Model for Gas Hydrate Equilibria Using a Variable Reference Chemical Potential: Part 1

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A new model developed for predicting the dissociation pressure of gas hydrates proposes that the host−host interaction can be affected by the guest molecules, thus requiring different values of the reference properties, $\Delta\mu_w^o$ and Δh_w^o, for each gas hydrate. We presume that the primary impact of the guest is to distort the lattice, although other factors, such as guest polarity, can have an impact. Experimentally based $\Delta\mu_w^o$ and Δh_w^o values for each gas hydrate show that these values vary from guest to guest, generally increasing with guest size. Using these experimentally determined reference values, the error between calculated and experimental dissociation pressures is reduced. A correlation between $\Delta\mu_w^o$ and the molecular size of the guest molecule (or the Kihara hard-core diameter 'a') is also developed for estimating values of $\Delta\mu_w^o$, where experimental data are absent (that is, methane in structure II hydrate with no other guests).

Introduction

Gas hydrates are of interest to the gas industry, not only because they plug gas and oil pipelines, but also because naturally occurring hydrates are a potentially abundant source of natural gas (Sloan, 1998; Smith et al., 1994). Gas hydrates are nonstoichiometric crystalline compounds formed by the physical combination of water and low molecular-weight gases, such as methane, propane, and isobutane (Holder et al., 1988), although some very large molecules can contribute to hydrate stability (Lederhos et al., 1992). In gas hydrates, water forms a lattice through hydrogen bonding. The resulting lattice has interstitial vacancies called cavities (small or large), which are partially filled with gases (Sloan, 1998). Their empty lattice is not stable and does not exist in nature.

In the 1950s, van der Waals and Platteeuw developed the statistical thermodynamic model for describing hydrate-phase equilibrium. Subsequently, Parrish and Prausnitz (1972) generalized this model to create a systematic approach to predicting equilibria from a wide variety of gases. In these models, the following assumptions were used (van der Waals and Platteeuw, 1959):

1. The nature of the guest molecules that are encapsulated does not affect the interaction of the water molecules of the hydrate lattice. For this assumption to be valid, the enclathrated molecule cannot distort the lattice structure or otherwise affect the molecular vibrations of the water.

2. The number of molecules encapsulated in one cavity is either zero or one.

3. The mutual interaction of the solute molecules is negligible.

4. Classic statistical mechanics are valid.

Holder and others (John et al., 1985, Zele et al., 1999) modified van der Waals and Platteeuw's hydrate equilibrium model in several ways. One important modification was the development of a corresponding states correlation to predict the deviation of Langmuir constants (which describe the affinity of a gas molecule for occupying a lattice cavity) from ideal (smooth cell) values (John et al., 1985). This modification allowed the Kihara parameters obtained from virial coefficient data to be used to describe the guest−host interaction. Until this development, hydrate potential parameters were usually experimental "fitting" parameters and had little relationship to potential parameters from other sources. The primary contribution of this model was to account for the deviation of the guest gas molecules' energy from that of the free rotation, free vibration assumption of the original van der Waals and Platteeuw model. This modification attributed all of the differences in predicted and calculated equilibrium pressures to this deviation.

Subsequently, Zele, Hwang, and Holder hypothesized that guests could impact the host−host interactions in the lattice (Zele et al., 1999; Hwang et al., 1993), invalidating the first assumption of the van der Waals and Platteeuw model. This

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conclusion was the basis for the present model, which uses the assumption that the lattice can be distorted due to the size of the guest molecules that are enclathrated, although the variable chemical potential is the core concept and if it is caused by something other than distortion, the model still pertains. Tanaka (1993) also considered the distortion in the hydrate cages around xenon and carbon tetrafluoride guests. In that work, he showed that the small xenon atoms did not distort the hydrate cages, but large carbon tetrafluoride distorted the small cages. Crystallographic data, lattice simulations, evidence of variable thermal expansivity (Zele et al., 1999), and the simple recognition that the force that a guest exerts on the cage will affect its structure all suggest that the hydrate structure, and thus the chemical potential, will depend upon the guest. Davidson et al. (1986) suggest that the variation of lattice parameter with guest size is approximately 0.2 Å, and that the larger variations shown by the crystallographic data may be an experimental error. However, even small variations can have an impact on the reference chemical potential, and this is the concept most important to the present treatment. Westacott and Rodger (1997) and Klauda and Sandler (2000) also used a variable chemical potential to calculate hydrate equilibria, although the latter study did this in terms of a variable empty-lattice vapor-pressure and did not use the van der Waals and Plateeuw model. If a guest affects the host–host interaction, the reference (273.15 K, 0 kPa) chemical potential difference between the theoretical empty lattice and water must be modified to account for this. In this concept, a guest-dependent reference chemical potential difference, $\Delta\mu_w^o$, is necessary for predicting the equilibrium conditions for simple and mixture hydrates (Zele et al., 1999). Kihara parameters from virial coefficient data are used, thus maintaining the advantage of Holder and coworkers' earlier approach.

