

Sensitivity Analysis of Hydrate Thermodynamic Reference Properties Using Experimental Data and *ab Initio* Methods

Zhitao Cao, Jefferson W. Tester, and Bernhardt L. Trout*

Department of Chemical Engineering and Energy Laboratory, Massachusetts Institute of Technology, Room 66-556, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Received: March 18, 2002; In Final Form: May 21, 2002

Various sets of thermodynamic reference properties currently available in the literature were examined by applying the van der Waals and Platteeuw model to predict monovariant three-phase equilibria for hydrate-forming binary mixtures from 260 to 320 K. Two recent and well-accepted experimental studies of cyclopropane hydrates by Dharmawardhana et al. (1980, 1981) with analysis by Holder et al. (1984) ($\Delta\mu_w^0 = 1299$ J/mol, $\Delta H_w^0 = 1861$ J/mol) and the NMR study of xenon hydrates by Handa and Tse (1986) ($\Delta\mu_w^0 = 1287$ J/mol, $\Delta H_w^0 = 931$ J/mol) were revisited. The deviations introduced by experimental uncertainties were found to be large enough to cause significant changes in the prediction of dissociation pressures. The methodology and parameters fitted to various pure and binary hydrate systems provided by Sloan (1998) were also employed in our calculations for methane hydrates using the Lennard-Jones and Devonshire (LJD) approximation and the Soave–Redlich–Kwong (SRK) or the Peng–Robinson (PR) equation of state. The comparison between the experimental data and software prediction provided by Sloan (1998) is in good agreement over the low-temperature range (<290 K), but there are significant differences at high temperatures (290–320 K). The methane–water intermolecular potential from our previous *ab initio* study was also used to obtain the reference properties with small deviations ($\Delta\mu_w^0 = 1236 \pm 4$ J/mol, $\Delta H_w^0 = 1703 \pm 62$ J/mol), and the resulting parameters were able to give the best prediction over the entire temperature range using the *ab initio* potential. More importantly, the use of the *ab initio* potential removes the need for adjusting fitted potential parameters to make up for errors in the reference parameters. Statistical variations (\pm) at the 95% confidence limit computed for our data and those from previous researches are found to be significantly smaller using our method. Note that these statistical variations do not take into account systematic error, which is possible in both the experimental and *ab initio* cases. Sensitivity analyses based on both the LJD approximation and our *ab initio* study were performed. The value of $\Delta\mu_w^0$ was found to be much more sensitive to the three-phase equilibria prediction of methane hydrates than ΔH_w^0 . For example, a variation in $\Delta\mu_w^0$ of ± 10 – 20 J/mol results in an error of 5%–10% in the predicted dissociation pressure.

Introduction

Clathrate hydrates are ice-like crystalline inclusion compounds formed in the presence of molecules such as argon, methane, ethane, cyclopropane, or carbon dioxide. These guest molecules stabilize a number of host lattice structures consisting of hydrogen-bonding networks of water molecules via van der Waals dispersive interactions. The two commonly occurring hydrate structures are known as structure I (sI) and structure II (sII) hydrates, which have been studied extensively.^{1,2} A new structure, structure H (sH), was discovered by Ripmeester et al.³ in 1987. A statistical thermodynamics model for hydrate equilibria was developed by van der Waals and Platteeuw in 1959,⁴ and then generalized by Parrish and Prausnitz for prediction of the hydrate dissociation pressures.⁵ The method of phase-equilibria prediction was further simplified by Holder et al.⁶ in 1980 to eliminate the need for the reference hydrate by introducing a universal set of reference properties for each type of structure. This established the methodology for most of the later thermodynamic and equilibrium calculations of gas hydrates.⁷

TABLE 1: Differences in Thermodynamic Properties between Ice and the Empty Hydrate Lattice (Adapted from Sloan⁷)

structure I		structure II		reference
$\Delta\mu_w^0$	ΔH_w^0	$\Delta\mu_w^0$	ΔH_w^0	
699	0	820	0	van der Waals and Platteeuw (1959)
		366–537		Barrer and Ruzicka (1962)
		833		Scortland and Robinson (1964)
1255.2	753	795	837	Child (1964)
1264	1150		808	Parrish and Prausnitz (1972)
1155	381		0	Holder (1976)
1297	1389	937	1025	Dharmawardhana, Parrish and Sloan (1980)
1299	1861			Holder, Malekar, and Sloan (1984)
1120	931	1714	1400	John, Papadopoulos, and Holder (1985)
1297				Davidson, Handa, and Ripmeester (1986)
1287	931	1068	764	Handa and Tse (1986)

Accurate values of reference properties are critical inputs to the statistical model. Investigators typically determine two thermodynamic reference parameters, $\Delta\mu_w^0$ and ΔH_w^0 . Table 1 lists reported values obtained from various calculations and

* To whom correspondence should be addressed.

experimental techniques. The variation in parameters is large enough to affect the prediction of the model significantly. Given the large variation in parameters, there is likely to be significant error. This error is generally addressed by adjusting parameters in the intermolecular potentials in an ad hoc way, yielding aphysical parameters.

Three different sets of reference parameters are considered to be the most accurate from independent studies by Dharmawardhana et al.^{8,9} and Holder et al.,¹⁰ Handa and Tse,¹¹ and Sloan.⁷ Dharmawardhana et al.^{8,9} used an experimental apparatus developed at the Colorado School of Mines that allowed precise measurement of cyclopropane hydrate compositions thus giving the values of $\Delta\mu_w^0$ and ΔH_w^0 over a range of experimental P – T conditions (not just at reference P_0 and T_0 conditions). Holder et al.¹⁰ at the University of Pittsburgh developed a rigorous empirical correlation method for using the same set of experimental data to evaluate $\Delta\mu_w^0$ and ΔH_w^0 for a sI hydrate. Handa and Tse¹¹ at the National Research Council in Canada performed an independent study to evaluate the reference properties from calorimetry-assisted determinations of the overall composition of xenon hydrate and the relative degree of occupancy of the two kinds of hydrate cavities near the reference P_0 and T_0 conditions using proton-decoupled ^{129}Xe NMR spectroscopy. Sloan⁷ at the Colorado School of Mines refined the reference parameters by fitting the chemical potential difference, $\Delta\mu_w^0$, to both pure and binary mixture hydrates while keeping the same value of enthalpy difference¹² and used these parameters in the program CSMHYD to predict phase equilibria for various pure and mixture hydrates.

