Excess Gibbs Potential Model for Multicomponent Hydrogen Clathrates

Sangyong Lee,[†] Prasad Yedlapalli,[‡] and Jae W. Lee*,[‡]

Department of Chemical and Natural Gas Engineering, Texas A&M University, Kingsville, Texas 78363, and Department of Chemical Engineering, The City College of the CUNY, New York, New York 10031

A new thermodynamic calculation procedure is introduced to predict the equilibrium conditions of multicomponent gas hydrates containing hydrogen. This new approach utilizes an excess Gibbs potential term to account for second- or higher-order water-cavity distortions due to the presence of multiple guest species. The excess Gibbs potential describes changes in reference chemical potentials according to different compositions of guest mixtures in the hydrate phase. To determine the equilibrium conditions of multicomponent gas hydrates, the excess Gibbs potential term is incorporated to the Lee−Holder model along with the Zele−Lee−Holder cell distortion model. For binary gas hydrates between hydrogen and the other gas molecule, the predicted equilibrium pressure deviates within 10−20% from the experimental value. For the ternary and quaternary mixture hydrates, the model prediction is reasonably good but its error increases with increasing pressure and temperature under the presence of THF.

1. Introduction

Gas hydrates are crystalline compounds, also known as clathrates. Their general formula is $(G)_n(H_2O)_p$ where G is Gas, n is the number of gas molecules, and p is the number of water molecules physically associated with gas molecules. Hydrogen forms structure-II gas hydrates with 136 water molecules and 24 cavities per unit cell. Those 24 cavities consist of 16 small cavities and 8 large cavities. Although 12 pentagonal faces (D-5^{12}: dodecahedron) make one small cavity, 12 pentagons and 4 hexagons (H-$5^{12}6^4$: hexakaidecahedron) make one large cavity. It was confirmed experimentally[1] that the gas hydrate contains 61 ± 7 hydrogen molecules per unit cell and the general formula of hydrogen hydrates is $H_2(H_2O)_2$. Two hydrogen molecules are stably enclathrated in a small cavity, and four hydrogen molecules are stably enclathrated in a large cavity.[1,2]

Around 50 g of hydrogen gas molecules can be held in one liter of solid water cavities (5.0 wt %) in the form of hydrates.[3] It is synthesized at 2000−3000 bar and 240−249 K and can be preserved at 140 K under ambient pressure.[1] Because of this excellent storage capacity, H_2 hydrates can be used as a storage medium to secure the supply of H_2. However, this technique can be economically competitive and widely applied only if H_2 hydrates are formed at lower pressures. Two research institutes recently synthesized a low-pressure H_2 hydrate combined with THF (tetra-hydrofuran) hydrates around 50 bar and 280 K,[4] and 120 bar and 270 K.[5] The design of hydrogen storage in clathrates requires an accurate prediction of dissociation pressures with temperature. However, no general thermodynamic model has been available for determining the phase equilibrium conditions of hydrogen-containing multicomponent hydrates. This is a very important task in minimizing the storage pressure of hydrogen in clathrates and in maximizing hydrogen density by optimizing the composition of any promoter.

We have proposed multiscale modeling for pure hydrogen hydrates by combining ab initio calculations and statistical thermodynamics.[6] By extending the previous study, this work will develop a new calculation procedure to predict low-pressure hydrogen hydrate equilibria with hydrate-forming gas mixtures including a promoter (THF). The key idea of this article is the incorporation of excess Gibbs potential terms into the Zele−Lee−Holder and the Lee−Holder cell distortion models[7−9] in order to consider second-order or higher-order cavity distortions due to the presence of multicomponents in cavities. We will first introduce a new multicomponent excess Gibbs potential model and propose a new thermodynamic calculation procedure. Here, we will assume that the first-order cavity distortion due to a single gas molecule is more dominant than the second-order distortion due to binary gas mixtures and the second-order distortion dominates over higher-order cavity distortion of ternary or quaternary guest mixtures. We will apply this new excess Gibbs potential model to binary, ternary, and quaternary gas hydrates formed from mixtures of hydrogen and other molecules such as THF, propane, ethane, and methane.

2. New Excess Gibbs Potentials for Mixture Hydrates

Water cavity distortion is the change of host water cavity size due to guest gas molecules. It was reported in X-ray diffraction and neutron scattering experiments.[10−12] The cavity distortion may come from the attractive and repulsive forces between host water molecules and guest gas molecules according to guest molecules' size, shape, and polarity. This cavity distortion is directly related to the change of water chemical potential and has been reflected in the change of the reference chemical potential difference (RCPD) with respect to different gas guest molecules by Holder and his colleagues.[7−9,13] They proposed cavity distortion models of single gas components[7−8] and binary gas mixtures.[9] They use the assumption that the hydrate cavity would be distorted due to the size of the gas molecule in it. From molecular dynamic simulations, Zele et al.[7] determined a correlation between cavity radius and RCPD.

* Corresponding author. 140th Street and Convent Ave, Department of Chemical Engineering, The City College of the CUNY, New York 10031. Tel: 212-650-6688. Fax: 212-650-6660. E-mail: lee@che.ccny.cuny.edu.
† Texas A&M University.
‡ The City College of the CUNY.