Theoretical Background

At equilibrium, the chemical potentials of water in the hydrate and other coexisting phases are identical. If liquid water is present (van der Waals and Plateeuw, 1959),

$$\mu_w^L(T,P) = \mu_w^H(T,P), \quad (1)$$

where $\mu_w^L(T,P)$ is the chemical potential of pure liquid water and $\mu_w^H(T,P)$ is the chemical potential of hydrate at temperature, T, and pressure, P. Using μ^β, the chemical potential of an unoccupied hydrate lattice as reference state, Eq. 1, would be (Holder et al., 1988)

$$\Delta\mu_w^L = \Delta\mu_w^H, \quad (2)$$

where

$$\Delta\mu_w^L = \mu^\beta - \mu_w^L$$
$$\Delta\mu_w^H = \mu^\beta - \mu_w^H.$$

The statistical thermodynamics model for hydrate phase developed by van der Waals and Plateeuw (1959) is

$$\Delta\mu_w^H = -RT \sum_{i=1}^{2} \nu_i \ln\left(1 - \sum_j \theta_{ij}\right) \quad (3)$$

where ν_i is the number of i-type cavities per water molecule, and θ_{ij} is the fractional occupancy of i-type cavities with j-type molecules. It is expressed as (Holder, 1988)

$$\theta_{ij} = \frac{C_{ij}f_i}{1 + \sum_j C_{ij}f_j}, \quad (4)$$

where f_j is the fugacity of gas component j, and C is the temperature-dependent Langmuir constant. For calculating the fugacity coefficients in the gas phase, the Peng-Robinson equation is used. John and Holder (1981) suggested including the contribution of more distant water molecules as "second" and "third" shells, according to their distance from the cavity center. Because of the exponential form, the second or third shell contribution can change C by several orders of magnitude. The smooth cell Langmuir coefficient can be calculated as

$$C_{ij} = \frac{1}{kT} \int_0^R 4\pi r^2 \exp\left(-\frac{W_1(r) + W_2(r) + W_3(r)}{kT}\right) dr, \quad (5)$$

where $W_1(r)$, $W_2(r)$, and $W_3(r)$ are smooth cell potentials of the first, second, and third shells based upon the Kihara potential function, and R is the radius of the hydrate cavity (Zele, 1994) or first shell. Since we have presumed that the lattice is distorted by the guest, different integration radii are used in equations when the lattice is distorted. However, this concept is not core to the model. Zele et al. (1999) developed an empirical correlation between the first shell radii of all cavities and $\Delta\mu_w^o$

$$R = A + B \times \Delta\mu_w^o. \quad (6)$$

In Eq. 6, $\Delta\mu_w^o$ is in cal/mol, and R is in Å. Constants A and B for three water shells of each type of cavity are listed in Table 1. This correlation results in cavity radii that vary by no more than 0.2 Å.

The chemical potential difference, $\Delta\mu_w$, is a function of pressure and temperature only and can be written as

$$d\left(\frac{\Delta\mu_w}{RT}\right) = -\left(\frac{\Delta h_w}{RT^2}\right) dT + \left(\frac{\Delta V_w}{RT}\right) dP, \quad (7)$$

where Δh_w is the molar enthalpy difference and ΔV_w is the volume difference between the theoretical empty hydrate and

Table 1. Constants Used in Obtaining Cavity Radii from $\Delta\mu_w^o$

Cavity Constants	Structure I			Structure II		
	Shell 1	Shell 2	Shell 3	Shell 1	Shell 2	Shell 3
Small A (Å)	3.75	6.34	7.79	3.75	6.47	7.84
B (Å mol/cal)	3.64	6.44	7.44	3.84	6.65	8.03
Large A (Å)	4.02	6.85	8.02	4.56	7.24	8.52
B (Å mol/cal)	3.87	6.56	7.67	4.69	7.45	8.78

