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# A Generalized Model for Predicting Equilibrium Conditions for Gas Hydrates

**A modification of van der Waals and Platteeuw's (1959) hydrate equilibrium model which incorporates the effect of spherical asymmetry is developed. A corresponding states correlation is used to predict the deviation of Langmuir constants from ideal values. In this model the Kihara parameters obtained from hydrate equilibrium data agree well with those obtained from virial coefficient data.**

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## SCOPE

Gas hydrates are crystalline solids in which water forms a hydrogen bonded lattice with large interstitial vacancies called cavities. These cavities must be partially occupied by small gas molecules such as methane, nitrogen, or propane. Although some of the cavities will always be empty, the water lattice cannot form in the absence of gas; only through the physical interaction between the encaged gas molecules and the water lattice is the hydrate structure stabilized. In recent years much effort has been devoted to modeling the conditions at which hydrates will form.

The prediction of phase equilibria in gas hydrate forming

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systems is similar in many ways to the prediction of vapor-liquid equilibria. In both instances, models are developed based upon theoretical considerations and model parameters are then fitted using experimental data. However, in prediction of hydrate phase equilibria the macroscopic phase behavior is based upon a detailed molecular description of the physical interactions. Because hydrates are crystalline in nature, the specific relative locations of the water molecules in the hydrate phase are known exactly. The gas molecules are trapped in the interstices or cavities of the water lattice and each molecule is localized within one cavity. Hence, the relative locations of the gas molecules are also well defined. It is because the relative locations of the gas and water molecules are known that a molecularly based theory can be readily used.

Historically, the development of hydrate equilibrium predictions has focused on obtaining more experimental data and then refitting whatever model parameters are being used. While having experimental data is always useful, in this work we have focused our effort on fundamental modifications of the molecular model which take into account, (1) longer range interactions, (2) asymmetry in the gas-water interactions, and (3) restrictions of rotation and vibration of the gas molecules in the hydrate cavities. An empirical corresponding states correlation is used to account for this last effect.

By improving the model used for predicting hydrate equilibria, the model (Kihara) parameters fitted to binary (one gas + water) equilibrium pressure data are more realistic. In order to accurately extend hydrate equilibrium predictions to multicomponent systems, the model parameters must be representative of the true molecular characteristics. The model modifications incorporated in this work are fundamental, theoretically valid changes which help achieve a more valid description of molecular interactions.

## CONCLUSIONS AND SIGNIFICANCE

The principles of corresponding states have been applied to the prediction of hydrate equilibria with the result that the Kihara parameters used for predicting hydrate equilibria agree very well with those obtained from virial coefficient and viscosity data (Tee et al., 1966). This success was achieved by incorporating more of the hydrate phase molecular interactions and by accounting for the asymmetry in such interactions. The correlations developed are used to calculate a parameter, $Q^*$, which is universal for all gases in a given hydrate cavity. This parameter is a multiplicative correction to the ideal Langmuir constant, $C^*$, and it is correlated with the Kihara parameters ($\sigma$,$\epsilon$) of the enclathrated gases and with their acentric factor ($\omega$).

Because of the agreement between the Kihara parameters obtained from gas phase and hydrate phase data, the relative values of the Langmuir constants of a gas in the two hydrate cavities are likely to be more realistic than in previous studies which used more simple ideal models. As discussed in the text, by accurately estimating the Langmuir constants in each of the two cavities (as opposed to allowing compensating errors), hydrate equilibrium predictions can be extended to mixtures and the results for multicomponent system are quite good. For the methane/ethane/propane system, predicted and calculated dissociation pressures agree within 4.6%. Typical errors in predicted pressures for a given system are 3 to 10% of experimental pressures.

### BACKGROUND

The characteristics of the two hydrate structures known to form with light nonpolar gases are given in Table 1. It is very important to the prediction of hydrate equilibria to note that each structure has two different size cavities. Because the cavities are of different sizes, there exist some gas molecules such as propane, which can fit into the large cavity, but not into the small cavity. In such cases the gas to water ratio is much lower (about $1/17$ for propane in structure II hydrate) than for gas molecules which enter both cavities (about $1/6$ for methane in structure I hydrate).

The classical Langmuir type adsorption theory used in predicting gas hydrate equilibrium was originally developed by van der Waals and Platteeuw (1959) and has since been modified and improved by others (Marshall et al., 1964; Parrish and Prausnitz, 1972; Holder et al., 1980; John and Holder, 1981, 1982a). In the original and modified models each cavity is considered to be an adsorption site which can contain zero or one gas molecule. The fractional portion of sites (cavities) which are occupied varies from gas to gas, and with temperature and pressure, and the problem of calculating hydrate equilibria is basically one of calculating the physical interaction between the gas molecules and the crystal lattice.

In their original model, van der Waals and Platteeuw (VDWP) assumed that the gas molecules only interact with the nearest neighbor water molecules, which are the water molecules forming a specific cavity. They further assumed that the water molecules are "smeared" over a sphere of radius $R$, which is characteristic of that cavity; i.e., they used a "smoothed cell" potential. In this context they further assumed that a Lennard-Jones potential describes the gas-water interaction. Subsequent modifications focused on changing this potential model and culminated in the present day use of spherical core Kihara potential function (an appropriate algorithm is described by John and Holder, 1982a).

