An Investigation of Gas Hydrates Formation Energetics

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DOI 10.1002/aic.10374

A method was developed and implemented for predicting enthalpies of gas hydrate formation, which are required for the efficient design of gas hydrate-based processes. The proposed method is based on the statistical thermodynamic theory of solid solutions and it is thermodynamically consistent. It allows delineation of the various energetic contributions, does not resort to empirical constants enforced by regressions and applies to any simple or multicomponent bulk hydrate equilibrium system at the hydrate point or beyond it. The application of the method was demonstrated for several simple, double and multicomponent gas hydrate systems with one or two equilibrium hydrate phases. It was found that a major energetic component in hydrate formation is the heat of enclathration, defined as the residual enthalpy of the enclathrated gas. All example applications indicated that this property is a constant, independent of temperature, pressure and composition, characteristic only of the individual gas and it was regressed by a general corresponding states analytical expression. © 2005 American Institute of Chemical Engineers
AIChE J, 51: 1258-1273, 2005
Keywords: gas hydrates, enthalpy, dissociation, formation, encagement

Introduction

Gas hydrates are solid crystalline nonstoicheiometric compounds formed by inclusion of certain volatile components into the voids of a host water lattice. The whole structure is stabilized by hydrogen bonds between water molecules and van der Waals forces between guest and host molecules. Gas hydrates belong to the more general class of clathrate compounds. Naturally occurring gas hydrates may be found in either of two distinct cubic structures, called structure I and structure II. Each of these structures contains two types of cavities. Each cavity can occlude only one guest molecule of the appropriate size. The number and the size of the cavities are different for each structure. An empty hydrate lattice is thermodynamically unstable and cannot physically exist.

Since their discovery in 1811 by Sir H. Davy, research on gas hydrates was motivated purely by scientific curiosity, until 1934 when Hammerschmidt rediscovered gas hydrates as plugs in gas transmission pipelines. Then, a new era of intense theoretical and experimental research started, aiming also at combating gas hydrates in the Petroleum Industry. Many important works appeared subsequently with turning points the works of von Stackelberg and coworkers, who elucidated in 1954 the crystal structure of gas hydrates by X-ray diffraction measurements and van der Waals and Platteeuw[1], who in 1959 presented the statistical thermodynamic theory of clathrate solutions. A listing of contributions to gas hydrates research is cited in the book of Sloan[2].

Currently, gas hydrates are being considered as working substances for such diverse processes as, for example, the desalination of sea water, the storage and transportation of natural gas, the depletion of flue gases from CO_2, and, as a future energy source following the discovery of immense quantities of gas hydrates in sediments in the ocean bottoms, with methane as the major component. Of these, the exploitation of natural gas hydrates reserves by effecting *in situ* decomposition is one of the most important areas for the current and the future gas hydrate research and much work has already been done.

Gas hydrate formation (or dissociation) is a heat-transfer

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limited process. Heat released during gas hydrate formation may affect the temperature and pressure of the system. Thus, correct calculations of the calorimetric properties of gas hydrates are important for the efficient design and operation of any gas hydrate related process. Traditionally, the enthalpy of dissociation of gas hydrates is calculated from experimental gas hydrate equilibrium data by application of the Clapeyron or its approximation, the Clausius-Clapeyron equation. However, the Clapeyron equation is not useful when pressure is higher than the hydrate point, where, however, gas hydrates really exist. It has not been investigated so far how the results from the Clapeyron equation compare to the dissociation of gas hydrates at pressures much higher than the hydrate point pressure. On the other hand, the statistical thermodynamic theory, presented by van der Waals and Platteeuw[1], which is the obvious proper basis for thermodynamic calculations of gas hydrates, has not been deployed until now for the development of a general scheme for calculation of the enthalpy of hydrate formation from any gas hydrate forming mixture at any temperature and pressure conditions.

Here, we present, after a brief account of previous related works, a method, based on the ideal solid solution theory for precise calculations of formation enthalpies of simple or multicomponent gas hydrates. This method is engaged to the model developed during past years at Heriot-Watt University by this author[3,4]. The proposed method is general and rigorous, within clearly defined assumptions. We believe that it can serve as a reliable tool for engineering design while helping to gain insight into the energetic phenomena associated with bulk gas hydrate formation.

Previous Work

Experimental measurements of the enthalpy of dissociation are not easily obtained and such data are very scarce. Handa[5,6] reported accurate calorimetric data below the ice point for the gas hydrates of Xe, Kr, CH_4, C_2H_6, C_3H_8 and i-C_4H_{10}. Lievois et al.[7] and Rueff et al.[8] reported a number of experimental data for the methane hydrate above the ice point. More recently, Kang et al.[9] determined the enthalpy of dissociation of hydrates of carbon dioxide, nitrogen, and mixtures of them, using an isothermal microcalorimeter appropriately modified by them.

Before further proceeding to the presentation of previous relevant works, is it expedient to define and clarify certain terms and issues that have raised questions in the past.

Clapeyron equation

The formation of gas hydrate is an exothermic equilibrium process, which may be represented by the equation

$$\text{Gas} + n\text{H}_2\text{O}(\alpha/\text{L}) \rightarrow \text{Hydrate(s)} \tag{1}$$

where the aqueous phase may be ice, denoted α, or liquid, denoted L, and the hydrate phase is a separate solid (s) phase. The number of mol of hydrated water per mol of encaged gas is the *hydration number*, denoted n. Except for the cases of simple gas hydrates or gas hydrates with an azeotropic composition, the composition of the gas in Eq. 1 should differ greatly from the composition of the actual equilibrium gas phase. At least one gas hydrate forming component must be involved.

The hydrate point at a fixed temperature of a closed system at equilibrium, consisting of any number of open phases and any number of components, is defined generally as the minimum pressure required for the appearance of just a minute hydrate crystal. When the process of hydrate formation is univariant, by virtue of the phase rule, as, for example, it is the three components system (C_1, C_3, H_2O) at four phases (V-L_h-L_w-H^{II}) equilibria, fixing the temperature suffices to fix all intensive variables, even if it is an open system. In this case, the hydrate mass need not be minute, theoretically at least, and any mass of gas hydrate or any other phase may participate at equilibrium. If some more components are added to the previous system, for example, a black oil, the system is polyvariant in the sense of the phase rule. In the latter case, for the construction of a hydrate point p-T line, the system must be closed and one has to adhere to the definition of the hydrate point, which is equivalent to fixing one extensive variable. However, it is practicaly impossible to observe a minute gas hydrate crystal in a black oil. To circumvent this problem, one has to construct two p-T lines at a fixed system volume: one for the four-phase, V-L_h-L_w-H^{II}, equilibria and one for the three-phase V-L_h-L_w equilibria. The intersection of these two lines gives the hydrate point V-L_h-L_w-H^{II}, of the closed system at the particular fixed volume. The experiment is then repeated at different volumes.

The enthalpy of the gas hydrate formation reaction per mol of encaged gas $\Delta h^f \equiv \Delta h^{\alpha/\text{L}+\text{G}\rightarrow\text{H}}$, is the heat released when one mol of a gas mixture and n mol of water combine and are converted into hydrate at the prevailing conditions of thermodynamic equilibrium. Since heat is released during the formation of gas hydrates, the enthalpy of the gas hydrate formation reaction must be negative by convention. The hydrate dissociation reaction is the inverse of (1) and the heat of dissociation is conventionally positive: $\Delta h^d = -\Delta h^f$. Of course, the enthalpy of hydrate dissociation does not include any sensible enthalpy change, that is, the heat associated with the definite amount of temperature increase practically required to cause dissociation.

When gas hydrate formation is a univariant equilibrium reaction, or, more generally, when a pressure-temperature equilibrium gas hydrate formation phase boundary curve of a closed system is available, the thermodynamic Clapeyron equation, $dp/dT = \Delta S/\Delta V$, may be applied at points along the p-T equilibrium line to calculate the enthalpy of the transformation Δh^f, under the imposed restrictions. In the presence of an excess gas phase, the enthalpy of gas hydrate formation according to Eq. 1, may be calculated by the Clausius-Clapeyron equation in the following form

$$\frac{d\ln p}{d(1/T)} = \frac{\Delta h^f}{zR} \tag{2}$$

where p is the dissociation pressure at temperature T, z is the compressibility factor of the equilibrium gas phase, and R is the universal gas constant. The compressibility factor may be easily calculated at the dissociation conditions from an equation of state. The value of the derivative should be computed at a fixed temperature from experimental data of dissociation pressures against the absolute temperature. Plots of the logarithm of experimental dissociation pressures vs. the inverse absolute temperature maintain a nearly constant slope over a restricted temperature range.

The Clapeyron or the Clausius-Clapeyron equations had served for more than 100 years for the calculation of the enthalpy changes associated with gas hydrate transformations. It is recognized that the heats of hydrate formation calculated by the Clapeyron equation show fair agreement with experimental data[5,6]. Roberts et al.[10], Barrer and Edge[11], and Skovborg and Rasmussen[12] derive analytically the Clapeyron equation for simple gas hydrates. The precise meaning of dp/dT in systems that are univariant in the sense of the phase rule is illustrated in the standard thermodynamics textbooks of Prigogine and Defay[13] and Tester and Modell[14], the latter with applications to gas hydrates. Yet, the Clapeyron equation is a general thermodynamic, macroscopic, relation, and as such, cannot directly delineate molecular interactions.

Sloan and Fleyfel[15] by using the Clausius-Clapeyron equation reached a generalized conclusion about the relation of the enthalpy of dissociation to the size of the guest molecules. There are two recent contributions that revive the method. Yoon et al.[16] used an improved form of the Clausius-Clapeyron equation to determine the hydration number and the heat of dissociation of several simple gas hydrates. Anderson[17] has applied the Clapeyron equation to determine the enthalpy of dissociation and the hydration number of carbon dioxide as a function of temperature. These works are further discussed in a subsequent section, in comparison to our present results.

The Clapeyron equation may also be applied for indirect calculation of the hydration number n, of simple gas hydrates. As suggested by de Forcrand[18], successive application of the equation for I-G-H and L_w-G-H equilibria near the quadruple point I-L_w-G-H would give the respective enthalpies. Then

$$n = (\Delta h^{L_w+G\rightarrow H} - \Delta h^{\alpha+G\rightarrow H})/\Delta h^{L_w\rightarrow\alpha} \tag{3}$$

Subsequently, many authors have applied this method of de Forcrand[18]. Results with this method for several gas hydrates are provided by Davidson[19].

