Generalized Model for Predicting Phase Behavior of Clathrate Hydrate

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An improved and generalized model was developed to predict the dissociation pressures of hydrate-forming gases and the complicated phase behavior of multicomponent hydrate systems. Based on the van der Waals-Platteeuw theory with the Kihara spherical-core potential function, a new equation for the water fugacity in the filled hydrate phase is provided. Instead of vapor pressures of ice for conventional approaches, it adopts the molar enthalpy difference between ice and liquid water. Since it always maintains its unique form whether the hydrates coexist with ice or water, it can be successfully applied to predict the multiphase equilibria of simple and mixed hydrate systems. The fugacities of all components in vapor and liquid phases coexisting with hydrates were calculated by the Soave-Redlich-Kwong (SRK) equation of state incorporated with the modified Huron-Vidal second-order mixing rule. Lower and upper quadruple points and neighboring four three-phase curves around these quadruple points were described correctly by this model calculation. The Kihara potential parameters for the interaction between water and gas molecules are presented by fitting experimental dissociation pressures. Various types of systems involving hydrate mixtures containing either two guest components or inhibitors were extensively tested to examine the model's potential applicability to predicting the complicated phase equilibria.

Introduction

Clathrate hydrates (or gas hydrates) are crystalline compounds which are formed by the physically stable interaction between water and relatively small guest molecules occupied in the cavities built by water molecules. They have been classified into three distinct structures I, II, and H by the difference in the cavity shape and size of hydrates. Structure I and II hydrates are composed of two types of cages, one small and one large. The unit crystalline of structure I consists of two pentagonal dodecahedron (5^{12}) and six tetrakaidecahedron ($5^{12}6^2$) cavities. The $5^{12}6^2$ means that the cavity is a polyhedron consisting of 12 pentagonal and 2 hexagonal faces. Structure II hydrates have sixteen 5^{12} and eight $5^{12}6^4$ cavities

(Sloan, 1998). Structure H hydrates are formed with three types of cavity, 5^{12}, $4^3 5^6 6^3$, 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).

The plugging of natural gas pipelines has been the well-known problem caused by the hydrate formation. The gas hydrate formation has been used for the concentration process of aqueous organic solutions (Huang et al., 1965, 1966) or other biological processes (Nguyen et al., 1989) and the desalination process of seawater (Parker, 1942; Barduhn et al., 1962; Barduhn, 1967, 1968). It is well known that vast quantities of methane in the form of the gas hydrate exist in the permafrost zone and the subsea sediment. Recently, the disposal of global warming gases, mainly carbon dioxide, on the

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ocean floor by using the hydrate formation process has been carefully studied (North et al., 1998; Saito et al., 2000). On the basis of the above 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 thermodynamic model for predicting the phase behavior of hydrates systems would be of importance.

A variety of thermodynamic models for the calculation of phase equilibrium properties of the hydrate system has been discussed and reviewed in the literature (Berecz and Balla-Achs, 1983; Holder et al., 1988; Sloan, 1998; Englezos, 1993). The first basic approach for the prediction of hydrate dissociation pressures was carried out by van der Waals and Platteeuw (1959) using the statistical thermodynamics based on the classical Langmuir type adsorption theory. They assumed that each cavity could contain at most one guest molecule, there are no interactions between the encaged molecules, and the internal partition functions of encaged molecules are taken those of free guest molecules. Only London forces are important in their model for describing the interaction between host water and guest molecules. They used the Lennard-Jones-Devonshire cell theory to consider the gas molecule moving about in a spherical cavity formed by host water molecules. Based on this fundamental approach, Mckoy and Sinanoglu (1963) suggested that, for the prediction of dissociation pressures for the hydrates of the rodlike molecules, the Kihara potential give better results than Lennard-Jones potentials. The Kihara potential parameters for the interaction between the host water and guest molecules such as CO_2, N_2, O_2, and CH_4 were calculated by geometric-mean and hard-sphere approximation. Parrish and Prausnitz (1972) reported the Kihara potential parameters for 15 hydrate-forming guest components by reducing the dissociation pressure data for binary hydrate systems, and determined new values of the thermodynamic properties of empty hydrate. Because the empty hydrate lattice is thermodynamically unstable and its physical properties cannot be measured, their proposed values have been effectively used for the calculation of hydrate phase equilibria by many researchers. In addition they also presented the systematic algorithm for the calculation of hydrate formation conditions from gas mixtures. Holder et al. (1980) suggested a simplified model which is considerably by direct integration of the chemical potential difference with temperature and pressure along the equilibrium dissociation line to eliminate the need for reference hydrate curves.

The ability of thermodynamic models to predict the complicated phase equilibria of the hydrate systems has been checked by many researchers. In order to avoid the dependence of the potential function on the mutual solubility of the gas and water, Lundgard and Mollerup (1991, 1992) obtained the Kihara parameters by fitting the dissociation pressures along only the hydrate-ice-vapor curve. In addition, they investigated the influence of the uncertainty of the lattice cavity size on the phase behavior prediction of hydrate-forming systems. Molecular simulation techniques such as Monte Carlo (MC) simulation and molecular dynamics may be powerful tools to describe the potential field in the non-

spherical cavity. A method to calculate the Langmuir constants of guest molecules in a hydrate cavity using the MC simulation technique was first proposed by Tester et al. (1972). Several workers (Tse et al., 1983a,b, 1984, 1986; Tse and Klein, 1987; Rodger, 1991) also presented and examined the molecular simulation models to study the potential energy field in the cavities. It is well known that the molecular simulation approach has the advantage of considering the guest-guest interactions, as well as the guest-host interactions, for an infinite hydrate lattice. It should not be neglected, however, that these models require more computation time than the classical adsorption theory for the calculation of the chemical potential in the cavities. The classical thermodynamic approaches using fugacity equality between hydrate and water phases have been developed recently (Chen and Guo, 1998; Klauda and Sandler, 2000). In particular, these models removed the need for reference energy parameters used in the van der Waals and Platteeuw model.

The addition of solutes such as alcohols, electrolytes, and polymers causes inhibition of the hydrate formation conditions by altering the state of the liquid phase. This change plays a great role in lowering the activity of water in the liquid phases. Theoretical study on the inhibition of gas hydrates by methanol has been carried out by many workers (Anderson and Prausnitz, 1986; Munck et al., 1988; Du and Guo, 1990). In most cases, the activity coefficient model such as the UNIQUAC equation is used for calculating the fugacity of condensable components in the liquid phase. For noncondensable gases, the fugacity in the liquid phase is obtained from empirical Henry's law correlations. With these models, the inhibition effect of methanol on the hydrate formation conditions can be correctly predicted. However, it should be noted that the proposed method may be not suitable for the hydrate formation of low water soluble components at high temperatures and moderately water soluble hydrate formers such as carbon dioxide hydrates because the solubility of these compounds in water is significant (Anderson and Prausnitz, 1986).

The objective of this study is to present a method for accurately predicting the phase equilibria of hydrate systems, based on the theory of van der Waals and Platteeuw. The fugacity of all components in the vapor and liquid phases is calculated by using the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) incorporated with the modified Huron-Vidal second-order (MHV2) mixing rule (Dahl and Michelsen, 1990). Here, the modified UNIFAC group contribution model is used as the excess Gibbs energy for the MHV2 model. The use of the equation of state (EOS) has the advantage of providing a consistent representation of vapor-liquid equilibria up to high pressures, whereas the activity coefficient approach is suitable for liquid phases at low pressures. Thus, as pointed out by Englezos and Bishnoi (1991) and Englezos (1993), the MHV2 model combining the benefits of both approaches can be effectively used for predicting the highly complicated phase behavior of the hydrate systems. A thermodynamically consistent approach for calculating the fugacity of ice is newly provided on the basis of fundamental thermodynamic considerations. By using this approach, we correctly describe not only the lower quadruple point, but also the neighboring four three-phase curves. Finally, the proposed model is supported by favorable compari-

son of calculated and experimental results for the complicated hydrate systems.