Given the range of parameter values cited in the literature and the absence of a quantitative comparison of their prediction performance, it was unclear which set of reference parameters should be used in phase-equilibria and kinetic studies. In addition, the quantitative sensitivity of phase-equilibrium predictions to reference property values has not been reported. As a result, we undertook a comparative study to clarify and quantify the magnitude of these effects with the hope of providing a more representative set of parameter values.

Methodology

In the statistical model developed by van der Waals and Platteeuw,⁴ the difference in chemical potential between a clathrate and an empty host lattice is expressed as

$$\Delta\mu^{\beta-H} = RT \sum_i v_i \ln(1 + \sum_J C_{ji} \hat{f}_J) = RT \sum_i v_i \ln(1 - \sum_J y_{ji}) \quad (1)$$

where v_i is the number of type i cavities per water molecule, \hat{f}_J is the fugacity of guest molecule J , which is usually calculated from a suitable equation of state (EOS), such as Peng–Robinson EOS,¹³ C_{ji} is the Langmuir constant of guest molecule J in cage i , and y_{ji} is the fractional occupation probability of guest J in cavity i (y_{ji} is related to the mole fraction of the guest molecule in the water clathrate), given by an expression similar to the Langmuir isotherm

$$y_{ji} = \frac{C_{ji} \hat{f}_J}{1 + \sum_i C_{ji} \hat{f}_J} \quad (2)$$

Note that C_{ji} is defined as $Z_{ji}/(kT)$, which is the configurational integral. The phase equilibrium of clathrate hydrates is described in the context of a two-component (water[w]–guest[J]) system with monovariant behavior requiring these coexisting phases with

$$\begin{aligned} \mu_w^H &= \mu_w^{L \text{ or } \alpha} \\ \mu_w^{\beta-H} &= \mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^{L \text{ or } \alpha} = \Delta\mu_w^{\beta-L \text{ or } \alpha} \end{aligned} \quad (3)$$

where μ_w^β is the chemical potential hypothetical empty hydrate lattice with no cages occupied by guest molecules, μ_w^H is the chemical potential of water in the hydrate phase, and $\mu_w^{L \text{ or } \alpha}$ is the chemical potential of water in the solid ice phase (α) or liquid aqueous phase (L) depending on whether the temperature is below 273.15 K or not. Following the approach proposed by Holder et al.,⁶ we can express the chemical potential difference between the water in the hypothetical empty lattice (β) and the water in the hydrate phase (H) as

$$\begin{aligned} \frac{\Delta\mu_w^{\beta-H}(T,P)}{kT} &= \frac{\Delta\mu_w^{\beta-L \text{ or } \alpha}(T,P)}{kT} = \frac{\Delta\mu_w^{\beta-\alpha}(T_0,0)}{kT_0} - \\ &\int_{T_0}^T \left[\frac{\Delta H_w^{\beta-L \text{ or } \alpha}}{kT^2} \right] dT + \int_0^P \left[\frac{\Delta V_w^{\beta-L \text{ or } \alpha}}{kT} \right] dP - \ln a_w^L \end{aligned} \quad (4)$$

where $\Delta\mu_w^{\beta-\alpha}(T_0,0)$ is the reference chemical potential difference at the reference temperature, T_0 , usually taken to be 273.15 K, and zero pressure, and $\Delta V_w^{\beta-L \text{ or } \alpha}$ is the volume difference between the empty lattice and the water in the hydrate phase. The temperature dependence of the enthalpy difference, $\Delta H_w^{\beta-L \text{ or } \alpha}$, is given by

$$\Delta H_w^{\beta-L \text{ or } \alpha} = \Delta H_w^{\beta-L \text{ or } \alpha}(T_0) + \int_{T_0}^T \Delta C_p^{\beta-L \text{ or } \alpha} dT \quad (5)$$

with the heat capacity difference, $\Delta C_p^{\beta-L \text{ or } \alpha}$, approximated by

$$\Delta C_p^{\beta-L \text{ or } \alpha} = \Delta C_p^{\beta-L \text{ or } \alpha}(T_0) + \Delta b^{\beta-L \text{ or } \alpha}(T - T_0) \quad (6)$$

where $\Delta b^{\beta-L \text{ or } \alpha}$ is an empirical constant representing a first-order linear dependence of heat capacity on the temperature. The volume difference, $\Delta V_w^{\beta-L \text{ or } \alpha}$, is assumed constant (independent of T and P), and the additional term involving the activity of water in the aqueous liquid phase, a_w^L , is defined by

$$a_w^L = \frac{\hat{f}_w^L}{\hat{f}_w^+} \quad (7)$$

where \hat{f}_w^L is the fugacity of water in the water-rich aqueous phase and \hat{f}_w^+ is the water fugacity in the reference state, which is chosen to be a pure water phase at T and P of the mixture; thus, $\hat{f}_w^+ = f_w(T,P,\text{pure})$.