Excess Gibbs Potential Model

J. Phys. Chem. B, Vol. 110, No. 51, 2006 **26123**

In this work, we aim at generalizing the water cavity distortion arising from the occupancy of multicomponent mixtures in the cavity. Here, we call the cavity distortion of a single guest hydrate the first-order (or primary) distortion, whereas that of the binary gas hydrate is called the second-order (or secondary) distortion, and those of more than two species are called the third- or higher-order distortion. If there are no second- and higher-order cavity distortions, then the ideal mixing rule gives the reference chemical potential difference (RCPD) of water in eq 1[9]

$$\Delta\mu_{mix}^{o,ideal} = \sum_i \Delta\mu_i^o Z_i \qquad (1)$$

where Z_i is the water-free mole fraction of a guest component in the hydrate phase and $\Delta\mu_i^o$ is the water RCPD that is the result of the primary distortion due to the presence of pure component i in the water cavity.

However, real mixtures have an excess Gibbs energy contribution due to second- and higher-order cavity distortions. Thus, the change in the RCPD for mixture hydrates can be given by

$$\Delta\mu_{mix}^o = \Delta\mu_{mix}^{o,ideal} + \Delta\mu_{mix}^{o,excess} \qquad (2)$$

Our central assumptions of excess RCPD changes ($\Delta\mu_{mix}^{o,excess}$) from the third- or higher-order distortion in multicomponent hydrates are the following: (1) The RCPD change from third- or higher-order distortion is much smaller than that from the second-order distortion, and (2) the excess RCPD of a multicomponent system can be expressed as the combination of that of each binary mixture. These two assumptions tell us that we can use the linear combination of binary excess Gibbs potential terms for describing second- or higher-order distortion as given by eq 3

$$\Delta\mu_{mix}^{o,excess} = \sum_{i=1}^{c-1}\sum_{j=i+1}^{c} P_{ij}\Delta\mu_{mix,ij}^{o,excess} = \sum_{i=1}^{c-1}\sum_{j=i+1}^{c} P_{ij}(A_{ij} + B_{ij}(Z_i - Z_j))Z_i Z_j \quad (3)$$

where A_{ij} and B_{ij} are interaction parameters between components i and j and are experimentally determined and P_{ij} is the probability term that is given by

$$P_{ij} = \frac{Z_i Z_j}{\sum_{i=1}^{c-1}\sum_{j=i+1}^{c} Z_i Z_j} \qquad (4)$$

The probability terms (P_{ij}'s) differentiate the dominance of binary guests i and j according to their compositions in the hydrate phase. It should be noted that there is no P_{ii} term (i.e., P_{11} or P_{22}) in eq 4 because P_{ii} is related to cavity distortion due to a single guest molecule and its effect is already considered in the primary distortion.[8] For binary guest mixtures, the number of components (c) is equal to 2. Then, P_{12} (or P_{21}) is equal to 1 in eq 4. Thus, the following equation describes excess water RCPD due to binary guest mixtures:

$$\Delta\mu_{mix}^{o,excess} = Z_1 Z_2\{A_{12} + B_{12}(Z_1 - Z_2)\} \qquad (5)$$

3. New Simulation Procedure for Multicomponent Mixture Hydrates

To generalize the simulation procedure for determining equilibrium conditions, we incorporate the new excess chemical
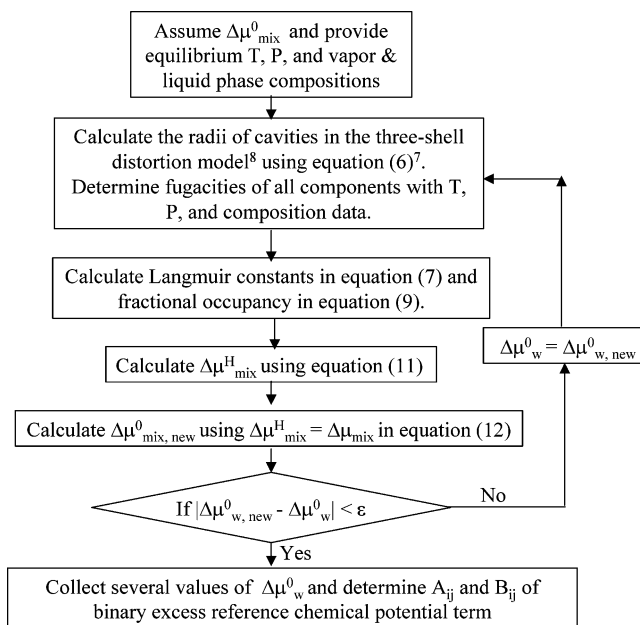

Figure 1. Flowchart for determining the binary parameters in excess reference chemical potential difference.

potential term of the previous section to the Lee−Holder Model.[8−9] The Zele−Lee−Holder correlation[7] is used to update cavity diameters according to the RCPD changes.

3.1. Estimation of Binary Parameters in Excess Reference Chemical Potential Difference (RCPD). The determination of binary interaction parameters (A_{ij} and B_{ij}) requires an initial guess of $\Delta\mu_{mix}^o$ and experimental values of temperature, pressure, and vapor- and liquid-phase compositions of guest mixtures as shown in Figure 1. From the initial guess of $\Delta\mu_{mix}^o$, we calculate the three-shell radii of small and large cavities of structure-I and -II hydrates by using the following equation:[7]

$$R = \alpha + \beta\Delta\mu_{mix}^o \qquad (6)$$

where R is a cavity radius and parameters α and β are available in Lee and Holder (2001)[8] for all three shells.