Thermodynamic Model

General hydrate equilibrium model

The equilibrium criteria of the hydrate-forming mixture are based on the equality of fugacity of the specified component i in all phases which coexist simultaneously

$$\hat{f}_i^H = \hat{f}_i^L = \hat{f}_i^V \left(= f_w^I \right) \qquad (1)$$

where H stands for the hydrate phase such structure I or II, L for the liquid phase such as the water-rich or guest-rich liquid phases, V for the vapor phase, and I for ice. Each of hydrate structures, I, II, and H must be considered as one independent phase because the mixed or double hydrates can possibly exist for the systems containing one or more guest components.

Thermodynamic models for predicting hydrate phase equilibria have been focused mainly on three-phase behavior of hydrate, ice and vapor (H-I-V) or hydrate, water-rich liquid and vapor (H-L$_w$-V).

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

$$\mu_w^H = \mu_w^{MT} + RT \sum_m \nu_m \ln \left(1 - \sum_j \theta_{mj} \right) \qquad (2)$$

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

$$\theta_{mj} = \frac{C_{mj} \hat{f}_j^V}{1 + \sum_k C_{mk} \hat{f}_k^V} \qquad (3)$$

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 $\Delta \mu_w^{MT-H} \left(= \mu_w^{MT} - \mu_w^H \right)$ is obtained from the following equation

$$\Delta \mu_w^{MT-H} = RT \sum_m \nu_m \ln \left(1 + \sum_j C_{mj} \hat{f}_j^V \right) \qquad (4)$$

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

$$\hat{f}_w^H = f_w^{MT} \exp \left(\frac{-\Delta \mu_w^{MT-H}}{RT} \right)$$

$$= f_w^{MT} \exp \left[-\sum_m \nu_m \ln \left(1 + \sum_j C_{mj} \tilde{f}_j^V \right) \right] \qquad (5)$$

where f_w^{MT} represents the fugacity of water in the hypothetical empty hydrate lattice. The Langmuir constant considers 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

$$C_{mj} = \frac{4\pi}{kT} \int_0^\infty \exp \left[\frac{-\omega(r)}{kT} \right] r^2 dr \qquad (6)$$

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

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

$$\Gamma(x) = 4\epsilon \left[\left(\frac{\sigma}{x-2a} \right)^{12} - \left(\frac{\sigma}{x-2a} \right)^6 \right], x > 2a \qquad (7)$$

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 up all guest-water interactions in the cavity, we obtain the spherical-core potential

$$\omega(r) = 2z\epsilon \left[\frac{\sigma^{12}}{R^{11}r} \left(\delta^{10} + \frac{a}{R}\delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left(\delta^4 + \frac{a}{R}\delta^5 \right) \right] \qquad (8)$$

where

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

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

The fugacity of water in the empty hydrate lattice f_w^{MT} is calculated by one of the following two expressions depending on the equilibrium temperature. If the equilibrium temperature is below the ice point

$$f_w^{MT} = f_w^I \exp \left(\frac{\Delta \mu_w^{MT-I}}{RT} \right) \qquad (10)$$

and above the ice point

$$f_w^{MT} = f_w^L \exp \left(\frac{\Delta \mu_w^{MT-L}}{RT} \right) \qquad (11)$$

where $\Delta \mu_w^{MT-I} = \mu_w^{MT} - \mu_w^I$ and $\Delta \mu_w^{MT-L} = \mu_w^{MT} - \mu_w^L$, respectively. The fugacity of pure liquid water at the speci-

fied temperature and pressure f_w^I is calculated by the SRK equation of state.

Holder et al. (1980) suggested the method to simplify the chemical potential difference between empty hydrate and reference state as follows

$$\frac{\Delta \mu_w^{MT-I}}{RT} = \frac{\Delta \mu_w^0}{RT} - \int_{T_0}^{T} \frac{\Delta h_w^{MT-I}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{MT-I}}{RT} dP \quad (12)$$

$$\frac{\Delta \mu_w^{MT-L}}{RT} = \frac{\Delta \mu_w^0}{RT} - \int_{T_0}^{T} \frac{\Delta h_w^{MT-I} + \Delta h_w^{\text{fus}}}{RT^2} dT$$
$$+ \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{\text{fus}}}{RT} dP \quad (13)$$

where T_0 is 273.15 K, the normal melting point of water, $\Delta \mu_w^0$ is the chemical potential difference between empty hydrate and water at T_0 and zero absolute pressure, and Δh_w^{fus} and Δv_w^{fus} are, respectively, the molar difference in enthalpy and volume between ice and liquid water. As pointed out by Parrish and Prausnitz (1972), the molar difference in enthalpy and volume between empty hydrate and ice Δh_w^{MT-I} and Δv_w^{MT-I} is assumed to be independent of temperature and pressure, but only depends on the type of hydrate structure. Similarly, the fugacity of water in the filled hydrate lattice is computed by either of the following two expressions depending also on temperature,

$$\hat{f}_w^H = f_w^I \exp\left(\frac{\Delta \mu_w^{MT-I}}{RT} - \frac{\Delta \mu_w^{MT-H}}{RT} \right) \quad (14)$$

and

$$\hat{f}_w^H = f_w^L \exp\left(\frac{\Delta \mu_w^{MT-L}}{RT} - \frac{\Delta \mu_w^{MT-H}}{RT} \right) \quad (15)$$

Choice of fugacity of ice

Judging from the complete phase behavior of hydrate mixtures, the lower quadruple point Q_1 at which four phases H, I, L_w, and V coexist in equilibrium must be located exactly at an intersection of four three-phase H-L_w-V, H-I-V, H-I-L_w, and I-L_w-V curves. However, most of the efforts to calculate Q_1 have been focused on the intersection point of only two three-phase H-L_w-V and H-I-V curves. Moreover, one cannot confirm the continuity of the fugacity of water in filled hydrate phase at Q_1, because the fugacity calculated with Eq. 14 is quite different from that with Eq. 15. Thus, without any appropriate model for the fugacity of ice, it is impossible to ensure the consistency of the fugacity calculated by Eqs. 14 and 15 at Q_1. In general, the fugacity of ice is computed from

$$f_w^I = P^{\text{sat}} \varphi_w^{\text{sat}} \exp\left[\int_{P^{\text{sat}}}^{P} \frac{v_w^I}{RT} dP \right] \quad (16)$$

When this equation is used for the fugacity of ice, it can be easily seen that the continuity of the fugacity of water in filled

hydrate phase at Q_1 is not guaranteed. As mentioned previously, a new approach for calculating the fugacity of ice was attempted in this work to overcome the inherent limitation of Eq. 16. At the lower quadruple point, the following expressions must hold for the fugacity of ice and pure liquid water (de Swaan Arons and Diepen, 1963)

$$\ln f_w^I = \ln P^{\text{sat}, I} + \int_0^P \frac{v_w^I}{RT} dP \quad (17)$$

and

$$\ln f_w^L = \ln P^{\text{sat}, L} + \int_0^P \frac{v_w^L}{RT} dP \quad (18)$$

whence

$$\ln \frac{f_w^I}{f_w^L} = \ln \frac{P^{\text{sat}, I}}{P^{\text{sat}, L}} + \int_0^P \frac{v_w^i - v_w^L}{RT} dP \quad (19)$$

where superscript L denotes supercooled (hypothetical-liquid) water. Using the Clausius-Clapeyron equation

$$\ln \frac{P^{\text{sat}, I}}{P^{\text{sat}, L}} = - \int_{T_0}^{T} \frac{\Delta h_w^{\text{fus}}}{RT^2} dT \quad (20)$$

