PSRK Method for Gas Hydrate Equilibria: I. Simple and Mixed Hydrates

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A thermodynamic model using the predictive Soave-Redlich-Kwong (PSRK) group contribution method to calculate the fugacities of all components in the vapor and liquid phases in equilibrium with the coexisting hydrate phase is proposed. Since the PSRK method together with the UNIFAC model takes the gas–gas interaction in the vapor and liquid phases into account, the phase equilibria of mixed gas hydrates can be successfully reproduced. This approach greatly improves upon the accuracy of the modified Huron-Vidal second-order (MHV2) model, especially for three-guest hydrate systems. Based on experimentally determined X-ray data, an accurate representation for the molar volume of the structure I (sI) hydrate is provided and used for predicting the equilibrium dissociation of methane hydrate at high pressures. Using this correlation, it is possible to reduce noticeable errors in dissociation predictions of high-pressure hydrate formers. Complete phase behavior, including a new quadruple point, which is predicted to be 272.6 K and 7.55 MPa, for cyclopropane hydrate, is presented by the proposed model calculation. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 203–214, 2004
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Introduction

Gas hydrates are crystalline compounds that are composed of host water cages and guest gas molecules. There are various cavities capable of entrapping gas molecules in an open network of water molecules. Depending on the difference in

cavity shape and size of hydrates, gas hydrates can be divided into three distinct structures I, II, and H. The unit crystalline of structure I (sI) consists of two pentagonal dodecahedron (5^{12}) and six tetrakaidecahedron ($5^{12}6^2$) cavities. Structure II hydrates (sII) have sixteen 5^{12} and eight $5^{12}6^4$ cavities (Sloan, 1998). Structure H hydrates (sH) are formed with three types of cavities, 5^{12}, $4^35^66^3$, and $5^{12}6^8$, and require a large guest molecule with a small help gas for cavity stability (Ripmeester et al., 1987; Ripmeester and Ratcliffe, 1990). Recently it has been known that a new structure of methane hydrate as a filled ice can stably exit at pressures higher than 2 GPa (Loveday, 2001a,b). Udachin and Ripmeester (1999) also reported a new

clathrate hydrate structure showing bimodal guest hydration based on the stacking of structure cage layers. They suggested that a wide variety of naturally occurring guest molecules, such as methane, hydrogen sulfide, and carbon dioxide, can be incorporated in the new structure to form more stable hydrate layers. Interestingly, hydrogen hydrate can be formed with the classic sII structure and an approximate hydrate number of 2 (Mao et al., 2002).

There has been considerable interest in research on natural gas hydrates during the past 50 years, since it was recognized that the plugging of gas pipelines in natural gas transportation was primarily due to gas hydrate formation between water and guest components such as methane, ethane, propane, and other light hydrocarbons. A large amount of the dissociation equilibrium data for gas hydrate has been reported in the literature and is well summarized by Sloan (1998) and Berecz and Balla-Achs (1983). In particular significant efforts have also been devoted to the investigation of the phase behavior of multicomponent systems containing gas hydrates. An important practical feature of gas hydrate is that vast quantities of methane in the form of the gas hydrate exist in the permafrost zone and the subsea sediment (Kvenvolden, 1999). To develop the method for commercially producing natural gases from hydrate layers, the accumulation of a lot of information on phase equilibria of gas hydrates, especially multicomponent mixed hydrates, would be of importance. On the other hand, the disposal of global warming gases, mainly carbon dioxide, on the ocean floor using the hydrate-formation process has been carefully studied (North et al., 1998; Saito et al., 2000). Several field experiments were conducted to test and prove ideas for carbon dioxide ocean disposal by *in situ* hydrate formation (Brewer et al., 1999; Pelzer et al., 2002). On the basis of these studies, it is necessary to possess considerable knowledge concerning hydrate formation conditions over a wide range of temperatures, pressures, and solute concentrations. It is well known, however, that there is only a limited amount of experimental data on the hydrate-forming conditions. For this reason, studies on the development of a thermodynamic model for predicting the phase behavior of hydrates systems would be important.

The primary purpose of this article is to critically evaluate the predictive Soave-Redlich-Kwong (PSRK) group contribution method (Holderbaum and Gmehling, 1991; Fischer and Gmehling, 1996; Gmehling et al., 1997; Horstmann et al., 2000) for predicting the phase equilibria of gas hydrate. In our previous work (Yoon et al., 2002), we developed a new model to predict the complicated phase behavior of simple and mixed gas hydrates. The Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972), together with the modified Huron-Vidal second-order (MHV2) mixing rule (Dahl and Michelsen, 1990), was used for calculating the fugacity of all components in the vapor and liquid phases. The modified UNIFAC group contribution model was also used as the excess Gibbs energy for the MHV2 model. Based on the van der Waals-(Platteeuw theory with the Kihara spherical-core potential function (van der Waals and Platteeuw, 1959), this model could describe correctly some peculiar phase behaviors at lower and upper quadruple points and neighboring four three-phase curves around these quadruple points. However, the MHV2 model may not be able to describe the phase equilibria of multiguest hydrate systems, since it does not take into account the gas–gas interaction in the vapor and liquid phases, which is assumed to be zero. It also should be noted that the MHV2 model considers several light hydrocarbons, such as ethane, propane, ethylene, and propylene, as a new group of components even though they can be treated without introducing new model parameters in the UNIFAC frame. Holderbaum and Gmehling (1991) reported that these problems can be resolved clearly using the PSRK model by testing the vapor–liquid predictions for light hydrocarbon systems.

Recently, the classic thermodynamic approaches using fugacity equality between hydrate and water phases have been developed (Chen and Guo, 1998; Klauda and Sandler, 2000). These models removed the need for empirically fitting intermolecular parameters used in the van der Waals and Platteeuw model. Lee and Holder (2002) developed a method for gas hydrate equilibria using a variable reference chemical potential. They provided a correlation in terms of the molecular size of the guest component for estimating reference properties where experimental data are absent. However, for application of these methods to multicomponent systems, it still requires many of the gas–gas interaction parameters or Henry's law constants to describe the solubility behavior of guest molecules in the water phase at high pressure. Using the group contribution concept minimizes the parameter fitting or estimating efforts, and makes it possible to accurately predict the phase behavior of the macromolecular and multicomponent system without introducing new interaction parameters.