Until recently, the other assumptions incorporated in the VDWP model had not been evaluated properly. However John and Holder (1981, 1982a) have shown that the assumptions mentioned above give manifestly incorrect results when calculating hydrate equilibria. In these two studies, the modifications necessary (1) for incorporating second neighbor effects, and (2) for characterizing the hydrate cavities as smooth, have been developed. It can be rigorously shown that these corrections give a fundamentally improved model for spherical molecules when using the spherical core Kihara potential.

If, however, one wishes to model the physical interaction with nonspherical molecules, the calculations must incorporate the effect of the angular orientation of the gas molecule in the hydrate cavity. For small linear molecules it is possible to develop a good statistical model for describing the gas-cavity interactions in the hydrate phase, but for polyatomic molecules the task would be extremely difficult. For such an approach, detailed information about each gas molecule would be required. For example, studies (Davidson and Ripmeester, 1978) have shown that $n$-butane can only fit into the large cavity of structure II and then only in the gauche form.

TABLE 1. STRUCTURE OF GAS HYDRATES (VAN DER WAALS AND PLATTEEUW, 1959)

| | Structure I | Structure II |
|---|---|---|
| Small cavities per unit cell | 2 | 16 |
| Large cavities per unit cell | 6 | 8 |
| Water molecules per unit cell | 46 | 136 |
| Small cavities per water molecule, $\nu_1$ | 1/23 | 2/17 |
| Large cavities per water molecule, $\nu_2$ | 3/23 | 1/17 |

TABLE 2. CELL CHARACTERIZATIONS IN THE FOUR CAVITIES OF STRUCTURE I AND STRUCTURE II HYDRATE

| | First Shell | Second Shell | Third Shell |
|---|---|---|---|
| Structure I | $R$ = 387.5 pm | $R$ = 659.3 pm | $R$ = 805.6 pm |
| Small Cavity | $z$ = 20 | $z$ = 20 | $z$ = 50 |
| Structure I | $R$ = 415.2 pm | $R$ = 707.8 pm | $R$ = 828.5 pm |
| Large Cavity | $z$ = 21 | $z$ = 24 | $z$ = 50 |
| Structure II | $R$ = 387.0 pm | $R$ = 666.7 pm | $R$ = 807.9 pm |
| Small Cavity | $z$ = 20 | $z$ = 20 | $z$ = 50 |
| Structure II | $R$ = 470.3 pm | $R$ = 746.4 pm | $R$ = 878.2 pm |
| Large Cavity | $z$ = 28 | $z$ = 28 | $z$ = 50 |

In the present work, rather than trying to develop a very complex set of potential functions it has been decided to model the hydrate phase interactions using the spherical core Kihara model with a perturbation type parameter to account for the nonspherical nature of gas-water interactions (which result in restricted rotations and vibrations) when aspherical guests are enclathrated.

## MODEL

For calculation of hydrate equilibria, the following equation is solved

$$\Delta\mu_w^H = RT \sum_{i=1}^{2} \nu_1 \ln\left(1 + \sum_j C_{ij}\phi_j y_j P\right) \tag{1}$$

where $\nu_i$ is the ratio of cavities (of type $i$) to water molecules in the hydrate phase, and $\phi_j$ and $y_j$ are the fugacity coefficient and mole fraction, respectively, of gas species $j$ which is in equilibrium with the hydrates. The quantity $\Delta\mu_w^H$ is the chemical potential difference between the occupied hydrate and the completely empty (hypothetical) hydrate lattice. Its dependence on temperature and pressure are described by Holder et al. (1980).

Equation 1 can be numerically solved for pressure if the Langmuir constant $C$ is known. The present model suggests a new method of calculating $C_{ij}$. The smoothed-cell Langmuir constant is (without subscripting),

$$C = \frac{4\pi}{kT}\int_0^R (e^{-W(r)/kT})r^2 dr \tag{2}$$

where, $W(r)$ is the smoothed-cell radial potential function obtained using the appropriate potential; it is specific to each cavity-gas combination. Here $r$ is the radial distance of the enclathrated gas molecule from the cavity center. In the present modified model

$$W(r) = W_1(r) + W_2(r) + W_3(r) \tag{3}$$

where $W_1$, $W_2$, and $W_3$ ae the smoothed-cell potential contributions of the first, second, and third shell (of water molecules), respectively. The second and third shell contributions are quite important (John and Holder, 1982a) and have not been used in previous models. Table 2 lists the cell characteristics needed for calculation of the cell potentials.

Unfortunately, Eqs. 2 and 3 cannot reasonably predict hydrate equilibria except for spherical molecules such as argon, krypton, and methane even though the interaction with all three shells is included. To overcome this deficiency (which also exists in single-shell models), investigators have arbitrarily adjusted the Kihara size ($\sigma$) and energy parameters ($\epsilon$) so that good agreement was obtained between experimental and calculated three-phase (water + gas + hydrate and ice + gas + hydrate) equilibrium pressures. The concept was first used by Kobayashi and coworkers (Marshall, Saito, and Kobayashi, 1964) and developed by Parrish and Prausnitz (1972). It has been used, sometimes in modified form, in most applications since.