Thus, the fugacity of ice is related to that of pure liquid water by the following equation

$$f_w^I = f_w^L \exp\left(- \int_{T_0}^{T} \frac{\Delta h_w^{\text{fus}}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{\text{fus}}}{RT} dP \right) \quad (21)$$

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. When we insert Eq. 21 into Eq. 14, the resulting expression for the fugacity of water in the filled hydrate phase is equal exactly to Eq. 15. Therefore, regardless of temperature range of the hydrate system considered, we can obtain a unique expression for the fugacity of water in the filled hydrate phase as follows

$$\hat{f}_w^H = f_w^L \exp\left[\frac{\Delta \mu_w^0}{RT} - \int_{T_0}^{T} \frac{\Delta h_w^{MT-I} + \Delta h_w^{\text{fus}}}{RT^2} dT \right.$$
$$\left. + \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{\text{fus}}}{RT} dP - RT \sum_m \nu_m \ln\left(1 + \sum_j C_{mj} \hat{f}_j^V \right) \right]$$
$$(22)$$

Here, the fugacities of supercooled water and all components in vapor phase, f_w^L and $\hat{f}_j^V$ were calculated using the SRK equation of state incorporated with the MHV2 mixing rule. As stated by several workers (Dahl and Michelsen, 1990; Dahl et al., 1991; Dahl and Macedo, 1992; Yoon et al., 1993), the
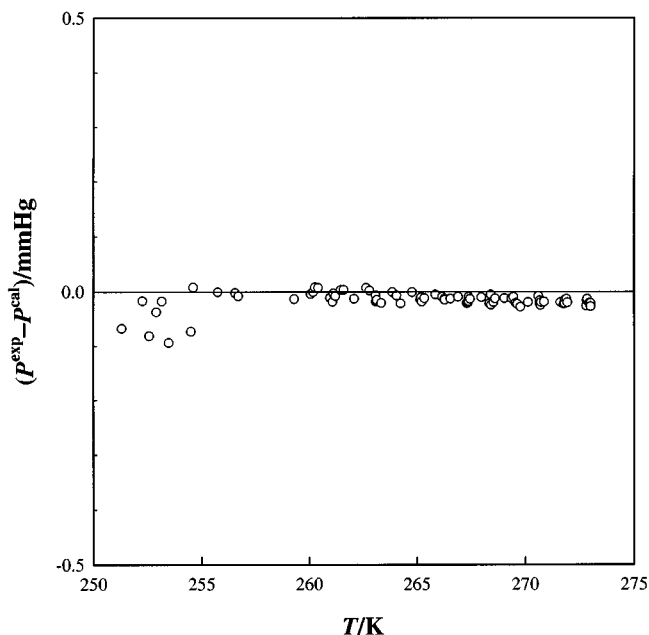
Figure 1. Deviation between experimental and calculated vapor pressures of supercooled water.

The experimental data from Kraus and Greer (1984) are used.

MHV2 mixing rule could be successfully applicable to the prediction of multicomponent VLE over a wide range of temperature and pressure. Any appropriate excess Gibbs energy model for the VLE calculations can be used for the Huron-Vidal mixing rules. In the present study, we used only the modified UNIFAC group-contribution model with the interaction parameters given elsewhere (Dahl et al., 1991). It should be noted, however, that the modified UNIFAC model is used not for calculating the activity coefficients of components in liquid phase, but for the MHV2 mixing rule to combine the SRK equation of state with the excess Gibbs energy model.

Heat capacity difference between ice and liquid water

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

$$\Delta h_w^{\text{fus}} = \Delta h_w^{\text{fus}}(T_0) + \int_{T_0}^{T} \Delta C_p dT \qquad (23)$$

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

where $\Delta C_p^0 = -38.13$, $\beta = 0.141$, $C_1 = -1.05253 \times 10^4$, $C_2 = 8.45606 \times 10^6$, $C_3 = -2.26357 \times 10^9$, $C_4 = 2.02637 \times 10^{11}$, $D_1 = -1.10556 \times 10^3$, $D_2 = 19.8314$, $D_3 = -1.17898 \times 10^{-1}$, $D_4 = 2.35259 \times 10^{-4}$, $T_H = 233$ K, and $T_G = 133$ K. For temperatures below T_G, the value of ΔC_p is assumed to be zero. The values of ΔC_p^0 and β are obtained from Parrish and Prausnitz (1972), while the constants C_i are calculated using the heat capacity data of Angell et al. (1973) for supercooled water and Giauque and Stout (1936) for ice. In calculation of the constants D_i, two boundary conditions at T_H and T_G and difference in total entropies of water and ice are taken into account (Angell et al., 1973). The remaining variable is chosen arbitrarily to reflect the thermodynamically reasonable shape of the heat capacity curve. The last term of Eq. 24 is to give the glass transition behavior of supercooled water at T_G (Ghormley, 1957; McMillan and Los, 1965; Angell and Sare, 1970; Angell et al., 1973). In fact, the spike behavior of the heat capacity curve at T_H is physically meaningless as pointed out by Angell et al. (1973). To resolve this aspect, it is necessary to correct the resulting equations by introducing more terms into Eq. 24. It is easily expected, however, that the use of Eq. 24 does not make significant discrepancy in thermodynamic calculations, particularly when they are used for calculating the fugacity of ice as shown in next section of this article.

Validity of the new equation for calculating the fugacity of ice

For the vapor-solid equilibria of pure water, we can write the general equation for the equilibrium condition as follows

$$f_w^V = P\varphi_w^V = f_w^I \qquad (25)$$

When we use Eq. 16 for the fugacity of ice, the equality of Eq. 25 is automatically satisfied at the saturation conditions because the fugacity is expressed as a function of pressure deviated from the saturation pressure by the Poynting correction. In contrast, as earlier discussed, the proposed equation for the fugacity of ice does not use the saturation pressure data, but requires only the thermodynamic properties and fugacities of supercooled water calculated from the SRK-EOS. It is obvious, therefore, that the use of Eq. 21 cannot exactly reproduce the saturation pressure of ice. Nevertheless, it may be reasonable to adapt this proposed equation only if it exhibits a satisfactory capability of predicting the saturation pressures of ice. First of all, let us consider the prediction of the vapor pressure of supercooled water in order to check the validity of the fugacity of supercooled water calculated from the SRK-EOS. As can be seen from Figure 1, the pre-
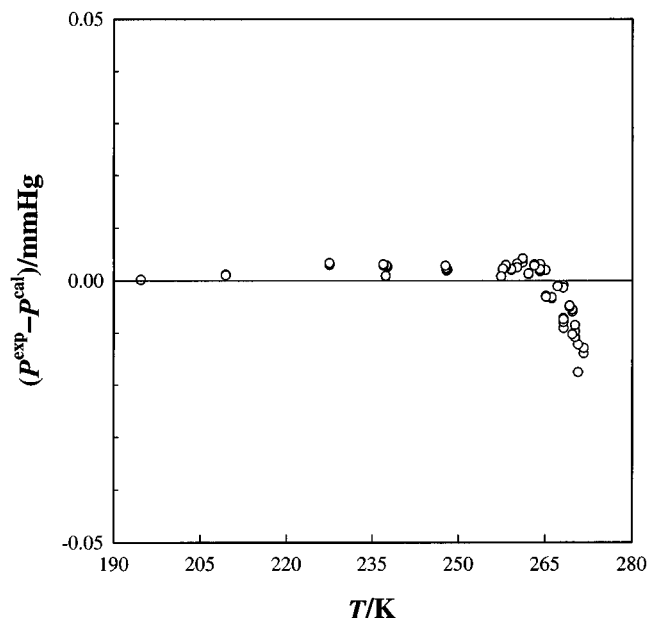
$$\Delta C_p = \begin{cases} \Delta C_p^0 + \beta(T - T_0) & T \geq T_0 \\[2mm] C_1 + \dfrac{C_2}{T} + \dfrac{C_3}{T^2} + \dfrac{C_4}{T^3} & T_0 > T \geq T_H \\[2mm] D_1 + D_2 T + D_3 T^2 + D_4 T^3 - \dfrac{T - T_G}{T_H - T_G} \ln \dfrac{T - T_G}{T_H - T_G} & T_H > T > T_G \end{cases} \qquad (24)$$

Figure 2. Deviation between experimental and calculated vapor pressures of ice.