The calculated cavity radii in eq 6 are used to determine the Langmuir constants that are given by

$$C_{ij} = \frac{1}{kT}\int_{V_{cell}}\exp\left\{\frac{-[W_1(r) + W_2(r) + W_3(r)]}{kT}\right\}dV \quad (7)$$

where C_{ij} is a Langmuir constant of component j in an i-type water cavity and $W_1(r)$, $W_2(r)$, and $W_3(r)$ are the smooth cell potentials for the first, second, and third shells.[14] We will use their analytical forms that were derived from the corresponding pair potential models.[6,15]

Experimental data of temperature, pressure, and compositions are used to calculate the fugacity of individual components in the vapor and liquid phases. The gas-phase fugacity of each component in the mixture is determined by the Peng−Robinson Equation of State.[16] The liquid-phase fugacity for component j (i.e., THF) is calculated using the following equation[17−18]

$$f_j = x_j\phi_j P \qquad (8)$$

where x_j is the liquid mole fraction of component j, ϕ_j is the fugacity coefficient of component j in the liquid phase, and P is the system pressure.

Using the Langmuir constants and the fugacity of all of the components, we can determine the fractional occupancy of guest

26124 *J. Phys. Chem. B, Vol. 110, No. 51, 2006*

Lee et al.

components that is given by

$$\theta_{ij} = \frac{C_{ij}f_j}{1 + \sum_j C_{ij}f_j} \tag{9}$$

where θ_{ij} is the fractional occupancy of component j in water cavity i. The hydrate phase composition for component j (Z_j) is calculated by normalizing fractional occupancy with respect to the sum of fractional occupancies in small and large cavities.

$$Z_j = \frac{\sum_i \nu_i \theta_{ij}}{\sum_j \sum_i \nu_i \theta_{ij}} \tag{10}$$

All fractional occupancies of guest components are used to calculate the chemical potential difference of water in the hydrate phase as given in eq 11[19]

$$\Delta\mu_{mix}^H = -RT \sum_{i=1}^{2} \nu_i \ln(1 - \sum_j \theta_{ij}) \tag{11}$$

where ν_i is the number of i-type cavities per water molecule.

At equilibrium, this hydrate phase chemical potential difference is equal to the water (or ice) phase chemical potential difference that is given[20] by

$$\frac{\Delta\mu_{mix}}{RT} = \frac{\Delta\mu_{mix}^o}{RT_o} - \int_{T_o}^{T} \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta V_w}{RT} dP - \ln\gamma_w x_w \tag{12}$$

The first term on the right-hand side is the reference chemical potential difference between the theoretical empty hydrate and liquid water at its reference state (273.15 K, 0 Pa). The second and the third terms are the changes in the chemical potential difference due to changes in temperature and pressure, respectively. The necessary parameters (Δh_w and ΔV_w) in the second and third terms are available in the literature.[21] Here, we use an ideal mixing rule for the reference enthalpy difference (Δh_w^o) of water in the guest mixture when integrating the second term. The last term is the chemical potential change due to the solubility of gas and organic component (i.e., THF) in the water phase. The water activity coefficient (γ_w) is determined by the NRTL (non-random-two-liquid) model.[22] At equilibrium, $\Delta\mu_{mix}^H$ is equal to $\Delta\mu_{mix}^H$ and all the other terms in eq 12 are calculated except $\Delta\mu_{mix}^o$. Thus, we can determine $\Delta\mu_{mix}^o$ and iterate until we have a converged solution as shown in Figure 1. Once several values of $\Delta\mu_{mix}^o$ are obtained over different binary hydrate compositions, we determine A_{ij} and B_{ij} coefficients in the binary excess reference chemical potential term of eq 3 or 5.

3.2. Prediction of Equilibrium Conditions for Binary and Multicomponent Hydrates. The previously determined binary parameters (A_{ij} and B_{ij}) are used to estimate the excess RCPD of multicomponent hydrates in eq 3 and finally to determine equilibrium pressures for given temperatures. The same procedure can be used to determine equilibrium temperatures for given pressures. The calculation procedure is as follows:

(1) For given temperature and gas- and liquid-phase compositions with A_{ij} and B_{ij}, we make an initial guess of pressure (P) and RCPD ($\Delta\mu_{mix}^o$).
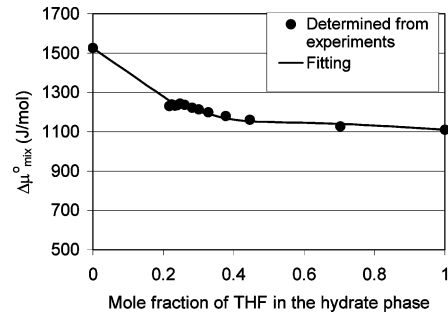

Figure 2. RCPD of the THF$-$H$_2$ mixture determined by Sloan and co-workers' data[4,26] and Lee's data.[5]

TABLE 1: Reference Parameters of Pure Hydrates Determined by Three-Shell Distortion

component	structure	$\Delta\mu_i^0$ (J/mol)	Δh_i^0 (J/mol)
H$_2$	II	1527.81[1,6]	733.4644[1,6]
THF	II	1109.998[25]	1400.00[21]
CH$_4$	II	1810.995[a]	1404.569[8]
CH$_4$	I	1218.421[17]	1404.569[8]
C$_2$H$_6$	II	1486.589[a]	1871.503[8]
C$_2$H$_6$	I	1780.247[17]	1871.503[8]
C$_3$H$_8$	II	1689.509[17]	1419.213[8]

[a] Optimized values from CH$_4-$C$_3$H$_8$ and C$_2$H$_6-$C$_3$H$_8$ binary dissociation pressure data.[17,26]

(2) Calculate cavity radii in eq 6 and fugacity of all guest components using the Peng$-$Robinson EOS and eq 8. Then, determine the Langmuir constants in eq 7 and the fractional occupancies of all guest species in eq 9.