Thermodynamic Model for Phase Equilibria of Gas Hydrate

The chemical potential of water in the hydrate phase μ_w^H is generally derived from statistical mechanics in the van der Waals and Platteeuw model

$$\mu_w^H = \mu_w^{MT} + RT \sum_m \nu_m \ln\left(1 - \sum_j \theta_{mj}\right) \qquad (1)$$

where μ_w^{MT} is the chemical potential of water in the hypothetical empty hydrate lattice, ν_m is the number of cavities of type m per water molecule in the hydrate phase, and θ_{mj} is the fraction of cavities of type m occupied by the molecules of component j. This fractional occupancy is determined by a Langmuir-type expression

$$\theta_{mj} = \frac{C_{mj}\hat{f}_j^V}{1 + \sum_k C_{mk}\hat{f}_k^V} \qquad (2)$$

where C_{mj} is the Langmuir constant of component j on the cavity of type m and $\hat{f}_j^V$ is the fugacity of component j in the vapor phase with which the hydrate phase is in equilibrium. The chemical potential difference between the empty hydrate and filled hydrate phases $\Delta\mu_w^{MT-H} (= \mu_W^{TM} - \mu_w^H)$ is obtained from the following equation

$$\Delta\mu_w^{MT-H} = RT \sum_m \nu_m \ln\left(1 + \sum_j C_{mj}\hat{f}_j^V\right) \qquad (3)$$

The fugacity of water in the hydrate phase $-\hat{f}_w^H$ is easily derived as follows

$$\hat{f}_w^H = f_w^{MT}\exp\left(\frac{-\Delta\mu_w^{MT-H}}{RT}\right) = f_w^{MT}\exp\left[-\sum_m \nu_m \ln\left(1 + \sum_j C_{mj}\hat{f}_j^V\right)\right] \tag{4}$$

where f_w^{MT} represents the fugacity of water in the hypothetical empty hydrate lattice. The Langmuir constant allows for the interactions between guest and water molecules in the hydrate cavities. Using the Lennard-Jones-Devonshire cell theory, van der Waals and Platteeuw presented the Langmuir constant as a function of temperature

$$C_{mj} = \frac{4\pi}{kT}\int_0^\infty \exp\left[\frac{-\omega(r)}{kT}\right]r^2\,dr \tag{5}$$

where T is the absolute temperature, k is the Boltzmann's constant, r is the radial distance from the cavity center, and $\omega(r)$ is the spherical-core potential. In the present study, the Kihara potential with a spherical core is used for the cavity potential function because it has been reported that it gives better results than the Lennard-Jones potential for calculating the hydrate dissociation pressures (Mckoy and Sinanoglu, 1963) and is given by

$$\Gamma(x) = \infty, \quad x \le 2a$$

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

where x is the central distance between two molecules. The values of the Kihara hard-core parameter, a, are given in the literature (Parrish and Prausnitz, 1972), while the values of the Kihara energy and size parameters, ϵ and σ, are determined by fitting the model to the experimental hydrate equilibrium data. By summing all guest-water interactions in the cavity, we obtain the spherical-core potential

$$\omega(r) = 2z\epsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right] \tag{7}$$

where

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right] \tag{8}$$

and z and R are the coordination number and the average radius of the cavity, respectively.

In previous work (Yoon et al., 2002), we presented a new expression for the fugacity of ice related to that of pure liquid water

$$f_w^I = f_w^L\exp\left(-\int_{T_0}^T \frac{\Delta h_w^{fus}}{RT^2}\,dT + \int_0^P \frac{\Delta v_w^{fus}}{RT}\,dP\right) \tag{9}$$

This equation does not need the expression of the vapor pressure of ice, and only uses the physical property difference between the ice and supercooled liquid water. Therefore, we can obtain a unique expression for the fugacity of water in the filled hydrate phase as follows

$$\hat{f}_w^H = f_w^L\exp\left[\frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{MT-I} + \Delta h_w^{fus}}{RT^2}\,dT\right.$$
$$\left. + \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{fus}}{RT}\,dP - \sum_m \nu_m \ln\left(1 + \sum_j C_{mj}\hat{f}_j^V\right)\right] \tag{10}$$

Here, the fugacities of supercooled water and all components in the vapor phase, f_w^L and $\hat{f}_j^V$ were calculated using the PSRK group-contribution method combined with the UNIFAC model (Hansen et al., 1991).

The molar enthalpy difference between the ice and liquid water is given by

$$\Delta h_w^{fus} = \Delta h_w^{fus}(T_0) + \int_{T_0}^T \Delta C_P\,dT \tag{11}$$

Depending on the temperature range considered, the heat-capacity difference between ice and liquid water, ΔC_p is given by

$$\Delta C_P = \begin{cases} \Delta C_P^0 + \beta(T - T_0) & T \ge T_0 \\[2mm] C_1 + \dfrac{C_2}{T} + \dfrac{C_3}{T^2} + \dfrac{C_4}{T^3} & T_0 > T \ge T_H \\[2mm] D_1 + D_2 T + D_3 T^2 + D_4 T^3 & \\[1mm] \quad - \dfrac{T - T_G}{T_H - T_G}\ln\dfrac{T - T_G}{T_H - T_G} & T_H > T > T_G \end{cases} \tag{12}$$

By the hyperquenching experiments, a new value for the glass transition temperature of supercooled water was found to be 165 K and was recently reported in the literature (Velikov et al., 2001). This temperature is about 30 K higher than the commonly accepted value over the past 50 years (Ghormley, 1957; McMillan and Los, 1965; Angell and Sare, 1970; Angell et al., 1973; Mishima and Stanley, 1998). On the basis of this revised value, we present here a new parameter set for the heat-capacity difference between ice and liquid (or supercooled) water as follows: $\Delta C_P^0 = -38.13$, $\beta = 0.141$, $C_1 = -1.05253 \times 10^4$, $C_2 = 8.45606 \times 10^6$, $C_3 = -2.26357 \times 10^9$, $C_4 = 2.02637 \times 10^{11}$, $D_1 = -1.78631 \times 10^3$, $D_2 = 26.6606$, $D_3 = -1.35114 \times 10^{-1}$, $D_4 = 2.37259 \times 10^{-4}$, $T_H = 233$ K, and $T_G = 165$ K. For temperatures below T_G, the value of ΔC_p is assumed to be zero.

PSRK Group-Contribution Method

The PSRK group-contribution method is based on the SKR equation of state

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (13)$$

where the mixture parameter b is derived from the conventional mixing rule

$$b = \sum_{i=1}^{n} x_i b_i \quad (14)$$

Huron and Vidal (1979) originally developed a new method for deriving a mixing rule in connection with the excess Gibbs energy, and thus they obtained an equation relating excess Gibbs energy at infinite pressure to the a/b parameter of the SRK equation of state using the following equation

$$g_\infty^E = RT \left[\ln \varphi - \sum_{i=1}^{n} x_i \ln \varphi_i \right] \quad (15)$$

where φ and φ_i are the fugacity coefficients of the solution mixture and pure component i, respectively. Michelsen (1990a,b) proposed a modified formulation of the Huron-Vidal mixing rule which uses the SRK equation of state and a reference pressure of zero. The resulting equation could be obtained in the following explicit form

$$q_i \left(\alpha - \sum_{i=1}^{n} x_i \alpha_i \right) + q_2 \left(\alpha^2 - \sum_{i=1}^{n} x_i \alpha_i^2 \right) = \frac{g_0^E}{RT} + \sum_{i=1}^{n} x_i \ln \left(\frac{b}{b_i} \right) \quad (16)$$

where $\alpha = a/bRT$ and $\alpha_i = a_i/b_i RT$. The recommended values of q_1 and q_2 for the modified Huron-Vidal first-order (MHV1) mixing rule are -0.539 and 0, respectively, and those for the MHV2 mixing rule are -0.478 and -0.0047, respectively (Dahl and Michelsen, 1990). The simplest first-order approximation is used in the PSRK model

$$\alpha = \frac{1}{A_1} \left[\frac{g_0^E}{RT} + \sum_{i=1}^{n} x_i \ln \left(\frac{b}{b_i} \right) \right] + \sum_{i=1}^{n} x_i \alpha_i \quad (17)$$