The ideal solid solution model

Van der Waals and Platteeuw[1], assuming no interactions between encaged molecules, presented thermodynamic equations that describe a solid hydrate phase as an ideal solid solution of the encaged compounds in the metastable host lattice. Their equations served as the basis of all ensuing thermodynamic models for the prediction of gas hydrate dissociation pressures.

For the chemical potential difference between the water in the filled hydrate and the empty lattice $\Delta_{\mu w}^{H-\beta}$, van der Waals and Platteeuw[1] obtained the following relation

$$\frac{\Delta\mu_w^{H-\beta}}{RT} = \sum_{m=1}^{2} \nu_m \ln\left(1 - \sum_{j=1}^{c^H} \theta_{mj}\right) \tag{4}$$

where v_m is the number of cavities of type m per water molecule in the hydrate lattice, c^H is the number of hydrate forming gases and θ_{mi} is the fraction of cavities of type m occupied by guest i. This equation characterizes an ideal solid solution in the sense that the properties of gas hydrates depend only on the concentration of the guests in the two types of cavities. The fractional cavity occupancies θ_{mi}, are given by the following relation

$$\theta_{mi} = \frac{C_{mi}f_i}{1 + \sum_{k=1}^{c^H} C_{mk}f_k} \tag{5}$$

where C_{mi} is the Langmuir-type constant of component i in the cavity m, and f_i is the fugacity of component i in the hydrate phase. The Langmuir-type constants can be calculated by the application of an intermolecular potential for gas-water interactions, if the cell potential parameters had been previously determined for example, from second virial coefficient data. However, much more satisfactory predictions[20] had been attained when the potential parameters were treated as fitting constants to adjust model predictions on experimental hydrate equilibrium data. The thermodynamic equations used for the calculation of gas hydrate phase equilibria and a scheme for an example phase equilibria calculation are given in Appendix A. The model depends on a number of constants, of which most important are the potential parameters and the chemical potential and enthalpy differences between the empty hydrate lattice and ice, at the ice point and zero pressure, the latter denoted, $\Delta\mu_w^0$ and Δh_w^0, respectively.

The heat of encagement of a gas i into a cavity m can be rigorously calculated from the equations provided by the ideal solid solution theory. Barrer and Edge[11] studied experimentally at various temperatures the absorption of Ar, Kr and Xe in the small cavities of the structure II hydrate of $CHCl_3$, at conditions where all large cavities of the hydrate were occupied by $CHCl_3$. From their data, they calculate by Eq. 5 the respective values of the Langmuir type equilibrium constants C_{mi}, where $m = 1$ in this case. From the slope of the curve C_{mi} vs. $1/T$, they deduced the heat of intercalation according to the following thermodynamic equation

$$\Delta h_{mi} \equiv \Delta h^{\beta_m+G_i\rightarrow H} = -R\frac{d\ln C_{mi}}{d(1/T)} \tag{6}$$

where β indicates the empty hydrate lattice. Having calculated $\Delta h^{\alpha+G\rightarrow H}$, $\Delta h^{\beta+G\rightarrow H}$ and n, they calculate the heat of formation of the empty hydrate lattice from ice by the application of the following relation

$$\Delta h^{\alpha+G\rightarrow H} = \Delta h^{\beta+G\rightarrow H} + n\Delta h_w^{\alpha\rightarrow\beta} \tag{7}$$

Davidson[19] calculates the total enthalpy of encagement of a gas i as the sum

$$\Delta h_i^{\beta+G_i\rightarrow H} = n\sum_{m=1}^{2}\nu_m\theta_{mi}\Delta h_{mi} = -nR\sum_{m=1}^{2}\nu_m\theta_{mi}\frac{d\ln C_{mi}}{d(1/T)}$$

$$= nRT^2\sum_{m=1}^{2}\nu_m\theta_{mi}\frac{d\ln C_{mi}}{dT} \tag{8}$$

Then, the enthalpy of formation of the empty lattice from ice, that is, the second term of the rhs of Eq. 7, is adjusted to fit data of hydrate formation enthalpies (obtained via the Clapeyron equation). According to the results of Davidson[19], the enthalpy $\Delta h_w^{\alpha \rightarrow \beta}$, of the transformation of ice to the empty hydrate lattice of structure I hydrate varies between 0.588 and 1.04 kJ/mol, with no pronounced trend with molecular size. An average value 0.795 kJ/mol is reported. A larger value, 1.55 kJ/mol, is reported for the studied structure II hydrates. The same Eq. 8 is used by Handa and Tse[21] to calculate enthalpies of encagement of xenon and krypton in individual gas hydrate cavities of either structure.

Davidson[19] calculates the heats of encagement of Xe in the small cavities and ethane in the large cavities of structure I and propane in the large cavities of structure II to be -30.7, -30.0 and -53.0 kJ/mol, respectively. According to Handa and Tse[21], the heats of encagement of Xe in the small and the large cavity are $-$ 30.219 and $-$ 32.528 kJ/mol, respectively. Such tabulated data may be used to calculate (reproduce) heats of hydrate formation from a pure gas and ice or liquid water near the ice point. For example, the enthalpy of propane hydrate formation is the sum $-$ 53.0 kJ/mol gas + 17.01 mol $H_2O \times 1.55$ kJ/mol $H_2O = -26.6$ kJ/mol or $-53.0 + 17.01 \times (1.55 - 6.01) = -128.9$ kJ/mol. The corresponding experimental values, as reported by Handa,[6] are $-$ 27.0 kJ/mol and $-$ 129.2 kJ/mol.

Proposed Model

For the calculation of the enthalpy of gas hydrate formation from liquid water and multicomponent hydrate forming gases, we consider a closed system consisting of open phases, and we start with the obvious enthalpy balance relation

$$\Delta H^f = \sum_{i=1}^{c} n_i^{G'} \bar{h}_i^{G'} + \sum_{i=1}^{c} n_i^{L'} \bar{h}_i^{L'} + n_w^{L'} \bar{h}_w^{L'} + \sum_{i=1}^{c^H} n_i^{H} \bar{h}_i^{H} + n_w^{H} \bar{h}_w^{H} - \left(\sum_{i=1}^{c} n_i^{G} \bar{h}_i^{G} + \sum_{i=1}^{c} n_i^{L} \bar{h}_i^{L} + n_w^{L} \bar{h}_w^{L} \right), \quad i \neq w,\ c \geq c^H \tag{9a}$$

where c is the number of components i in the gas and liquid water phases, excluding water, w is the index of water, c^H is the number of components participating in the formation of the gas hydrate, n_a^A and $\bar{h}_a^A$ are, respectively the number of mol and the partial molar enthalpy of component a in phase A, superscripts G, L and H indicate, respectively, the gas, aqueous liquid and hydrate phase, and the prime ($'$) indicates the final equilibrium state. The concurrent mass conservation restrictions are

$$(n_i^{G'} - n_i^{G}) + (n_i^{L'} - n_i^{L}) = -n_i^{H} \quad \text{and} \quad (n_w^{L'} - n_w^{L}) = -n_w^{H} \tag{9b}$$

For further development, it is advantageous to choose $\sum_{i=1}^{c^H} n_i^H = 1$, so that n_w^H is the hydration number, already denoted n.

To simplify Eq. 9, we assume that: (a) The composition of the final gas phase, that is, the gas phase in equilibrium with hydrate and water, is very nearly the same as the initial gas phase. This means that the gas phase is in large excess so that the formation of any certain mass of gas hydrate would not affect appreciably its composition. The assumption is strictly true at the hydrate point and it is valid for most practical purposes, if the pressure in not too high. Because of this assumption, the partial molar properties of the gas phase would be considered to remain unchanged. (b) The water-rich liquid phase, being a solution of mostly permanent gases, can be considered as an infinitely dilute solution. This means that the second term of the lhs of the first of Eq. 9b can be neglected, and that the partial molar enthalpy of water in the water-rich liquid may be regarded nearly equal to the molar enthalpy of pure water $\bar{h}_w^L \approx h_w^L$. Now, Eq. 9a is reduced in the following form

$$\Delta h^f = \sum_{i=1}^{c^H} n_i^H \bar{h}_i^H + n\bar{h}_w^H - \sum_{i=1}^{c} n_i^H \bar{h}_i^G - nh_w^L \tag{10a}$$

If we replace the molar enthalpy of water by the molar enthalpy of ice in Eq. 10a, the equation would produce the enthalpy of formation of gas hydrate by gas and ice. Therefore, a more generally applicable form of the equation is

$$\Delta h^f = \sum_{i=1}^{c^H} n_i^H \bar{h}_i^H + n\bar{h}_w^H - \sum_{i=1}^{c} n_i^H \bar{h}_i^G - nh_w^{a/L} \tag{10b}$$

Multiplication and division of the rhs of the last equation by $(1+n)$ gives the equation

$$\Delta h^f = (1+n)\left(\sum_{i=1}^{c^H} x_i^H \bar{h}_i^H + x_w^H \bar{h}_w^H - \sum_{i=1}^{c} x_i^H \bar{h}_i^G - x_w^H h_w^{a/L} \right) \tag{11}$$

Since only mole fractions of the hydrate phase appear in the earlier equation, the superscript H over x_i is obsolete and it is dropped in the subsequent treatment.

The mole fraction of the encaged gaseous component i may be calculated by the expression

$$x_i = \frac{\sum_{m=1}^{2} \nu_m \theta_{mi}}{1 + \sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^H} \theta_{mj}}, \quad i \neq w \tag{12a}$$

and the mole fraction of water in the solid hydrate phase is

$$x_w = \frac{1}{1 + \sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^H} \theta_{mj}} \tag{12b}$$

The hydration number n, is given by the equation

$$n = \frac{x_w}{\sum_{i=1}^{c^{\mathrm{H}}} x_i} = \frac{1}{\sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^{\mathrm{H}}} \theta_{mj}} \tag{13}$$

so it is

$$\sum_{i=1}^{c^{\mathrm{H}}} x_i = \frac{1}{1+n} \tag{14a}$$

Note, that the gas released by complete decomposition of the gas hydrate would have the dry basis gas hydrate composition, that is

$$y_i = \frac{x_i}{\sum_{i=1}^{c^{\mathrm{H}}} x_i} = (1+n)x_i \tag{14b}$$

If we add and subtract from the term in parentheses of the rhs of Eq. 11 the quantity $x_w h_w^{\beta} + \sum_{i=1}^{c^{\mathrm{H}}} x_i h_i^*$ where h_w^{β} is the molar enthalpy of the empty hydrate lattice and h_i^* is the molar enthalpy of an ideal gas i at the same temperature and pressure as the equilibrium gas, and take into account the last relations Eq. 13 and Eq. 14b, we obtain

$$\Delta h^f = \sum_{i=1}^{c^{\mathrm{H}}} y_i(\bar{h}_i^{\mathrm{H}} - h_i^*) + n(\bar{h}_w^{\mathrm{H}} - h_w^{\beta}) - (h^{\mathrm{G}} - h^*) - n(h_w^{\alpha/\mathrm{L}} - h_w^{\beta}) \tag{15}$$

where

$$h^{\mathrm{G}} - h^* = \sum_{i=1}^{c^{\mathrm{H}}} y_i(\bar{h}_i^{\mathrm{G}} - h_i^*) \tag{16}$$

The various terms of Eq. 15 show clearly the energetic contributions to the transformation. If desired, each of the first two terms can be calculated via the solid solution theory, as detailed later. The third term is calculated from an equation of state for the gas phase. Finally, the enthalpy difference between ice and the empty hydrate lattice is a reference property of the solid solution model, determined by forcing agreement of the model with experimental hydrate data, and it is a constant characteristic of each structure. Values of this quantity from various sources are cited by Handa and Tse[21].