(3) From fractional occupancies, calculate the hydrate phase composition of all guest components and then update $\Delta\mu_{mix}^o$. From the $\Delta\mu_{mix}^o$, recalculate the cavity radii and the Langmuir constants.

(4) Determine the hydrate phase chemical potential difference in eq 11 and equate this to eq 12. Then determine a new value of equilibrium pressure. If the difference between this pressure and the initial guess (or previous pressure) is not within tolerance limit, then go to step 2 and iterate until the difference is less than the tolerance. Otherwise, finish the iteration with a final equilibrium pressure.

4. THF$-$H$_2$ Binary Hydrates

THF enters only the large cavities of structure-II clathrates,[23] whereas H$_2$ can enter both small and large cavities with occupancies of 2 and 4, respectively.[1-5] The 2H$_2$ or 4H$_2$ molecules in the cavities are treated as a single rigid cluster and the corresponding Exp-6 potential parameters between water and each H$_2$ cluster are available in our previous work.[6] Table 1 shows the RCPD ($\Delta\mu^o$) and the reference enthalpy difference (Δh^o) for pure hydrates that are estimated using experimental data from the previous literature indicated in the table. We use the Lennard-Jones potential form for THF ($\sigma = 5.08$ Å and $\epsilon/k = 519$ K) in the literature[24] and its smooth cell potential form [$W(r)$] can be derived by letting the core radius of the Kihara potential be equal to zero. The three-shell cavity distortion model[8,14] also estimates the RCPD of the pure THF hydrate as 1109.998 J/mol using an equilibrium temperature of 277.65 K at 1 atm[25] and a standard value of $\Delta h^o = 1400$ J/mol.[21]

By following the procedure in the previous section (Section 3.1), we determine the RCPD ($\Delta\mu_{mix}^o$) of THF$-$H$_2$ binary hydrates using the experimental temperature and pressure[4,5,26] as shown in Figure 2. Here, the solubility of H$_2$ in the aqueous phase is ignored (i.e., $x_W = 1 - x_{THF}$). A_{12} and B_{12} are estimated

Excess Gibbs Potential Model

J. Phys. Chem. B, Vol. 110, No. 51, 2006 **26125**

| Tempature	Pressure	Prediction	Fractional Occupancy			H2 wt%
(K)	EXP (MPa)	(MPa)	2H2(small)	4H2(large)	THF(large)	(storage)
278.00	0.83	1.29	0.1545	0.0001	0.9998	0.40
279.00	3.21	2.52	0.2607	0.0003	0.9996	0.68
279.51	5.00	4.00	0.3579	0.0005	0.9994	0.94
280.30	7.50	6.26	0.4644	0.0009	0.9990	1.22
281.13	10.00	8.82	0.5481	0.0013	0.9986	1.44
281.90	12.50	11.32	0.6079	0.0017	0.9981	1.59
283.20	17.50	15.96	0.6852	0.0025	0.9973	1.80
284.50	22.50	21.27	0.7436	0.0034	0.9965	1.95
286.00	27.00	28.45	0.7963	0.0044	0.9954	2.09
287.00	31.00	33.99	0.8250	0.0051	0.9947	2.17
289.00	42.50	47.30	0.8715	0.0064	0.9935	2.30
291.00	54.00	64.39	0.9073	0.0074	0.9925	2.39
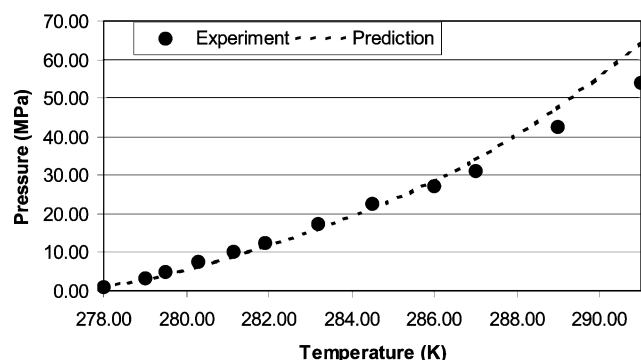
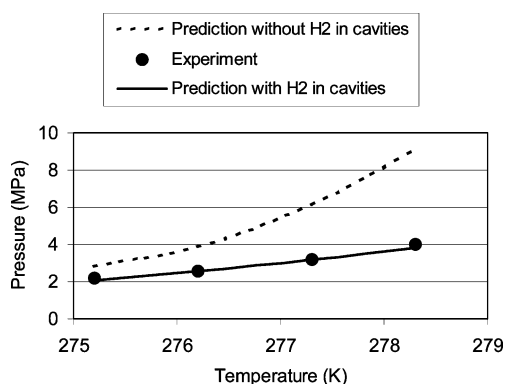**Figure 3.** Equilibrium of the THF−H$_2$ hydrate determined from experiments[4,5,26] and prediction.