The recommended value of $A_1 = q_1 = -0.539$ has been changed to $A_1 = -0.64663$ in the PSRK model, which yields better results at higher pressures (Holderbaum and Gmehling, 1991). Thus, the fugacity coefficient for the PSRK model is given by

$$\ln \hat{\varphi}_i = \ln \frac{RT}{P(v - b)} + \left(\frac{1}{v - b} - \frac{\alpha}{v + b} \right) b_i - \bar{\alpha}_i \ln \left(\frac{v + b}{v} \right) \quad (18)$$

where

Table 1. Lattice and Thermodynamic Properties of Gas Hydrates Used in This Study

	Structure I	Structure II
Ideal structure*	$3M_1 \cdot M_2 \cdot 23H_2O$	$M_1 \cdot 2M_2 \cdot 17H_2O$
Number of water molecules/ unit cell	46	136
Number of small cavities/ unit cell	2	16
Number of large cavities/ unit cell	6	8
Average radius of small cavities, Å	3.95	3.91
Average radius of large cavities, Å	4.3	4.73
Coordination number of small cavities	20	20
Coordination number of large cavities	24	28
$\Delta\mu_w^0$, J/mol	1,264	883
Δh_w^{MT-I}, J/mol	1,151	808
Δv_w^{MT-1}, cm^3/mol	3.0	3.4
Δh_w^{fus}, J/mol		$-6,011$
Δv_w^{fus}, cm^3/mol		1.6

*M_1 and M_2 are large and small cavities, respectively.

$$\bar{\alpha}_i = \left(\frac{\partial(n\alpha)}{\partial n_i} \right)_{T,P,n_j} = \frac{1}{A_1} \left(\ln \gamma_i + \ln \frac{b}{b_i} + \frac{b_i}{b} - 1 \right) + \alpha_i \quad (19)$$

Here, the activity coefficient γ_i is calculated using the UNIFAC model. Very recently Chen et al. (2002) proposed a modified version of the PSRK model to resolve some problems observed in the vapor–liquid equilibrium prediction of strong asymmetric mixtures. However, in this work we consider only the original PSRK model because the interaction parameters between guest and water molecules for the modified PSRK model are not yet available.

Results and Discussion

As shown in Table 1, the lattice and thermodynamic properties of the empty hydrate lattice suggested by Parrish and Prausnitz (1972) are used in the model calculation because their values give a very good agreement between experimental and calculated hydrate dissociation pressures. In our previous work (Yoon et al., 2002), we did not take the compressibility of gas hydrate into account, and therefore the effect of pressure on the hydrate lattice was assumed to be negligible. It should be noted, however, that this simple approach may result in some large deviations between experimental and predicted dissociation pressures for methane hydrate, particularly at high-pressure conditions over 100 MPa (Klauda and Sandler, 2000). Based on experimental X-ray diffraction data (Tse, 1987; Hirai et al., 2000), the molar volume of the empty hydrate lattice for each structure has been expressed as a function of temperature and pressure (Klauda and Sandler, 2000)

$$v_{w,I}^{MT}(T, P) = (11.835 + 2.217 \times 10^{-5}T + 2.242$$

$$\times 10^{-6}T^2)^3 \frac{10^{-30}N_A}{46} - 8.006 \times 10^{-9}P + 5.448 \times 10^{-12}P^2$$

$$(20)$$

$$v_{w,II}^{MT}(T, P) = (17.13 + 2.249 \times 10^{-4}T + 2.013 \times 10^{-6}T^2$$

$$+ 1.009 \times 10^{-9}T^3)^3 \frac{10^{-30}N_A}{136} - 8.006 \times 10^{-9}P$$

$$+ 5.448 \times 10^{-12}P^2 \quad (21)$$

where N_A is the Avogadro's number, and T and P are the equilibrium temperature and pressure given in K and MPa units, respectively. When compared with the values calculated from the X-ray diffraction data for methane hydrate at high-pressure conditions (Hirai et al., 2000), the molar volume predicted using these equations is within an average percent absolute deviation (% AAD) of 2.5. In the present study, the suggested approach is also used to resolve inaccuracies for methane hydrate and is applied to all gas hydrate-formers. For a more accurate prediction, we propose the revised parameters for the molar volume of sI hydrate as follows

$$v_{w,I}^{MT}(T, P) = (11.835 + 2.217 \times 10^{-5}T + 2.242$$

$$\times 10^{-6}T^2)^3 \frac{10^{-30}N_A}{46} + 1.6155 \times 10^{-9}P - 2.5054$$

$$\times 10^{-12}P^2 + 2.2561 \times 10^{-14}P^3 \quad (22)$$

This equation is in excellent agreement with the experimental values, and therefore the % AAD is less than 0.1. For convenience, we call PSRK and MHV2 with the correlation, depending on the temperature and pressure, PSRK-VT and MHV2-VT, respectively.