The major difficulty in the above approach is that the Kihara parameters needed for calculating hydrate equilibria cannot be related to the Kihara parameters found from viscosity and second virial coefficient data (Tee et al., 1966). Our earlier work has shown that there are several sets of Kihara parameters which can be used to calculate a single Langmuir constant (Holder et al., 1980; Holder and Manganiello, 1982), but more important, for gases which fit into two cavities, there exist many pairs of Langmuir constants which will closely predict the experimental dissociation pressures of binary (one gas species + water) hydrates, e.g., methane-hydrate. Only one of these pairs can be correct. If prediction of hydrate formation from a single gas were all that was needed, the arbitrary selection of Kihara parameters would be useful although theoretically unsound. The wrong Kihara parameters, the wrong cell potentials, and the wrong Langmuir constants would lead to the *right dissociation pressures.*

However, in most practical cases hydrates are formed from gas mixtures such as a mixture of methane, ethane, and propane. The Langmuir constants for each gas are independent of the composition of the gas, and for each species in a mixture the Langmuir constant will be the same as it is in the pure gas. The contribution to $\Delta\mu_w$ is composed of a contribution from the small cavity (1) and the large cavity (2)

$$\Delta\mu_w^H = \Delta\mu_1^H + \Delta\mu_2^H \tag{4}$$

where

$$\Delta\mu_i^H = RT\,\nu_i \ln\left(1 + \sum_j C_{ji} y_j \phi_j P\right)$$

In a pure gas hydrate, where $j = 1$, if $\Delta\mu_1^H$ is too low and $\Delta\mu_2^H$ is too high (at a given pressure), their sum may be correct. However, consider hydrates formed from a mixture of methane and propane. Propane is too large to fit into the small cavity ($C = 0$) and its Langmuir constant in cavity 2 is about 600 times as large as that of methane. Hence $\Delta\mu_1^H$ is determined solely by the methane Langmuir constant and $\Delta\mu_2^H$ is, for practical purposes, determined by the propane Langmuir constant. Errors in the Langmuir constants will produce corresponding errors in $\Delta\mu_1^H$ and $\Delta\mu_2^H$, which, except in the most fortuitous cases, will not be mutually cancelled. Hence, the calculated equilibrium pressure will be wrong. Only if the Langmuir constants for each species in each cavity is correct will the dissociation pressure be correct.

It is clear that a more theoretically sound basis of calculating $C_{ji}$ is needed if dissociation pressures of mixtures are to be accurately calculated. To do this all of the cell potentials need to be included and the Kihara parameters must be theoretically based.

### Selection of Kihara Parameters

The Kihara parameters selected for calculation of the gas-water interaction in the hydrate phase are determined from traditional mixing rules

$$\begin{aligned} \sigma &= (\sigma_g + \sigma_w)/2 \\ \epsilon &= (\epsilon_g \epsilon_w)^{1/2} \\ a &= (a_g)/2 \end{aligned} \tag{5}$$

where $\sigma_g$ is the Kihara distance parameter for gas-gas interactions and $\sigma_w$ is the corresponding parameter for water. The Kihara parameters ($\sigma_g$ and $\epsilon_g$) of Parrish and Prausnitz typically differed from the gas-phase (virial coefficient and viscosity) parameters by 50%, and a variation of $\sigma$ or $\epsilon$ by 50% will result in a several orders of magnitude change in $C_{ji}$. In contrast, we require that the gas Kihara parameters be "very close," typically within 5%, to parameters calculated from virial coefficient and viscosity data (Tee et al., 1966) and we require that a single set of parameters be applicable to water for calculation of gas-water hydrate phase interactions. Theoretically the Kihara parameters in the gas and hydrate phases should agree, and when agreement is obtained the calculated Langmuir constants are more likely to accurately distribute the contribution to hydrate stability between the large and small cavities. Because of the extreme sensitivity of $C_{ji}$ to $\sigma$ and $\epsilon$ it is, unfortunately, not possible to require that the gas phase and hydrate phase Kihara parameters ($\sigma_g$, $\epsilon_g$, $a_g$) be exactly identical and still get reasonable predictions. The mixing rules (Eq. 5) are somewhat arbitrary, and the variation between gas and hydrate phase parameters can be attributed to a small binary-interaction

TABLE 3. REFERENCE PROPERTIES OF STRUCTURE I AND STRUCTURE II HYDRATES

| | Structure I | Structure II |
|---|---|---|
| $\Delta\mu_w^0$ J/mol | 1,120 | 931 |
| $\Delta h_w^o$ J/mol* | 1,714 | 1,400 |
| $\Delta v_w$ cc/mol** | 2.9959 | 3.39644 |
| $\sigma_w$ pm | 356.438 | 356.438 |
| $\epsilon_w/k$ | 102.134 | 102.134 |
| $a_w$ pm | 0 | 0 |
| $\Delta C_{pw}$ | $-34.583 + 0.189\ (T - T_o)$; $T > T_o$ | $-36.8607 + 0.1809\ (T - T_o)$; $T > T_o$ |
| $\Delta C_{pw}$ | $3.315 + 0.0121\ (T - T_o)$; $T < T_o$ | $1.029 + 0.00377\ (T - T_o)$ $T < T_o$ |
| $a_o$: Small Cavity | 35.3446 | 35.3446 |
| $a_o$: Large Cavity | 14.1161 | 782.8469 |
| $n$: Small Cavity | 0.973 | 0.973 |
| $n$: Large Cavity | 0.826 | 2.3129 |
| $T_0 = 273.15$ K | | |

* In the liquid water region, subtract 6,011 J/mol from $\Delta h_w^o$.
** In the liquid water region, add 1.6 cc/mol to $\Delta v_w$. (From crystallographic data on von Stackelberg and Müller, 1954.)

parameter type of correction which is incorporated into the Kihara parameters used in the hydrate phase. Hence slight differences in the gas and hydrate phase Kihara parameters are justified.

Without further modification this approach will work for spherical molecules. Despite the fact that only a single shell potential $[W_1(r)]$ was used, the approach described above was successful for methane/argon/krypton systems (Holder et al., 1980). However, when nonspherical moelcules are included, the model is not effective and a modification is required to account for the effects of molecular asphericity.