Figure 4. Equilibrium of the C$_3$H$_8$−H$_2$ hydrate from experimental data[28] and prediction.
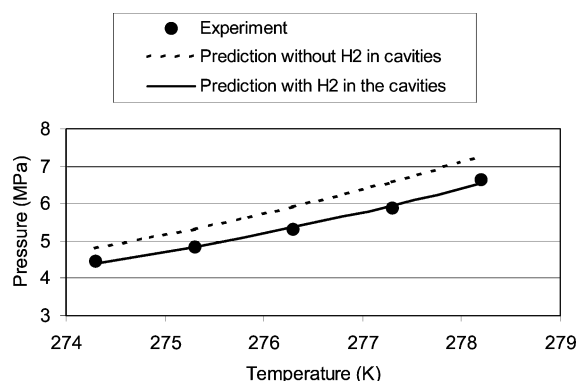

Figure 5. Equilibrium of the CH$_4$−H$_2$ hydrate from experimental data[28] and prediction.

as −698.8684 J/mol and 614.6900 J/mol by fitting these values of $\Delta\mu^o_{mix}$ to eq 5 as shown in Table 2. Figure 2 shows a good fit of the curve and its correlation coefficient is 0.945.

Equation 5 with the values of A_{12} and B_{12} is used to predict equilibrium pressure for given temperatures as described in Section 3.2. Figure 3 shows that the predicted pressure deviates from the experimental values by 10% but its error increases to
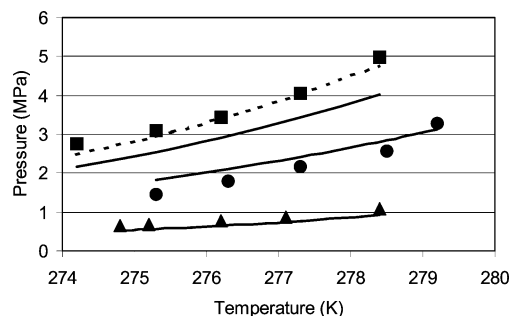

Figure 6. Equilibrium prediction for the H$_2$−CH$_4$−C$_3$H$_8$ and H$_2$−CH$_4$−C$_2$H$_6$−C$_3$H$_8$ hydrates. H$_2$, C1, C2, and C3 in the vapor phase: filled triangle - 44.89, 30.3, 0.0, and 24.81 mol %;[28] filled circle - 79.14, 12.37, 3.58, and 4.91 mol %;[28] filled square - 92.11, 2.79, 0.0, and 5.1 mol %.[28] Solid lines, prediction with P_{ij}; dotted line, prediction without P_{ij}.

TABLE 2: Binary Parameters in Equation 5 for Several Binary Hydrates

components i and j	structure	A_{ij} (J/mol)	B_{ij} (J/mol)	correlation coeff (R^2)
THF−H$_2$[4,5,26]	II	−698.868	614.690	0.945
THF−CH$_4$[29]	II	1231.927	1493.779	0.899
C$_3$H$_8$−H$_2$[28]	II	437.222	−415.802	0.800
H$_2$−CH$_4$[28]	I	25095.23	28132.02	0.993
C$_3$H$_8$−CH$_4$[17]	II	15.01	−408.471	0.817
C$_3$H$_8$−C$_2$H$_6$[27]	II	408.1921	−603.659	0.886

20% when the temperature reaches 291 K. In this calculation, we allow the hydrogen clusters to enter both small and large cavities to see whether the proposed calculation procedure predicts the fractional occupancies of H$_2$ and THF correctly. With the THF mole fraction of 0.056 and 0.048 in the aqueous phase,[4−5] the fractional occupancy of H$_2$ is much less than 1% in the large cavity and most of THF occupies the large cavity as shown in Figure 3. It represents the previous experimental results correctly[4−5] because hydrogen molecules hardly enter the large cavity when the THF mole fraction in the aqueous phase is higher than 0.02. The H$_2$ storage density is also shown in Figure 3. Because THF mostly occupies the large cavity, its maximum storage capacity is around 2 wt % under 5.6 and 4.8 mol % of THF in the aqueous solution. This is the same result observed in the previous experimental works.[4−5]

5. Other Binary Hydrates

In this section, we estimate the binary parameters of the excess RCPD of other binary hydrates because our final goal is to predict the multicomponent hydrates' equilibrium conditions using eq 3. Table 1 shows the reference values of pure hydrates, and Table 2 shows the binary parameters (A_{ij} and B_{ij}) for binary hydrates using experimental values.[4,5,17,26,27−29] For the binary hydrates between H$_2$ and the other guest molecule, experimental temperature and pressure data with respect to different gas compositions are available in the recent literature.[4,5,26,28−30]

One important question here is whether hydrogen molecules stay only in the gas phase or if they can enter the small and large cavities of structure-II clathrates together with a second guest component under a reasonable pressure (1−10 MPa). The experimental proof of hydrogen's occupancy together with THF in the cavities is given by Florusse et al. (2004)[4] and then by Lee et al. (2005).[5] In the early eighties, Holder et al. (1983)[30] synthesized hydrates with a hydrogen-rich gas containing H$_2$ (78.4 mol %) and light hydrocarbons. At that time, it was not
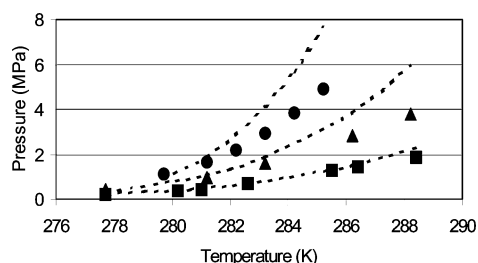
Figure 7. Equilibrium prediction for the H_2-CH_4-THF hydrates with 6 mol % of THF in the aqueous phase without P_{ij} terms. H_2 and C_1 in the vapor phase: filled square - 34.74 and 65.26 mol %;[29] filled triangle - 69.71 and 30.29 mol %;[29] filled circles - 89.13 and 10.87 mol %.[29]