Once reference state values for $\Delta\mu_w^0 \equiv \Delta\mu_w^{\beta-\alpha}(T_0,0)$, $\Delta H_w^0 \equiv \Delta H_w^{\beta-\alpha}(T_0)$, $\Delta C_p^{\beta-L \text{ or } \alpha}(T_0)$, and $\Delta V_w^{\beta-L \text{ or } \alpha}(T_0)$ are specified, $\Delta\mu_w^{\beta-H}(T,P)$ can be computed at T and P of interest using eqs 3–6. Alternatively, the relationships can also be used to fit the reference properties. Holder et al.¹⁰ integrated and rearranged eqs 3–6 in the following form:

$$\frac{\Delta\mu_w^{\beta-H}(T,P)}{RT} + \frac{(\Delta C_p^{\beta-L \text{ or } \alpha}(T_0) - \Delta b^{\beta-L \text{ or } \alpha} T_0) \ln(T/T_0)}{R} - \frac{2\Delta C_p^{\beta-L \text{ or } \alpha}(T_0) - \Delta b^{\beta-L \text{ or } \alpha} T_0^2}{2R} \left[\frac{1}{T_0} - \frac{1}{T} \right] + \frac{\Delta b^{\beta-L \text{ or } \alpha}}{2R} (T - T_0) - \frac{P\Delta V_w^{\beta-L \text{ or } \alpha}(T_0)}{RT} + \ln a_w^L = \frac{\Delta\mu_w^0}{RT_0} + \frac{\Delta H_w^{\beta-L \text{ or } \alpha}(T_0)}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (8)$$

In the experimental condition for the cyclopropane hydrate,^{8,9} water is in liquid phase; therefore,

$$\Delta H_w^{\beta-L \text{ or } \alpha}(T_0) = \Delta H_w^{\beta-L}(T_0) = \Delta H_w^{\beta-L}(T_0) + \Delta H_w^{\alpha-L}(T_0) = \Delta H_w^0 + \Delta H_w^{\alpha-L}(T_0) \quad (9)$$

where $\Delta H_w^{\alpha-L}(T_0)$ is the latent heat of ice. If the left-hand side of eq 8 is defined as the variable Y , then

$$Y = \frac{\Delta\mu_w^0}{RT_0} + \frac{\Delta H_w^0 + \Delta H_w^{\alpha-L}(T_0)}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (10)$$

where Y is a function of the experimental conditions (T , P , composition) and other constants, namely, $\Delta b^{\beta-L \text{ or } \alpha}$, $\Delta C_p^{\beta-L \text{ or } \alpha}(T_0)$, and $\Delta V_w^{\beta-L \text{ or } \alpha}(T_0)$.

If the fundamental equations derived above capture the behavior of the system correctly, a plot of the experimental value of Y vs $(1/T - 1/T_0)$ should yield a straight line of which the intercept and slope will give the values of $\Delta\mu_w^0$ and ΔH_w^0 . An evaluation of this hypothesis was based on the experimental cyclopropane data obtained by Dharmawardhana et al.,^{8,9} when cyclopropane forms a sI hydrate, as listed in Table 2. Because cyclopropane occupies only the large cage in the sI hydrate, the fractional occupation probability can be rigorously related to the composition data by

$$y_{J2} = \frac{n_{\text{cyc}}}{n_{\text{cage}}} = \frac{n_{\text{cyc}}}{6n_{\text{water}}/46} \quad (11)$$

where n_{cyc} , n_{water} , and n_{cage} are the measured moles of the C_3H_6 , H_2O molecules, and large cages in the hydrate. The activity of water in the potassium chloride solution, a_w^L , was calculated from tabulated freezing-point depression data (CRC Handbook of Chemistry and Physics, 1977/1978, p D242) by the following common thermodynamic expression for such colligative property variations:¹⁴

$$\ln a_w^L = \frac{-\Delta H_w^{\alpha-L}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \quad (12)$$

where T_f and T are the freezing-point temperatures of pure water ($T_f = 273.15$ K) and water in a salt solution at the composition of the experiment, respectively.

Another independent study using sI xenon hydrates was performed by Handa and Tse.¹¹ They used ^{129}Xe NMR spectroscopy to measure the fractional occupation probabilities and, with these quantities, eq 1 to estimate $\Delta\mu_w^0$. Note that in doing this, they assumed that their experimental conditions, $T = 273.15$ K and $P = 1.467$ bar, were equivalent to the reference state used by almost all researches, $T_0 = 273.15$ K and $P_0 = 0$ bar. The error introduced by the pressure difference,

TABLE 2: Experimental Data of Cyclopropane for Filling the Structure I Hydrate (Adapted from Dharmawardhana et al.^{8,9})

T (K)	P (kPa)	mole of $c\text{-C}_3\text{H}_6$	mole of H_2O	salt concn (N)
280.170	176.25	0.034 82	0.269 20	0.010 45
278.475	142.39	0.042 76	0.330 99	0.010 66
278.275	138.39	0.046 02	0.356 18	0.010 65
278.150	135.99	0.033 62	0.260 32	0.010 46
278.685	128.28	0.031 18	0.241 40	0.010 45
277.425	124.02	0.023 85	0.184 71	0.010 33
277.150	120.12	0.046 58	0.360 77	0.010 66
276.900	115.75	0.045 68	0.353 72	0.010 67
276.655	115.20	0.041 56	0.321 91	0.010 59
276.150	101.24	0.051 71	0.400 55	0.010 74
275.915	102.74	0.049 22	0.381 44	0.010 71
275.690	99.35	0.060 63	0.470 04	0.010 90
275.455	96.69	0.041 82	0.324 22	0.010 61
275.355	95.35	0.047 59	0.368 89	0.010 69

1.47 bar, is extremely small compared with other terms in eq 4, as found by our calculations.