For the calculation of the residual partial molar enthalpies of encaged gases, we use the following thermodynamic relation

$$\bar{h}_i^{\mathrm{H}} - h_i^* = -RT^2\left(\frac{\partial \ln f_i}{\partial T}\right)_{P,x_j} \tag{17}$$

Formulas and algorithms necessary for the calculation of the derivatives of the logarithms of fugacities of enclathrated species vs. temperature were reported in a previous communication[4].

The difference $(\bar{h}_w^{\mathrm{H}} - h_w^{\beta})$ is obtained in a similar manner

$$\left(\frac{\partial(\Delta\mu_w^{\mathrm{H}-\beta}/RT)}{\partial T}\right)_{P,x_j} = \left(\frac{\partial \ln(f_w^{\mathrm{H}}/f_w^{\beta})}{\partial T}\right)_{P,x_j} = -\frac{\bar{h}_w^{\mathrm{H}} - h_w^{\beta}}{RT^2}, \quad j \neq w. \tag{18}$$

By partial differentiation of Eq. 4, we get

$$\left(\frac{\partial(\Delta\mu_w^{\mathrm{H}-\beta}/RT)}{\partial T}\right)_{P,x_j} = -\sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^{\mathrm{H}}} \theta_{mj}\left(\frac{\partial \ln f_j}{\partial T} + \frac{d \ln C_{mj}}{dT}\right) \tag{19}$$

and by eliminating the lfs' of the last two relations we obtain

$$\bar{h}_w^{\mathrm{H}} - h_w^{\beta} = RT^2 \sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^{\mathrm{H}}} \theta_{mj}\left(\frac{\partial \ln f_j}{\partial T} + \frac{d \ln C_{mj}}{dT}\right) \tag{20}$$

A numerical method for the calculation of cavity occupancies θ_{mi}, is detailed elsewhere[4]. The Langmuir-type constants C_{mj} are functions of temperature only, and the derivatives of their logarithms can be calculated as detailed in Appendix B. For simple gas hydrates in that the large cavities only are occupied, that is, $\theta_{11} = 0$, then the rhs of Eq. 20 is exactly equal to zero, because in such a case it is has been shown[4] that $(\partial \ln f_1/\partial T) = -d \ln C_{21}/dT$. Therefore, in such a case, the partial molar enthalpy of water in the hydrate phase is equal to that of the empty hydrate lattice $\bar{h}_w^{\mathrm{H}} = h_w^{\beta}$.

The residual molar enthalpy of the gas phase $(h^{\mathrm{G}} - h^*)$ can be calculated via the rigorous thermodynamic relation

$$\bar{h}_i^{\mathrm{G}} - h_i^* = -RT^2\left(\frac{\partial \ln \phi_i^{\mathrm{G}}}{\partial T}\right)_{P,x_j} \tag{21}$$

where ϕ_i^{G} is the fugacity coefficient of component i in the gas phase. These coefficients can be calculated with any equation of state for the gas phase. In this implementation, we use the EoS proposed by Avlonitis et al.[22]

Equation 11 can be further simplified by combining the first two terms in a simple expression. Substitution of equations 12, 17, and 20 into Eq. 15 gives the enthalpy of hydrate formation, in terms of calculable quantities

$$\Delta h^f = nRT^2 \sum_{m=1}^{2} \nu_m \sum_{j=1}^{c^{\mathrm{H}}} \theta_{mj} \frac{d \ln C_{mj}}{dT} + RT^2 \sum_{i=1}^{c^{\mathrm{H}}} y_i\left(\frac{\partial \ln \phi_i^{\mathrm{G}}}{\partial T}\right)_{P,x_j} - n(h_w^{\alpha/\mathrm{L}} - h_w^{\beta}) \tag{22}$$

The first term of the rhs of the earlier equation is always negative, since the Langmuir-type constant decreases with temperature. This term represents the quantity of heat that is

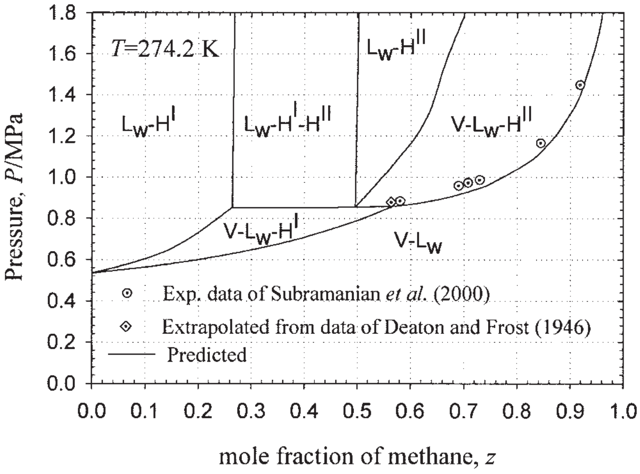

Figure 1. Predicted phase diagram of the system methane, ethane, and excess water.

released when a gas hydrate is formed by encagement of one mol of an ideal gas mixture into n mol of water comprising the empty hydrate structure. The residual enthalpy of the gas, ($h^G - h^*$), as well as the enthalpy of transformation of the empty hydrate into ice ($h_w^\alpha - h_w^\beta$), are normally small negative quantities. In the next section, it is demonstrated that the residual enthalpy of the gas contributes insignificantly at lower pressures so that it may be stated that the enthalpy of gas hydrate formation is dependent on pressure to the extent that the latter affects the hydrate composition. The term ($h_w^\alpha - h_w^\beta$) may be considered a constant, even at higher pressures, because ice (Ih) and gas hydrates have similar values of isothermal compressibility, as shown in the next section (for str. I, though). The temperature and pressure dependence of the enthalpy of melting of ice ($h_w^L - h_w^\alpha$), was ignored, as such, an accuracy surpasses the ability of the model, and it is taken as a constant equal to 6.010 kJ/mol[23].

Application

The hydrate phase equilibria prediction program that we deploy here, has been extensively tested in the past against all the then available experimental data[3,24]. Nevertheless, prior to applying this method we had investigated the capability of the phase equilibria model to predict correctly the experimental phase equilibria findings of the last years in cases where other works had been reported in the literature as failed. Figure 1 shows the results of our present calculations for the system methane, ethane and excess water for pressures up to 1.8 MPa, that has been studied experimentally by Subramanian et al.[25], including Raman spectroscopy. It is clear that this phase diagram shows the same correct phase equilibria features as those cited by the latter authors. However, our model predicts that phase transitions occur at comparatively lower methane concentrations, except the upper transition (not included in the figure) for which our prediction coincides with that of the experimentalists. We may note that Ballard and Sloan[26] reported that some commercial hydrate prediction programs also underpredict the lower transition point while all well match the upper one. In our view of this situation, a readjustment of the parameters of the phase equilibria model should be aided by additional V-L-H^{I} and V-L-H^{II} phase equilibria experimental data. Therefore, the phase equilibria model was further used in this study as it stands.

Simple gas hydrates

For simple gas hydrates, Eq. 11 reduces to the following form

$$\Delta h^f = (\bar{h}_1^H - h_1^*) + n(\bar{h}_w^H - h_w^\beta) - (h_1^G - h_1^*) - n(h_w^{\alpha/L} - h_w^\beta) \tag{11a}$$

The first three terms of the righthand side of this equation can be calculated from the ideal solid solution model and an E_0S, as detailed earlier. The molar change of enthalpy for transforming ice into empty hydrate lattice, appearing in the last term, could be determined by forcing agreement of Eq. 11a to the experimental calorimetric data of Handa[5,6], reported at 273.15 K and 101.325 kPa. Unfortunately, we experienced in this study a certain scatter of the values of this property, with no clear trend. This is also noticed by other authors[19,21]. The values $h_w^\alpha - h_w^\beta$ that we obtained range from -1.184 kJ/mol for $CH_4 \cdot 6.00H_20$ (str. I) to -1.040 kJ/mol for $C_3H_8 \cdot 17.01H_20$ (str. II). A somewhat absolutely larger value, -1.302 kJ/mol, was obtained for $C_2H_6 \cdot 7.67H_20$ (str. I). It is clear that the previous procedure is inconsistent because the model[3], as noted before, already incorporates the value of this quantity and its present extension should reproduce it. The values that have been incorporated in the model[3], are those obtained by Dharmawardhana et al.[47] from their cyclopropane hydrate compositional data, and these are $-$ 1.389 kJ/mol for structure I and $-$ 1.025 kJ/mol for structure II. Now, the deviation between input and output parameters is 6.3% for structure I (cyclopropane-ethane), and 1.4% for structure II (cyclopropane-propane). Evidently, these results indicate consistency of our model and demonstrate the compatibility of the two independent experimental data that are different in nature.