Figure 8. Equilibrium of the H_2-CH_4-THF hydrates. H_2 and C1 in the vapor phase: filled triangle - 69.71 and 30.29 mol %.[29]

sure that hydrogen molecules could enter the cavities and no potential models were available for hydrogen hydrates. However, Zhang et al. (2000, 2005)[28-29] argued based on their experiments that hydrogen molecules could enter the cavities of structure-II clathrates. They reported that when light hydrocarbons form hydrates with hydrogen gas the fugacity of the hydrocarbon in the mixture is usually lower than that of pure hydrocarbon at given temperature and pressure. Thus, this lowered fugacity can give a lower fractional occupancy of the hydrocarbon and can provide room for hydrogen molecules to enter the cavities.

Figure 4 shows the experimental data[28] of a gas mixture of H_2 and C_3H_8 with two sets of calculation results. One prediction result (dotted line) is obtained with no hydrogen in the cavity and the other prediction (solid line) uses the excess RCPD in eq 5 with hydrogen being present in the cavity of structure II. It is clear from these results that the former prediction is much worse than the latter and hydrogen molecules can enter the cavities.

This is also true of the CH_4 and H_2 mixture. Figure 5 shows one set of experimental data[28] and the two predictions by assuming structure-I clathrate: the dotted line is without hydrogen in the cavity, and the solid line is with hydrogen being allowed to enter the small cavity of structure-I clathrate using the binary parameters in Table 2. Note that the small cavity is the same dodecahedron for both structure I and structure II. Thus, the only place that hydrogen molecules enter is the small cavity if structure I is assumed for the H_2-CH_4 mixture.
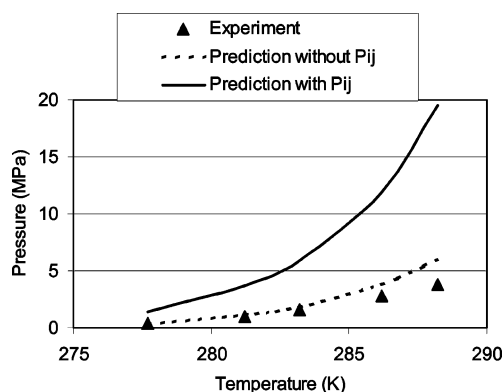
Now, another important question is how to ascertain that structure I goes with the H_2-CH_4 mixture rather than structure II. Because H_2 forms structure-II hydrates,[1-5] we are not completely sure that the binary mixture forms structure-I clathrates. One possible way to determine the binary hydrate structure is to first estimate RCPDs using experimental data and to compare these values to the ideal mixing rule. If the estimated RCPD seriously deviates from the values estimated by the ideal mixing rule in eq 1, then the second-order cavity distortion is allowed more significantly than it is. If we calculate the difference between experimentally estimated RCPD and the RCPD from the ideal mixing rule ($|\Delta\mu^o_{mix,experimental} - \Delta\mu^o_{idealmixing}| = |\Delta\mu^{o,excess}_i|$), then the lower difference could give a preferable hydrate structure. Using the experimental data,[28] the structure-I case for the binary mixture gives a $\Delta\mu^o_{mix,experimental}$ of 1183 to 1208 J/mol and a $\Delta\mu^o_{idealmixing}$ of 1221 to 1225 J/mol (by using $\Delta\mu^o_i = 1527.81$ for hydrogen) with the methane mole fraction of 0.98 to 0.99 in the hydrate phase. If we assume structure II for the binary mixture, then the experimental data[28] gives a $\Delta\mu^o_{mix,experimental}$ of 1025 to 1037 J/mol and a $\Delta\mu^o_{idealmixing}$ of 1780 to 1797 J/mol with the methane mole fraction of 0.89 to 0.95 in the hydrate phase. The excess RCPD ($|\Delta\mu^{o,excess}_{mix}| = |\Delta\mu^o_{mix,experimental} - \Delta\mu^o_{idealmixing}|$) in structure I is at largest 40 J/mol, whereas that in structure II is 760 J/mol. It means that the second-order distortion is much higher in structure II than structure I and occurs abnormally. Thus, structure I may be preferred for the H_2-CH_4 binary mixture.