The experimental data from Jancso et al. (1970) is used.

Table 1. Lattice Properties of Gas Hydrates

	Structure I	Structure II
Ideal structure	$M_1 \cdot 3M_2 \cdot 32H_2O$	$M_1 \cdot 2M_2 \cdot 17H_2O$
No. of water molecules/ unit cell	46	136
No. of small cavities/ unit cell	2	16
No. of large cavities/ unit cell	6	8
Avg. radius of small cavities, Å	3.95	3.91
Avg. radius of large cavities, Å	4.3	4.73
Coordination no. of small cavities	20	20
Coordination no. of large cavities	24	28

diction results are in excellent agreement with the experimental data even though the data below about −15°C are somewhat scattered. Based on these results, it is clear that the vapor pressure of supercooled water can be accurately reproduced by the SRK-EOS. In addition, this result implies that the vapor pressure of supercooled water follow closely the extrapolated behavior of stable liquid water above 0°C. Next, we consider the prediction of the vapor pressure of ice by using the proposed equation for the fugacity of ice. Figure 2 illustrates the difference between the experimental data and the calculated results. The available data cover the temperature ranging from −1 to −80°C (Jancso et al., 1970). From this figure, it is likely that there is a satisfactory agreement between the experimental and calculated results. It is found that the average percent absolute deviation (% AAD) between the calculated and measured results is 4.6. Consequently, the new expression for the fugacity of ice proposed in this study may provide the promising results for any thermodynamic calculation.

Results and Discussion

Dissociation pressures of simple hydrate-formers

The fugacities of all components in the vapor and liquid phases are calculated using the SRK equation of state incorporated with the MHV2 mixing rule (SRK-MHV2). The modified UNIFAC group contribution model is also used as the excess Gibbs energy for the MHV2 model. In the previous work, we have tested and proven the applicability of the MHV2 model for accurate prediction of the high-pressure phase equilibria of aqueous systems containing carbon dioxide and several alcohols (Yoon et al., 1993; Kim et al., 1994). Further, it has been widely known that the MHV2 model could be successfully applicable to the prediction of high-

pressure multiphase equilibria such as vapor-liquid-liquid equilibria over a wide range of temperature and pressure (Dahl and Michelsen, 1990; Dahl et al., 1991). Thus, it is noteworthy to expect that this model may be quite suitable for predicting the phase behavior of the hydrate systems containing a variety of hydrocarbon inhibitors, particularly, under high-pressure conditions. Only nine hydrate-forming gases would be considered in this work since the modified UNIFAC interaction parameters between solvent groups and gases are not sufficiently available in the literature.

The lattice and thermodynamic properties of gas hydrates used in the model calculation are listed in Tables 1 and 2, respectively. In Table 3, the sources and the ranges of temperature of hydrate data used for data reduction are listed. Also included are Kihara potential parameters for guest-water interactions of nine gases. The Kihara potential parameters are determined using the values for lattice and thermodynamic properties of empty hydrate lattice suggested by Parrish and Prausnitz (1972), because their values give a very good agreement between experimental and calculated hydrate dissociation pressures. Furthermore, since the effect of pressure on the hydrate lattice was assumed to be negligible, the compressibility of hydrates was not taken into account in this study. As mentioned earlier, the compositions of all fluid phases coexisted with hydrates are calculated by using the SRK-MHV2. This calculation procedure does not require the Henry's law constant correlation to describe gas solubility in liquid water. The Kihara parameters may be obtained independently of the mutual solubility between gas and water by constraining the model to the experimental dissociation pressures along the H-I-V curve. In this case, the Kihara parameters become insensitive to the choice of equations of state because the fugacity coefficients in that region are close to

Table 2. Thermodynamic Properties of Gas Hydrates

	Unit	Structure I	Structure II
$\Delta\mu_w^0$	J/mol	1,264	883
Δh_w^{MT-I}	J/mol	1,151	808
Δv_w^{MT-I}	cm³/mol	3.0	3.4
Δh_w^{fus}	J/mol	−6,011	
Δv_w^{fus}	cm³/mol	1.6	

Table 3. Kihara Potential Parameters for Guest-Water Interaction and Data Sources of Hydrate Dissociation

Guest	$a,^*$ Å	σ, Å	ϵ/k, K	Ref.[†]	Temp., K
Methane	0.30	3.2408	153.2	1, 2, 3, 4, 5, 6, 7, 8, 9, 10	148−320
Ethane	0.40	3.4383	175.0	1, 6, 7, 11, 12, 13, 14	200−288
Ethylene	0.47	3.3228	173.1	15, 16, 17	269−305
Propane	0.68	3.4435	187.4	1, 8, 10, 11, 18, 19, 20, 21	247−279
Propylene	0.65	3.4419	177.8	11, 22	273−274
Carbon dioxide	0.72	2.9327	169.5	1, 7, 19, 23, 24, 25, 26	151−283
Oxygen	0.36	2.9580	133.2	27, 28	267−291
Nitrogen	0.35	3.1308	123.8	4, 5, 27, 28	268−305
Hydrogen sulfide	0.36	3.2000	201.7	29, 30	250−303

[*]Parrish and Prausnitz (1972).
[†](1) Deaton and Frost (1946); (2) Kobayashi and Katz (1949); (3) McLeod and Campbell (1961); (4) Marshell 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).

unity (Lundgard and Mollerup, 1992). However, when the experimental data covering the H-I-V region is only limited or not available, this approach cannot be correctly applied for accurate determination of Kihara parameters. Furthermore, the Kihara parameters obtained by fitting only H-I-V data cannot be used effectively to predict the hydrate phase equilibria at high temperatures and pressures. Thus, in the present study, all experimental dissociation pressures covering both the H-I-V and H-L_w-V regions are used for the present model calculation.

The carbon dioxide hydrate was taken as a typical example of phase behavior of simple hydrates. Figure 3 shows the phase diagram for carbon dioxide hydrate over a wide range of temperature and pressure. The calculated results showed an excellent agreement with the experimental data. In particular, it should be noted that the lower and upper quadruple points designated by Q_1 and Q_2, respectively, are calculated by considering the thermodynamic basis that the four three-phase curves must meet at one quadruple point, as previously described. Thus, two almost vertical lines, structure I hydrate-Ice-water-rich liquid (H_I-I-L_w) and I-L_w-V, must branch at the lower quadruple point Q_1. Moreover, the lower quadruple point serves as a temperature limitation under which ice can coexist with hydrates because the slope of the H_I-I-L_w curve is negative. Of course, the compositions of all phases including hydrate phase at the quadruple points can be exactly specified by our model calculation. The calculated lower and upper quadruple points of simple hydrate systems considered in this study are listed and compared with experimental values in Table 4.