In earlier studies,^{15,16} we developed a methane–water pair potential using first-principles methods and applied it successfully to the prediction of the phase equilibria of methane hydrates. With a specified ab initio methane–water pair potential, cage occupation probabilities can be calculated using eq 2 by numerically evaluating the Langmuir constants (C_{ji}) at any specific T and P of interest. The same fitting approach developed by Holder et al.¹⁰ can be applied to determine the reference properties from the ab initio pair potential. A key difference is that experimentally determined y_{ji} 's are not needed in our case to evaluate $\Delta\mu^{\beta-H}$ in eq 1 because they can be directly calculated from numerical integration of Langmuir constants. The only experimental data needed for this approach is the readily available methane hydrate P – T equilibrium data. This gives us the great advantages that we have up to 100 data points in the fitting procedure and that we eliminate the uncertainty introduced by the composition measurements that are hard to perform accurately in practice over a wide temperature range.¹⁷

In an earlier study,¹⁵ reference property values were shown to affect significantly the prediction of phase equilibria for the methane hydrate using either the Lennard-Jones and Devonshire (LJD) approximation or an ab initio pair potential with multiscale guest–host interactions included. Although much research has been devoted to estimating and correlating reference property values, a comprehensive, quantitative evaluation of parameter uncertainty and sensitivity to the prediction of phase equilibria has not appeared. Our objective was to perform such analysis for sI hydrate systems. In this work, both the LJD method, which assumes spherical symmetry and takes into account only the first shell of water hosts, and the ab initio method, including five shells of guest–host interaction, were evaluated by varying the values of $\Delta\mu_w^0$ or ΔH_w^0 systematically to examine their influence on the dissociation pressure prediction of methane hydrates.

Results and Discussion

In this section, we present results using the methodologies introduced in the previous section. The same set of experimental data was used by Dharmawardhana et al.^{8,9} and Holder et al.¹⁰ First, we refitted Dharmawardhana's experimental data^{8,9} as listed in Table 2 to eq 10. All of the constant parameters are the same as those used in our previous study,¹⁵ and all are summarized in Table 3. The resulting line fit is listed in Table 1S (Supporting Information), plotted in Figure 1a, and compared

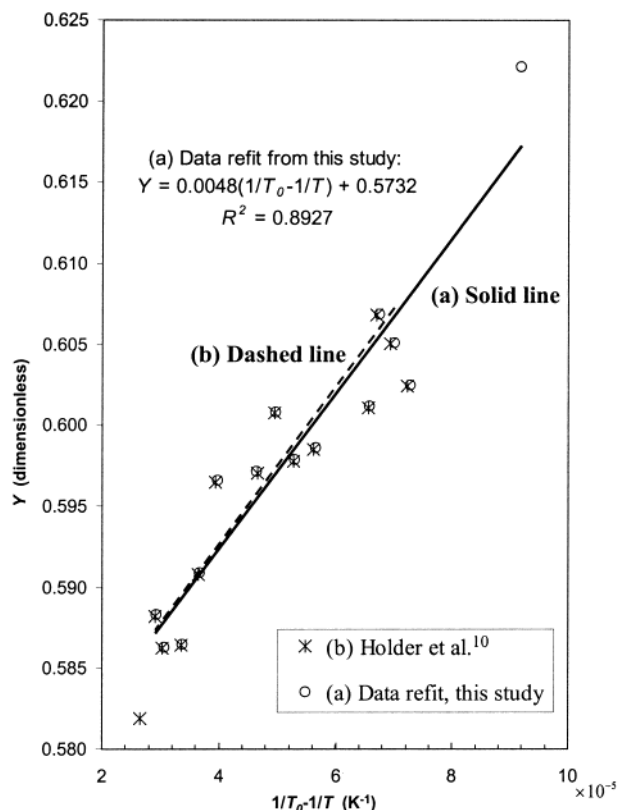


Figure 1. Comparison of the regression of the Dharmawardhana's experimental data from this study (a) with earlier results (b) (Plot b is adapted from Holder et al.).¹⁰

TABLE 3: Thermodynamic Reference Properties of Structure I Water Clathrate

reference condition ($T_0 = 273.15$ K, $P_0 = 0$ atm)	
Latent Heat (T_0, P_0)	
$\Delta H_w^{\alpha-L}$, J mol ⁻¹	-6009.5
Volume Differences (T_0)	
$\Delta V_w^{\beta-\alpha}$, m ³ mol ⁻¹	3.0×10^{-6}
$\Delta V_w^{L-\alpha}$, m ³ mol ⁻¹	-1.598×10^{-6}
Heat Capacity Differences ($T > T_0$)	
$\Delta C_p^{\beta-L}$, J mol ⁻¹ K ⁻¹	-38.12
$\Delta b^{\beta-L}$, J mol ⁻¹ K ⁻²	0.141

with the original plot by Holder et al.¹⁰ in Figure 1b. For the sake of comparison, we used the same axis convention, in which the x axis is $(1/T_0 - 1/T)$ and the slope yields $-(\Delta H_w^0 + \Delta H_w^{\alpha-L})/R$ and not $(\Delta H_w^0 + \Delta H_w^{\alpha-L})/R$. There is one main discrepancy between parts a and b of Figure 1. All of the data points in both plots match except one point at $T = 280.17$ K at which the corresponding x axis value, $(1/T_0 - 1/T)$, should be 9.17×10^{-5} . As a result of this apparent miscalculation, we could not reproduce the values of the reference properties in the original paper using the data given in Table 2. (Holder et al.¹⁰ gave $\Delta \mu_w^0 = 1299$ J/mol and $\Delta H_w^0 = 1861$ J/mol, while our refit gave $\Delta \mu_w^0 = 1302$ J/mol, $\Delta H_w^0 = 2019$ J/mol.) However, the main purpose of our refit was not to find the "correct" values of reference properties but to investigate the effect of experimental uncertainties. Both parts a and b of Figure 1 show significant scatter around the correlation line for the 14 data points given with a correlation coefficient R^2 of 0.89. Given the scatter, the reference properties obtained from this fitting procedure are likely inadequate to be used for all sI hydrates. It