Apparently though, the value of $h_w^\alpha - h_w^\beta$ for structure I, as obtained for large molecules entering only the large cavity of either structure, is not appropriate for gas hydrates when methane is the main gas component. The enthalpy difference between ice and the empty hydrate lattice does not have a constant value, not even for the same guest at different concentrations. These variations may result from nonidealities, such as the stretching of the host lattice, that are not accounted for by the ideal solid solution theory (for a treatment of this problem, see Lee and Holder[27]). The variation of $h_w^\alpha - h_w^\beta$ with temperature might be calculated according to the thermodynamic equation

$$(h_w^\alpha - h_w^\beta)_T = (h_w^\alpha - h_w^\beta)_{T_o} + \int_{T_0}^{T} \Delta c_{P,w}^{\alpha-\beta} dT \tag{23}$$

where $\Delta c_{P,w}^{\alpha-\beta}$ is the molar heat capacity difference between ice and the empty hydrate lattice. This correction is nearly zero and can be neglected for methane and xenon[21]. The temperature dependence of $\Delta c_{P,w}^{\alpha-\beta}$ for ethane and propane, given by Avlonitis[4], is also a small number and correction is not necessary. Reoptimization of the reference parameters would not resolve

Table 1. Enthalpy Changes for Formation of Some Simple Gas Hydrates

Guest	Source	T/K	P^d (MPa)	n	$\bar{h}_1^H - h_1^*$ (kJ/mol)	$\bar{h}_w^H - h_w^\beta$ (kJ/mol)	$h^G - h^*$ (kJ/mol)	Δh^f (kJ/mol)
N_2	This work	185.0	0.867	5.84	−19.66	0.080	−0.147	−13.21
		270.0	13.94	6.29	−20.06	0.136	−0.893	−12.03
	Yoon et al.[16]	271.93		6.34				−12.18
CH_4	This work	185.0	0.0690	5.81	−25.11	−0.0057	−0.025	−18.73
		270.0	2.41	6.04	−25.11	−0.023	−0.474	−18.13
	Handa[5]	185.0		6.00				−17.78
	Yoon et al.[16]	272.90		6.07				−17.53
Xe	This work	225.0	0.0157	6.05	−31.07	−0.279	−0.0093	−26.09
		270.0	0.138	6.27	−31.19	−0.261	−0.064	−25.87
	Handa[6]	225.0		5.90				−26.40
C_2H_6	This work	220.0	0.0424	7.70	−35.83	0.000	−0.036	−27.33
		270.0	0.412	7.76	−35.74	0.000	−0.271	−26.93
	Handa[5]	220.0		7.67				−26.23
	Yoon et al.[16]	273.10		7.77				−24.13
C_3H_8	This work	235.0	0.0233	17.00	−44.91	0.000	−0.036	−27.87
		270.0	0.148	17.01	−44.82	0.000	−0.185	−27.62
	Handa[5]	235.0		17.01				−27.07
	Yoon et al.[16]	273.13		17.00				−26.97
iC_4H_{10}	This work	245.0	0.0218	17.01	−48.95	0.000	−0.045	−31.89
		270.0		17.01	−48.86	0.000	−0.174	−31.67
	Handa[5]	245						−31.07
CO_2	This work	260.0	0.705	6.14	−27.80	−0.351	−0.146	−21.59
		270.0	0.848	6.19	−27.81	−0.476	−0.145	−21.42
	Anderson[17]	270.15	0.977					−23.50
	Yoon et al.[16]	272.12		6.23				−20.60

the issue, as it seems to be a consequence of the limitations inherent in the ideal solid solution model. Throughout this study, we used for $h_w^\alpha - h_w^\beta$ the constant values −1.100 kJ/mol for structure I and −1.000 kJ/mol for structure II. These values correspond to a rough mean of values reported in the literature.

The predictions of the model with these parameters for I-G-H equilibria are presented in Table 1 for selected temperatures for each guest, together with any available experimental data. In Table 1, the data of Handa[5,6] are recorded at the mid-temperature of the range, where the hydrate sample was actually prepared and the enthalpy of the transformation was measured. In doing so, we removed the corrections made by the latter author via an equation similar to Eq. 23. This was necessary to avoid possible confusion, because the enthalpy of hydrate formation at 273.15 K is different from the enthalpy of the same reaction having taken place at a much lower temperature and then reduced to 273.15 K in the above manner, at least to the extent that hydration numbers differ.

Our predictions are also presented in graphical form, as a function of temperature, along with literature data in Figures 2, 3, 4, 5, 6, 7 and 8, each figure corresponding to a different guest. As it may be seen, trends common in all figures are the constancy of each of the individual enthalpies of enclathration ($\bar{h}_1^{\mathrm{H}} - h_1^*$), and of gas hydrate formation Δh^f, while n changes with temperature. Unless otherwise stated, all experimental data appearing in the figures were retrieved from Sloan[2].

Double gas hydrates

Results of application of Eq. 15 at the hydrate point H-I-V and H-Lw-V, of the system methane-propane-water, with 88.3 mol % methane on a dry basis, are presented in Figure 9 from 265 K to 280 K. In this system, the larger guest, propane, can not enter the small cavities and occupies most of the large cavities of the structure II gas hydrate. Therefore, the smaller

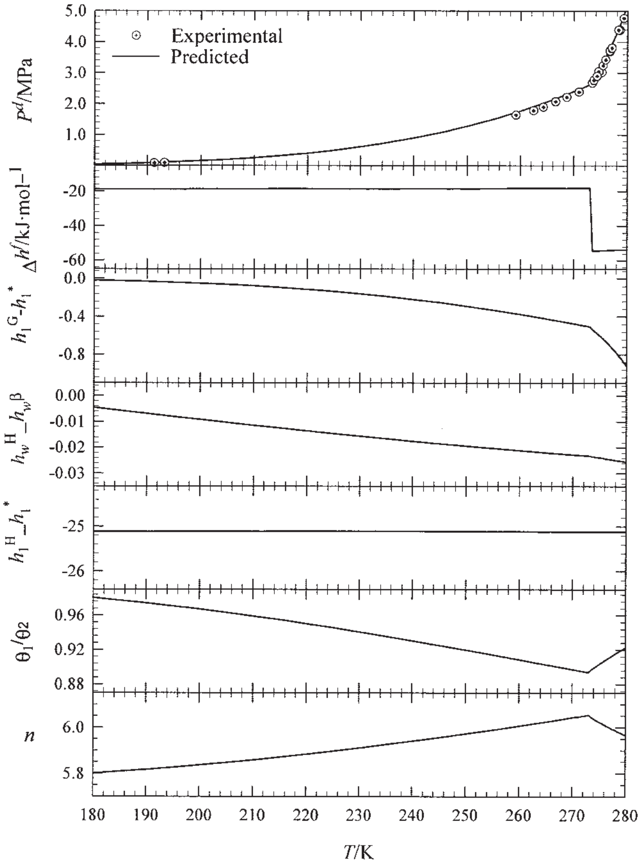

Figure 2. Energetic and equilibrium properties of methane gas hydrate formation as functions of temperature.

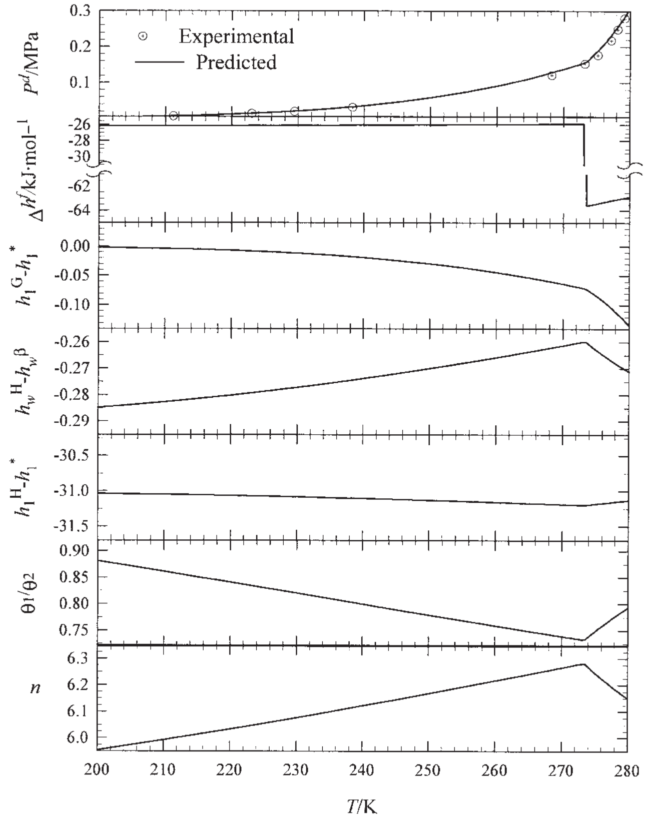

Figure 3. Energetic and equilibrium properties of xenon gas hydrate formation as functions of temperature.

guest, methane, rests mostly in the small cavities. As more methane is absorbed into the hydrate unit cell, propane is desorbed. Increase of temperature and pressure causes reduction of the hydration number. Below the ice point *n* is almost constant, ranging from 9.037 to 8.983, while above the ice point it suffers severe reduction down to 7.744 at 280 K. In the latter case, it is also observed a substantial absolute reduction of the molar enthalpy of hydrate formation from -79.51 to -72.02 kJ/mol. Note that the residual enthalpy of enclathration of methane and propane retain a constant value in the whole region of temperatures, though for propane it is about 7% higher in comparison to the value calculated for the simple gas hydrate.

As a second example of double gas hydrates, we studied the system methane-ethane-water in the hydration region at T = 277.6 K with molar composition 0.65 – 0.35 –1.00, respectively. Thermodynamic stability analysis, according to the method proposed by Avlonitis et al.[28], shows that the hydrate point is H^{II}-Lw-V at dissociation pressure p^d =1.3418 MPa, where the hydration number *n* is 7.79, and the enthalpy of formation is $\Delta h^f = -67.96$ kJ/mol. The liquid water phase disappears at p = 1.3512 MPa, where all water is transformed into gas hydrate having structure II, with n =7.74 and $\Delta h^f = -67.70$ kJ/mol. The behavior of the system at higher pressures is depicted in Figure 10. At p = 2.189 Mpa, a second hydrate phase having structure I appears that reaches a maximum molar phase fraction 0.2862 at 3.810 MPa before disappearing at p = 6.120 MPa. The variation of *n* with pressure is quite substantial for the structure II hydrates ranging from 7.74 to 6.23, while *n* of the structure I hydrate exhibits remarkable stability at the same conditions. The latter differences are also reflected in the

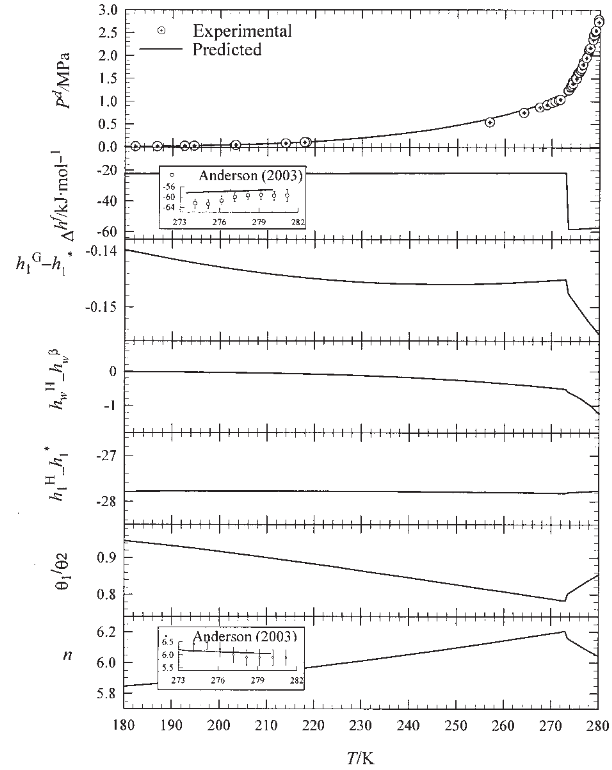

Figure 4. Energetic and equilibrium properties of carbon dioxide gas hydrate formation as functions of temperature.