The accurate prediction of I-L_w-V curve for the binary hydrate systems does not depend on the used specific hydrate model, but requires a judicious means for calculating the fugacities of water in ice, water-rich liquid, and vapor phases. As precisely indicated in Figure 4, the earlier expression for the fugacity of ice does not provide the reliable prediction of the I-L_w-V curve. By increasing the system pressure, the deviations between the experimental and predicted results became considerably large. The erroneous prediction of the lower quadruple point seems to be unavoidable when the conventional approach is used. When applying the Peng-Robinson equation of state (Peng and Robinson, 1976) instead of the SRK equation of state for model calculations,
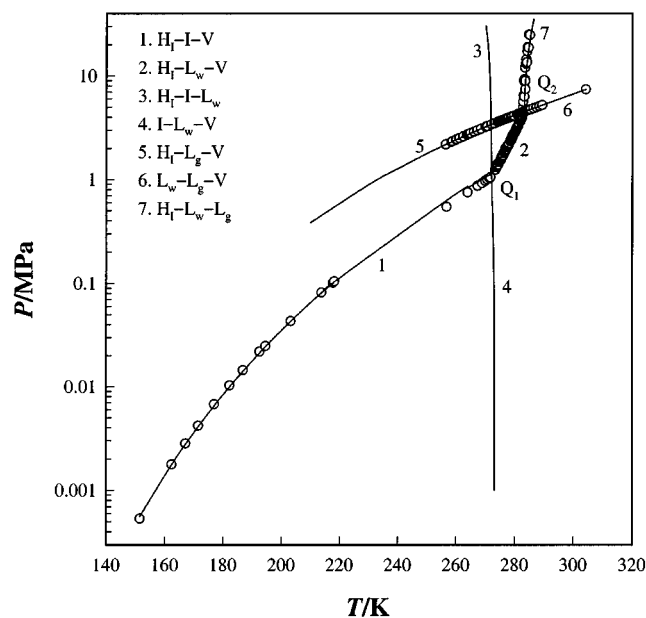
Figure 3. Pressure-temperature diagram of the binary carbon dioxide and water system.

Q_1 and Q_2 designate the lower and upper quadruple points, respectively.

the same tendency was observed as with the SRK equation of state. This implies that the best choice of the equation of state cannot improve the accuracy for predicting the lower quadruple point and I-L_w-V curve. In addition, since the mutual solubility between water and a guest component is very low, the effect of the MHV2 mixing rule on the I-L_w-V prediction becomes negligible. Therefore, as discussed earlier, this problem must be attributed to the fugacity of ice, which became a strong motive for going into the present study. The new approach gave an excellent agreement with the experimental I-L_w-V data for nitrogen hydrate system. Three different phase boundaries of the H_I-I-V, H_I-L_w-V and H_I-I-L_w curves were also successfully reproduced by the present model even though the pressure conditions appeared to be relatively high. Since most of the past investigations regarding

Table 4. Calculated and Experimental Lower and Upper Quadruple Points of Simple Hydrate Systems

	Q_1				Q_2			
	Calculated		Experimental		Calculated		Experimental	
	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)
Methane*	2.532	272.90	2.521	272.8[†]				
Ethane	0.472	273.10	0.473	273.1[†]	3.402	287.70	3.303	287.4[§]
Ethylene*	0.526	273.06	0.545	272.9[†]				
Propane	0.164	273.13	0.171	273.1[†]	0.559	278.62	0.562	278.4[‖]
Propylene	0.467	273.05	0.473	273.1[†]	0.608	274.18	0.600	274.1[#]
Carbon dioxide	1.133	272.12	1.049	271.9[†]	4.424	283.25	4.468	283.3[##]
Oxygen*	11.06	272.26	11.09	272.2[†]				
Nitrogen*	14.36	271.93	14.24	271.8[†]				
Hydrogen sulfide	0.096	272.89	0.093	272.8[‡]	2.293	302.70	2.239	302.7[‡]

*No upper quadruple points exists. [†]Estimated from H-I-V and H-L_w-V equilibrium data of references in Table 3. [‡] Selleck et al. (1952). [§]Reamer et al. (1952). [‖] Verma (1974). [#]Estimated by Parrish and Prausnitz (1972). [##]Robinson and Mehta (1971).
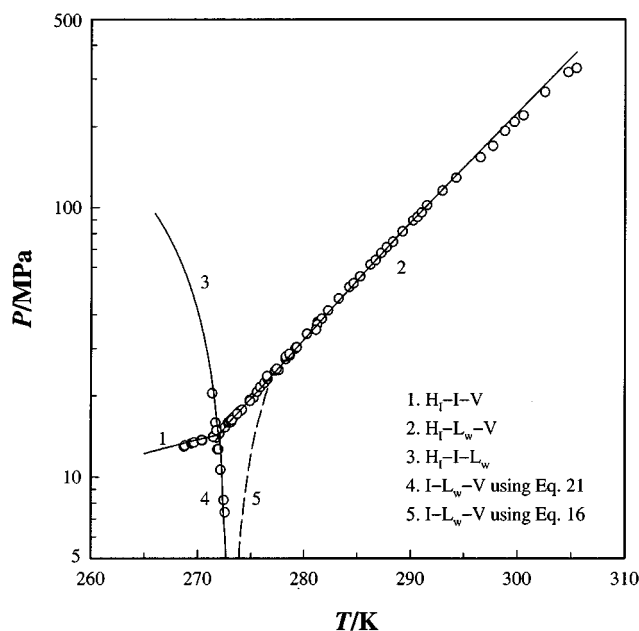

Figure 4. Pressure-temperature diagram of the binary nitrogen and water system.

1. H_I-I-V
2. H_I-L_w-V
3. H_I-I-L_w
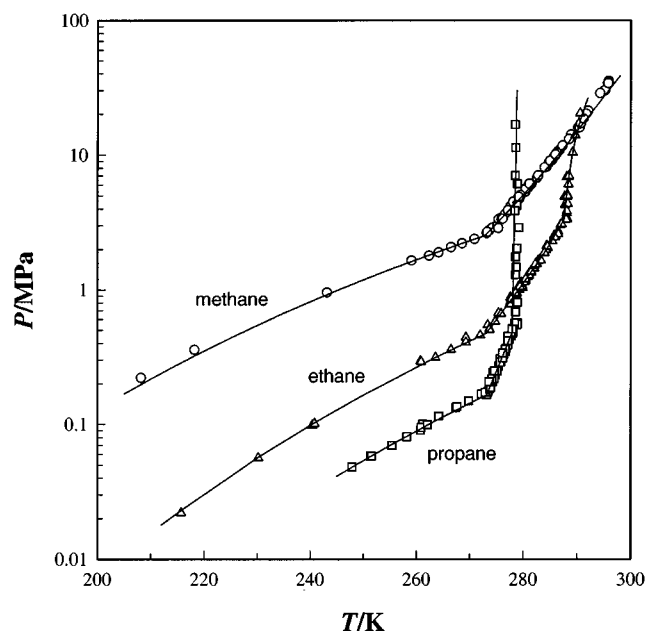4. I-L_w-V using Eq. 21
5. I-L_w-V using Eq. 16

Figure 5. Three phase H-I-V and H-L_w-V curves of simple methane, ethane, and propane hydrates.

the hydrate phase behavior have been limited to the H-I-V and H-L_w-V curves, no actual experimental H_I-I-L_w data have been reported with the exception of nitrogen and oxygen systems.

