of the reference state heat capacity difference ΔC_{pw}^o and constant b are taken from Parrish and Prausnitz (1972).

The mole fraction of water x_w is very close to unity due to the low aqueous solubility of the hydrate forming components. The solubility of a guest component k in the pure liquid water phase x_k is found by using the Krichevsky and Kasarnovsky (1935) expression:

$$x_w=1-x_k=1-\frac{f_k}{H_{kw}\exp\left(\frac{PV}{RT}\right)} \quad (15)$$

where f_k is the fugacity of component k, P is the pressure, V is the partial molar volume of the guest species, R is the gas constant, T is the temperature, and H_{kw} is Henry's law constant fitted to solubility data as a function of temperature in the form:

$$H_{kw} = \exp\left(A + \frac{B}{T}\right) \qquad (16)$$

where the fitted constants A and B are taken from Holder et al. (1988) for methane. The solubility of methane in these liquid hydrocarbons has yet to be measured experimentally.

The other parameters which need to be known to solve Eq. 12 are the reference properties $\Delta\mu_w^o$, Δh_w^o, and Δv_w. The value of the volume difference between the empty hydrate lattice and ice (Δv_w) for structures I and II have been established by the X-ray diffraction data of von Stackelberg and Muller (1954). The value of the other two parameters, $\Delta\mu_w^o$ and Δh_w^o, have been determined by various investigators for structures I and II. The determination of these values is discussed by Dharmawardhana et al. (1980, 1981) and Holder et al. (1984). However, no two sets of these reference properties are identical, and a particular set of values is compatible only when used in conjunction with all the other optimized parameters used in that particular model. Recent calorimetric studies by Handa et al. (1986) have yielded more accurate values for $\Delta\mu_w^o$ and Δh_w^o for sI and sII hydrates. These calorimetric studies have verified the experimental value of $\Delta\mu_w^o$ obtained by Dharmawardhana et al. (1981) for sI hydrates.

Reduction of Data

The solution of the model is based on a minimization of the two expressions for the chemical potential given by Eqs. 3 and 12. However, initially there are nine unknown parameters: the Kihara core parameters σ_S, ϵ_S and a_S for the small molecule, the Kihara core parameters σ_L, ϵ_L and a_L for the large guest molecule, and the values of the reference state parameters for sH hydrate, $\Delta\mu_w^o$, Δh_w^o, and Δv_w. The number of unknowns have to be reduced before the optimization process.

The three Kihara core parameters for methane are fixed using the values of Erickson (1983) which have also been incorporated in the hydrate prediction program CSMHYD developed by the Colorado School of Mines (Sloan, 1984). These parameters in Table 2 were obtained after a comprehensive optimization of many sets of methane data, including binary and multicomponent mixtures.

Of the three core parameters for the large guest molecule, one of them, the core radius a_L, is fixed using viscosity and virial coefficient data by Tee et al. (1964). Since the core radius a_L is not a very sensitive parameter in the statistical model, assuming a fixed value for a_L is justified, as shown later. Another relatively insensitive parameter is the reference enthalpy difference Δh_w^o. Initially the value Δh_w^o of sH is assumed to be equal to that of sI. The assumed value of Δh_w^o is 931 J/mol, the enthalpy difference determined by Handa calorimetrically for sI. This assumed value of Δh_w^o was adjusted later to give the best possible fit for the sH equilibrium data.

Table 2. Optimized Kihara Core Parameters

Guest Type	a (Å)	σ (Å)	ϵ/k (K)
Methane*	0.3834	3.165	154.54
Isopentane	0.9867	3.118	279.99
Neohexane	1.0480	3.068	348.74
Methylcyclohexane	1.0693	4.539	475.22
Adamantane	1.3378	2.781	579.96

*Core parameters for methane from Sloan (1990).