TABLE 4: Calculated $\Delta \mu_w^0$ Value at Different Fractional Occupation Probabilities within the Experimental Uncertainty^a

	base value $\langle y_{ji} \rangle$	upper limit	lower limit
y_{H1}	0.7161	$\langle y_{ji} \rangle + 0.0161$	$\langle y_{ji} \rangle - 0.0161$
y_{H2}	0.9808	$\langle y_{ji} \rangle + 0.0070$	$\langle y_{ji} \rangle - 0.0070$
$\Delta \mu_w^0$ (J/mol)	1296.8	1437.7	1198.8

^a Experimental data are taken from ref 11.

is also worth pointing out that the variation of Holder's $\Delta \mu_w^0$, refitted by us, at the 95% confidence interval was only ± 13 J/mol.

However, this statistical analysis does not account for the full extent of the experimental uncertainties. There may be systematic errors.¹⁷ In Handa and Tse's¹¹ independent study to obtain the thermodynamic properties of empty lattices of sI and sII clathrate hydrates, the two fractional occupation probabilities, inputs to eq 1, were given with experimental error limits. We recalculated $\Delta \mu_w^0$ at both the upper and lower bounds of these experimental errors. The results are shown in Table 4, in which our calculated value of $\Delta \mu_w^0$, 1297 J/mol, was different from the value of 1287 J/mol reported by Handa and Tse.¹¹ In addition, the variation of the calculation of $\Delta \mu_w^0$ was 240 J/mol (from 1198 to 1438 J/mol) using the reported range in cell occupation probabilities. Nonetheless, the computed result is in close agreement with the original xenon ¹²⁹NMR study by Davidson et al.,¹⁷ which estimated of $\Delta \mu_w^0 = 1297 \pm 110$ J/mol. Davidson et al.¹⁷ also pointed out that the error limits reported by Holder et al.,¹⁰ as 299 ± 10 J/mol, were greatly underestimated. Although the total of 20 J/mol is consistent with our regression study that gave a range of $26 (\pm 13)$ J/mol, it reflects only the statistical error in the linear regression of eq 10 based on the assumption that all of the experimental data points are accurate. Therefore, we agree with Davidson and co-workers¹⁷ in asserting that the Holder et al.¹⁰ error limits were underestimated because they did not consider experimental uncertainties in hydrate composition measurements, which may be large.

In this study, we also evaluated the often-cited values of reference-state properties ($\Delta \mu_w^0 = 1263$ J/mol, $\Delta H_w^0 = 1389$ kcal/mol) recommended by Sloan⁷ in 1998. For comparison, we used the LJD approximation and the same approach to predict the dissociation pressure of methane hydrates used by others previously. Our own code and the Colorado School of Mines code CSMHYD⁷ were used to generate results. All input parameters used in our code are listed in Table 5 with effort to match those used earlier by Sloan.⁷ Two different $PVTx_i$ equations of state (EOS), the Soave-modified Redlich-Kwong (SRK) and the Peng-Robinson (PR), were used in our calculation to model nonidealities in the fluid phase. Experimental equilibrium three-phase dissociation pressure data compiled by Sloan¹⁸ were used, including 97 points for the methane-water system from 148.8 to 320.1 K. Results are compared in Figure 2. Figure 2 parts a and b are the same plot in different scales to illustrate the comparison more clearly over the entire temperature range. Although the LJD approximation has been shown to be inaccurate in representing guest-host interactions on a molecular scale from earlier analysis in our group,^{16,19,15} careful, yet aphysical, adjustment of the Kihara potential parameters has been shown to provide a good empirical correlation of the methane hydrate phase equilibria at low temperatures ($T < 290$ K). Nonetheless, this empirical model, which is based on fitted parameters and the LJD approximation, shows significant deviations from experiment at high temperatures, as shown in

TABLE 5: Parameter Values Used in Calculations of This Study

vdW-P model ^a	CH ₄ -H ₂ O Kihara LJD approximation ^a	LJD approximation ^a	CH ₄ critical point properties ^b
$\Delta\mu_w^0 = 1263$ J/mol	$\epsilon/k = 154.54$ K	sI small cage: $z = 20$, $R = 3.95$ Å	$T_c = 190.4$ K
$\Delta H_w^0 = 1389$ J/mol	$\sigma = 3.1650$ Å		$P_c = 46$ bar
$\Delta H_w^{L-\alpha} = 6009.5$ J/mol	$a = 0.3834$ Å	sI large cage: $z = 24$, $R = 4.33$ Å	$\omega = 0.011$
$\Delta V_w^{\beta-\alpha} = 3.0 \times 10^{-6}$ m ³ /mol			
$\Delta V_w^{L-\alpha} = 1.598 \times 10^{-6}$ m ³ /mol			
$\Delta C_p^{\alpha-L} = 38.12 - 0.141(T - 273.15)$			