The pressure-temperature phase behavior of simple methane, ethane, and propane hydrate systems forming two distinctive types of hydrate structures I and II is presented in Figure 5. For methane hydrates, the experimental data covering only the temperature range of 200−300 K are depicted in this figure. For all these three systems, the predicted results agree well with experimental data over whole ranges of temperature and pressure. Even though the Kihara potential parameters are determined by fitting the experimental data of the H-I-V and H-L_w-V curves, the almost vertical curves of the three hydrate-water-rich liquid-gas-rich liquid (H-L_w-L_g) phases are perfectly reproduced for ethane and propane hydrate systems. These curves may serve as a temperature limit under which hydrates are capable of coexisting with other

phases in equilibrium. In fact, the H-L_w-L_g curve of the ethane hydrate system seems to have a slightly positive slope, while that for the propane hydrate system is nearly vertical. One of the most surprising results is that our model calculation perfectly reproduces this phase behavior. At an earlier time, Anderson and Prausnitz (1986) used the molar volume difference between the empty hydrate lattice and ice as 1.2 cm^3/mol instead of the experimental value of 3.4 cm^3/mol to calculate the H-L_w-L_g curve for the propane hydrate system and its inhibition by methanol. They insisted that this modification was needed to diminish particularly the rapid increase of water fugacity in the hydrate phase with increasing pressure and which is only applied to propane hydrate, but strangely not in ethane hydrates. However, in the present work, we directly used 3.4 cm^3/mol for the value of the molar volume difference and confirmed that the H-L_w-L_g curve for propane hydrate could be correctly calculated with this value. Furthermore, it is worthy to note that, by the model calcula-

Table 5. Average Absolute Deviations of Predicted Hydrate Dissociation Pressures of Simple Hydrate-Formers[*]

Guest	Temp., K	Pres., MPa	N_p	Sloan (1998)		This Work	
				% AAD	Structure	% AAD	Structure
Methane	148–320	0.005–400	92	8.8	I	9.3	I
Ethane	200–288	0.008–3.3	59	8.4	I	2.0	I
Ethylene	269–305	0.47–103	63	5.9	I	5.5	I
Propane	247–279	0.04–0.57	65	5.7	II	3.2	II
Propylene	273–274	0.46–0.60	15	3.2	II	0.6	II
Carbon dioxide	151–283	0.0005–4.4	92	6.0	I	3.1	I
Oxygen	267–291	9.9–95	50			2.5	II
Nitrogen	268–305	12–330	72	6.6	II	1.9	II
Hydrogen sulfide	250–303	0.03–2.3	29	7.1	I	2.6	I

[*]Data source: references in Table 3.

tion, the slope of the H-L$_w$-L$_g$ curve starting from the upper quadruple point of 278.62 K and 0.559 MPa increases steeply with a small increase of temperature until the equilibrium temperature and corresponding pressure is 278.69 K and 12.54 MPa, respectively. In our model calculation, at temperatures above 278.69 K, propane hydrates cannot exist in the equilibrium state because the slope turns negatively. In the case of propylene hydrate forming hydrate structure II the slope of the H-L$_w$-L$_g$ curve has been found to be always negative. When the value of the molar volume difference is smaller than 3.2 cm^3/mol, we can expect that the slope of the H-L$_w$-L$_g$ curve for both propane and propylene hydrates becomes always positive over the whole range of temperatures as shown in other systems forming structure I hydrate. In practice, we can expect the pressure-induced compression of hydrate molar volumes at pressures above 50 MPa (Hirai et al., 2000; Klauda and Sandler, 2000). If the molar volume difference of hydrates is expressed as a function of temperature and pressure, the predicted shape of the H-L$_w$-L$_g$ curve of propane hydrates at high pressures might be changed.

In Table 5, the % AADs of the predicted dissociation pressures for simple hydrate-formers are presented and compared with the results calculated by the program CSMHYD.EXE (Sloan, 1998). It has been found that the predictions of our model are more accurate than those of Sloan model except for methane hydrates. For methane hydrates, the agreement between the model and experimental values is not completely satisfactory for the entire temperature range of 150–320 K, and % AADs of 24.5 and 21.1 for the temperature ranges of 150–200 and 300–320 K, respectively. As indicated by Klauda and Sandler (2000), a change of the reference enthalpy or heat capacity, and an accurate description of hydrate molar volume that depends on temperature as well as pressure, must be considered to resolve inaccuracies. However, in this work, we do not take into account the compressibility of hydrates. The effect of pressure on the hydrate lattice is assumed to be negligible.

Mixed guest systems

In order to examine the potential applicability of our proposed model to the complicated systems, the hydrate-forming characteristics of the multiguest systems were first closely investigated for the mixed methane and propane hydrates and both the experimental and calculated dissociation pressures of this system agreed well over a wide range of concentra-
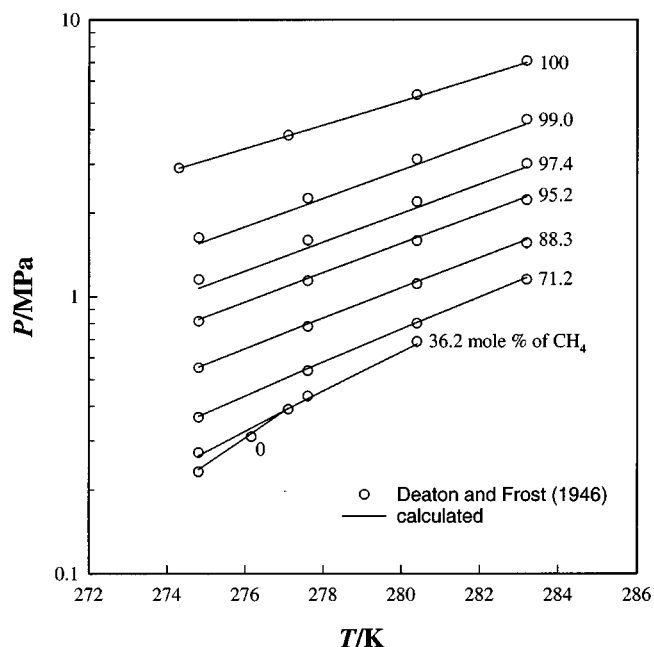

Figure 6. Dissociation pressures of the mixed methane and propane hydrates.

tions, as shown in Figure 6. While pure methane forms structure I hydrate and occupies both the small and large cavities of the hydrate lattice, pure propane forming the structure II hydrate apparently enters only the large cavities because the molecular diameter of propane is too large to occupy the small cavities. The occupancy of methane molecules to small cavities in the structure II makes the mixed methane and propane hydrates more stable than those formed solely by propane. The close examination of hydrate structure formed by the methane-propane-water mixtures reveals that, for a majority of compositions, structure II hydrates are most stable except for the hydrates formed by a very propane-dilute mixture (Holder and Hand, 1982). The detailed phase behavior of this system is presented through the pressure-composition (p-x) diagrams on the basis of the water-free concentration, as will be shown in Figures 8 and 9. For all concentration ranges measured experimentally, only structure II hydrate is found to exist in equilibrium. This peculiar phase behavior can be clearly supported by thermodynamic calculation. As shown in
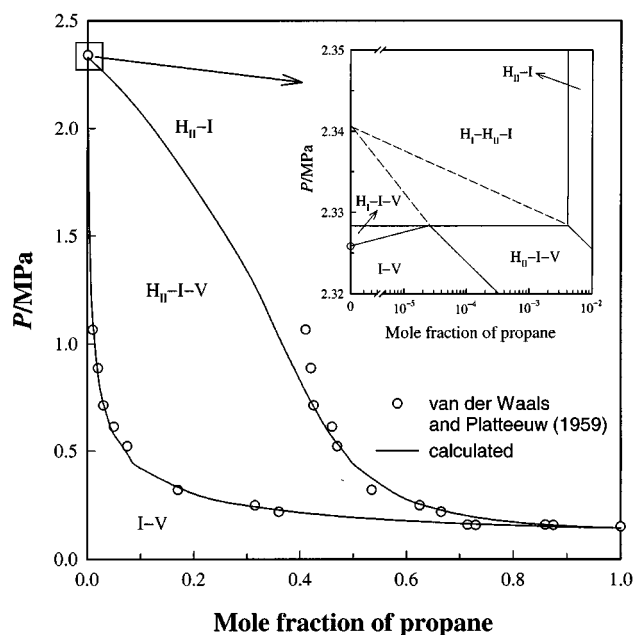
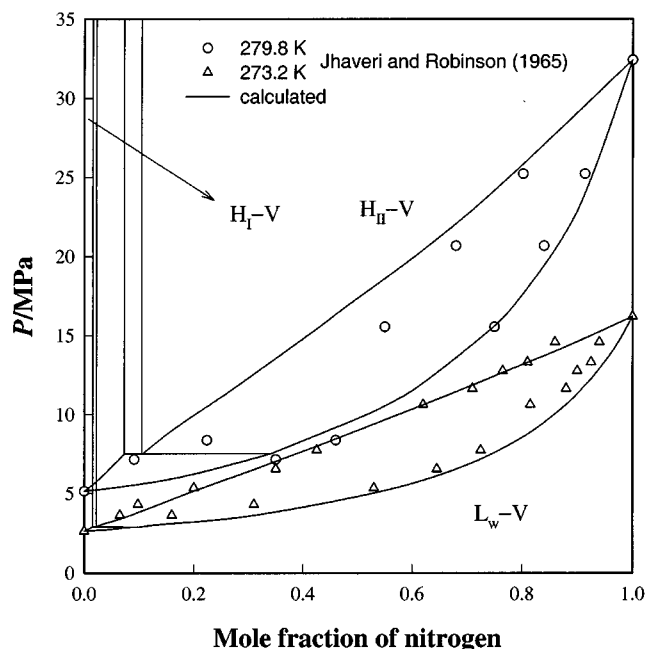**Figure 7. Pressure-composition diagram of the mixed methane and propane hydrate system at 270.15 K.**