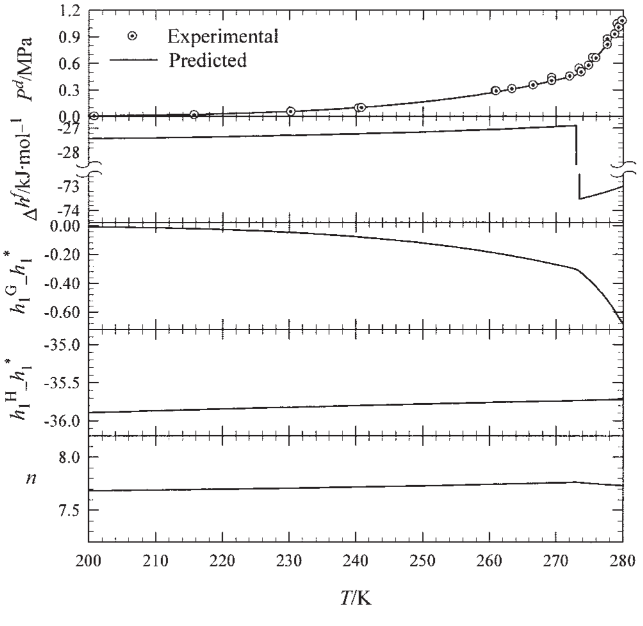

Figure 5. Energetic and equilibrium properties of ethane gas hydrate formation as functions of temperature.

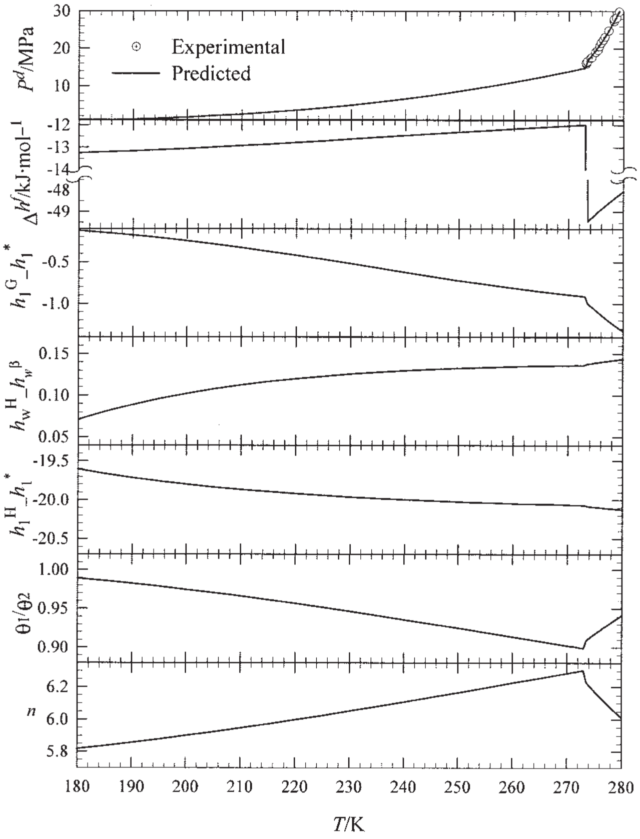

Figure 6. Energetic and equilibrium properties of nitrogen gas hydrate formation as functions of temperature.

variation of Δh^f, where the range for the structure II hydrate is from − 67.66 to − 58.10 while for the structure I, within its region of stability, is from −61.66 to − 59.03 kJ/mol. It may be noted that at the pressure 4.00 MPa, the two structures have equal values of Δh^f. Our predictions show that the residual enthalpy of enclathration of methane retains its constant value, independent of structure. However, for ethane this happens only in structure I, while in structure II its residual enthalpy of enclathration appears about 8% higher.

Multicomponent gas hydrates

We chose to study the mixture having the composition (in mol fraction) methane 0.364, ethane 0.541 and propane 0.095 with water at 285.0 K. There is a region of equilibrium of this system where gas hydrates of both structures, I and II, coexist[28]. It should be noted that for structure I hydrates, propane is a non-hydrate-forming substance. Here, we added 0.2 mol of water per mol of the gas mixture and then, according to our stability calculations, the three-phase region H^I-H^{II}-V existed between 2.830 and 2.990 MPa. In this region, the hydration number range was from 6.362 to 6.337 for structure I, and from 7.945 to 7.841 for structure II, while the corresponding enthalpies of formation range was from −63.03 to −62.80 for structure I, and from −70.36 to − 69.74 kJ/mol for structure II. At higher pressures, both the hydration number and the absolute enthalpy of formation continue to decrease smoothly. The values of the enthalpies of enclathration appear constant within the whole region. In particular, for methane the constant value was the same as that observed before for simple and double gas hydrates, that is about -25.0 kJ/mol. The enthalpy of enclathration of ethane in structure I was the same as in simple and double gas hydrates of the same structure, that is about -35.5 kJ/mol, but in structure II was the same as in the double gas hydrate of the same structure, that is, about -38.4 kJ/mol.

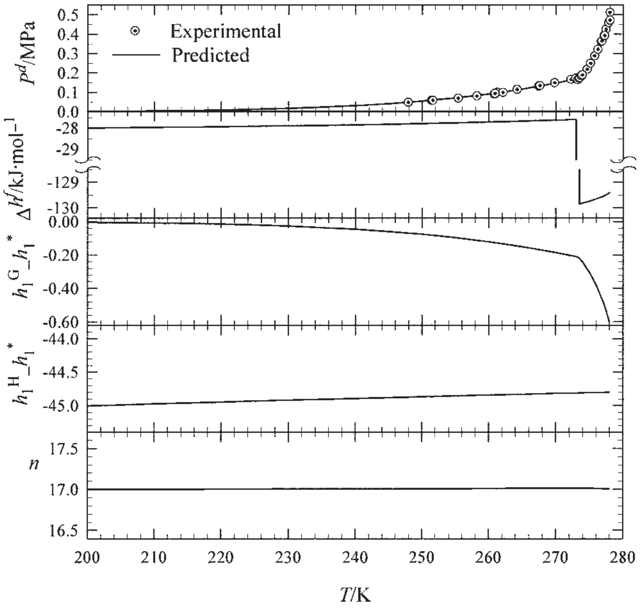

Figure 7. Energetic and equilibrium properties of propane gas hydrate formation as functions of temperature.

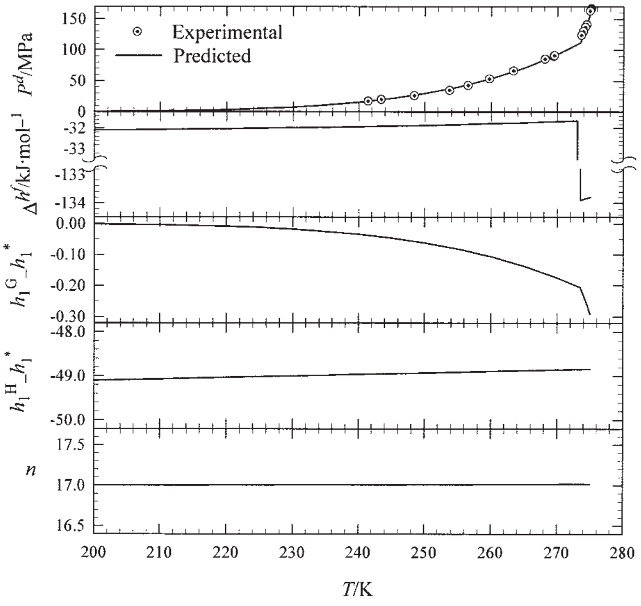

Figure 8. Energetic and equilibrium properties of *i*-butane gas hydrate formation as functions of temperature.

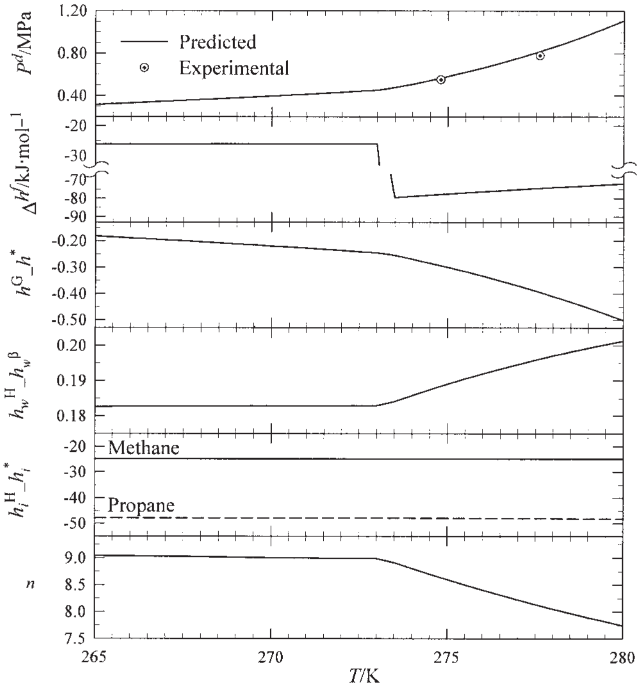

Figure 9. Energetic and equilibrium properties of a methane-propane double gas hydrate formation as functions of temperature.

The composition of the equilibrium gas phase was C_1 88.3 mol % on a dry basis.

Similarly, the enthalpy of enclathration of propane hydrate was the same as in the double hydrate, that is, about -48.2 kJ/mol.

As a final example application, we studied at the same temperature the system consisting of the previous mixture but enriched with 40 mol % N_2 on a dry basis. The hydrate point of this system is H^{II}-Lw-V and occurs at 4.12 MPa with hydration number 7.617 and enthalpy of formation -67.42 kJ/mol. At higher pressures, that is in the two-phase region, these properties decrease with pressure and at 8.56 MPa their values are 6.730 and -61.468 kJ/mol, respectively. The enthalpy of enclathration of nitrogen was -20.5 kJ/mol, that is, about equal to that of the simple nitrogen hydrate. The enthalpies of enclathration of the other components were the same as those in the previous example.