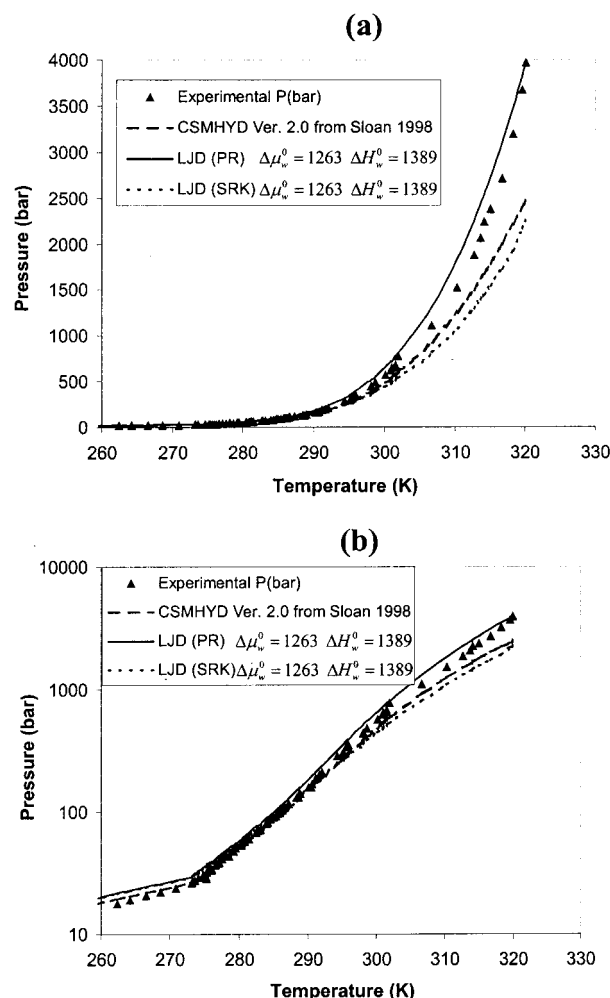
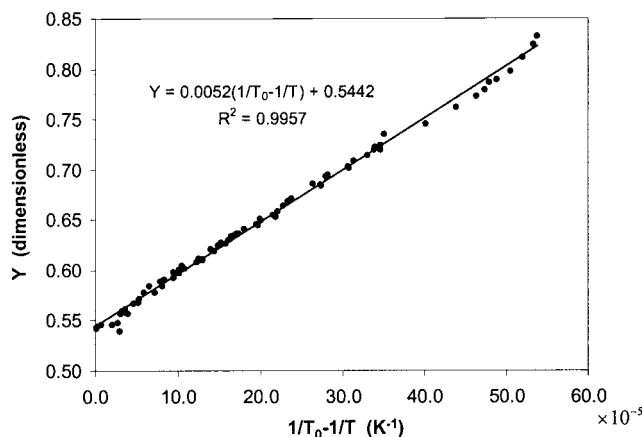
^a From ref 7. ^b From ref 22.**Figure 2.** Comparison of predicted and experimental monovariant phase equilibrium for the methane-water hydrate system.

Figure 2 and listed in Table 2S (Supporting Information). Moreover, the choice of EOS has a significant effect on phase-equilibria prediction because the fugacity of the guest molecule is far from being ideal at extremely high pressures. Such clearly visible complexities justify the need to develop a robust methane-water potential¹⁶ and to treat guest-host molecular interactions in the clathrate hydrate structure consistently and explicitly.¹⁵

As mentioned in the methodology section, we were able to obtain reference property values directly from the ab initio potential and methane hydrate P - T phase equilibrium constraints. Without the need for the composition data, we incorporated 97 monovariant P - T data points¹⁸ for the methane-water system in our regression. Results are given in Table 3S (Supporting Information) and Figure 3. The fitted reference

**Figure 3.** Fit of 97 experimental data points for methane hydrates using the ab initio potential to calculate the cage occupancies. The correlation is defined by eq 10.**TABLE 6: Recommended Reference Property Parameters for sI Hydrate Systems Based on the Best Fit of the Methane Hydrate Using the ab Initio Potential from Our Previous Study¹⁶**

reference parameters at 273.15 K, 0 bar	fitted values (J/mol)	95% confidence interval (J/mol)
$\Delta\mu_w^0$	1236	± 4
ΔH_w^0	1706	± 62

properties ($\Delta\mu_w^0 = 1236 \pm 4$ J/mol, $\Delta H_w^0 = 1703 \pm 62$ J/mol), listed in Table 6, are well within the range obtained in previous studies given in Table 1. The line fit had a highly linear correlation ($R^2 = 0.996$) with a 95% confidence level range of only ± 4 J/mol for $\Delta\mu_w^0$ and ± 4 J/mol for ΔH_w^0 from the regression analysis. This is promising because the regression analysis using the ab initio method does not depend on the experimental uncertainties associated with the difficult hydrate composition measurement. The experimental error in the P - T equilibrium measurements will introduce some uncertainty, but the temperature and pressure measurement can be considered accurate with the current experimental techniques. Of course, all of this assumes that our ab initio potential is highly accurate.¹⁶

Given these caveats, the excellent linear relationship observed in Figure 3, using our ab initio pair potential confirms, to some extent, that the van der Waals and Platteeuw model is valid for the methane-water system. Note that the scatter in Figure 1 does not include any uncertainty associated with systematic experimental error in the composition measurement.^{8,9} Direct measurements of hydrate compositions are known to be difficult, frequently because of the problem presented by the presence of excess water.¹¹ Therefore, the experimental cyclopropane composition tends to be lower than it should if all excess water is removed. This lower composition will result in a higher fitted chemical potential difference, $\Delta\mu_w^0$. This partially explains

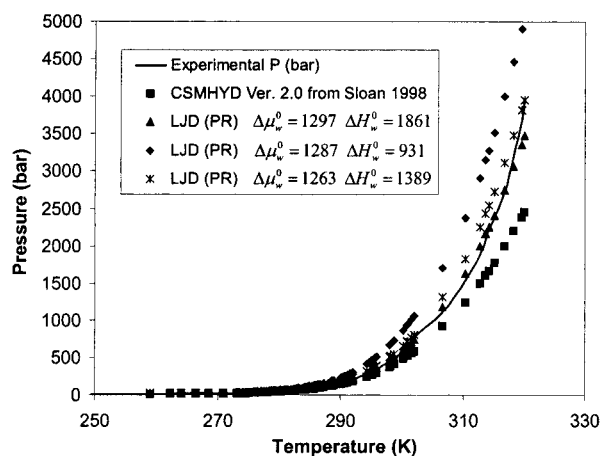


Figure 4. Sensitivity analysis results using the LJD method and different sets of reference state estimates from the literature.

why Holder et al.'s fitting method¹⁰ based on composition measurement gave a higher value of 1297 J/mol as compared to our first-principles value, 1236 J/mol. We also varied all of the number of moles of water by -0.0005 mol (see Table 2) in the calculation to see how changes in the fourth decimal place would affect the result. The regression result changed drastically from $\Delta\mu_w^0 = 1302$ J/mol, $\Delta H_w^0 = 2019$ J/mol to $\Delta\mu_w^0 = 1320$ J/mol, $\Delta H_w^0 = -253$ J/mol. The sign change of ΔH_w^0 indicates the significant impact of experimental uncertainty on the fitted reference parameters.