Figure 1 shows the flow diagram of the model calculation of the hydrate formation condition for gas mixtures. The fugacities of all components in the vapor and liquid phases are calculated using the PSRK and the other three models. To provide a group-contribution concept the UNIFAC model is used as the excess Gibbs energy for the PSRK and PSRK-VT models (Holderbaum and Gmehling, 1991), whereas the modified UNIFAC model is used for the MHV2 and MHV2-VT models (Dahl et al., 1991; Yoon et al., 2002). The % AADs between the measured and calculated dissociation pressures for simple hydrate-formers are presented in Table 2. Also listed in the table are the prediction results using four different models of MHV2, MHV2-VT, PSRK, and PSRK-VT. As mentioned previously, the MHV2 model considers gas components such as ethane and propane as new group components even though they can be treated without introducing new model parameters in the original UNIFAC frame. Therefore, we cannot calculate the phase equilibria of cyclopropane and isobutane hydrates because the interaction parameters between them and water have not yet been available. When using the PSRK model, it is possible to predict the hydrate dissociation pressures of all simple hydrate-formers including cyclopropane and isobutane. Since no actual experimental data of X-ray diffraction for sII hydrate depending on pressure have been reported, we investigate the effect of variable volume parameters on dissociation prediction only for sI hydrate. As can be seen in Table 2, it seems that the PSRK-VT and MHV2-VT models using the hydrate volume correlation suggested by Klauda and Sandler (2000) exhibit better correlation with experimental dissociation pressures than the PSRK and MHV2 models, especially for
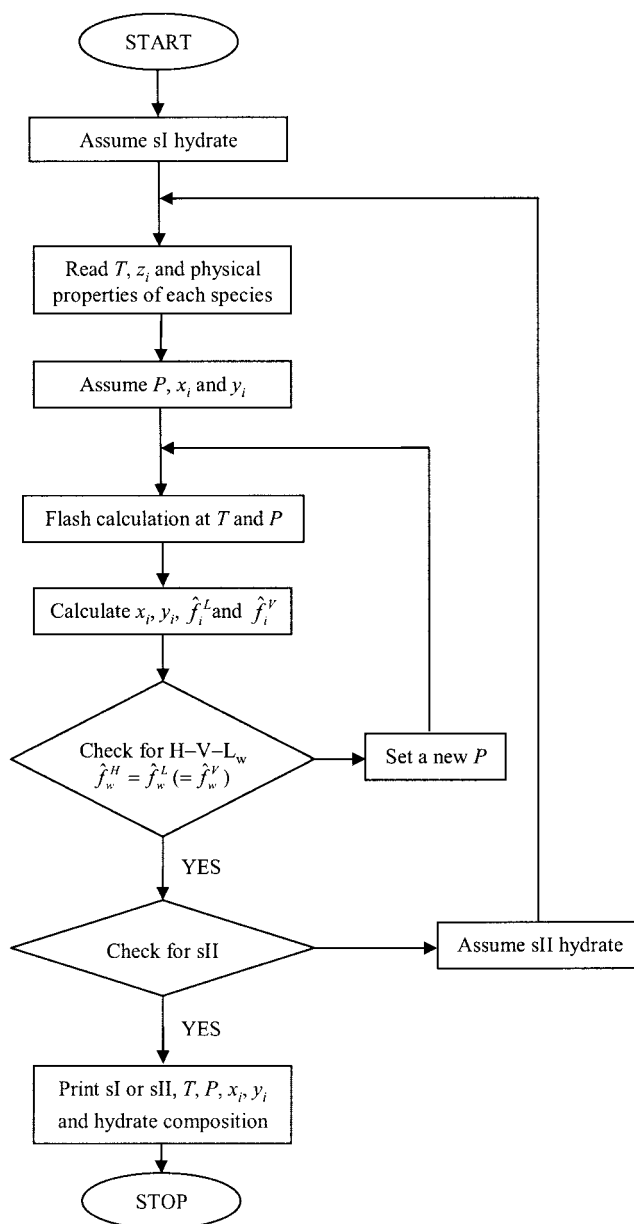

Figure 1. Flow diagram for hydrate formation calculation for gas mixtures.

high-pressure hydrate-formers such as methane and ethylene hydrates. However, the Klauda and Sandler correlation is still very inaccurate in dissociation prediction of methane hydrate at high-pressure conditions, even though it is very effective for predicting the dissociation pressures at low-pressure conditions, as shown in Figures 2 and 3. In contrast, our correlation perfectly reproduces the dissociation behavior of methane hydrate at both high- and low-pressure conditions. This result implies that an accurate description of hydrate molar volume depending on pressure as well as temperature must be considered to resolve inaccuracies in dissociation predictions at high-pressure conditions. At extremely high pressures, noticeable errors may be caused by a very small change in hydrate molar volume, because the effect of the Poynting correction would be of significance. We note that Klauda and Sandler (2000) have

Table 2. Average Absolute Deviations of Predicted Hydrate Dissociation Pressures of Simple Gas Hydrates

Guest	Struc.	T, K	P, MPa	N_p	Ref.*	% AAD			
						MHV2	MHV2-VT	PSRK	PSRK-VT
CH_4	I	148–320	0.005–400	92	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	9.3	4.7 (6.8)[†]	6.7	4.4 (5.7)
C_2H_6	I	200–288	0.008–3.3	59	1, 6, 7, 11, 12, 13, 14	2.0	1.8 (1.8)	1.9	1.9 (1.9)
C_2H_4	I	269–305	0.47–103	63	15, 16, 17	5.5	3.8 (4.7)	5.4	3.6 (5.1)
C_3H_8	II	247–279	0.04–0.57	65	1, 8, 10, 11, 18, 19, 20, 21	3.2	n.a.[††]	3.3	n.a.
C_3H_6	II	273–274	0.46–0.60	15	11, 22	0.6	n.a.	0.8	n.a.
CO_2	I	151–283	0.0005–4.4	92	1, 7, 19, 23, 24, 25, 26	3.1	3.0 (3.0)	2.9	2.8 (2.9)
O_2	II	267–291	9.9–95	50	27, 28	2.5	n.a.	2.3	n.a.
N_2	II	268–305	12–330	72	4, 5, 27, 28	1.9	n.a.	5.5	n.a.
H_2S	II	250–303	0.03–2.3	29	29, 30	2.6	2.6 (2.6)	3.2	3.2 (3.2)
$i\text{-}C_4H_{10}$	II	240–275	0.017–0.17	53	10, 20, 31, 32, 33	n.a.	n.a.	2.1	n.a.
$c\text{-}C_3H_6$	I, II	237–290	0.008–0.57	35	34	n.a.	n.a.	1.1	n.a.

*(1) Deaton and Frost (1946); (2) Kobayashi and Katz (1949); (3) McLeod and Campbell (1961); (4) Marshall et al. (1964); (5) Jhaveri and Robinson (1965); (6) Galloway et al. (1970); (7) Falabella (1975); (8) Verma (1974); (9) de Roo et al. (1983); (10) Thakore and Holder (1987); (11) Reamer et al. (1952); (12) Holder and Grigoriou (1980); (13) Holder and Hand (1982); (14) Avlonites (1988); (15) Diepen and Scheffer (1950); (16) Snell et al. (1961); (17) van Cleef and Diepen (1962); (18) Miller and Strong (1945); (19) Robinson and Metha (1971); (20) Holder and Godbole (1982); (21) Patil (1987); (22) Clarke et al. (1964); (23) Unruh and Katz (1949); (24) Larson (1955); (25) Miller and Smythe (1970); (26) Ng and Robinson (1985); (27) van Cleef and Diepen (1960); (28) van Cleef and Diepen (1965); (29) Selleck et al. (1952); (30) Bond and Russell (1949); (31) Schneider and Farrar (1968); (32) Rouher and Barduhn (1969); (33) Wu et al. (1976); (34) Hafemann and Miller (1969).
[†]Calculated using Klauda and Sandler correlation.
[††]Not available.

provided their correlation for hydrate molar volume by fitting the dissociation data for sI methane hydrate at high pressures, whereas our correlation is presented by fitting the experimental values from X-ray diffraction data for sI methane hydrate at high pressures. Recently, it was suggested that sI methane hydrate transforms to sII hydrate at 100 MPa (Chou et al., 2000) and 1.1 GPa (Loveday et al., 2001b). In addition a quadruple point at 660 MPa and 315 K and the neighboring three-phase curve H_{II}–Lw–V have been observed by Dyadin et al. (1997). However, as there have been no X-ray diffraction data for sII methane hydrate covering a wide range of high

pressure, we cannot at present model the structural transition behavior of methane hydrate at high pressure.