Investigation of the effect of higher pressures

The proposed model, comprising Eqs. 9 to 22, is valid even if the hydrate crystal were considered compressible. For an estimate of the effect of the compressibility of the crystal on the hydrate properties, let the molar volume difference between the empty hydrate lattice and the stable water phase $\Delta v_w^{\beta-\alpha/L}$, be a function of both temperature and pressure. If the isothermal compressibility $k_T \equiv -(1/v)(\partial v/\partial p)_T$, of a condensed phase within the region of our interest is assumed independent of temperature and pressure[29], then the equation of state for that phase is

$$v(T, p) = v(T, p_0)\exp[-k_T(p - p_0)] \tag{24}$$

where $v(T, p_0)$ is the molar volume of the condensed phase at any temperature T and at a reference pressure p_0. The quantity $v(T, p_0)$ may be calculated for any pure water phase by application of the correlation (Eq. A.5) appearing in Appendix A. After introduction of Eq. 24, the isothermal integral of the molar volume differences appearing in Eq. A2, becomes

$$\int_0^P \frac{\Delta v_w^{\beta-\alpha/L}}{RT}\,dp = \frac{v_w^\beta}{RTk_T^\beta}\left(1 - e^{-k_T^\beta p}\right) - \frac{v_w^{\alpha/L}}{RTk_T^{\alpha/L}}\left(1 - e^{-k_T^{\alpha/L} p}\right), \quad p \gg p_0 \tag{25}$$

It is interesting to note that if the crystal were perfectly incompressible then $\lim_{k_T \to 0}(1 - e^{-k_T p})/k_T = 1$, so the result of the earlier integration is valid in any case.

According to the recommendations of Marion and Jakubowski[30], the isothermal compressibility of ice, at 1 bar and at 273.0 K is 2.02×10^{-4} MPa, while at 263 K is 1.13×10^{-4} MPa. For liquid water, the isothermal compressibility recommended by the same authors at 273.15 is 5.06×10^{-4} MPa, while at 283 K is 4.76×10^{-4} MPa. For comparison, Kell[31] recommends 5.089×10^{-4} MPa and 4.781×10^{-4} MPa, respectively.

The combined data at the ice point of Hirai et al.[32] and Davidson et al.[33] were used to fit Eq. 24. The result is shown in Figure 11, together with the confidence interval for 95% statistical probability of the fitted line. The estimated value of k_T

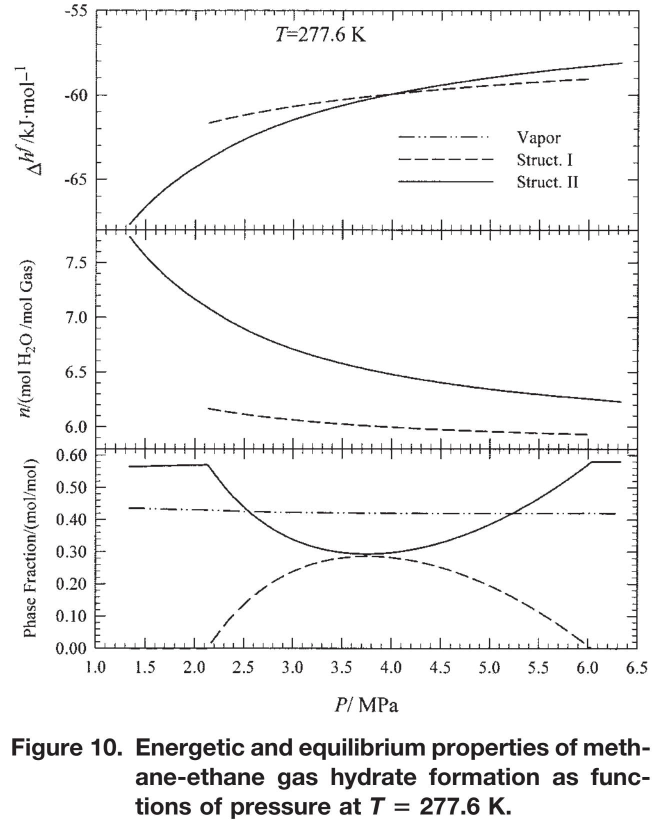

Figure 10. Energetic and equilibrium properties of methane-ethane gas hydrate formation as functions of pressure at T = 277.6 K.

The molar composition of the closed system was C_1 0.65, C_2 0.35 and H_2O 1.00.

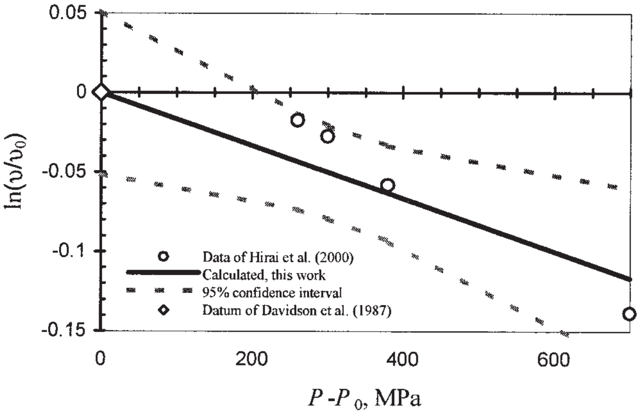

Figure 11. Isothermal compressiblity of methane hydrate at 273.15 K.

for the hydrate lattice (str. I) is $1.67 \times 10^{-}$ MPa, with a standard error $\pm 2.3 \times 10^{-5}$ Mpa, and a coefficient of determination $R^2 = 0.861$. The value obtained by Hirai et al.[32] exclusively from their own data, by fitting to the Birch-Murnaghan EoS, is 3.571×10^{-4} MPa, which clearly indicates that the datum of Davidson et al.[33] is significantly different from their's. It appears from this treatment that ice and gas hydrate (str. I) have quite similar values of isothermal compressibility. This means that compressibility should not have an appreciable effect on equilibria involving ice and gas hydrates at higher pressures.

The predictions of the hydrate model for methane hydrate, before and after substituting Eq. 25 in Eq. A.2, show that for hydrate point predictions the compressibility of the condensed equilibrium phases is not of any appreciable importance up to about 50 MPa. The introduction of Eq. 25 improves the accuracy of the phase equilibria predictions that are fair up to about 150 MPa. At still higher pressures the modified model overpredicts while the unmodified underpredicts the data. These results are shown in Figure 12. The two models provide almost identical predictions for the enthalpy of formation up to about 310.6 K, which corresponds to an experimental dissociation pressure 162 MPa, while the predictions are 175 MPa and 143 MPa, respectively for the modified and unmodified model. This is a turning point, because after that both models predict an absolute increase of the enthalpy of formation as the equilibrium temperature is increased, while before that point it was only very slightly absolutely decreasing. However, the increase calculated by the modified model is quite large, for example, while at 310.6 K the predicted enthalpies of formation by the modified and unmodified model are -50.9 and -50.5 kJ/mol, at 313.0 K they are -56.8 kJ/mol and -50.9 kJ/mol, respectively. The latter results are both erroneous, because the wrong prediction of the equilibrium pressure leads to the false calculation of the enthalpic contribution $(h_1^G - h_1^*)$, that is, the third term of Eq. 11a. This is the term that is actually rapidly changing along the equilibrium line while the rest of the terms remain almost constant.

Discussion

As it is evident from the data in Table 1, our present model corroborates in every case the results of Yoon et al.[16], which are derived by application of the Clausius-Clapeyron equation, as well as the experimental data of Handa[5,6]. Several conclusions may be drawn from the calculated data for simple gas hydrates in Table 1. At temperatures below the lower quadruple equilibrium point I-L_w-G-H, the values of Δh^f of all of the simple gas hydrates studied here are so slightly decreasing with temperature that they may be considered approximately constant. If both types of cavities are occupied, the hydration number n increases steadily with temperature. If, however, the guest component enters the large cavity only, the increase of n is almost negligible. Whatever the case, the hydration number is maximum at the lower quadruple point. Above the lower quadruple point, the hydration number decreases with temperature, but the decrease remains insensible for the hydrates of components entering the large cavity only. The values of Δh^f absolutely decrease monotonically with increasing temperature. At the quadruple point, they are absolutely minimum for I-G-H equilibrium and absolutely maximum for Lw-G-H equilibrium.

These findings are in qualitative accord with the data for carbon dioxide hydrate reported by Anderson[17], who used the Clapeyron equation. The latter author critically reviews the method, cites results from previous relevant works and proposes an efficient scheme for the calculation of ΔV. The deviation of these results to those of Anderson[17] for carbon dioxide is not large but, as shown in Figure 4, it is systematic and definite. We may argue, however, that the elegant analysis of Anderson[17] is based on the empirical fitting of experimental data of dissociation pressures by a higher order polynomial. However, as it may be pointed out, the excellent quality of the fit does not guarantee the quality of the experimental data or—more importantly—the physical significance of the derivatives of the fitted equation. On the other hand, our model does have inherent particular limitations for carbon dioxide, due to its large size relative to the size of the small cavities and its enhanced solubility in water. Perhaps, the combined errors from the two methods may have led to the noted discrepancy.

The Clausius-Clapeyron equation is not useful if a vapor phase does not coexist or at higher temperatures and pressures where the assumption of negligible condensed phase volume is

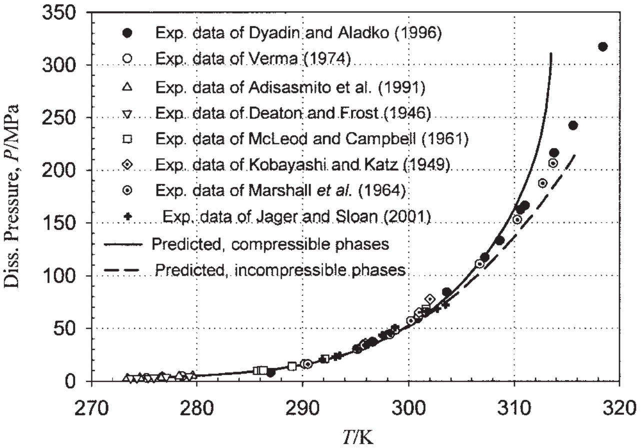

Figure 12. Model with compressible condensed phases, and the model with incompressible condensed phases.

not valid. In these cases the Clapeyron equation may be used. For example, Verma[34] and Ng and Robinson[35] had applied the Clapeyron equation to explain the slope dp/dT of their L_h-L_w-H^{II} equilibrium data of several double and multicomponent hydrate forming liquid mixtures. Jager and Sloan[36] conclude for methane hydrate that the Clausius-Clapeyron equation shows deviations when the pressure is higher than 20 MPa, while the Clapeyron is used by them up to about 70 MPa with satisfactory accuracy.