Source: Zele et al. (1999).

liquid-water phase. Holder, et al. (1982) provided the simple method for calculating the effect of temperature, pressure and composition on $\Delta\mu_w$

$$\frac{\Delta\mu_w}{RT} = \frac{\Delta\mu_w^o}{RT_o} - \int_{T_o}^{T}\frac{\Delta h_w}{RT^2}dT + \int_0^P\frac{\Delta V_w}{RT}dP - \ln\gamma_w x_w. \quad (8)$$

The first term is the chemical potential difference between the theoretical empty hydrate and liquid water at its reference state (273.15 K, 0 kPa), and the second term accounts for the change in chemical potential difference due to temperature, at zero pressure. The third term accounts for the change in chemical potential difference due to pressure, and the last term is the correction necessary when liquid water is present and accounts for the solubility of gas in the water or to the presence of a dissolved inhibitor. The activity coefficient, γ_w, accounts for the nonidealities of the solution. The gas solubility in water is calculated by use of the Krichevsky-Kasranovsky equation (Holder, et al. 1988).

In the present model, the reference chemical potential difference between the theoretical empty hydrate and liquid water, $\Delta\mu^o$, has different values for different guests because of the impact of the guest on the host−host interactions. Differ-

Figure 1. Algorithm for calculating $\Delta\mu_w^o$.

Table 2. $\Delta\mu_w^o$ for Hydrates

Guest Gas	Gas Dia. (Å)	Kihara Para. a (pm)	Cavities Occupied (O)		$\Delta\mu_w^o$ (cal/mol) Exp.
			Small	Large	
Structure I					
N_2	4.1	34.1	O	O	266
CH_4	4.36	26	O	O	259
Xe	4.58	25.2	O	O	194
H_2S	4.58	49.2	O	O	443
CO_2	5.12	67.7	O	O	542
C_2H_6	5.5	57.4		O	417
c-C_3H_6	5.8	74.5		O	408
Ethylene	6.1	53.3		O	419
Structure II					
Ar	3.8	21.7	O	O	248
Kr	4.0	23.2	O	O	196
c-C_3H_6	5.8	65.3		O	297
C_3H_8	6.28	74.5		O	354
i-C_4H_{10}	6.5	85.9		O	451

ent $\Delta\mu_w^o$ values are calculated from experimental vapor-pressure data for each simple gas hydrate. The value of $\Delta\mu_w^o$ for any guest is calculated based upon experimental data using the following procedure:

1. A value of $\Delta\mu_w^o$ is assumed for a specific simple gas hydrate, such as methane gas hydrate or propane gas hydrate at 273.15 K. Note that the experimental equilibrium dissociation pressure is available in all cases. The radii of each water shell is obtained from Eq. 6.

2. With the radii from Eq. 6, Langmuir constants are calculated for each cavity by using Eq. 5. The Kihara potential with parameters obtained from viscosity and virial coefficient data is used to obtain the cell potential.

3. $\Delta\mu^H$ is calculated using Eq. 3 with the Langmuir constants calculated from step 2.

4. The chemical potential difference between theoretical empty hydrate and water is calculated using Eq. 8. In this equation the second term would be zero at 273.15 K. The activity coefficient for water, which has a minor effect, is calculated by using the Krichevsky-Kasranovsky equation (Holder et al., 1988). Constants for heat-capacity calculations for empty hydrate and for water are obtained from the same source.

5. If the chemical potential difference of hydrate ($\Delta\mu^H$) and that of water ($\Delta\mu^w$) are not identical, a new $\Delta\mu_w^o$ is assumed, using an appropriate convergence method.

6. Repeat steps 2 to 5 until two chemical potentials become identical. This gives the reference chemical potential for a specific hydrate (methane).

The computer program is given in Figure 1 and $\Delta\mu_w^o$ values for each simple gas hydrate are listed on Table 2 (Holder et al., 1988). These can be considered experimental values in that they are obtained directly from these data. Very similar results would be obtained with the original vdWP model.