The value of the reference molar volume difference Δv_w is not known for sH. Davidson et al. (1987) have measured the lattice parameters for sH. For a rhombohedral unit cell, the lattice constants are $a = 12.26$ Å and $c = 10.17$ Å. From the unit cell formula of sH, there are 34 water molecules per unit crystal lattice. The volume occupied by these 34 water molecules in the unit crystal lattice can be calculated from the cell geometry since the lattice constants are known. Multiplying this volume by Avogadro's number of water molecules gives the volume of 1 mol of sH hydrate. By deducting the volume occupied by 1 mol of ice at 273.15 K and zero absolute pressure, the molar volume difference Δv_w between the empty hydrate lattice and ice can be calculated and is found to be equal to 3.85 cm^3/mol. Similar calculations for sI and sII using the method outlined above give values of Δv_w consistent with those obtained from X-ray diffraction by von Stackelberg and Muller (1954). In the absence of definitive single-crystal X-ray diffraction data, these calculations based on powder diffraction measurements provide an adequate measure for Δv_w of sH hydrate.

Thus, by making the above approximations, the nine original unknown parameters have been reduced to three: the core parameters of the large molecule σ_L and ϵ_L/k, and the reference chemical potential difference $\Delta\mu_w^o$ for sH hydrate. These three parameters have to be optimized for each of the four sH systems.

Results and Discussion

The optimization routine employed multidimensional minimization, that is, finding the minimum of a function of more than one independent variable. The downhill simplex method algorithm by Nelder and Mead (1965) was used. This method required only function evaluations and not derivatives. Using this technique, each of the four sH systems was regressed and optimum values for the three unknown parameters were obtained. These parameters were further refined by trying several values of the reference enthalpy difference Δh_w^o, finally settling for the value which gave the best fit with experimental data.

Table 2 lists the final optimized core parameters of all the sH formers used in this study. In our model, the core parameters σ and ϵ may be viewed as fitting constants, and so no correlation between the molecular size and the final optimized parameters can be expected. Thus, despite its larger size adamantane has an optimized value of σ which is smaller than that of methane. Table 3 lists the optimized reference properties $\Delta\mu_w^o$ and Δh_w^o, and the calculated volume difference Δv_w. The reference properties in Table 3 are common to all sH hydrate forming systems. Using these optimized parameters, an algorithm based on that of Parrish and Prausnitz (1972) for sI and sII was developed to determine the sH equilibrium pressures at a given temperature. Very good agreement was found between the experimental dissociation pressures and those determined by the model as shown in Figure 2. Table 4 compares the experimental equilibrium pressure to the corresponding

Table 3. Optimized Reference Property Differences Between Water in Empty Hydrate Lattice (β Phase) and Pure Water in Ice (α Phase)

$\Delta\mu_w^o$ (J/mol)	914.38
Δh_w^o (J/mol)*	846.57
Δv_w (cm^3/mol)**	3.85
ΔC_{pw}^o (J/mol·K)†	38.12
b (J/mol·K^2)†	0.141

*In the liquid water region subtract 6012.35 J/mol from Δh_w^o.
**In the liquid water region add 1.6 cm^3/mol to Δv_w.
†Parrish and Prausnitz (1972).

calculated pressure from the model at each equilibrium temperature for all the four *s*H systems. In each case, the pressures could be fit within ±5% of their experimental values.

Sensitivity Analysis

A sensitivity analysis on each of the parameters in the model was performed. The methane + isopentane system was selected as a basis, since its optimized parameters could fit the experimental data within ±1% of its experimental values. The effect on the predicted equilibrium pressures by changing any one of the core parameters of the small and large guest molecule or one of the reference properties was studied, while fixing the rest of the parameters at their optimized values.

The percentage change from the optimum value of each parameter required to cause a change of ±10% in the predicted equilibrium pressures was noted. Figures 3 to 5 show that the following changes were required in the core parameters of the large guest molecule: σ_L (±1-2%), ϵ_L/k (±4-5%) and a_L (±10-50%). Figures 6 to 8 show that the following changes were required in the core parameters of the small guest molecule: σ_S (±1%), ϵ_S/k (±2-3%) and a_S (±4-5%). Figures 9 and 10 show that the reference properties had to be changed by $\Delta\mu_w^o$ (±4%) and Δh_w^o (±50-120%). According to a sensitivity analysis with Δv_w, changes greater than 250% were required to make any significant impact on the predictions.