Figure 9. Pressure-composition diagram of the mixed methane and nitrogen hydrate system at 273.2 and 279.8 K.

Figure 7, the prediction result indicates that structure II hydrates can be stabilized by methane even though the mol fraction of propane is below 0.001. It can be also seen that slight changes in the system pressure make a large change in the composition of vapor phase. This is due to the stabiliza-

Figure 8. Pressure-composition diagram of the mixed methane and propane hydrate system at 275.15 and 278.15 K.

tion effect by methane molecules occupied in the small cavities of the structure II hydrate.

On the other hand, the limiting condition at near the dissociation pressure of pure methane hydrate is described by our model calculation, as drawn separately on an enlarged scale in Figure 7. This figure implies that the dissociation pressure of pure methane hydrates which form a *metastable* structure II hydrate must always exist and be located at a higher pressure than the dissociation pressure of structure I hydrate. In this region, propane molecules do not absorb in the structure I hydrate, but acts only as gas diluents or inhibitors. Thus, higher pressure is required for the formation of structure I hydrate inhibited by a small amount of propane. As a consequence, the four phase H_I-H_{II}-I-V equilibrium pressure must also exist between two dissociation pressures of structure I and structure II hydrates of pure methane. This phenomenon was observed in the comprehensive experiments carried out by Adisasmito and Sloan (1992). They investigated that the hydrate structural transition for the mixed hydrates of carbon dioxide and each of propane, isobutane, *n*-butane, and synthetic natural gas occurred at the highly carbon dioxide-concentrated regions. Evidently, the existence of the four phases of H_I-H_{II}-L_w-V caused by this structural transition was also confirmed in their work. From close examination of both the experimental results and theoretical predictions by our model, it can be decisively concluded that, at a specified temperature, the *metastable* hydrate structure only exists at the higher-pressure region than the dissociation pressure of stable hydrate. As pointed out by Adisasmito and Sloan (1992), the capability of demonstrating this phenomenon can be used as a strong factor to test the potential of thermodynamic models for prediction of the hydrate phase equilibria. As can also be seen from Figure 8, the similar
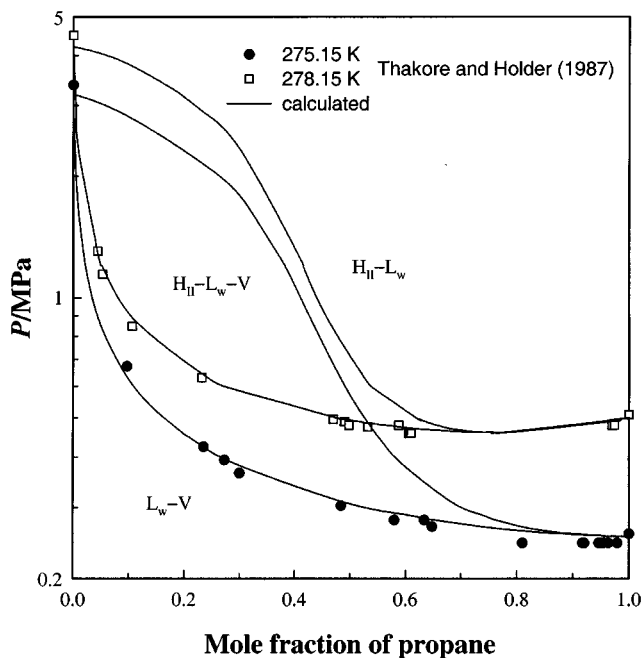
Table 6. Average Absolute Deviations of Predicted Hydrate Dissociation Pressures of Mixed Guest Systems

System	Temp., K	Pres., MPa	N_p	Ref.*	Sloan (1998) % AAD	Sloan (1998) Structure	This Work % AAD	This Work Structure
Methane-ethane	274–304	0.94–69	54	1, 2, 3	11.5	I	9.0	I, II
Methane-propane	270–305	0.15–69	78	1, 2, 4, 5	5.4	II	4.7	II
Methane-nitrogen	273–296	3.6–36	63	6	9.5	I, II	12.5	I, II
Methane-carbon dioxide	273–288	1.4–11	59	7, 8	2.9	I	3.2	I
Methane-hydrogen sulfide	276–296	1.0–6.8	20	9	7.4	I, II	7.4	I
Ethane-propane	273–284	0.44–2.1	60	10	13.4	I, II	10.6	I, II
Ethane-carbon dioxide	273–288	0.56–4.1	40	11	7.2	I	7.0	I
Propane-nitrogen	274–290	0.25–18	29	12	14.9	II	6.5	II
Propane-carbon dioxide	273–286	0.30–4.3	37	13	16.6	I, II	6.5	I, II

*(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) Noaker and Katz (1954); (10) Holder and Hand (1982); (11) Adisasmito and Sloan (1992); (12) Ng et al. (1977–1978); (13) Robinson and Metha (1971).

phase equilibria at two different temperatures are predicted by our model calculation. In these cases, the structural transition can be also anticipated at the highly methane-concentrated region, but it is eliminated from Figure 8 to avoid complexity. While the azeotropic conditions are experimentally observed at both temperatures (Thakore and Holder, 1987), our model predicts the azeotropic condition only at 278.15 K.

In Figure 9, the *p-x* diagram of the methane-nitrogen hydrate system is plotted on the basis of water-free concentration as a function of pressure. Even though there has been a controversy on which structure is more stable for nitrogen hydrates, we assume that nitrogen guest molecules form the structure II hydrate. Therefore, like the methane-propane hydrate system, the structural transition can be expected for this system. Calculated results show some deviations from the experimental data, especially at low temperatures and nitrogen-rich concentrations. It must be noted for this system containing mixed hydrate that, unlike the mixed methane-propane hydrate, the structural transition is observed over a wide range of concentrations. As the temperature increases, the occurrence of structural transition is shifted to the more nitrogen-rich condition. Accordingly, the composition range becomes enlarged over which structure I hydrate forms more preferably and stably.