The temperature dependence of the enthalpy term Δh_w can be given by Eq. 9.

$$\Delta h_W = \Delta h_W^0 + \int_{T_o}^{T}\Delta C_{P_W}dT, \quad (9)$$
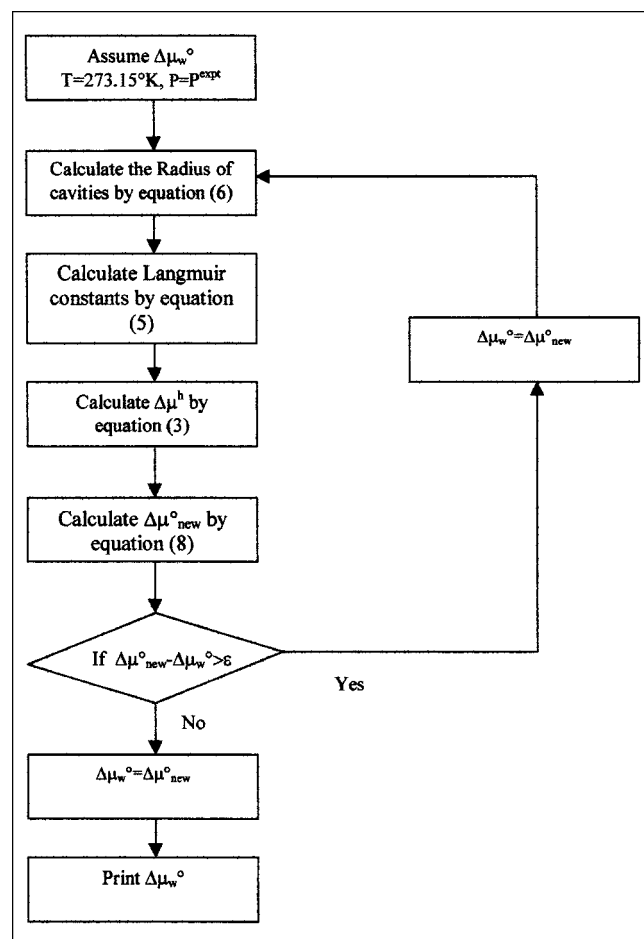
where, Δh_w^o is the reference enthalpy difference between the theoretical empty hydrate and the pure-water phase at 273 K, and ΔC_{Pw} is the heat-capacity difference between the theoretical empty hydrate and the pure-water phase. Both ΔC_{pw} and Δh_w^o are experimentally determined functions.

If the reference chemical potential difference depends upon each guest, the reference enthalpy difference will also depend upon each guest. This means that enthalpy of the corresponding empty lattice for each gas hydrate at 273 K, 0 kPa should have a different value (Hwang et al., 1993). It is possible to determine whether the experimental data suggest a variable reference enthalpy difference by using the model to calculate the difference for different hydrate-forming species. Equating Eqs. 3 and 8 gives

$$
- RT_F \sum_i \nu_i \ln\left(1 - \sum_j \theta_{ij}\right) = \frac{\Delta\mu_w^o T_F}{T_o} - T_F \int_{T_o}^{T_F} \frac{\Delta h_w}{T^2} dT
$$
$$
+ T_F \int_0^P \frac{\Delta V_w}{T_F} dP - T_F \ln \gamma_w x_w, \tag{10}
$$

where T_F is the temperature of the system, γ_w is the activity coefficient of water, and x_w is the mol fraction of water in the water-rich phase. This equation can be rearranged to give X and Y values after carrying out the appropriate integration,

$$
Y = \alpha \times X, \tag{11}
$$

where

$$
X = \left(\frac{1}{T_F} - \frac{1}{T_o}\right)
$$

$$
Y = \frac{\Delta\mu_w^o}{T_o} + \beta \ln\frac{T_F}{T_o} + \gamma(T_F - T_o) + \int_0^P \frac{\Delta V_W}{T_F} dP - \ln\gamma_w x_w
$$
$$
+ R \sum_i \nu_i \ln\left(1 - \sum_j \theta_{ij}\right),
$$

where

$$
\alpha = -\Delta h_w^o + \Delta C_{PW}^o T_o - \frac{b}{2} T_o^2 \tag{11a}
$$

$$
\beta = \Delta C_{PW}^o - b T_o, \qquad \gamma = \frac{b}{2}. \tag{11b}
$$

Here b is a constant fitted to experimental data (Holder et al., 1988). Using Eqs. 11, 11a, and 11b, Δh_w^o can be obtained from the slope of the graph X vs. Y. ΔC_{pw}^o and b values for Eqs. 11a and 11b are from Holder et al. (1988), and are given in Table 3. This is a universal approach to calculating experimental reference enthalpy differences; the method does not depend upon the assumption of a variable chemical potential difference. Values for Δh_w^o for ethane, krypton, carbon dioxide, and iso-butane hydrates are shown in Figure 2. Values for each hydrate studied is given in Table 4. The fact that different reference enthalpies are obtained from experimental data (Figure 2 and Table 4) strongly suggests that the concept of variable reference properties is valid. (Note that in Eq. 11, two different Δh_w^o values can be obtained from experimental data. One is the enthalpy difference between ice and the theoretical empty hydrate, while the other is that between liquid water and the theoretical empty hydrate. The difference between these two values is 6,011 J/mol·K, the enthalpy change between ice and water at 273.15 K (Holder, 1988), so in practice the experimental data allow the determination of only one independent value for Δh_w^o for each species.