### Aspherical Corrections

In order to correct for the fact that the guest-host interactions depart from the spherical smoothed-cell potential we have adopted a perturbation approach. We represent the true Langmuir constant $C$ by

$$C = Q^*C^* \tag{6}$$

where

$$C^* = \frac{4\pi}{kT}\int_0^R \exp\left(-\left[\frac{W_1(r) + W_2(r) + W_3(r)}{kT}\right]\right) r^2 dr$$

and $Q^*$ is an empirical function that corrects the Langmuir constant due to restricted motion of the gas molecule. Equation 6 requires that values of $Q^*$ be such that they give Langmuir constants, $C$, which are accurate. Thus, $Q^*$ accounts for all nonidealities in the molecular interactions between the enclathrated gas and the hydrate cavity. However, if this correction is theoretically valid there should be some general trends in $Q^*$ with molecular properties. These trends include:

1. $Q^*$ should be near 1.0 for spherical molecules in approximately spherical cavities since no aspherical corrections are needed.

2. $Q^*$ should decrease as molecular asymmetry increases; that is, as the acentric factor increases $Q^*$ should decrease. An asymmetric gas will have restricted movement in the hydrate cavity and will thus be less stable in a hydrate cavity than a spherical molecule with the same $\epsilon$ and $\sigma$. The lower stability is indicated by a lower value of $C$ (or $Q^*$). Hence $\omega$ should be a good correlating parameter.

3. $Q^*$ should decrease as the size of the gas molecule increases. More accurately, $Q^*$ should be proportional to the ratio of the molecular diameter to the cavity diameter (or cavity radius). We use $\sigma/(R - a)$ as a measure of the degree of tightness with which a molecule fits into a cavity.

4. $Q^*$ should decrease as the intermolecular interaction (as measured by $\epsilon$) increases. As $\epsilon$ increases, the preference for certain

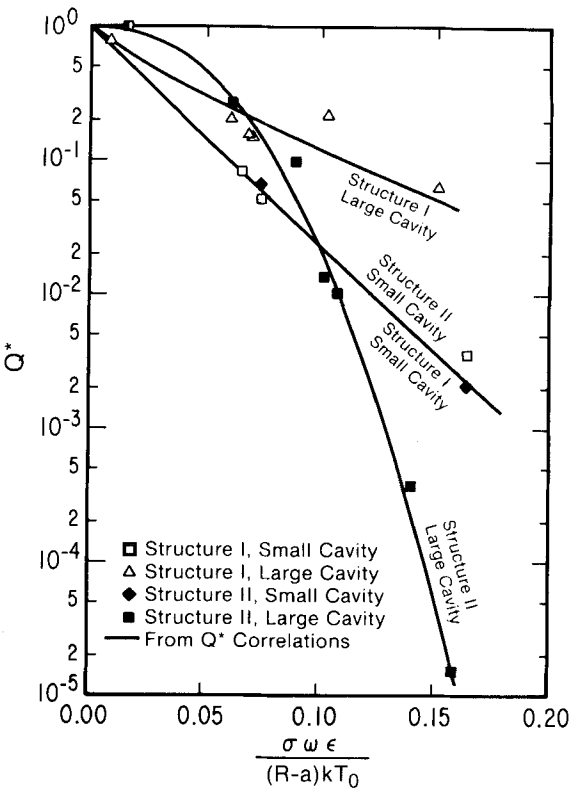


**Figure 1. The $Q^*$ correlations.**

orientations becomes larger, internal rotation is more restricted, and this restricted rotation is manifested in a decrease in $Q^*$. We thus use $\epsilon/kT$ as a correlating parameter.

Accordingly, the following empirical, corresponding states correlation for $Q^*$ was hypothesized

$$Q^* = \exp\left(-a_0\left[\omega\left(\frac{\sigma}{R-a}\right)\left(\frac{\epsilon}{kT_0}\right)\right]^n\right) \tag{7}$$

where $a_o$ and $n$ are empirical parameters which depend upon the particular cavity. For a given molecule $Q^*$ will be different for each cavity. Table 3 lists values of $a_o$ and $n$ for each cavity which are determined by forcing agreement between experimental and calculated dissociation pressures for 15 different gases. The strongest support for the theory developed here is its ability to predict the dissociation pressure of all gases studied with values of $a_o$ and $n$ which are independent of the gas species enclathrated. Initially we tried to keep $a_o$ and $n$ the same for all cavities. However, $Q^*$ is a measure of the asymmetry of interaction between the cavity and the gas molecule, and since each cavity has different degrees of asymmetry, different values of $a_o$ and $n$ are needed for each cavity.

Fortunately, for molecules such as propane and $n$-butane which only fit into the large cavity of structure II, values of $Q^*$ can be calculated exactly from experimental data. For other molecules such as methane, values of $Q^*$ can also be calculated from experimental data through a procedure to be described in a separate paper. Note that the correlations given by Eq. 7 fit these experimental values of $Q^*$ as shown in Figure 1.