Figure 4 shows the phase diagram for simple ethane and isobutane hydrates over a wide range of temperature and pressure. For isobutane hydrate, only the PSRK model is used to predict the dissociation behavior, because the correlation for molar volume of sII hydrate is not available. As shown in Figure 4, all calculated results show an excellent agreement with the experimental data for both hydrate systems except the high-pressure region over 100 MPa for ethane hydrate. At pressures higher than 100 MPa, the predicted results of the
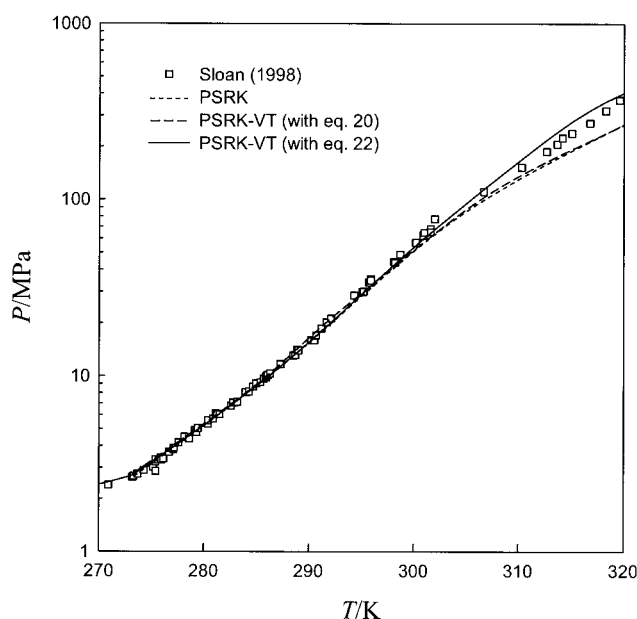

Figure 2. Comparison of experimental data with predicted results for methane hydrate in high-pressure H–L$_w$–V region.
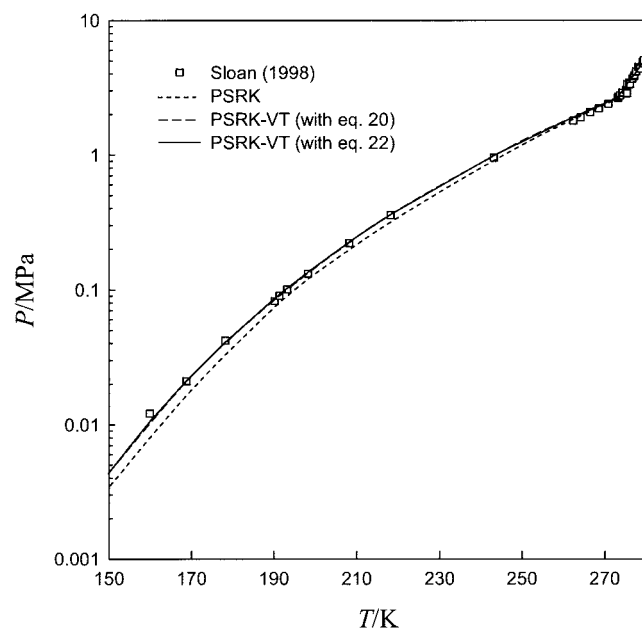

Figure 3. Comparison of experimental data with predicted results for methane hydrate in low-pressure H–I–V region.
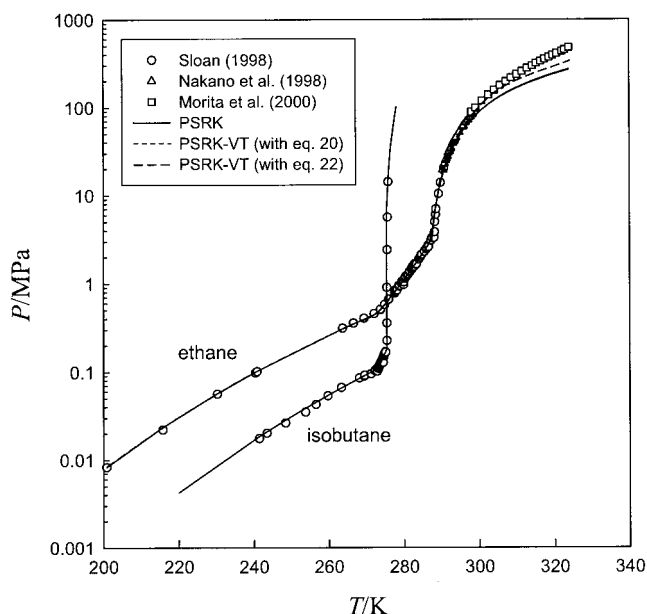
Figure 4. Comparison of experimental data with predicted results for ethane and isobutane.

Figure 6. *ET-x* Diagram of cyclopropane hydrate at 0.07 MPa.

PSRK-VT model with Eq. 22 are better than those of the PSRK and PSRK-VT models with Eq. 20, as was expected. The erroneous prediction of the high-pressure behavior of gas hydrate seems to be unavoidable for both PSRK and PSRK-VT models without an accurate representation of hydrate molar volume. Complete pressure–temperature behavior of cyclopro-

pane hydrate is shown in Figure 5. The cyclopropane hydrate may be taken as a typical example for testing the thermodynamic model, because it forms both sI and sII hydrates, depending on the formation condition. The PSRK model can accurately predict the entire phase behavior including the structural transition, as shown in Figure 5. One of the most surpris-
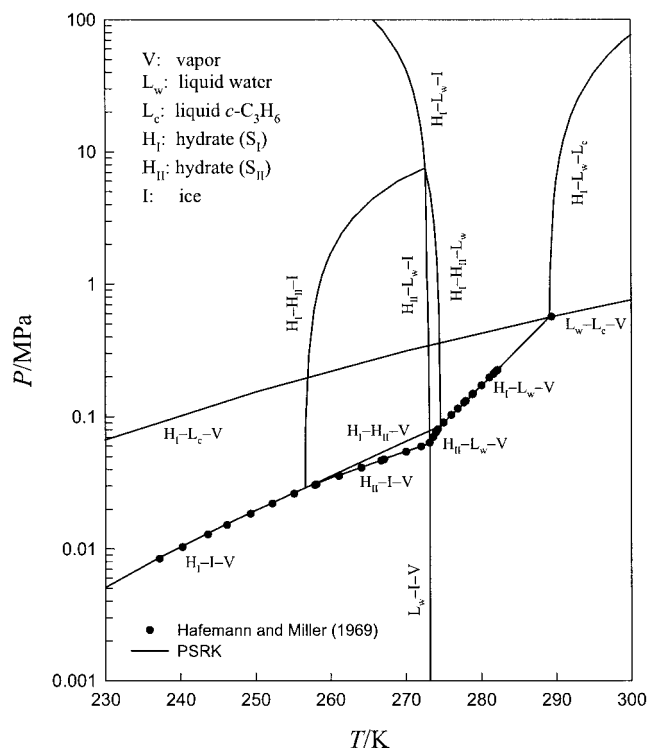