Experimental dissociation pressure data for different species at the ice point can be used to determine if a variable reference chemical potential exists. The experimental pressures suggest that it does. The slope of the experimental pressure-temperature curve determines the reference enthalpy difference, as given by Eq. 10. The experimental pressure temperature data suggest that a variable reference enthalpy difference is appropriate. A variable reference enthalpy can only exist if the chemical potential of the empty hydrate depends upon the guest.

Results and Conclusion

Experimental pressure−temperature hydrate equilibrium data give different reference chemical potential differences and different reference enthalpy differences for each hydrate-forming species. This is consistent with crystallographic data, molecular simulation, and calculated thermal expansivities that appear in the literature for these hydrates, all of which suggest that the hydrate lattice structure is affected by the guest species present. By using the reference chemical potential and enthalpy differences derived from experimental data, an accurate calculation of dissociation pressures for simple gas hydrates is achieved. In this model, a different $\Delta\mu_w^o$ value is obtained for each simple gas hydrate using the assumption that the lattice structure and energy is affected by the guest molecule. Assuming that size was an important consideration in determining the impact of a guest on the

Table 3. ΔC_{pw}^o and b Values for Structure I and II Hydrate

$T_o = 273.15$ K	Structure I	Structure II
ΔV_w (cm^3/mol)	2.9595	3.39644
ΔC_{pw} (cal/mol·K) $T > T_o$	$-9.222 + 0.0452(T - T_o)$	$-9.2879 + 0.04324(T - T_o)$
ΔC_{pw}^o (cal/mol·K) $(T - T_o)$	$0.7923 + 0.0289(T - T_o)$	$0.2459 + 0.000901(T - T_o)$

Source: Holder et al. (1988).
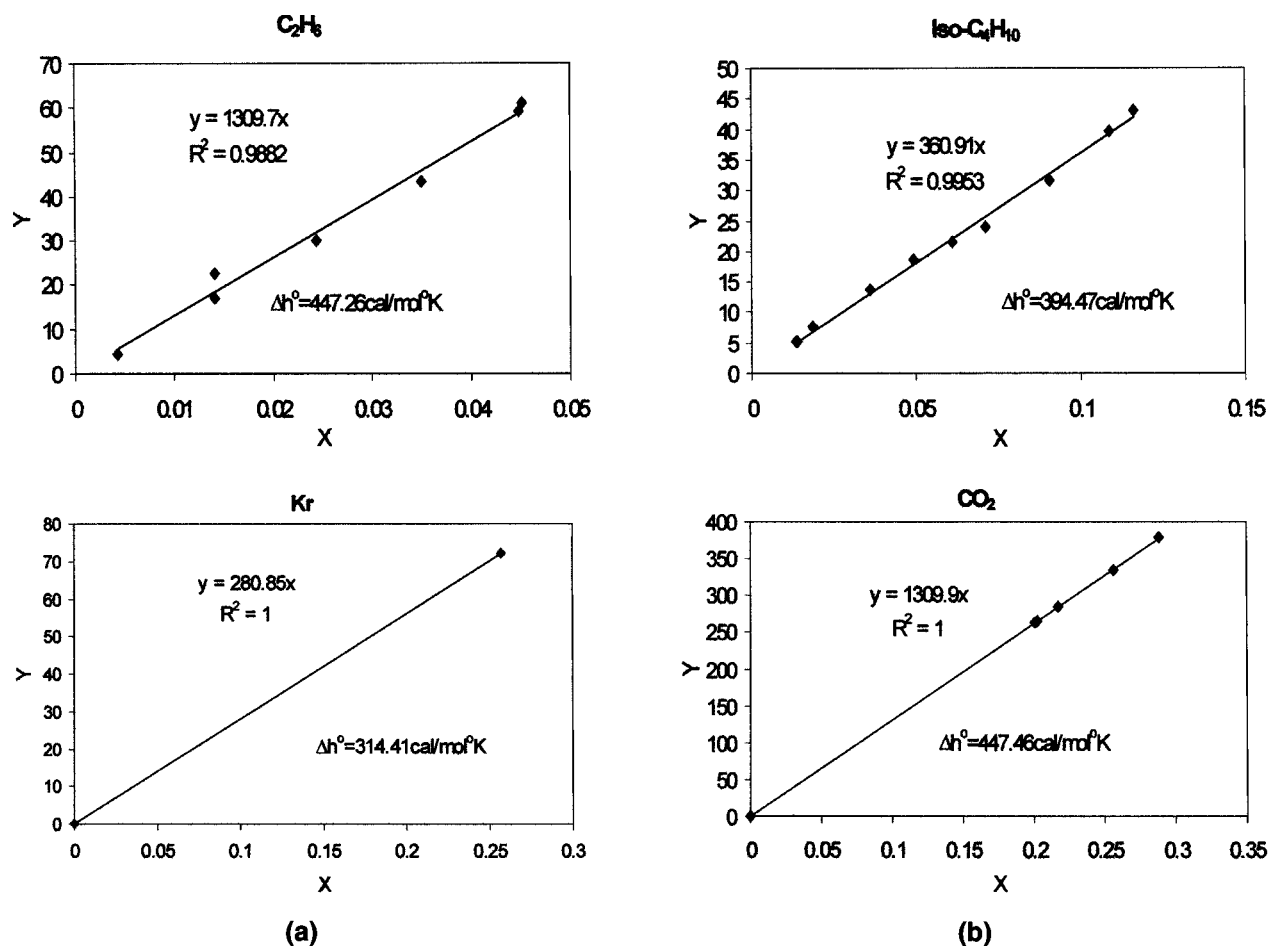*In the liquid water region add 1.6J/mol to ΔV_w.