In determining the values of $a_o$ and $n$ for each cavity, hydrate data covering the systems listed in Table 4 and referenced in Table 5 were used. As mentioned above, the Kihara parameters for each gas species were allowed to vary slightly from virial coefficient and viscosity parameter in order to get a good fit to experimental dissociation pressures. The final Kihara paraemters are listed in Table 6. Table 3 lists the reference properties used in this approach. They are determined according to the method of Holder et al. (1980) using experimental data. Methane/argon/krypton data at 273.16 K were used for determining the reference properties of structure I and methane/propane and methane/isobutane data at 273.16

TABLE 4. HYDRATE SYSTEMS STUDIED USING THE $Q^*$ CORRELATION METHOD

| Gas Species | Temp. Range, K | No. of Data Points | Average Error, % |
|---|---|---|---|
| Methane, Argon, Krypton, Methane/Argon, Methane/Krypton (Structure I) | 148–302 | 26 | 10.9 |
| Propane (Structure II) | 250–277 | 13 | 7.9 |
| Methane/Propane (Structure II) | 273–283 | 26 | 11.1 |
| Isobutane, Methane/Isobutane (Structure II) | 252–286 | 26 | 10.9 |
| Cyclopropane (Structure I) | 243–260<br>276–282 | 8 | 3.6 |
| Cyclopropane (Structure II) | 264–274 | 6 | 2.0 |
| Ethane/Propane (Structure I) | 275–280 | 8 | 2.0 |
| Ethane/Propane (Structure II) | 273–278 | 17 | 4.0 |
| Ethane, Methane/Ethane (Structure I) | 262–285 | 20 | 5.0 |
| Methane/Ethane/Propane (Structure I) | 275–285 | 13 | 4.6 |
| Methane/$n$-Butane (Structure II) | 252–283 | 35 | 8.8 |
| Ethylene (Structure I) | 274–288 | 11 | 2.3 |
| Carbon Dioxide, Carbon Dioxide/Methane (Structure I) | 276–285 | 15 | 3.4 |
| Carbon Dioxide/Propane (Structure II) | 273–282 | 13 | 6.7 |
| Propylene (Structure II) | 272–274 | 7 | 0.7 |
| Hydrogen Sulfide (Structure I) | 252–298 | 13 | 2.8 |
| Hydrogen Sulfide/Propane (Structure II) | 270.15 | 8 | 6.4 |
| Hydrogen Sulfide/Methane (Structure I) | 279–289 | 9 | 7.7 |
| Oxygen (Structure I) | 267–289 | 15 | 2.5 |
| Nitrogen (Structure I) | 268–289 | 11 | 3.2 |
| Xenon (Structure I) | 216–273 | 11 | 6.4 |
| Nitrogen/Methane (Structure I) | 273–255 | 44 | 10.4 |

TABLE 5. SOURCES OF HYDRATE EQUILIBRIUM DATA USED IN THIS STUDY

Sources not listed by Parrish and Prausnitz (1972).

| | |
|---|---|
| Pure Gases | |
| Methane | Falabella and Vanpee (1974) |
| Ethane | Falabella and Vanpee (1974) |
| Krypton | Holder et al. (1980) |
| Propane | Holder and Godbole (1981) |
| Isobutane | Holder and Godbole (1981) |
| Gas Mixtures | |
| Methane/Krypton | Holder et al. (1980 |
| Methane/Ethane | Holder and Grigoriou (1980) |
| Methane/Propane | Verma (1974) |
| Methane/Ethane/Propane | Holder and Hand (1982) |
| Ethane/Propane | Holder and Hand (1982) |
| Methane/Isobutane | Wu et al. (1976) |
| Methane/$n$-Butane | Ng and Robinson (1976a)<br>John and Holder (1982b) |

K were used for determining the reference properties of structure II. For structure I, the values of $Q^*$ for methane ($\omega = 0$ is used), argon, and krypton are zero, but in structure II, the $Q^*$ values of isobutane and propane were needed to determine the reference properties. These $Q^*$ values were determined from the experimental data on pure propane and pure isobutane.

## DISCUSSION

This study introduces a unified method for calculating hydrate equilibria for a variety of multicomponent gas mixtures over a range of temperatures and pressures. The $Q^*$ correlation method corrects for the nonideal behavior of gas molecules in the hydrate phase, based on the size and shape characteristics of the molecules. While the basic model is the one proposed by van der Waals and Platteeuw (1959), sufficient improvements have been made to make the model applicable to non-ideal gas species. Table 4 gives the general accuracy of this method and Tables 7 and 8 show the accuracy for two specific examples. Note that even though the Kihara parameters were not freely adjusted, the same accuracy was obtained for the methane, ethane, and propane system as was obtained by Dharmawardhana et al. (1980) who used this data in determining their Kihara parameters. Figures 2 and 3 show predicted results for the methane/isobutane and methane/ethane systems. We have evaluated the ability of this procedure to predict the dissociation pressure of the multicomponent systems of McLeod and Campbell (1961), Robinson and Hu Hon (1967), and Ng and Robinson (1976) with average errors of 23%, 26%, and 22% respectively, based upon experimental dissociation pressures. Calculations were not successful in predicting the results of hydrogen rich systems (Holder et al., 1983) where an average error of 51%