TABLE 3: Prediction of Ternary and Quaternary Hydrate Equilibria

cases: gas mol % $H_2/CH_4/C_2H_6/C_3H_8$	temp (K)	pressure (MPa)		$\Delta\mu^o_{mix}$ (J/mol)	$\Delta\mu^{excess}_{ij}$ (J/mol)			probability (P_{ij})		
		exptl[28]	pred		C3−H2	C3−C1	C3−C2	C3−H2	C3−C1	C3−C2
44.89/30.3/ 0.0/24.81	274.8	0.65	0.53	1725.14	5.61	−8.91	N/A	0.092	0.839	N/A
	275.2	0.68	0.56	1726.79	5.76	−7.68		0.092	0.836	
	276.2	0.77	0.66	1730.61	6.14	−4.76		0.094	0.828	
	277.1	0.88	0.76	1733.68	6.47	−2.36		0.095	0.821	
	278.4	1.08	0.92	1737.53	6.94	0.76		0.098	0.810	
92.11/2.79/ 0.0/5.10	274.2	2.74	2.15	1686.51	69.38	−8.75	N/A	0.587	0.235	N/A
	275.3	3.08	2.55	1685.76	72.96	−7.75		0.584	0.226	
	276.2	3.43	2.92	1684.96	75.56	−7.00		0.582	0.219	
	277.3	4.04	3.43	1683.79	78.37	−6.17		0.580	0.210	
	278.4	4.98	4.02	1682.43	80.80	−5.43		0.578	0.202	
79.14/12.37/ 3.58/4.91	275.3	1.46	1.84	1708.60	26.31	−2.84	0.46	0.254	0.515	0.010
	276.3	1.78	2.11	1708.80	27.39	−1.68	0.48	0.256	0.503	0.010
	277.3	2.16	2.42	1708.81	28.44	−0.66	0.49	0.257	0.491	0.010
	278.5	2.57	2.85	1708.59	29.69	0.40	0.50	0.260	0.477	0.009
	279.2	3.28	3.12	1708.35	30.42	0.93	0.50	0.261	0.469	0.009

Excess Gibbs Potential Model

J. Phys. Chem. B, Vol. 110, No. 51, 2006 **26127**

6. Multicomponent Hydrates

Using the parameters of binary hydrates in Table 2, eqs 3 and 4 can now predict the equilibrium condition of multicomponent hydrates. Figure 6 compares two predictions of ternary $H_2-CH_4-C_3H_8$ mixtures and one prediction of $H_2-CH_4-C_2H_6-C_3H_8$ quaternary mixture with experimental data.[28] structure II (sII) is used for the determination of ternary and quaternary hydrate equilibria because pure H_2 and most of the $C_3H_8-CH_4$ mixture form sII hydrates[27] and the $C_3H_8-C_2H_6$ binary mixture forms sII when the mole fraction of C_3H_8 in the vapor is more than 0.19.[27] For these multicomponent mixtures, we do not use the binary parameters (A_{ij} and B_{ij}) of H_2-CH_4, $H_2-C_2H_6$, and $CH_4-C_2H_6$ because there are no experimental data for structure-II clathrates to estimate these parameters. Figure 6 shows that the predictions of ternary $H_2-CH_4-C_3H_8$ are reasonably good with a maximum error of 20% of the equilibrium pressure. When a relatively small amount of H_2 is present in the gas phase (44.89%), the prediction result is excellent over the entire range of temperature and pressure. However, if the H_2 mole fraction increases to 92.11% in the vapor phase, then the prediction deviates by 20% of the experimental values. From the excess reference chemical potential difference in Table 3, it is obvious that the second-order distortion and its probability (P_{ij}) increases due to the $C_3H_8-H_2$ binary mixture as the hydrogen concentration increases in the vapor.

Because the binary parameters (A_{ij} and B_{ij}) of H_2-CH_4, $H_2-C_2H_6$, and $CH_4-C_2H_6$ are not available for the sII hydrate, the excess RCPD terms are reduced too much by multiplying the probability terms. This is reflected in Figure 6. If we do not use P_{ij} terms in eq 3 (i.e., $P_{ij} = 1$), then the prediction is much improved for the case of 92.11 mol % of H_2 as shown in Figure 6. The prediction for the other two cases without P_{ij} terms is nearly the same as the prediction with P_{ij} terms because the distortion is not so large in terms of the small excess RCPD terms.

Figure 7 compares the prediction results of H_2-CH_4-THF ternary hydrate equilibria with experimental data[29] when the mole fraction of THF in the aqueous phase is equal to 6%. Here, we also use the sII clathrates for the determination of equilibrium conditions because THF molecules only enter the large cavity of the sII clathrates.[23] The gas and THF solubility in aqueous solution is rigorously calculated using the commercial software called AspenPlus.[31] This prediction uses only two excess RCPD terms (THF$-H_2$ and THF$-CH_4$) without P_{ij} terms. The prediction is relatively good for the first case of low H_2 concentration (34.74%) in the vapor and for lower temperature in all cases. However, the prediction error increases as the H_2 mole fraction and temperature increases. The prediction error in pressure is very high for all cases when the probability terms (P_{ij}) are used. Figure 8 shows one case of the mole percent of H_2 equal to 69.71%. The excess RCPD is between -123 and -164 J/mol with P_{ij} being used (solid line) and between -162 and -356J/mol without P_{ij} being used (dotted line). Thus, if any of the binary parameters are not available, then our computational experience tells us that it is more feasible not to use the probability terms for reasonable predictions at least for H_2 with light hydrocarbons and THF.

7. Conclusions

We have proposed an excess Gibbs potential model to account for changes in RCPDs due to the water cavity distortion of multicomponent hydrates. A primary assumption is that the second-order distortion by binary guest components is much higher than higher-order distortions and the linear combination of second-order distortions can represent all of the higher-order distortions. The cavity distortion is reflected in the change of reference chemical potential differences that is a function of guest component composition in the hydrate phase. These reference chemical potential differences relate to the cavity radius change in the Zele$-$Lee$-$Holder model and are incorporated to the Lee$-$Holder model to predict multicomponent hydrogen hydrate equilibria. The prediction is quite good within a maximum deviation of 30% from experimental values. One possible source of error comes from our assumption of the dominance of second-order distortion and we may need to include higher-order distortions to improve the accuracy of prediction. The other error source is the absence of binary parameter data for binary mixtures in the structure-II cavity (i.e., H_2-CH_4, $H_2-C_2H_6$, etc.). However, this new thermodynamic procedure reasonably predicts equilibrium conditions and is applicable to the design of low-pressure H_2 storage in clathrates under mixtures or a promoter.