Figure 2. Δh_w^o Values: (a) ethane hydrate and krypton hydrate; (b) isobutane hydrate and carbon dioxide hydrate.

lattice properties, an attempt was made to correlate the experimentally derived $\Delta\mu_w^o$ with the Kihara size (σ, a) parameters. The relationship with the energy parameters (ϵ) was also examined. The correlation coefficients (R^2 values) or correlations between σ, ϵ, and a and $\Delta\mu_w^o$ are given in Table

5. In this table, the core radius of the guest molecule (or the Kihara hard-core parameter a) has the best correlation with $\Delta\mu_w^o$, as shown in Figure 3. The following correlation equations for gas hydrates structure I and structure II are obtained.

$$\text{Structure I:} \Delta\mu_w^o = 133.39 \exp\left(0.0213 \times a\right), \quad R^2 = 0.9058 \tag{12}$$

$$\text{Structure II:} \Delta\mu_w^o = 171.91 \exp\left(0.0101 \times a\right), \quad R^2 = 0.8810, \tag{13}$$

Table 4. Δh_w^o for Various Gas Hydrates ($T < 273.15$ K)

| | Gas Dia. (A) | Kihara Para. a (pm) | Cavity | | Δh_w^o (cal/mol) |
			Small	Large	
Structure I					
N_2	4.1	34.1	O	O	261.9
CH_4	4.36	26	O	O	335.7
Xe	4.58	25.2	O	O	292.2
H_2S	4.58	49.2	O	O	346.6
CO_2	5.12	67.7	O	O	447.5
C_2H_6	5.5	57.4		O	447.3
Cyclo-C_3H_6	5.8	74.5		O	407.9
Ethylene	6.1	53.3		O	135.7
Structure II					
Ar	3.8	21.7	O	O	393.6
Kr	4	23.2	O	O	314.4
Cyclo-C_3H_6	5.8	65.3		O	286.3
C_3H_8	6.28	74.5		O	339.2
Iso-C_4H_{10}	6.5	85.9		O	394.5

Table 5. Correlation Between Chemical Potential and Individual Kihara Parameters

| Correlating Parameter | Squared Correlation Coefficient, R^2 | |
	Structure I	Structure II
Cavity Diameter	0.353	0.832
σ	0.073	0.898
ϵ	0.679	0.257
a	0.905	0.881