The application of the Clausius-Clapeyron equation to calculate the enthalpies of dissociation of double and multicomponent gas hydrates from respective three phase V-L_w-H equilibrium data[2,37] had raised questions in the past[38] on the ground that the composition of the hydrate phase changes along the equilibrium line, and the phase rule does not indicate univariant equilibria. The answer has been that the hydrate nonstoichiometry is not thermodynamically prohibitive to the use of the Clapeyron or Clausius-Clapeyron equation[39] if it is applied precisely at one point of the equilibrium p-T line[40,41]. To this issue, we may add that for a closed system with any number of components at the equilibrium hydrate point (that is, where the mass of the hydrate phase participating in the equilibrium is exactly zero), the equilibrium is fixed if one only independent variable, for example, the temperature is fixed, by virtue of Duhem's theorem (Prigogine and Defay[13]). So, the pressure, the mass, and the composition of each equilibrium phase together with the fugacities of all species in the system are fixed. Then the available Gibbs-Duhem equations, being as many as the number of phases, may be algebraically combined, as dictated by the hydration reaction, to express the common term in them $(dp/dT)_e$, and that expression is, of course, nothing more than the usual Clapeyron equation. The change of composition along the equilibrium line of multicomponent hydrate equilibrium systems means that a large number of highly accurate experimental data are required in order to apply the Clapeyron equation at one or more points. Because such data are rarely available for mixed gas hydrates, it might be expected that either the more accurate Clapeyron equation or the simpler Clausius-Clapeyron equation can provide only one, roughly mean, estimate of the enthalpy of dissociation, for the range of the data.

It is clear from our results for simple gas hydrates in Table 1 that the most significant enthalpy contribution arises from the encagement of the gases from the ideal gas state $h_1^H - h_1^*$. This characteristic quantity of simple gas hydrates appears to be independent of the hydration number, the distribution between cavities, the temperature and the pressure. The residual enthalpy of the gas $h^G - h^*$, and the enthalpy change associated with the transformation of the metastable empty hydrate lattice to gas hydrate $n(\bar{h}_w^H - h_w^\beta)$, are both relatively small numbers, tending generally to cancel the effect of each other in the case of gas hydrates with both cavities occupied. In the case of gas hydrates with only the large cavity occupied, the first is a small number, due to the generally lower equilibrium pressures, while the second is exactly zero for simple gas hydrates. These facts explain the noted stability of the enthalpy of gas hydrate formation below the lower quadruple point. For example, from the data in Table 1 for methane hydrate, we have

$$\Delta h^f(270\text{ K}) - \Delta h^f(185\text{ K}) = 0 - 0.106 + 0.449 + 0.253 = 0.60\text{ kJ/mol}$$

Above the lower quadruple point, the hydration number decreases with temperature but the last term in Eq. 11a, that is $(h_w^L - h_w^\beta) = (h_w^L - h_w^\alpha) + (h_w^a - h_w^\beta)$, now becomes significant and changes sign as well. For example, for methane hydrate, we have

$$\Delta h^f(280\text{ K}) - \Delta h^f(274\text{ K}) = 0.00219 - 0.00673 + 0.223 + 0.244 = 0.46\text{ kJ/mol}$$

Overall, the enthalpy of gas hydrate formation changes along the equilibrium line in the same pattern whether below or above the ice point, but apparently with a greater rate in the latter case.

Since the ideal solid solution model is developed assuming no interactions between encaged molecules, we should expect that calculated heats of enclathration are independent from the hydration number, as well as from the synthesis of the enclathrated mixture. Indeed, in all of the example applications studied here, as computed by application of the ideal solid solution model, the heat of encagement from the ideal gas state of all gas hydrate formers is essentially constant at all conditions, irrespective of temperature, pressure, gas hydrate type and composition. These observations firmly corroborate our initial observation from simple gas hydrates that $\bar{h}_i^H - h_i^*$ is a constant characteristic only of the pure substance i. To estimate this constant, we have regressed the following corresponding states correlation

$$\frac{\bar{h}_i^H - h_i^*}{RT_{ci}} = 52.05 - 6.93 \ln T_{ci} + 0.394\omega_i T_{ci}^{0.675}, \qquad (26)$$

where T_{ci} is the critical temperature in K and ω_i is the accentric factor of component i. This equation fitted the data of Table 1, not including carbon dioxide, with an average absolute deviation 0.70%, while the maximum deviation was 1.75%, corresponding to propane.

This analysis does not support a direct relation between the enthalpy of dissociation above the ice point and the type of the cavity occupied by the guest(s), as has been suggested by Sloan and Fleyfel[15]. The heat of gas hydrate formation is the sum of two principal contributions: the heat of enclathration, which depends solely on the nature of the enclathrated molecules, and the heat of conversion of water (ice or liquid) into gas hydrate crystal, which depends on the hydration number. The major effect below the ice point is the first while above the ice point it is the second. The values in Table 1 reveal close proximity of the enthalpies of formation of the hydrates of Xe, C_2H_6 and C_3H_8, which, of course, is simply accidental and that there are substantial deviations among the values of Δh^f of the hydrates of Xe, CH_4 and CO_2, which are guests of the same cavities.

The establishment of a general analytical correlation for the enthalpies of enclathration did not led us to a generally applicable short-cut method for the calculation of gas hydrate formation conditions, since the latter depends also on the hydration number. This in turn depends on the thermodynamics of the system, which may be quite complex, as our example studies of double and mixed gas hydrates clearly demonstrate. Nevertheless, the incorporation of the algorithm proposed in this work into a hydrate phase equilibrium model is an efficient means for accurate predictions of the enthalpy of bulk gas hydrate formation. Our results at higher pressures clearly indicate that an isothermal compressibility that is a dependent variable of both temperature and pressure can be used to obtain perfect fits of experimental dissociation pressure data at higher pressures. This author is not aware of experimental data of isothermal compressibilities of gas hydrates such that would permit a bivariate regression. We should comment, however, that the extension of a phase equilibrium model to enthalpy calculations entails a danger common to any model used beyond its range of fit. When the predicted properties depend on the derivatives of a fitted property, they may be erroneous and they are always suspicious. In a previous work[3], we demonstrated the discrepancies normally associated with treating the cell potential parameters as empirical fitting constants, and we proposed a consistent methodology to overcome the problem and obtain unique and meaningful values of the potential parameters. Then, these unique parameters enabled calculation of the heat capacities of gas hydrates[4], as well as these calculations. Other authors, for example, Mehta and Sloan[42] for their work on structure H gas hydrate have also adopted that methodology. Thus, before attempting calculations of enthalpies on the basis of the ideal solid solution model, experimentally determined reference properties and unique cell potential parameters should be incorporated in the model.

In porous media, due to capillary phenomena, the gas hydrate equilibrium pressure increases as the pore size decreases and the heat of hydrate dissociation is lower than in the bulk, as Handa and Stupin[43] first had reported. The dissociation conditions of methane hydrate in porous glass was also measured by Uchida et al[44]. These experiments demonstrate that pore size affects not only the equilibrium pressure at a fixed temperature, but also the composition of the hydrate phase as well as the enthalpy of dissociation. Moreover, phase equilibria is affected not only by the size of the pores, but also by the pore-size distribution. The process of hydrate dissociation in porous media is only phenomenally univariant. In fact, gas hydrates in the smallest pores will dissociate first and those in the largest pores last so one might rather consider the $p = f(T)$ equilibrium dissociation line as representing an infinite series of equilibrium processes, each taking place in a different system, as long as the porous medium of interest is continuously changing properties during decomposition. Therefore, thermodynamic models for bulk gas hydrate equilibria are not directly applicable to gas hydrates in porous media. A theoretical model proposed by Klauda and Sandler[45], which accounts for pore-size distribution, was shown to provide improved predictions of phase equilibria in porous media. Clearly, the Clapeyron equation is not useful for enthalpy calculations of gas hydrate dissociation or formation in porous media. In this case, a differential approach might be adopted involving the proposed method on top of an appropriate phase equilibrium algorithm. In reality, however, the situation is much more complex. For example, coupling with a heat transfer model, taking into account pore-size distribution, is also needed. Evidently, to the end of accurate predictions of the phenomena associated with gas hydrate dissociation in porous media, further work is needed.

Conclusions

An extension of the ideal solid solution model was presented for the direct calculation of enthalpies of gas hydrate formation. The method can be applied at the hydrate formation point or beyond it, irrespective of the number of components and the number of hydrate phases that may be present. Extensive results were presented that compare well to results reported in the literature that had been obtained either by direct calorimetric measurements or by application of the Clapeyron equation on available hydrate point equilibrium data. This model may be a reliable tool for process engineering applications involving bulk gas hydrate formation at pressures not exceeding 150 MPa. However, the variation among predictions and the very limited number of direct experimental calorimetric measurements reported in the past dictates that more experimental work is needed, particularly with double or mixed gas hydrates.

In this study the various energetic components of the enthalpy of gas hydrate formation were delineated. Contrary to the common belief that the hydration number controls the heat of gas hydrate formation, it was found that below the lower quadruple point the major energetic component in gas hydrate formation is the residual enthalpy of enclathration. Moreover, it was demonstrated that the residual enthalpy of enclathration of a gas is a property of the gas itself, independent of the hydrate type and cavity, and also independent of the composition of the gas hydrate or the prevailing temperature and pressure. As a result, this property was regressed with fair accuracy by application of the principle of corresponding states. The latter correlation might possibly serve as part of a future short-cut method for gas hydrate equilibrium predictions.