Nomenclature

C_{ij}	Langmuir constant for component j in cavity i
f_j	fugacity of gas component j
k	Boltzmann constant, 1.38×10^{-23} J/ K
P	system pressure, Pa
P_{ij}	Probability of occupancy of components i and j in eq 4
T	absolute temperature, K
R	cavity radius, Å in eq 6, gas constant (8.314 J/mol K) in eq 12
W_1, W_2, W_3	first, second, third smooth cell potential, J
x_j	liquid mole fraction of component j
x_w	water mole fraction in liquid phase

Greek Letters

α, β	parameters in eq 6
γ_w	water activity coefficient in liquid phase
$\Delta\mu^o_{mix}$	water reference chemical potential difference of mixture hydrate, J/mol
$\Delta\mu^o_i$	water reference chemical potential difference of pure hydrate of component i, J/mol
$\Delta\mu^H_{mix}$	chemical potential difference of water in hydrate phase, J/mol
$\Delta\mu_{mix}$	chemical potential difference of water in liquid or ice phase, J/mol
Δh_w	molar enthalpy difference of water, J/mol
ΔV_w	molar volume difference of water, m³/mol
ϕ_j	fugacity coefficient of component j in the liquid phase
v_i	number of i-type cavities per water molecule
θ_{ij}	fractional occupancy of i-type cavities with j-type molecules

Abbreviation

RCPD	reference chemical potential difference

References and Notes

(1) Mao, W. L.; Mao, H. K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. *Science* **2002**, *297*, 2247.

(2) Patchkovskii, S.; Tse, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **2003,** *100*, 14645.

(3) Mao, W. L.; Mao, H. K. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 708.

(4) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. *Science* **2004**, *306*, 469.

(5) Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H. I.; Moudrakovski, L.; Ratcliffe, C. I.; Ripmeester, J. A. *Nature* **2005**, *434*, 743.

(6) Lee, J. W.; Yedlappali, P.; Lee, S. Y. *J. Phys. Chem. B* **2006**, *110*, 2332.

(7) Zele, S. R.; Lee, S.-Y.; Holder, G. D. *J. Phys. Chem. B* **1999**, *43*, 10250.

(8) Lee, S.-Y.; Holder, G. D. *AIChE J.* **2002**, *48*, 161.

(9) Lee, S.-Y.; Holder, G. D. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 614.

(10) Bertie, J. E.; Jacobs, S. M. *J. Chem. Phys.* **1982**, *77*, 3230.

(11) Davidson, D. W.; Handa, Y. P.; Ratcliffe, C. I.; Ripmeester, J. A.; Tse, J. S.; Dahn, J. R.; Lee, F.; Calvert, L. D. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 141.

(12) Tse, J. S.; Powell, B. M.; Sears, V. F.; Handa, Y. P. *Chem. Phys. Lett.* **1993**, *215*, 383.

(13) Hwang, M.-J.; Holder, G. D.; Zele, S. R. *Fluid Phase Equilib.* **1993**, *83*, 437.

(14) John, V. T.; Papadopoulos, K. D.; Holder, G. D. *AIChE J.* **1985**, *31*, 252.

(15) McKoy, V.; Sinanoglu, O. *J. Chem. Phys.* **1963**, *38*, 2946.

(16) Peng, D.Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

(17) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Mercel Dekker Inc: New York, 1998.

(18) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*, 6th ed.; McGraw Hill Company: New York, 2001.

(19) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.

(20) Holder, G. D.; Corbin, G.; Papadopoulos, K. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282.

(21) Holder, G. D.; Zetts, S. P.; Pradhan, N. *Rev. Chem. Eng.* **1988**, *5*, 1.

(22) Renon, H.; Prauanitz, J. M. *AIChE J.* **1968**, *14*, 135.

(23) Yamamuro, O.; Matsuo, T.; Suga, H.; David, W. I. F.; Ibberson, R. M.; Leadbetter, A. J. *Physica B* **1995**, *213 & 214*, 405.

(24) Gibanel, F.; Lopez, M. C.; Royo, F. M.; Santafe, J.; Urieta, J. S. *J. Solution Chem.* **1993**, *22*, 211.

(25) Wilson, P. W.; Lester, D.; Haymet, A. D. J. *Chem. Eng. Sci.* **2005**, *60*, 2937.

(26) Sloan, E. D. Data obtained through a private communication, 2005.

(27) Holder, G. D.; Hand, J. H. *AIChE J.* **1982**, *28*, 440.

(28) Zhang, S.; Chen, G.; Ma, C.; Yang, L.; Guo, T. *J. Chem. Eng. Data* **2000**, *45*, 908.

(29) Zhang, Q.; Chen, G.; Huang, Q.; Sun, C.; Guo, X.; Ma, Q. *J. Chem. Eng. Data* **2005**, *50*, 234.

(30) Holder, G. D.; Stephenson, J. L.; Joyce, J. J.; John, V. T.; Kamath, V. A.; Malekar, S. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 170.

(31) Aspen Plus 12.1, *Aspen Engineering Suite*; Aspen Tech, 2005.