Note: Using the equation $\Delta\mu_w^o = Ae^{BZ}$, where, A and B are constants and Z is the Kihara parameter.
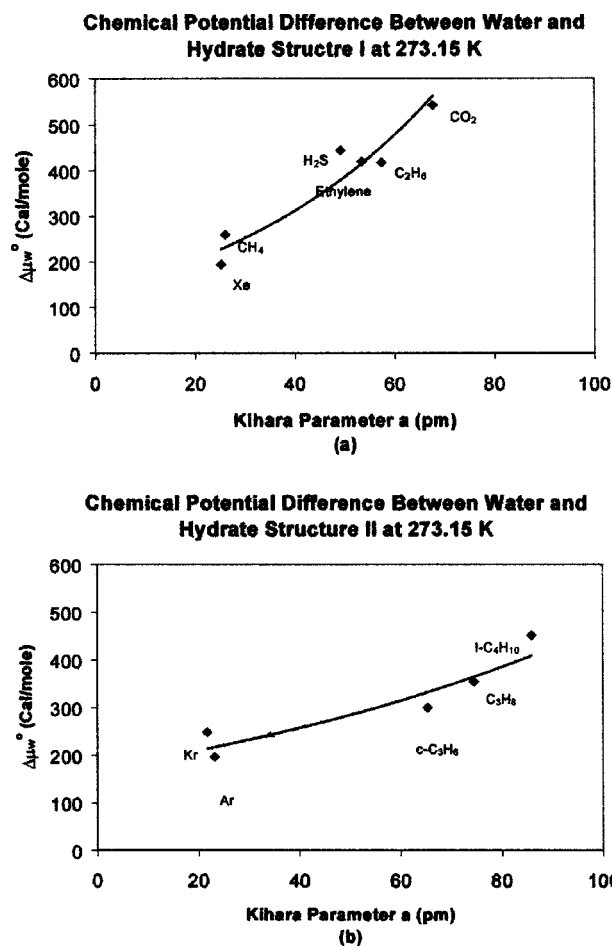
Figure 3. **Changes of chemical potential difference at 273.15 K for various guest gases.**

All experimental data used for optimization are from Sloan (1998).

where, a is the Kihara parameter (pm). By using these correlations, the chemical potential of the empty hydrate appropriate for any guest can be estimated without experiments.

Table 6. Error Comparison

| Guest | Error $(\%) = 100 \times \dfrac{1}{N} \displaystyle\sum_{N} \dfrac{\text{abs}(\Delta\mu_h - \Delta\mu_W)}{\Delta\mu_h}$ | |
	Correction of Δh_w^{o*}	Constant Δh_w^{o**}
Structure I		
CH_4	1.36	1.36
Xe	0.07	5.09
H_2S	0.54	0.70
CO_2	1.01	1.09
C_2H_6	0.73	1.62
Structure II		
Ar	1.03	1.23
Kr	1.40	1.59
N_2	1.47	3.01
C_3H_8	0.32	0.32
i-C_4H_{10}	0.20	0.39

*Error calculation between experimental value and calculated value with optimized $\Delta\mu^o$ for each hydrate.
**Error calculation between experimental value and calculated value with optimized $\Delta\mu^o$ and Δh^o.
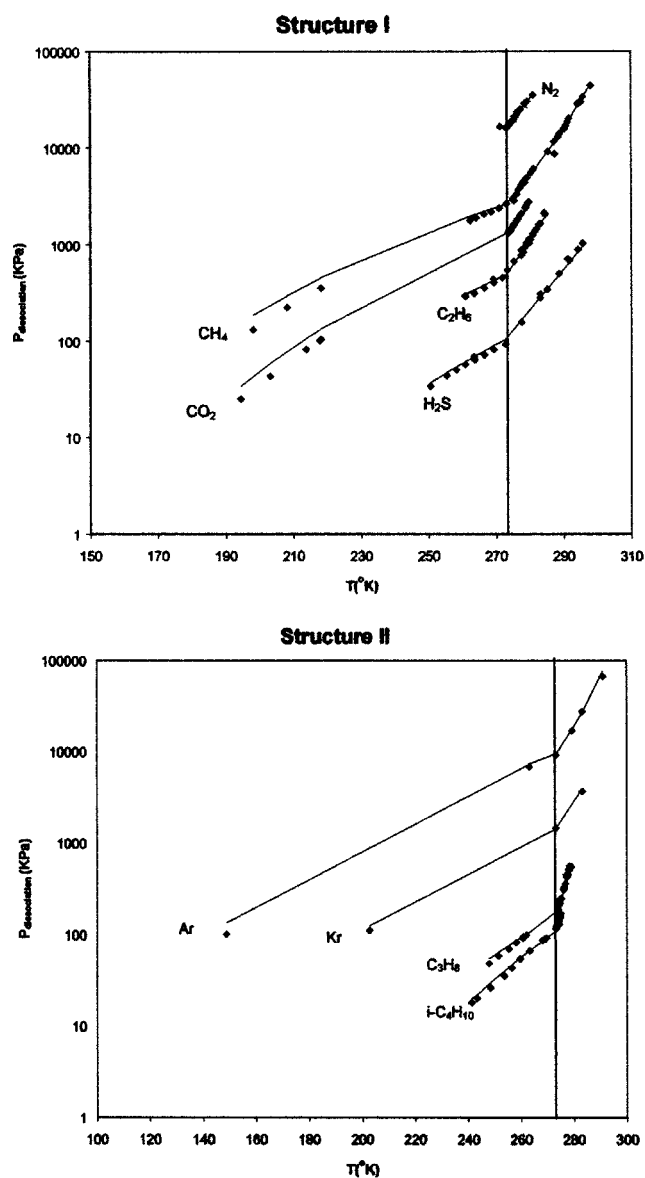
Figure 4. **Calculation Results for Structure I and Structure II Hydrates.**