Table 4. Comparison of Experimental and Calculated Pressures at the Equilibrium Temperatures of each *s*H system

	T, K	P_{Exp}, MPa	P_{Calc}, MPa	Abs. % Error
Isopentane	275.25	2.654	2.650	0.15
	276.25	2.978	2.989	0.36
	277.85	3.640	3.628	0.32
	278.95	4.150	4.151	0.02
Neohexane	276.01	1.598	1.585	0.81
	278.04	2.028	2.036	0.39
	279.20	2.391	2.347	1.84
	282.15	3.339	3.373	1.01
Methylcyclohexane	275.65	1.599	1.650	3.27
	277.65	2.137	2.131	0.28
	279.45	2.688	2.678	0.37
	281.15	3.357	3.321	1.07
Adamantane	275.09	1.779	1.692	4.89
	276.90	2.165	2.094	3.27
	278.42	2.510	2.501	0.35
	280.17	3.001	3.070	2.29

The above analysis shows that the molecular separation distance at zero potential energy σ is one of the most sensitive parameters in the model followed by the energy parameter ϵ/k and the reference chemical potential difference $\Delta\mu_w^o$. The spherical core radius of the large molecule a_L can tolerate large changes in its value without having any significant impact on the predicted equilibrium pressures. Thus, our initial assumption of fixing a_L using viscosity and virial coefficient correlations is justified. As pointed out by one of the referees of this article, the changes in a and σ are strongly correlated since both act in a roughly additive manner to increase the effective collision diameter. The effect of the reference enthalpy difference Δh_w^o on the predicted equilibrium pressures is also neg-

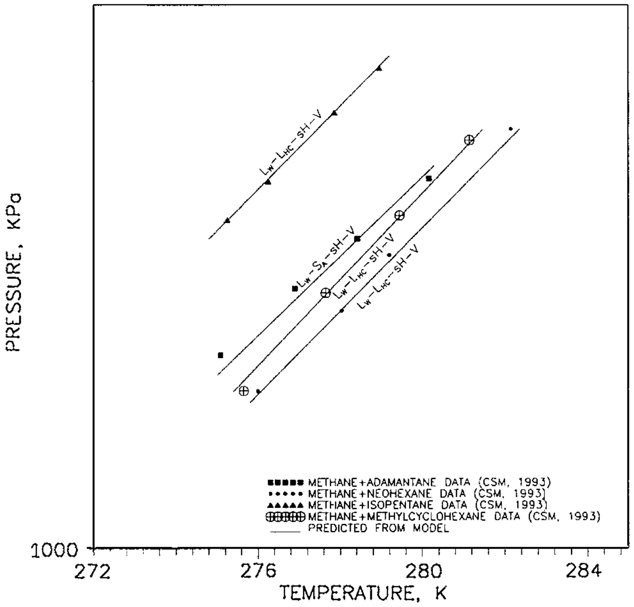

Figure 2. Experimental pressures and calculated pressures for four *s*H systems.

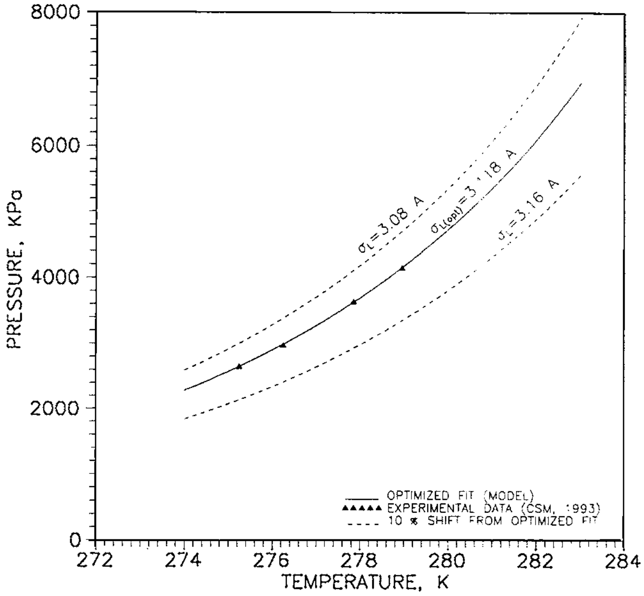

Figure 3. Sensitivity of σ_L on the predicted pressures.