Notation

$c_{p,i}$ = molar heat capacity of component i, J/mol·K
c^{H} = number of enclathrated components
c_{mi} = Langmuir type constant for a gas molecule i in a hydrate cavity m
f_i = fugacity of component i, Pa
H = enthalpy of a system, J
h = molar enthalpy, J/mol
$\bar{h}_i$ = partial molar enthalpy of component i, J/mol
k = Boltzmann's constant, 1.38066×10^{-23} J/K
n = hydration number, mol of hydration water per mol of enclathrated gas
n_i = number of mol of component i
p = system pressure, Pa
R = universal gas constant, 8.31451 J/mol·K
R = cell radius, m
r = radial distance from the center of the cavity
S = system entropy, J/K
T = absolute temperature, K
V = system volume, m^3
$w(r)$ = spherically symetric cell potential at distance r, J
x_j = mole fraction of component j
y_j = mole fraction of component j
z = compressibility factor, $z \equiv pv/RT$

Greek letters

α = index, ice
β = index, empty hydrate lattice
Δ = change in a property
θ_{mi} = fractional occupancy of type m cavities by component i
μ_i = chemical potential of component i, J/mol
ν_m = number of cavities of type m
υ = molar volume, m^3/mol
ϕ_i = fugacity coefficient of component i

Subscripts

h = index in L_h of a hydrocarbon-rich phase
i, j = gas component indices
m = cavity type index
w = index of water

Superscripts

d = dissociation direction
f = formation direction
G = index, gas phase
H = index, hydrate phase
I = index, ice
L_w = index, liquid water-rich phase
$*$ = ideal gas state at the system temperature and pressure
$\circ$ = reference state

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Appendix A

Thermodynamic equations of the gas hydrate phase equibrium model

The chemical potential of a pure water phase is a function of temperature and pressure only. Application of the thermodynamic relation

$$d\left(\frac{\mu}{RT}\right) = \left[\frac{\partial(\mu/RT)}{\partial T}\right]_P dT + \left[\frac{\partial(\mu/RT)}{\partial P}\right]_T dP$$
$$= -\frac{h}{RT^2}dT + \frac{v}{RT}dP \quad \text{(A1)}$$

to water in the empty hydrate lattice (β) and ice (α) - or liquid (L), as appropriate according to temperature- subtracting the latter from the first and then integrating from (T_0, 0) to (T, p), the following relation is finally obtained

$$\frac{\Delta\mu_w^{\beta-\alpha/\mathrm{L}}(T,P)}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_w^{\beta-\alpha/\mathrm{L}}}{RT^2}dT + \int_0^p \frac{\Delta v_w^{\beta-\alpha/\mathrm{L}}}{RT}dp \quad \text{(A2)}$$

where $\Delta\mu_w^{\beta-\alpha/\mathrm{L}} \equiv \mu_w^{\beta} - \mu_w^{\alpha/\mathrm{L}}$, μ_w^{β} and $\mu_w^{\alpha/\mathrm{L}}$ are, respectively, the chemical potential of pure water in the empty hydrate lattice (β) and ice (α), or the liquid (L) phase, whichever exists depending on the temperature, p is the equilibrium pressure, T_0 is the absolute temperature at the ice point, $\Delta h_w^{\beta-\alpha/\mathrm{L}}$ and $\Delta v_w^{\beta-\alpha/\mathrm{L}}$ are, respectively, the molar enthalpy difference at zero pressure, and the molar volume difference at a temperature T between an empty hydrate lattice and ice or liquid water.

The molar enthalpy difference between an empty hydrate lattice and ice or liquid water at zero pressure is a function of temperature

$$\Delta h_w^{\beta-\alpha/\mathrm{L}} = \Delta h_w^0 + \Delta h_w^{\alpha-\mathrm{L}} + \int_{T_0}^{T}\Delta c_{P_w}^{\beta-\alpha/\mathrm{L}}dT \quad \text{(A3)}$$

where is $\Delta h_w^{\alpha-L}$ the molar difference in enthalpy between ice and liquid water, and it is set equal to zero if $T < T_0$. $\Delta c_{P_w}^{\beta-\alpha/\mathrm{L}}$ is the heat capacity difference between the empty hydrate and ice or liquid water and it is generally a function of temperature. The heat capacity difference between the empty hydrate lattice and ice, $\Delta c_{P_w}^{\beta-\alpha}$, is set equal to zero[4]. For the heat capacity difference between ice and liquid water we use the equation recommended by Holder et al.[46] in J·mol^{-1}·K^{-1}.:

$$\Delta c_{P_w}^{\beta-\mathrm{L}} = -37.885 + 0.177(T - T_0) \quad \text{(A4)}$$

$\Delta\mu_w^0$ and Δh_w^0 are, respectively, chemical potential and enthalpy differences between the empty hydrate lattice and ice at the ice point T_0, and zero pressure. These were obtained experimentally by Dharmawardhana et al.[47].

The molar volumes of ice, hydrate I and II and liquid water are fitted[3] to the equation

$$v = v_0\lfloor 1 + k_1(T - T_0) + k_2(T - T_0)^2 + k_3(T - T_0)^3\rfloor \quad \text{(A5)}$$

The numerical values of the parameters of this equation are reported in the original article[3].

Equations A1 through to A5 give the value of the chemical potential of water in the empty hydrate phase relative to that of a pure water phase as a function of temperature and pressure. The chemical potential difference between water in a hydrate phase and pure water - in the ice or liquid state, depending on temperature - is calculated as

$$\Delta\mu_w^{\mathrm{H}-\alpha/\mathrm{L}} = \Delta\mu_w^{\mathrm{H}-\beta} + \Delta\mu_w^{\beta-\alpha/\mathrm{L}} \quad \text{(A6)}$$

where the first term is calculated by Eq. 4 of the statistical thermodynamic theory as detailed by Parrish and Prausnitz[20] and the second term of the righthand side as detailed earlier.

Then, the fugacity of water in the hydrate phase is obtained from

$$f_w^{\mathrm{H}} = f_w^{\alpha/\mathrm{L}}\exp\left(-\frac{\Delta\mu_w^{\mathrm{H}-\alpha/\mathrm{L}}}{RT}\right) \quad \text{(A7)}$$

where $f_w^{\alpha/\mathrm{L}}$ is the fugacity of pure water in its stable state at T and p. The fugacity of any component in a vapor or liquid phase is calculated from a cubic equation of state with unconventional nondensity-dependent mixing rules proposed by Avlonitis et al.[22]. The fugacity of water as ice is calculated by correcting the saturation fugacity at the same temperature by the Poynting factor.

As an example formulation of a phase equilibria problem, consider the calculation of the hydrate point of the three-phase V-L$_\mathrm{w}$-H equilibria of a system of c hydrate forming components with overall mol fractions z_i at a any fixed temperature T. Equality of the fugacity of each component in the two fluid phases, $f_{i1} = f_{i2}$, provides c equations. One more equation $f_{w1} = f_{w3}$, is provided by the equality of the fugacity of water in the hydrate phase in Eq. A7, to the fugacity of water in the vapor (or, in the water-rich liquid) phase. Besides, mol balance restrictions provide one equation for each of the components, that may be $z_i = \sum_{j=1}^{2} x_{ij}F_j$, and one equation for each fluid phase j, that may be $\sum_{i=1}^{c} x_{ij} = 1$. So, the total number of independent equations is $c+1+c+2 = 2c+3$. There are c +1unknowns for each fluid phase j, that is, x_{ij} and F_j, plus the equilibrium pressure p. So, the total number of unknowns equals the number of independent equations and the problem can be solved by the usual numerical methods for systems of nonlinear equations, as for example is the Newton-Raphson algorithm. Note, that in this problem the number of mol of the hydrate phase equals zero, $F_3 = 0$, and the mol fractions of all components in the hydrate phase are calculated as dependent variables using Equation 12.

Appendix B

Calculation of the Temperature Derivatives of the Langmuir-type Constants

The Langmuir-type constant, which accounts for gas-water interactions in the hydrate cavities, is given by the following relation (van der Waals and Platteeuw, 1959)

$$C_{mi}(T) = \frac{4\pi}{kT}\int_0^R \exp\left(-\frac{w(r)}{kT}\right)r^2dr \qquad \text{(B1)}$$

where m and i are the cavity and guest indices, respectively, and R is the radius of the cavity. To simplify notation we assign the symbol $\mathbf{I}_{mi}$ to the integral

$$\mathbf{I}_{mi} \equiv \int_0^R \exp\left(-\frac{w(r)}{kT}\right)r^2dr \qquad \text{(B2)}$$

By taking the logarithm of (1) and differentiating, we obtain for the derivatives

$$\frac{\partial \ln C_{mi}}{\partial T} = \frac{1}{\mathbf{I}_{mi}}\frac{\partial \mathbf{I}_{mi}}{\partial T} - \frac{1}{T} \qquad \text{(B3)}$$

and

$$\frac{\partial^2 \ln C_{mi}}{\partial T^2} = \frac{1}{\mathbf{I}_{mi}}\frac{\partial^2 \mathbf{I}_{mi}}{\partial T^2} - \frac{1}{\mathbf{I}_{mi}^2}\left(\frac{\partial \mathbf{I}_{mi}}{\partial T}\right)^2 + \frac{1}{T^2} \qquad \text{(B4)}$$

The derivatives of the integral with respect to temperature are calculated as follows

$$\frac{\partial \mathbf{I}_{mi}}{\partial T} = \frac{\partial}{\partial T}\int_0^R \exp\left(-\frac{w(r)}{kT}\right)r^2dr = \int_0^R \frac{\partial}{\partial T}\exp\left(-\frac{w(r)}{kT}\right)r^2dr$$

$$= \int_0^R \exp\left(-\frac{w(r)}{kT}\right)\frac{\partial}{\partial T}\left(-\frac{w(r)}{kT}\right)r^2dr$$

$$= \int_0^R \frac{w(r)}{kT^2}\exp\left(-\frac{w(r)}{kT}\right)r^2dr$$

or

$$\frac{\partial \mathbf{I}_{mi}}{\partial T} = \frac{1}{T}\int_0^R \frac{w(r)}{kT}\exp\left(-\frac{w(r)}{kT}\right)r^2dr \qquad \text{(B5)}$$

$$\frac{\partial^2 \mathbf{I}_{mi}}{\partial T^2} = \frac{\partial}{\partial T}\frac{\partial \mathbf{I}_{mi}}{\partial T} = -\frac{2}{kT^3}\int_0^R w(r)\exp\left(-\frac{w(r)}{kT}\right)r^2dr$$

$$+\frac{1}{T}\int_0^R \frac{w(r)}{kT}\exp\left(-\frac{w(r)}{kT}\right)\frac{\partial}{\partial T}\left(-\frac{w(r)}{kT}\right)r^2dr$$

$$\times\frac{\partial^2 \mathbf{I}_{mi}}{\partial T^2} = -\frac{2}{T}\frac{\partial \mathbf{I}_{mi}}{\partial T} + \frac{1}{T^2}\int_0^R \left(\frac{w(r)}{kT}\right)^2\exp\left(-\frac{w(r)}{kT}\right)r^2dr \qquad \text{(B6)}$$

The two new integrals appearing in Eqs. 5 and 6, as well as $\mathbf{I}_{\mathrm{mi}}$, are calculated numerically.

Manuscript received Dec. 31, 2003, and revision received Aug. 2, 2004.