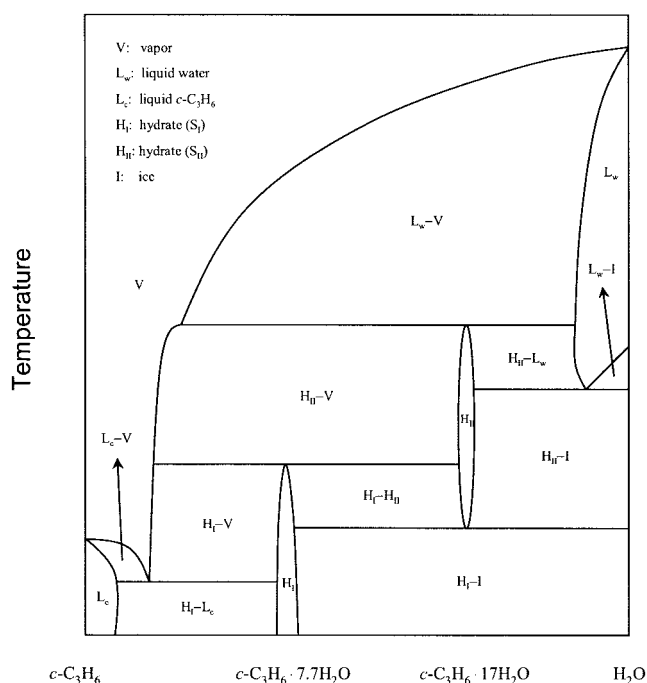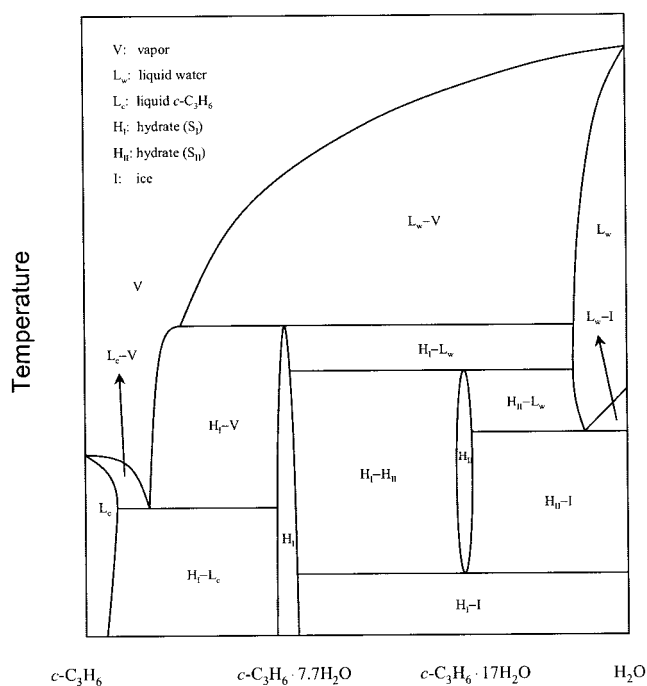**Figure 5. Complete *p-T* diagram of cyclopropane hydrate.**

Figure 7. *T-x* Diagram of cyclopropane hydrate at 0.3 MPa.

Table 3. Average Absolute Deviations of Predicted-Phase Equilibria of Mixed Gas Hydrates

System	Struc.	T, K	P, MPa	N_p	Ref.*	% AAD	
						MHV2	PSRK
CH_4-C_2H_6	I, II	274–304	0.94–69	54	1, 2, 3	9.0	8.8
CH_4-C_3H_8	I, II	270–305	0.15–69	78	1, 2, 4, 5	4.7	3.4
CH_4-N_2	I, II	273–296	3.6–36	63	6	12.5	12.3
CH_4CO_2	I	273–288	1.4–11	59	7, 8	3.2	2.4
C_2H_6-C_3H_8	I, II	273–284	0.44–2.1	60	9	10.6	10.2
C_2H_6-CO_2	I	273–288	0.56–4.1	40	10	7.0	5.6
C_3H_8-N_2	II	274–290	0.25–18	29	11	6.5	5.4
C_3H_8-CO_2	I, II	273–287	0.30–4.3	37	12	6.5	6.2
CH_4-C_3H_8-H_2S	I, II	275–301	0.33–4.3	13	13	14.7	8.1
CH_4-CO_2-H_2S	I	279–298	1.4–16	37	14	41.4	14.5

*(1) Deaton and Frost (1946); (2) McLeod and Campbell (1961); (3) Holder and Grigoriou (1980); (4) Thakore and Holder (1987); (5) van der Waals and Platteeuw (1959); (6) Jhaveri and Robinson (1965); (7) Unruh and Katz (1949); (8) Adisasmito et al. (1991); (9) Holder and Hand (1982); (10) Adisasmito and Sloan (1992); (11) Ng et al. (1977–1978); (12) Robinson and Metha (1971); (13) Schroeter et al. (1983); (14) Robinson and Hutton (1967).

ing results is that a new quadruple point, thermodynamically unique and an invariant condition, is carefully predicted to be 272.6 K and 7.55 MPa. At this quadruple point, four individual phases of sI hydrate (H_1), sII hydrate (H_{II}), liquid water (L_w), and ice (I) can coexist in equilibrium. As a result, four different three-phase boundaries of the H_I–H_{II}–Lw, H_I–H_{II}–I, H_1–L_w–I, and H_{II}–L_w–I curves can be successfully reproduced by the PSRK model, as shown in Figure 5. Unfortunately, the experimental evidence of phase behavior around the quadruple point has not yet been reported in the literature. Figures 6 and 7 show the composition-temperature behavior of cyclopropane hydrate at 0.07 and 0.3 MPa, respectively. Both figures are presented on the basis of the solid solution range concept described in

detail by Huo et al. (2002). Interestingly, the predicted hydrate numbers of cyclopropane sI and sII hydrates are about 7.7 and 17.0, which are very close to those of the ethane and propane hydrates, respectively (Handa, 1986).