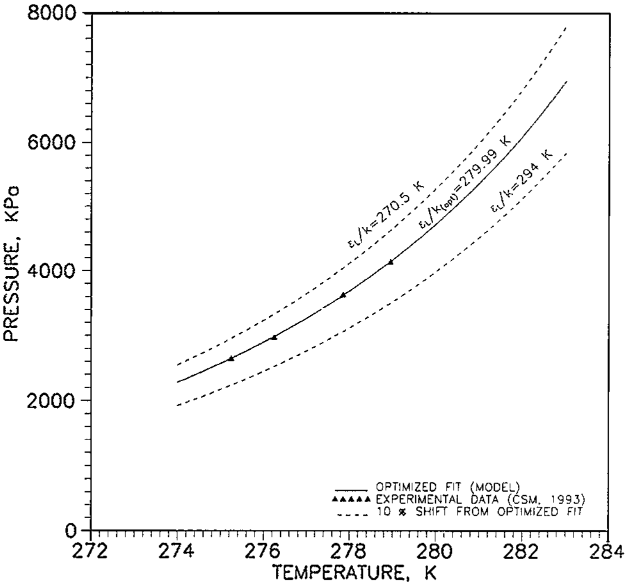

Figure 4. Sensitivity of ϵ_L/k on the predicted pressures.

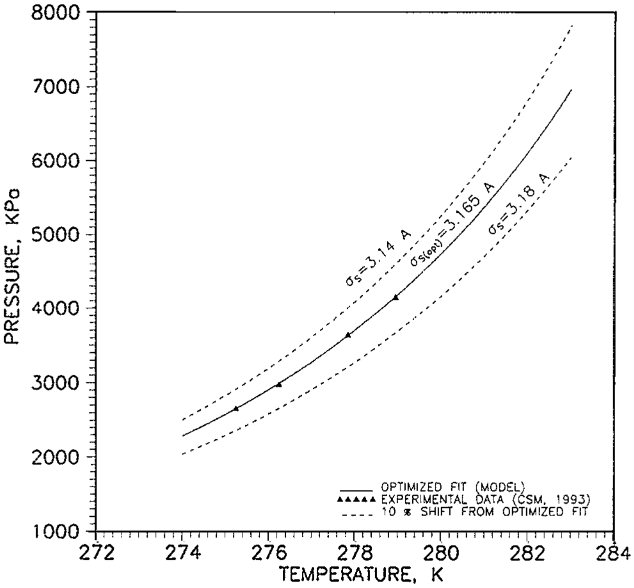

Figure 6. Sensitivity of σ_S on the predicted pressures.

ligible. Thus, our second assumption of starting with an initial fixed value of Δh_w^0 is also validated.

Conclusions

A thermodynamic model for the prediction of *s*H hydrates shows that good agreement with experimental phase-equilibria values can be obtained by using the optimized values of the core parameters and the reference properties. The sensitivity analysis determines the parameters which have the most pronounced effect on the output of the model and justifies some of the initial assumptions made in the model.

The model is the first step toward a thorough elucidation of the *s*H hydrate characteristics. It can serve as a guide for determining the phase equilibria of other *s*H forming systems, including other binary and multicomponent systems. The model can also be used to study possible transitions between hydrate structures. Future work will include these studies and incorporate this model into existing models available for the determination of phase equilibria of conventional hydrates.

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Notation

a = Kihara spherical core radius or lattice constant, Å

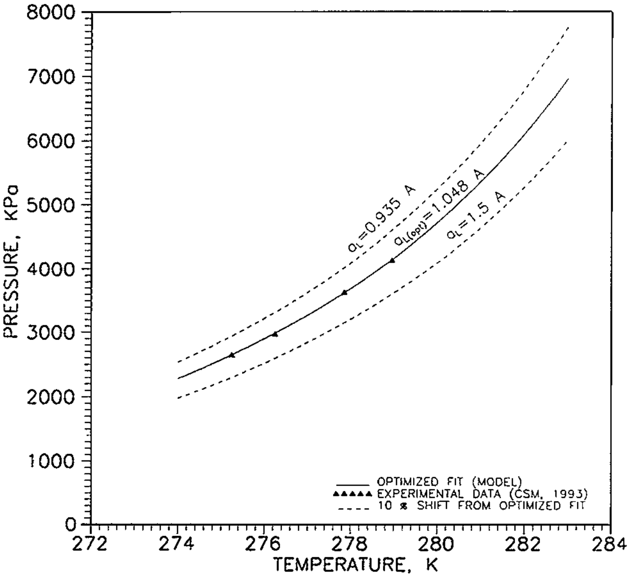

Figure 5. Sensitivity of a_L on the predicted pressures.