In Table 6, the % AADs of hydrate dissociation pressures predicted by both the present and Sloan models for the mixed guest systems are presented for comparison. As indicated in this table, the % AADs of the hydrate systems in which the structural transition occurs are greater than those forming only one hydrate structure. To overcome the inherent model limitations, it becomes essential to accurately predict the structural transition point by changing the model parameters such as the reference chemical potential and/or Kihara potential parameters. It has been reported that the methane-ethane mixtures can form structure II hydrates at certain compositions (Subramanian et al., 2000a,b). As can be seen in Table 6, the proposed model reasonably predicts the structural transition of this system, whereas the Sloan model does not. In our model calculation, the lower (sI → sII) and upper (sII → sI) structural transition points at 274.2 K are predicted to occur at 89.0 and 99.7 mol % methane, respectively, while the corresponding experimental values were determined to be 72.2–75.0 and 99.2–99.4 mol % of methane (Subramanian et al., 2000a,b). Although both values for sII → sI were found
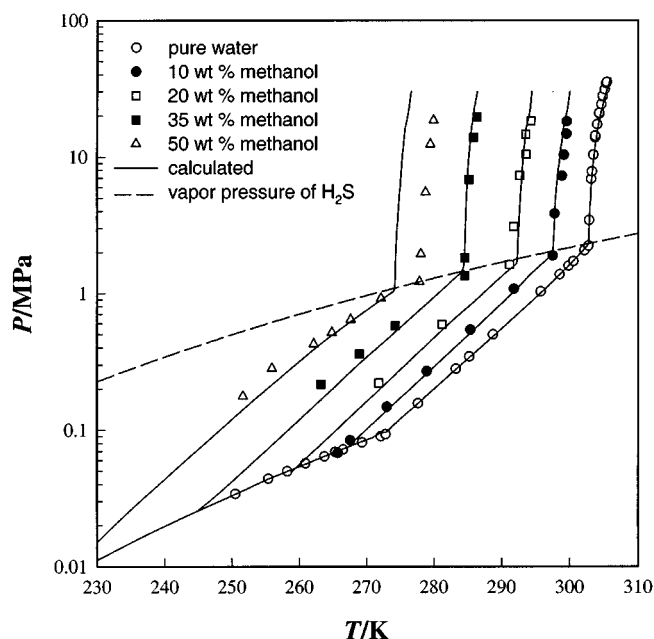
Figure 10. Inhibition of hydrogen sulfide hydrate by methanol.

to be almost identical, a little larger deviation between both values for sI → sII was produced. It must be, however, noted that, for the prediction of the mixed methane-ethane hydrate system containing two different guest components, the present approach uses the Kihara potential parameters determined only from the hydrate dissociation data of pure methane and ethane in order to predict the overall hydrate phase behavior, particularly, including its structural transition points. Interestingly, the Sloan model predicts the structural transition of the methane-hydrogen sulfide system, but the structure identification has not yet been reported.

Effect of inhibitors on hydrate formation

The inhibition effect of methanol on hydrate formation in the hydrogen sulfide-water and ethane-water systems are depicted in Figures 10 and 11, respectively. Even though the present model predicts fairly well under 35 wt. % of methanol, a noticeable deviation occurs at 50 wt. % methanol, particu-
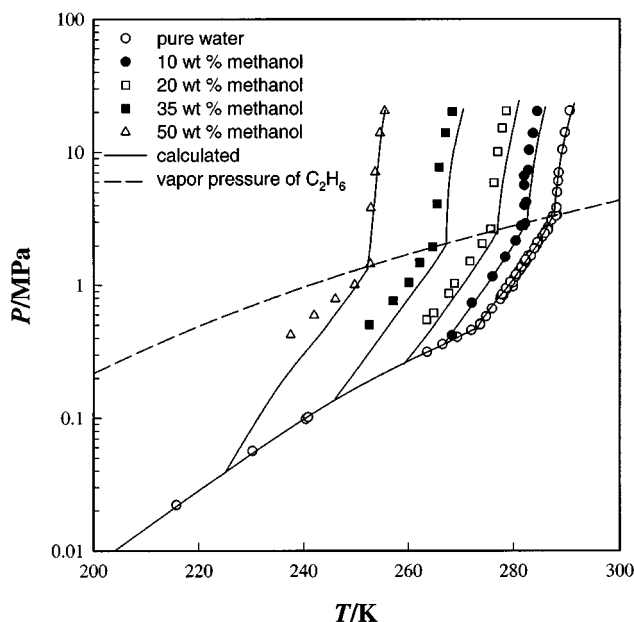
Figure 11. Inhibition of ethane hydrate by methanol.

larly for the H-L_w-L_g curve as shown in Figure 10. The systematic deviations between the experimental and calculated results of the ethane-water system inhibited by methanol are observed over the whole pressure and temperature ranges. These deviations may be attributed to the inadequacy of the modified UNIFAC interaction parameters used for the MHV2 model. In general the modified UNIFAC interaction parameters are determined by fitting the low-pressure and high-temperature VLE data. As previously described by Anderson and Prausnitz (1986), the use of UNIFAC parameters based on high-temperature data is probably responsible for the discrepancy since the hydrate data inhibited by methanol are mainly obtained below the ice-point temperature. Another possible source might come from data uncertainties resulting from the difficulty of experimental measurements. Judging from Figure 10, the possibility of systematic errors in experimental measurements for 50% of methanol becomes more feasible.

Conclusion

A generalized hydrate equilibrium model was developed for accurately predicting the complete phase behavior of simple and mixed hydrate systems. The proposed model used the Kihara potential for the interactions between gas and water molecules in hydrates on the basis of the theory of van der Waals and Platteeuw. The fugacities of all components in the vapor and liquid phases coexisting with hydrates were calculated by using the SRK-EOS incorporated with the MHV2 mixing rule. The Henry's law constant correlation for describing the gas solubility in liquid water was adopted to conventional models, but not required for the present approach. The UNIFAC group contribution model was also used as the excess Gibbs energy for the MHV2 model.

The present approach for predicting the fugacity of ice was confirmed to possess a great potential for examining the phase behavior of the complex hydrate-involving mixtures. By using this approach, the lower quadruple points and all possible phase boundaries of H-I-V, H-L_w-V, H-I-L_w and I-L_w-V around the lower quadruple point can be correctly described. The Kihara potential parameters for the interaction between water and nine hydrate-forming guests are provided by constraining the model to the experimental dissociation pressures of the H-I-V and H-L_w-V phase boundaries. In addition, the hydrate structural transition for the mixed hydrates such as the methane-propane hydrates was correctly described by the model calculation. The inhibition of gas hydrate by methanol was also checked to examine the potential applicability of the model to predicting the complicated phase equilibria. Although the modified UNIFAC interaction parameters are calculated by fitting the low-pressure and high-temperature VLE data, the agreement between the calculated and experimental results were found to be in an acceptable range.

Notation

a = Kihara hard-core parameter
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^V = fugacity of pure water in vapor phase
$\hat{f}_i^H$ = fugacity of component i in hydrate phase
$\hat{f}_i^L$ = fugacity of component i in liquid phase
$\hat{f}_i^V$ = fugacity of component i in vapor phase
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
P = pressure
$P^{sat,I}$ = saturation pressure of ice
$P^{sat,L}$ = saturation pressure of water
R = gas constant
r = radius of distance from the cavity center
T = temperature
T_0 = reference temperature, 273.15 K
v_w^I = molar volume of ice
v_w^L = molar volume of water
Δv_w^{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
ϵ = Kihara energy parameter
φ_w^{sat} = fugacity coefficient of water at saturation condition
φ_w^V = fugacity coefficient of water in vapor phase
$\Gamma(x)$ = Kihara potential function
μ_w^H = chemical potential of water in filled hydrate lattice
μ_w^I = chemical potential of ice
μ_w^L = chemical potential of water
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
$\Delta\mu_w^{MT-I}$ = difference in chemical potential of water between empty hydrate lattice and ice
$\Delta\mu_w^{MT-L}$ = difference in chemical potential of water between empty hydrate lattice and water

$\Delta\mu_w^0$ = 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
sat = saturation condition
w = water

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