Finally, on the basis of the previous results, sensitivity analyses were performed on phase-equilibria predictions of methane hydrates by varying the values of $\Delta\mu_w^0$ and ΔH_w^0 . The first and second results (Figure 1 and Table 4) above demonstrate the necessity to consider the large variation of the obtained reference parameters caused by inherent experimental errors. The third and fourth results (Figures 2 and 3) show that the LJD approximation and the Kihara potential with adjusted parameters are useful only at low temperatures (<290 K), while the method using the ab initio potential and explicit quadrature integration with five water host shells is superior over a wider temperature range (up to 320 K). We concluded that the fitted reference properties (reported in Table 6) estimated using the ab initio potential and our methodology are accurate within a theoretically consistent framework.

The goal of the sensitivity analyses was to study how much the prediction of dissociation pressures changed with respect to the variation within the error limit. Two cases using different methods for predicting dissociation pressures were examined: one using the LJD method⁷ and one using the ab initio method.¹⁵ In both cases, the same set of methane–water P – T equilibrium data¹⁸ was used and plotted for comparison in Figure 4. In the first case, our own code (the method was identical to what was used in CSMHYD program⁷ and the potential parameters were also taken from Sloan⁷) using the LJD approximation with the PR EOS was run at different sets of reference properties obtained by Holder et al.,¹⁰ Handa and Tse,¹¹ and Sloan.⁷ The results are shown in Figure 4 and Table 4S (Supporting Information). It can be seen that different sets of reference parameters cause significant changes of the pressure prediction—exceeding a factor of 1.5 at higher temperatures ($T > 290$ K). Most researchers cite the work by van der Waals and Platteeuw and use the LJD approximation and the Kihara potential to predict P – T behavior, but often they do not report the reference properties and Kihara parameters used in their calculations. Given their sensitivity, it is therefore important to know exactly

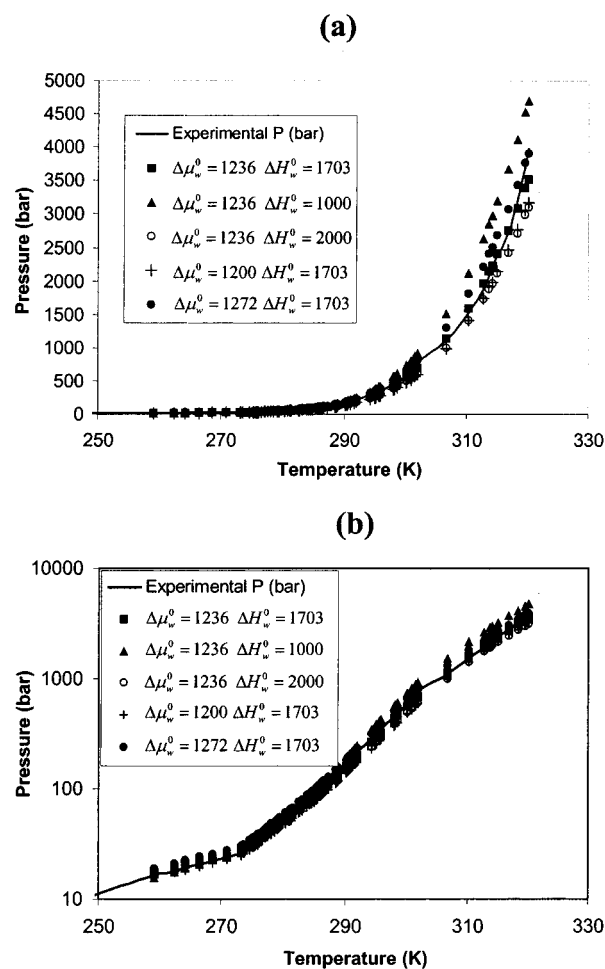


Figure 5. Sensitivity analysis results using ab initio method by systematically varying the reference values (Part a is a linear plot, and part b is a log–linear plot of the monovariant P – T phase equilibrium (predicted and experimental) for the methane–water hydrate system. Note that the variation of ΔH_w^0 is not symmetric but rather was selected to span the entire range of ΔH_w^0 values reported in the literature.).

which reference values were used to allow results of a given investigator to be both reproducible and transferable.

We also performed sensitivity analyses on our ab initio method. The fitted values of $\Delta\mu_w^0$ and ΔH_w^0 from our results (Figure 3) were selected as the base values. The variation of ΔH_w^0 was intentionally chosen to be much larger than that of $\Delta\mu_w^0$. The results are plotted in Figure 5 and listed in Table 5S (Supporting Information). Although ΔH_w^0 had a variation range of 1000 J/mol, the effect of the changes on the predicted pressure was comparable to a range of 72 J/mol for $\Delta\mu_w^0$. Hence, the three-phase monovariant equilibria prediction of methane hydrates was found to be much more sensitive to the value of $\Delta\mu_w^0$ than to the value of ΔH_w^0 at high temperatures ($T > 290$ K). This finding is consistent with qualitative statements made in earlier studies^{7,10} that the effect of the experimental uncertainties introduced into the value of ΔH_w^0 was not significant. In our case, a deviation of ± 36 J/mol in $\Delta\mu_w^0$ was large enough to result in a 50% change of pressure prediction at high temperatures ($T > 290$ K). We estimate that the $\Delta\mu_w^0$ value obtained from either experiments or calculations should be within ± 10 – 20 J/mol to result in errors in equilibrium pressures of 5%–10% of predicted values for all sl gas hydrates.