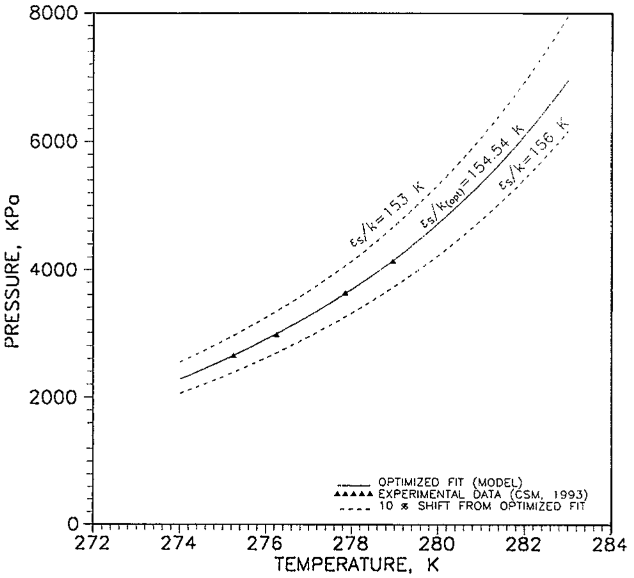

Figure 7. Sensitivity of ϵ_S/k on the predicted pressures.

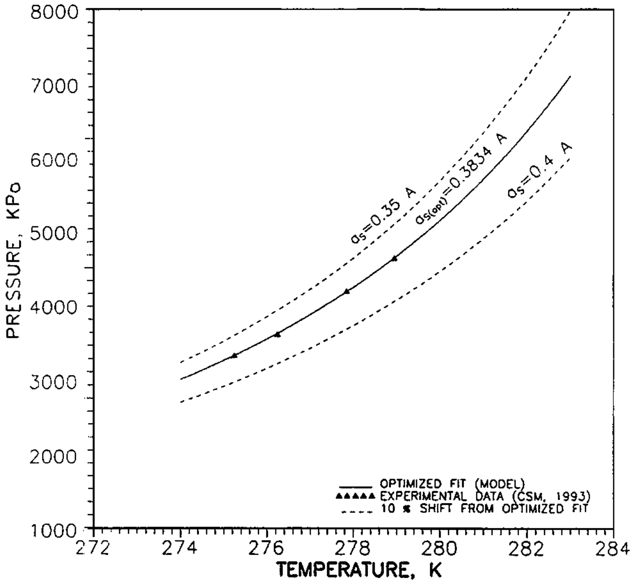

Figure 8. Sensitivity of a_S on the predicted pressures.

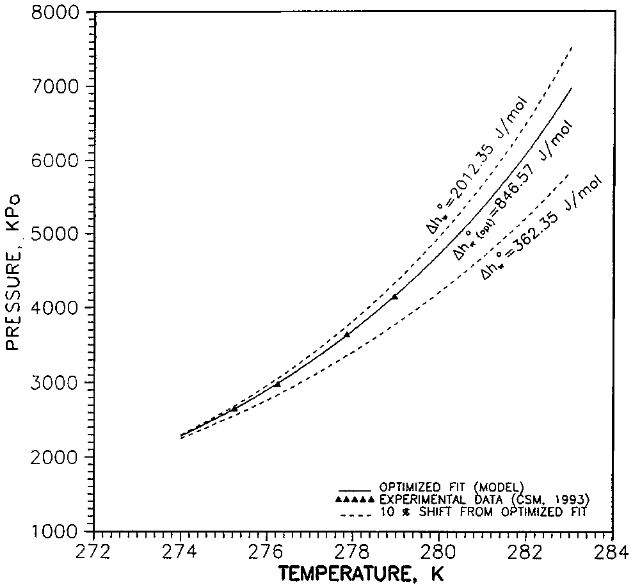

Figure 10. Sensitivity of Δh_w^o on the predicted pressures.