TABLE 6. COMPARISON OF TWO SETS OF KIHARA PARAMETERS

| Gas Species | Spherical Kihara Parameters from Tee, Gotoh, Stewart (1966) Correlations | | | | Optimal Kihara Parameters to be Used in the $Q^*$ Method | | | |
|---|---|---|---|---|---|---|---|---|
| | $\sigma_g^*$, pm | $\epsilon_g/k$, K | $a_g$, pm | $\omega$ | $\sigma_g^*$, pm | $\epsilon_g/k$, K | $a_g$, pm | $\omega$ |
| Methane | 363.8 | 195.48 | 26.0 | 0.007 | 350.1 | 197.39 | 26.0 | 0.000 |
| Ethane | 402.2 | 404.3 | 57.4 | 0.105 | 403.6 | 393.2 | 57.4 | 0.105 |
| Argon | 331.8 | 151.7 | 21.7 | 0.0 | 328.8 | 156.08 | 21.7 | 0.0 |
| Krypton | 355.1 | 210.3 | 23.2 | 0.0 | 353.1 | 216.4 | 23.2 | 0.0 |
| Nitrogen | 346.9 | 142.1 | 34.1 | 0.04 | 344.4 | 158.97 | 34.1 | 0.04 |
| Oxygen | 327.0 | 165.33 | 27.2 | 0.021 | 327.2 | 165.52 | 27.2 | 0.021 |
| Carbon Dioxide | 333.5 | 513.85 | 67.7 | 0.225 | 340.7 | 506.25 | 67.7 | 0.225 |
| Hydrogen Sulfide | 352.3 | 488.40 | 49.2 | 0.1 | 347.6 | 478.94 | 49.2 | 0.1 |
| Ethylene | 387.4 | 367.87 | 53.4 | 0.097 | 381.9 | 354.33 | 53.4 | 0.097 |
| Xenon | 386.5 | 290.8 | 25.2 | 0.0 | 364.8 | 314.51 | 25.2 | 0.0 |
| Propane | 440.6 | 542.78 | 74.5 | 0.152 | 439.9 | 539.99 | 74.5 | 0.152 |
| Isobutane | 474.6 | 628.6 | 85.9 | 0.176 | 483.8 | 662.09 | 85.9 | 0.176 |
| Normal Butane | 471.4 | 676.9 | 89.1 | 0.193 | 467.4 | 674.91 | 89.1 | 0.193 |
| Propylene | 427.5 | 531.05 | 71.4 | 0.148 | 423.2 | 527.91 | 71.4 | 0.148 |
| Cyclopropane | 418.5 | 554.4 | 65.3 | 0.128 | 419.1 | 602.40 | 65.3 | 0.128 |

TABLE 7. EQUILIBRIUM PREDICTIONS FOR PROPANE-CARBON DIOXIDE MIXTURES. (Data from Robinson and Mehta, 1971.)

| Composition mol. % $C_3$ | Temp. K | Pres. (experimental) kPa | Calculated Pressure kPa: Parris and Prausnitz* (1972) | Ng and Robinson (1976b) | This Work |
|---|---|---|---|---|---|
| 6.0 | 276.26 | 1,151 | 1,917 | 1,151 | 1,132 |
| 8.0 | 273.93 | 676 | 1,289 | 738 | 680 |
| 10.0 | 278.32 | 1,255 | 2,482 | 1,276 | 1,203 |
| 14.0 | 279.43 | 1,207 | 2,413 | 1,234 | 1,208 |
| 21.0 | 273.98 | 359 | 669 | 386 | 419 |
| 26.0 | 281.82 | 1,303 | 2,551 | 1,296 | 1,334 |
| 47.5 | 278.59 | 689 | 621 | 593 | 626 |
| 60.0 | 274.82 | 324 | 364 | 279 | 298 |
| 63.0 | 279.59 | 752 | 924 | 710 | 694 |
| 65.0 | 278.26 | 579 | 689 | 545 | 542 |
| 72.0 | 275.21 | 303 | 343 | 294 | 300 |
| 82.0 | 279.04 | 593 | 703 | 648 | 619 |
| 84.0 | 277.76 | 476 | 526 | 494 | 481 |
| | | Average Error: | 53.5% | 7.3% | 6.7% |

* As presented by Ng and Robinson (1976b).

TABLE 8. HYDRATE EQUILIBRIUM PREDICTIONS FOR THE METHANE/ETHANE/PROPANE SYSTEM (Data from Holder and Hand 1982)

| Temp. K | mole Fraction Methane | mole Fraction Ethane | mole Fraction Propane | Experimental Pressure kPa | Calculated Pressure* kPa | Calculated Pressure This Work kPa |
|---|---|---|---|---|---|---|
| 279.76 | 0.174 | 0.705 | 0.121 | 1,248 | 1,262 | 1,299 |
| 280.48 | 0.174 | 0.705 | 0.121 | 1,393 | 1,386 | 1,416 |
| 281.43 | 0.174 | 0.705 | 0.121 | 1,586 | 1,544 | 1,587 |
| 282.21 | 0.174 | 0.705 | 0.121 | 1,779 | 1,696 | 1,745 |
| 283.98 | 0.174 | 0.705 | 0.121 | 2,165 | 2,068 | 2,177 |
| 281.37 | 0.364 | 0.542 | 0.094 | 1,724 | 1,710 | 1,737 |
| 282.48 | 0.364 | 0.542 | 0.094 | 2,006 | 1,924 | 1,978 |
| 283.76 | 0.364 | 0.542 | 0.094 | 2,275 | 2,227 | 2.302 |
| 284.98 | 0.364 | 0.542 | 0.094 | 2,758 | ** | 2,672 |
| 275.76 | 0.454 | 0.457 | 0.089 | 917 | 731 | 1,005 |
| 280.76 | 0.454 | 0.457 | 0.089 | 1,682 | 1,744 | 1,763 |
| 282.04 | 0.454 | 0.457 | 0.089 | 1,882 | 1,986 | 2,042 |
| 285.15 | 0.454 | 0.457 | 0.089 | 2,758 | ** | 2,956 |
| | | | | Average Error: | 4.6% | 4.6% |

* Dharmawardhana et al. (1980).
** Values not reported.

was obtained (calculated pressures were too low).