In closing, we emphasize that the reference parameters were obtained within the framework of the van der Waals and

Platteeuw model,⁴ for both previous work^{8–11} and our ab initio study. Therefore, the four basic assumptions of the model⁴ are always made. The first assumption is the rigid lattice approximation, which neglects differences in the water–water interactions between the empty and filled lattices. Our results, as discussed above, tend to validate this approximation and the others, at least for this system. As discussed in the Introduction, experimental errors in the determination of the reference parameters are generally addressed by adjusting parameters in the intermolecular potentials in an ad hoc way, yielding aphysical parameters. The value of using the ab initio potential for methane–water interactions, which was validated by several independent phase and spectroscopic experiments,^{15,16} is to provide a set of parameters that should be physically relevant without the need for ad hoc adjustment of parameters. Consequently, the set of reference properties that we obtained could be a physically based input to applications such as indirect experimental determination of methane hydrate's cage occupancies via Raman spectroscopy.^{20,21} Finally, the statistical error of ± 4 J/mol that we obtained in $\Delta\mu_w^0$ using the ab initio potential does not take into account possible systematic errors in our potential. Even though our potential was validated with respect to nonhydrate data (see above and ref 16), the high degree of sensitivity could make systematic errors possible. It would be nice to validate our reference properties on another system, such as xenon hydrates, but to do this, we would need to compute the ab initio potential for xenon–water interactions. This would be another study in itself.

Conclusions

This study clearly indicates the importance of having accurate values for the empty clathrate lattice reference state for both chemical potentials and enthalpies. Uncertainties in currently available experimentally derived values in the literature are large enough to affect both the quality and reliability of regressed potential parameters needed to deploy the van der Waals and Platteeuw model. A set of representative reference property parameters with small statistical errors was obtained using an ab initio method to generate a guest–host pair potential and an accurate means of estimating the Langmuir constant with five shells of water host interactions included. A sensitivity analysis illustrated the importance of selecting values of reference properties obtained from the literature and underscores the need for more accurate and precise experimental techniques to provide $\Delta\mu_w^0$ values to within a few joules per mole.

Acknowledgment. The authors thank the Idaho National Environmental Engineering Laboratory (INEEL) and the MIT Energy Laboratory for their support of this research. We also gratefully acknowledge insightful discussions with Prof. William Green, Brian Anderson, and other members of our research groups at MIT, Dr. Kevin Sparks, Prof. Dendy Sloan at Colorado School of Mines, and Drs. Robert Cherry and Rick Colwell and others from INEEL.

Supporting Information Available: Tables reporting the raw data used in Figures 1–5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) McMullan, R. K.; Jeffrey, G. A. *J. Chem. Phys.* **1965**, *42*, 2725.
- (2) Mak, T. C. W.; McMullan, R. K. *J. Chem. Phys.* **1965**, *42*, 2732.
- (3) Ripmeester, J. A.; Tse, J. A.; Ratcliffe, C. I.; Powell, B. M. *Nature* **1987**, *325*, 135.
- (4) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.
- (5) Parrish, W. R.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 26.
- (6) Holder, G. D.; Corbin, G.; Papadopoulos, K. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282.
- (7) Sloan, E. D., Jr. *Clathrate hydrates of natural gases*, 2nd ed., revised and expanded; Marcel Dekker: Monticello, 1998.
- (8) Dharmawardhana, P. B.; Parrish, W. R.; Sloan, E. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 410.
- (9) Dharmawardhana, P. B.; Parrish, W. R.; Sloan, E. D. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 306.
- (10) Holder, G. D.; Malekar, S. T.; Sloan, E. D. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 123.
- (11) Handa, P. Y.; Tse, J. S. *J. Phys. Chem.* **1986**, *90*, 5917.
- (12) Sloan, E. Personal communication, 2001.
- (13) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
- (14) Dickens, G. R.; Qinby-Hunt, M. S. *J. Geophys. Res., [Solid Earth]* **1997**, *102*, 773.
- (15) Cao, Z.; Tester, J. W.; Sparks, K. A.; Trout, B. L. *J. Phys. Chem. B* **2001**, *105*, 10950.
- (16) Cao, Z.; Tester, J. W.; Trout, B. L. *J. Chem. Phys.* **2001**, *115*, 2550.
- (17) Davidson, D. W.; Handa, Y. P.; Ripmeester, J. A. *J. Phys. Chem.* **1986**, *90*, 6549.
- (18) Sloan, E. D. *Clathrate hydrate of natural gases*; Marcel Dekker Inc.: New York, 1990.
- (19) Sparks, K. A.; Tester, J. W.; Cao, Z.; Trout, B. L. *J. Phys. Chem. B* **1999**, *103*, 6300.
- (20) Uchida, T.; Hirano, T.; Ebinuma, T.; Narita, H.; Gohara, K.; Mae, S.; Matsumoto, R. *Environ. Energy Eng.* **1999**, *45*, 2641.
- (21) Sum, A. K.; Burruss, R. C.; Sloan, E. D. *J. Phys. Chem. B* **1997**, *101*, 7371.
- (22) Tester, J. W.; Modell, M. *Thermodynamics and its applications*, 3rd ed.; Prentice-Hall: Upper Saddle River, NJ, 1997.