For propane hydrate, our model does predict the retrograde hydrate melting for the three-phase equilibrium curve of H–L_w–$L_{C_3H_8}$. The slope of the H–L_w–$L_{C_2H_8}$ curve, starting from the upper quadruple point of 278.71 K and 0.574 MPa, increases steeply with a small increase in temperature until the equilibrium temperature and corresponding pressure is 278.78 K and 10.41 MPa, respectively. At temperatures above 278.78 K, propane hydrate cannot exist in the equilibrium state because the slope turns negatively. For comparison, we note that the upper dissociation point at 278.2 K is predicted to be 58.0 MPa, which closely matches 60.0 MPa predicted by Ballard and Sloan (2001), but it is different from 26.84 MPa predicted by Klauda and Sandler (2003). However, as described in our previous work (Yoon et al., 2002), we can expect the pressure-
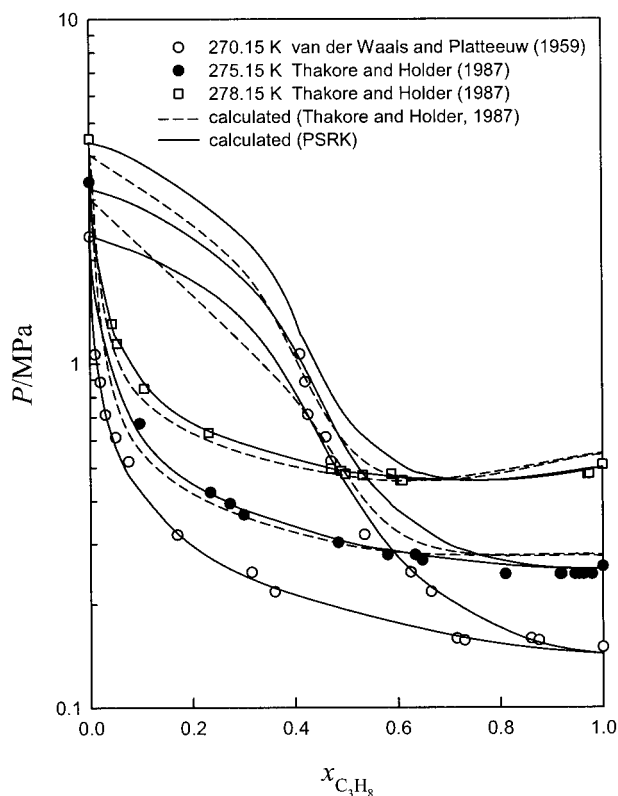

Figure 8. *P-x* Diagram for methane–propane hydrate system at 270.15, 275.15, and 278.15 K.
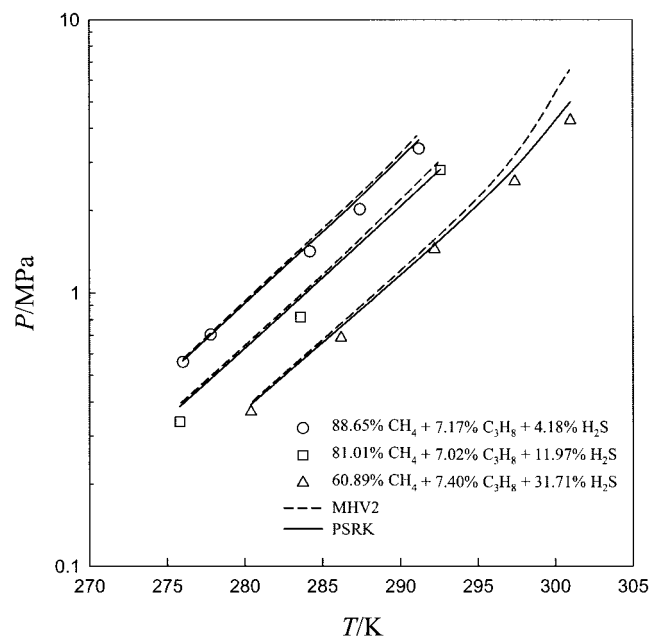

Figure 9. Dissociation pressures for methane–propane–hydrogen sulfide hydrates.
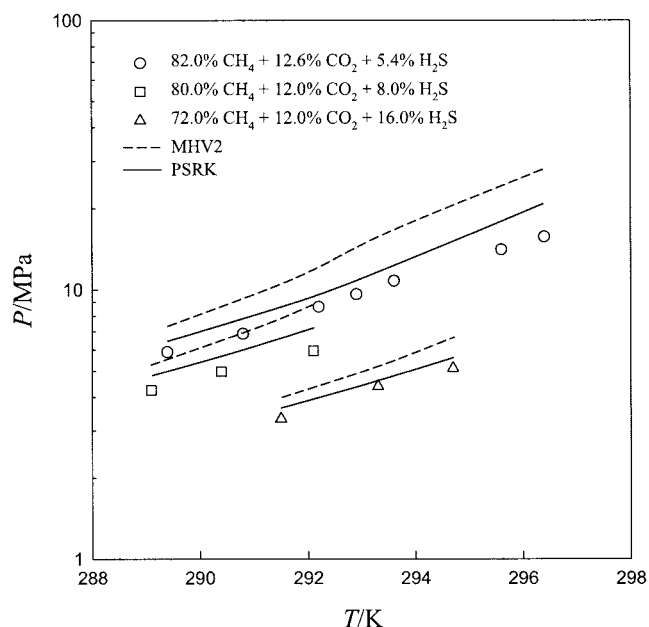
Figure 10. Dissociation pressures for methane–carbon-dioxide–hydrogen sulfide hydrates.

induced compression of hydrate molar volumes at pressures above 50 MPa (Hirai et al., 2000; Klauda and Sandler, 2000). Hence, if the molar volume difference of sII hydrate is expressed as a function of temperature and pressure, the predicted shape of the H–L_w–$L_{C_3H_8}$ curve of propane hydrate at high pressures might be changed.