The improvements on the van der Waal method as advanced by Parrish and Prausnitz (1972) lead to a good method for predicting hydrate equilibria for a number of gas species. However, the $Q^*$ correlation method has certain advantages. First, the $Q^*$ correlation method has been applied to a variety of multicomponent gas mixtures over a wide range of temperatures and pressures. This is especially true for nonideal gas species such as carbon dioxide and hydrogen sulfide that form structure I hydrates but which help stabilize structure II hydrates when present in mixtures containing large molecules such as the propanes and the butanes (Ng and Robinson, 1976b). The $Q^*$ correlation method is more accurate than other methods in predicting equilibria for species that form both structure I and II hydrates at different pressures and temperatures.

Secondly, the Kihara size parameters used in the $Q^*$ correlation method are universal empirical characterizations of the effective size and asymmetry of the gas molecules. While the Kihara parameters have been optimized to obtain a better agreement between experimental and calculated dissociation pressures, the optimal values still agree closely with the values obtained from second virial coefficient and viscosity data.

Additionally, the effective Kihara size parameters obtained using the combination rules qualitatively predict whether a given gas molecule can enter a particular cavity; these predictions are in accordance with experimentally determined hydrate numbers. The Kihara parameters listed by Parrish and Prausnitz (1972) are not as physically realistic. For example, the Kihara size parameters of ethane indicate that the molecule is capable of entering the small cavity of either structure, while experimentally determined hydrate compositions of ethane indicate that the molecule can enter only the large cavities. To compensate for this, their algorithm arbitrarily required that ethane be excluded from the small cavity. Our calculations *predict* that ethane is effectively excluded from the small cavity.

A particular advantage that results from the present model is the ability to distinguish between the different effects of nonidealities in the four different hydrate cavities. Because the stability of the hydrate phase comes about from the different interactions of the guest molecule with each of the two cavities of the equilibrium structure, it is quite easy to find a set of Kihara parameters which overemphasize the contribution from one cavity while underemphasizing the contribution from the other. This misinterpretation, which is inherent in earlier models, did not prevent the model from fitting the dissociation pressure of a pure component, but it did lead to serious errors for some gas mixtures where the contributions of each species to each cavity must be well defined in order to accurately estimate hydrate dissociation pressures. The present model helps considerably in defining the contributions in different cavities and hence should be superior in predicting dissociation pressures

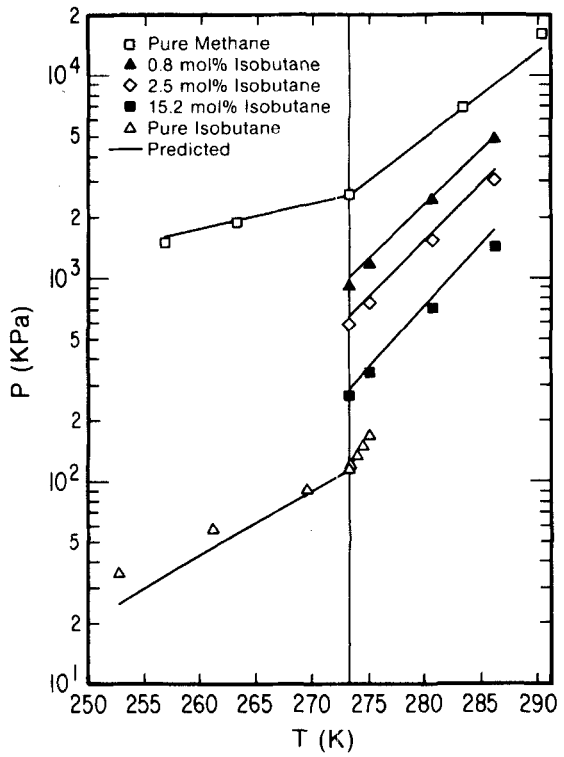


**Figure 2. Calculation of hydrate equilibrium: methane/isobutane hydrates (experimental data from Holder and Godbole, 1981; Rouher and Barduhn, 1969; Wu et al., 1976).**

of gas mixtures.

The development of the $Q^*$ correlation method was based on a semitheoretical approach. The approach has examined, from a fundamental viewpoint, the effects on hydrate stability caused by structural asymmetry of the cavities, secondary gas-water interactions, and restrictions on molecular motion within the hydrate cavities. To use the $Q^*$ correlation method, smoothed-cell Langmuir constants are to be calculated using the cell characteristics listed in Table 2; the Langmuir constants are to be corrected using the appropriate correlations from Eq. 7, with the optimal Kihara parameters listed in Table 6. When these Langmuir constants are used together with the reference properties listed in Table 3, accurate calculations of hydrate equilibrium for the 15 gas species studied (and their mixtures) result. The Kihara parameters of the gas species used in the study together with the acentric factors are sufficient to calculate hydrate equilibrium conditions. Thus a three-parameter molecular theory of corresponding states is valid for the hydrates of nonpolar or weakly polar molecules, the three parameters being the Kihara energy parameter, the Kihara distance parameter, and the acentric factor.