All experimental data are from Sloan (1998).

From an engineering point of view, this is valuable, for example, in obtaining the values of $\Delta\mu_w^o$ in structure II for guest molecules that normally form structure I (methane). Using the present model, such values will be needed if equilibrium is to be predicted from gas mixtures that contain structure I formers (methane) and structure II formers (propane), since the mixture may form only one structure at most conditions.

The Δh_w^o values for each simple gas hydrate are also obtained. The value of calculation Δh_w^o from experimental data is shown in Table 6. While the intention of this study is to propose a more physically based model, its ability to predict accurate pressures (Figure 4; Table 7) suggests that the model can be accepted for industrial applications. The greatest improvement in predicted dissociation pressures occurs for Kr, N_2, and ethane hydrate.

Table 7. Error Calculation Between Experimental Dissociation Pressure and Calculated Dissociation Pressure

Guest	Temperature Range (K)	Error (%)
Structure I		
N_2	273–282	1.7
CH_4	198–298	7.2
Xe	216–273	2.9
H_2S	251–302	7.1
CO_2	250–282	10.6
C_2H_6	260–285	5.3
$c\text{-}C_3H_6$	245–265, 275–285	7.6
Ethylene	274–297	8.1
Structure II		
Ar	148–288	10.0
Kr	203–283	7.0
$c\text{-}C_3H_6$	265–277	2.1
C_3H_8	248–280	6.0
$i\text{-}C_4H_{10}$	241–275	4.1

Note: $\text{Error (\%)} = \dfrac{\text{abs}(P_{\text{experimental}} - P_{\text{calculated}})}{P_{\text{experimental}}} \times 100.$

Notation

a = Kihara core radius parameter, pm
C_{ij} = Langmuir constant, kPa^{-1}
f = fugacity coefficient
k = Boltzmann constant, $\text{erg} \cdot \text{K}^{-1}$
P = pressure, kPa
R = gas constant
T = temperature, K
X_w = mol fraction of water
W_1, W_2, W_3 = cell potential for first, second, and third cell, $\text{kj} \cdot \text{mol}^{-1}$

Greek letters

Δh_w^o = moral enthalpy difference between the empty hydrate lattice and pure water at 273.15 K and 0 atm, $\text{J/mol} \cdot \text{l}$
$\Delta \mu_w^o$ = difference of chemical potential of water and theoretical empty hydrate at 273.15 K and 0 pressure, J/mol
$\Delta \mu_w^L$ = difference of chemical potential of water in the unoccupied hydrate lattice and in the water, J/mol
$\Delta \mu_w^H$ = difference of chemical potential of water in the unoccupied hydrate lattice and of occupied hydrate, J/mol
ΔC_{Pw} = molar heat-capacity difference between the empty hydrate lattice and pure water phase, $\text{J/mol}^{-1} \cdot \text{K}^{-1}$
ϵ = Kihara intermolecular well-depth parameter, J^{-1}
μ_β = chemical potential of water in the unoccupied hydrate lattice J/mol
γ_w = activity coefficient of water
ν_i = ratio of small or large cavities to water molecules in a unit cell
θ_{ij} = fraction of i-type cavities occupied by a j-type gas molecule
σ = Kihara core-to-core distance parameter, pm

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