A = Henry's law constant fitted to solubility data
b = temperature coefficient in heat capacity difference expression, J/mol·K^2, or lattice constant, Å
B = Henry's law constant fitted to solubility data
C_{ki} = Langmuir constant of type k molecule in type i cage, MPa
ΔC_{pw} = heat capacity difference between empty hydrate lattice (β phase) and ice (α phase), J/mol·K
ΔC_{pw}^o = reference heat capacity difference between empty hydrate lattice (β phase) and ice (α phase) at 273.15 K, J/mol·K
f_k = fugacity of component k
H = hydrate phase
H_{kw} = Henry's law constant for solubility of gas in water
i = subscript denoting cavity type
k = subscript denoting molecule type, or Boltzmann's constant, J/K
L_{HC} = liquid hydrocarbon phase
L_w = liquid water phase
N = integer constant

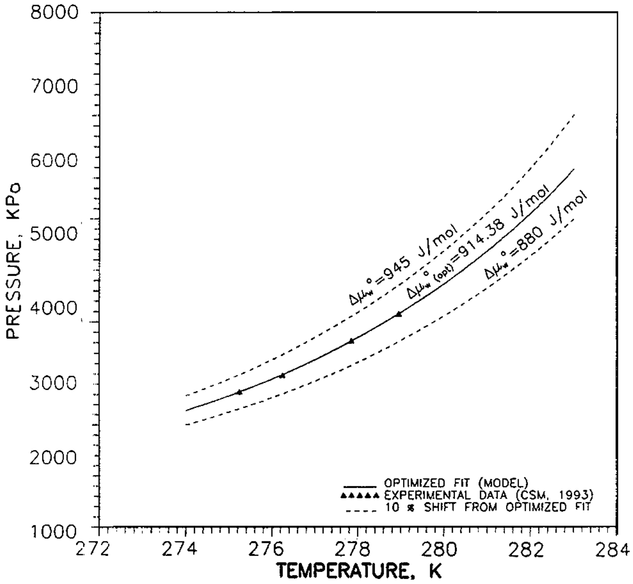

Figure 9. Sensitivity of $\Delta\mu_w^o$ on the predicted pressures.

P = pressure, MPa
P_o = dissociation pressure at 273.15 K, MPa
P_{ref} = reference hydrate dissociation pressure
r = radial distance from the center of the molecule, Å
R = gas constant, J/mol/K, or cavity radius, Å
sat = superscript denoting saturation
s = solid phase, or superscript denoting small guest molecule
sH = structure H hydrate
sI = structure I hydrate
sII = structure II hydrate
S_A = solid adamantane phase
T = temperature
T_o = reference temperature, 273.15 K
v = molar volume, cm^3/mol
V = vapor phase or partial molar volume
Δv_w = volume difference between empty hydrate lattice (β phase) and ice (α phase), cm^3/mol
w = water phase
x = molecular separation distance between guest and water molecular cores, Å
x_k = mole fraction of component k in water
x_w = mole fraction of water in water-rich phase
y_k = mole fraction of component k in the vapor phase
z = coordination number, that is the number of oxygens at the periphery of a cavity

Greek letters

α = superscript denoting the ice phase
β = superscript denoting the empty hydrate lattice
γ = activity coefficient
Γ = Kihara Potential of guest-water interaction, J/mol
ϵ = depth of intermolecular potential well, J/molecule
μ = chemical potential, J/mol
$\Delta\mu_w$ = chemical potential difference between empty hydrate lattice (β phase) and ice (α phase), J/mol
$\Delta\mu_w^o$ = reference chemical potential difference between empty hydrate lattice (β phase) and ice (α phase) at 273.15 K and zero absolute pressure, J/mol
ν_i = number of cavities of type i per water molecule in a unit hydrate crystal
σ = distance between molecular cores of guest and water at zero potential energy, Å
Φ = fugacity coefficient

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