The % AADs of hydrate dissociation pressures predicted by both the PSRK and MHV2 models for the mixed guest systems are presented in Table 3. It can be easily seen that the % AADs of the hydrate systems in which the structural transition occurs are greater than those forming only one hydrate structure. For all mixed hydrate systems considered in this work, the prediction results of the PSRK model are more accurate than those of the MHV2 model. In particular, for the ternary guest systems such as methane–propane–hydrogen sulfide and methane–carbon-dioxide–hydrogen sulfide hydrates, the difference in deviation values between the PSRK and MHV2 models becomes larger. As stated earlier, this may be due to the inherent limitation of the MHV2 model that the gas–gas interaction in the vapor and liquid phases is not taken into account. The phase

behavior of the methane–propane hydrate mixture is presented through the pressure-composition ($p - x$) diagram on the basis of the water-free concentration, as shown in Figure 8. The predicted results by the PSRK model are also compared with those of Thakore and Holder (1987). The PSRK model predictions are in good agreement with the experimental data and much better agreement than the Thakore and Holder model. For the $p - x$ experimental data at 275.15 and 278.15 K, the % AADs of the PSRK and the Thakore and Holder models are 2.6 and 6.9, respectively. We note that the structural transition for this system can be anticipated at the highly methane-concentrated region, as described previously (Yoon et al., 2002). Figures 9 and 10 compare the PSRK model with the MHV2 model for three-guest methane–propane–hydrogen sulfide and methane–carbon–dioxide–hydrogen sulfide hydrates, respectively. As can be clearly seen in both figures, the PSRK model is superior to the MHV2 model. Thus, we can conclude that the interaction between the gas molecules should be considered to be accurately predicting the dissociation behavior of mixed gas hydrates. Large deviations in the MHV2 model predictions can come from inappropriate assumption that all gas–gas interaction parameters are zero. In Table 4, we summarize the Kihara potential parameters for the four different models considered in this study.

Conclusion

In this article, we provide a new method for predicting the phase equilibria of gas hydrates using the PSRK group-contribution model. The fugacity of all the components in the vapor and liquid phases of the coexisting hydrates is calculated by the PSRK group-contribution method together with the UNIFAC model. Based on the van der Waals–Platteeuw theory with the Kihara potential function, the fugacity equation of water in the hydrate phase, which is coupled with the PSRK model, can be used to accurately predict the dissociation behavior of simple hydrates. Since this approach takes into account the interaction between gas molecules with the help of the PSRK and UNI-FAC model, it greatly improves upon the accuracy of the MHV2 model for mixed gas hydrates. In particular, for three-guest hydrate systems, such as methane–propane–hydrogen sulfide and methane–carbon dioxide–hydrogen sulfide, the PSRK model resolves noticeable errors of the MHV2 model. This implies that the interaction between gas molecules should be taken into account when accurately predicting the dissociation behavior of mixed gas hydrates.

Table 4. Fitted Kihara Potential Parameters for Gas–Water Interaction

Guest	a,* Å	MHV2		MHV2-VT		PSRK		PSRK-VT	
		σ, Å	ϵ/k, K	σ, Å	ϵ/k, K	σ, Å	ϵ/k, K	σ, Å	ϵ/k, K
CH_4	0.30	3.2408	153.2	3.1872	155.6	3.2402	153.1	3.1718	157.0
C_2H_6	0.40	3.4383	175.0	3.4333	174.9	3.4146	174.5	3.4149	174.5
C_2H_4	0.47	3.3228	173.1	3.3114	173.1	3.2842	173.3	3.2827	173.3
C_3H_8	0.68	3.4435	187.4	n.a.	n.a.	3.3445	196.5	n.a.	n.a.
C_3H_6	0.65	3.4419	177.8	n.a.	n.a.	3.5446	173.9	n.a.	n.a.
CO_2	0.72	2.9327	169.5	2.9318	169.5	2.9317	169.9	2.9305	169.9
O_2	0.36	2.9580	133.2	n.a.	n.a.	2.9544	133.5	n.a.	n.a.
N_2	0.35	3.1308	123.8	n.a.	n.a.	3.0958	123.5	n.a.	n.a.
H_2S	0.36	3.2000	201.7	3.2000	201.7	3.2000	201.6	3.2000	201.6
i-C_4H_{10}	0.80	n.a.	n.a.	n.a.	n.a.	3.3872	190.6	n.a.	n.a.
c-C_3H_6	0.50	n.a.	n.a.	n.a.	n.a.	3.4560	210.8	n.a.	n.a.

*Parrish and Prausnitz (1972).

Dissociation prediction for the cyclopropane and isobutane hydrates is carried out using the PSRK model, with the interaction parameter between them and water in the original UNIFAC frame. It is interesting to note that a new quadruple point for cyclopropane hydrate, which has not been reported yet, is predicted by the proposed model.

An accurate representation for hydrate molar volume, which depends on temperature and pressure, is provided. Using this equation, the error between experimental and calculated dissociation pressures for methane hydrate at high-pressure conditions is reduced.

Acknowledgments

Notation

a = Kihara hard-core parameter
a = parameter in the SRK equation of state
A_1 = mixing rule constant in Eq. 17
b = parameter in the SRK equation of state
C_{mj} = Langmuir constant of component j on the cavity of type m
ΔC_p = heat capacity difference between ice and water
ΔC_P^0 = heat capacity difference between ice and water at T_0
f_w^I = fugacity of ice
f_w^L = fugacity of pure water in liquid phase
f_w^{MT} = fugacity of water in empty hydrate lattice
f_w^H = fugacity of water in hydrate phase
f_w^L = fugacity of component i in liquid phase
$\hat{f}_i^V$ = fugacity of component i in vapor phase
g_0^E = excess Gibbs energy at zero pressure
g_∞^E = excess Gibbs energy at infinite pressure
Δh_w^{fus} = molar enthalpy difference between water and ice
Δh_w^{MT-I} = enthalpy difference between empty hydrate lattice and ice
k = Boltzmann's constant
N_A = Avogadro's number
P = pressure
q_1, q_2 = mixing rule constants in Eq. 16
R = gas constant
R = average radius of the cavity
r = radius of distance from the cavity center
T = temperature
T_0 = reference temperature, 273.15 K
T_G = glass transition temperature of supercooled water, 165 K
v = molar volume
$v_{w,I}^{MT}$ = molar volume of structure I empty hydrate lattice
$v_{w,II}^{MT}$ = molar volume of structure II empty hydrate lattice
Δv^{fus} = molar volume difference between water and ice
Δv_w^{MT-I} = volume difference between empty hydrate lattice and ice
x = central distance between two molecules
x_i = mole fraction of component i in mixture
z = coordination number of the cavity

Greek Letters

α = parameter in the SRK equation of state, $\alpha = a/bRT$
ϵ = Kihara energy parameter
φ = fugacity coefficient
$\hat{\varphi}_i$ = fugacity coefficient of component i in mixture
$\Gamma(x)$ = Kihara potential function
γ_i = activity coefficient of component i in mixture
μ_w^H = chemical potential of water in filled hydrate lattice
μ_w^{MT} = chemical potential of water in empty hydrate lattice
$\Delta\mu_w^{MT-H}$ = difference in chemical potential of water between empty and filled hydrate lattice
$\Delta\mu_w^0$ = difference in chemical potential of water between empty hydrate lattice and water at T_0 and zero absolute pressure
ν_m = the number of cavities of type m per water molecule in the hydrate lattice

σ = Kihara size parameter
θ_{mj} = fraction of cavities of type m occupied by component j
$\omega(r)$ = spherical-core potential function

Superscripts and Subscripts

0 = reference state
fus = fusion
H = hydrate
i, j = component
I = ice
L = liquid water
m = cavity type m
MT = empty
V = vapor
w = water

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