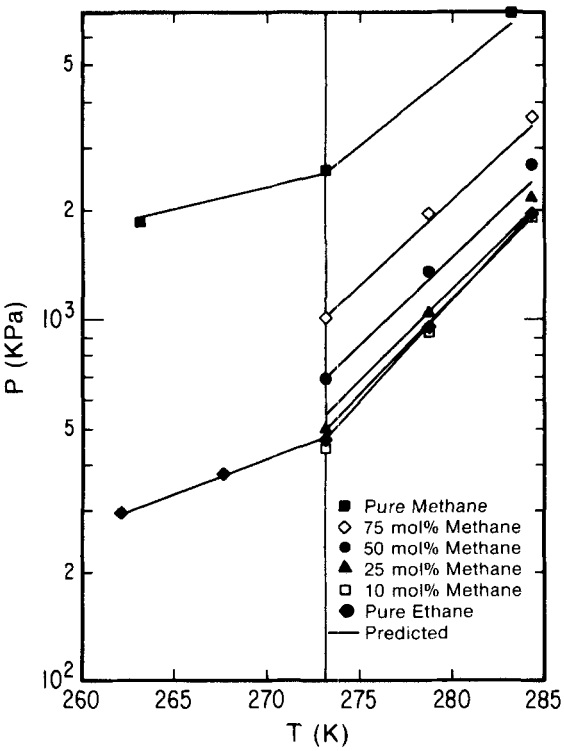


**Figure 3. Calculation of hydrate equilibrium: methane/ethane hydrates (experimental data from Falabella and Vanpee, 1974; Roberts et al., 1940; Holder and Grigoriou, 1980).**

## NOTATION

$a_o$ = correlation constant in Eq. 7
$a_g$ = Kihara core diameter of a gas molecule, pm
$a_w$ = Kihara core diameter of a lattice water molecule, pm; $a_w = 0$
$a$ = core parameter to be used in smoothed-cell-potential calculations, pm; $a = (a_w + a_g)/2.0 = a_g/2.0$
$b$ = temperature coefficient of heat capacity difference between $\beta$ and pure $\alpha$ phases kJ·mole$^{-1}$K$^{-2}$
$C$ = true Langmuir constant, MPa$^{-1}$
$C^*$ = ideal spherical Langmuir constant, MPa$^{-1}$
$\Delta C_{pw}$ = molar heat capacity difference between $\beta$ and pure $\alpha$ phases, kJ·mol$^{-1}$·K$^{-1}$
$\Delta C^o_{pw}$ = $\Delta C_{pw}$ at 273.15 K, kJ·mol$^{-1}$
$H$ = hydrate phase
$\Delta h_w$ = molar enthalpy difference between $\beta$ and pure $\alpha$ phases, kJ·mol$^{-1}$
$\Delta h^o_w$ = $\Delta h_w$ at 273.15 K and 0 kPa, kJ·mol$^{-1}$
$k$ = Boltzman constant
$n$ = correlation constant in Eq. 7
$P$ = pressure, MPa
$Q^*$ = Ratio of true Langmuir constant $C$ to smoothed-cell Langmuir constant $C^*$. $Q^*$ is the correction factor for the smoothed-cell Langmuir constant.
$R$ = gas constant
$R$ = radius of a hydrate cavity, pm
$r$ = radial distance of gas molecule from center of hydrate cavity, pm
$T_o$ = 273.15 K
$T$ = temperature, K
$\Delta V_w$ = difference in molar volume between $\beta$ and $\alpha$ phases, cc-mol$^{-1}$
$W$ = cell potential, kJ·mol$^{-1}$
$w$ = subscript indicating a water phase
$X_w$ = mole fraction water in $\alpha$ phase
$z$ = coordination number of a hydrate water shell

### Greek Letters

$\beta$ = subscript indicating metastable phase of unoccupied hydrate lattice
$\epsilon_g$ = depth of molecular potential well for binary Kihara potential between two gas molecules, kJ·mol$^{-1}$
$\epsilon_w$ = depth of molecular potential well for binary Kihara, potential between two lattice water molecules, kJ·mole$^{-1}$
$\epsilon$ = depth of molecular potential well for binary Kihara potential describing interaction of a lattice water molecule and a gas molecule $\epsilon = (\epsilon_g \epsilon_w)^{1/2}$
$\mu$ = chemical potential, kJ·mol$^{-1}$
$\Delta\mu^{\beta}_w$ = chemical potential difference between $\beta$ and stable hydrate ($H$) phases, kJ·mol$^{-1}$
$\Delta\mu^o_w$ = chemical potential difference between $\beta$ and ice phases at 273.15 K and 0 kPa, kJ·mol$^{-1}$
$\nu_i$ = number of cavities of type $i$ per water molecule of the hydrate structure

$\sigma_g$ = core-to-core Kihara distance parameter for a gas molecule at which distance the binary potential is 0, pm

$\sigma_g^*$ = center-to-center Kihara distance parameter for a gas molecule = $\sigma_g + a_g$

$\sigma_w$ = core-to-core Kihara distance parameter for a lattice water molecule at which distance the binary potential is 0, pm

$\sigma$ = core-to-core distance parameter for interaction between a gas molecule and a lattice water molecule, pm

$\omega$ = acentric factor

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# Effect of Temperature on Crystallization and Dissolution Processes in a Fluidized Bed


**The influence of temperature on crystallization and dissolution kinetics in a fluidized bed was investigated. Values of activation energies were determined and a correlation between the rate constants of secondary nucleation and of the surface integration step of crystal growth was presented.**



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## SCOPE

The Arrhenius equation is widely used to present the effect of temperature on kinetics of overall crystal growth, of dissolution, and of primary and secondary nucleation, despite the well-known fact that this equation is essentially valid for chemical reaction kinetics. Similarly, the driving force for crystallization—i.e., supersaturation—is usually expressed in terms of absolute concentration difference but not, as theoret-


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