

Augmented stability of hydrogen clathrate hydrates by weakly polar molecules

Takato Nakayama, Kenichiro Koga, and Hideki Tanaka^{a)}

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Kitaku, Okayama 700-8530, Japan

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Thermodynamic stability of hydrogen clathrate hydrates has been examined in a wide range of pressure based solely on the intermolecular interactions involved. We show that the stability is indeed augmented by a second guest species (here acetone) called a promoter, a consequence of which is notable reduction in the dissociation pressure of the hydrates encaging hydrogen alone. This evaluation is made by extension of the van der Waals–Platteeuw theory combined with semi-grand-canonical Monte Carlo (GCMC) simulations where the number of hydrogen molecules is allowed to vary while those of host water and promoter acetone molecules are fixed. The GCMC simulations then provide various types of cage occupancies of hydrogen from single to quadruple, from which the chemical potential of water in the clathrate hydrate is obtained as a function of the cage occupancy by acetone and the pressure. These occupancies are used to calculate the chemical potential of water in the clathrate hydrate. The stability is estimated by comparison of the chemical potential of water in the clathrate hydrate with that in hexagonal ice. We show the extent to which the dissociation pressure is reduced with increasing the occupancy of the larger cages by acetone. © 2009 American Institute of Physics. [doi:10.1063/1.3271341]

I. INTRODUCTION

Clathrate hydrates are nonstoichiometric compounds made from water and guest molecules.¹ Clathrate hydrates are stable only when guest molecules occupy most of the cages. It has long been believed that each cage accommodates at most one guest molecule.¹ The thermodynamic stability of the clathrate hydrates has been accounted for by van der Waals and Platteeuw (vdWP) under the assumption of single occupancy.² Dissociation pressures of many clathrate hydrates have been successfully predicted by the vdWP theory with accurate intermolecular interactions.¹ An assumption in the original vdWP theory that host water lattice is not affected by inclusion of guest molecules is reasonable for small guest molecules but it is not so for guest molecules large enough to alter the host vibrational motions significantly.^{3–5} It was shown that a simple modification of the vdWP theory enables to treat multiple occupancy in a single cage.⁶

Since the discovery of hydrogen clathrate hydrate, it attracted considerable attention due to its potential use as hydrogen storage.^{7,8} A hydrogen clathrate hydrate is identified with structure II, which is made by both 12- and 16-hedra. Considering the size of a hydrogen molecule, multiple occupancies are expected at a high pressure where a hydrogen clathrate hydrate is formed.⁹ In fact, each larger cage accommodates maximally four hydrogen molecules while a smaller one encages at most two molecules according to the original report. It is, however, pointed out later that the highest occupancy in the smaller cage seems to be limited to be one.

The cage occupancy of hydrogen clathrate hydrate has

been examined by grand canonical/NPT Monte Carlo (GC/NPT MC) simulations for wide ranges of temperature and pressure.¹⁰ The simulations were carried out with a fixed number of water molecules and a fixed chemical potential of the guest species so that hydrogen molecules can be created or removed in the clathrate. This hybrid type of the GCMC simulation turned out to be very useful to calculate the cage occupancy correctly, in which it is allowed to adjust itself under a preset pressure so as to take account of compression or expansion by a hydrostatic pressure. It was found that the smaller cage in structure II is practically incapable of accommodating more than a single guest molecule even at pressures as high as 500 MPa, which agrees with the recent experimental investigations.^{8,11,12} The larger cage was found to encapsulate maximally four hydrogen molecules but its occupancy is dependent significantly on the chemical potential of hydrogen, which is related to the pressure of the bulk hydrogen outside.

One of the key issues toward the practical use of a hydrogen clathrate is to explore possibilities for reduction of its dissociation pressure. It is stable only at pressures above 200 MPa and its cage occupancy by hydrogen is almost saturated around at 500 MPa. Such high pressures make it difficult to handle this substance by simple containers. To overcome this inconvenience, some molecules called promoters are added to increase its stability. They are mostly large molecules accommodated in the larger cages so as to stabilize the clathrate while hydrogen molecules occupy both the smaller and the remaining larger cages. For example, the dissociation pressure can be fairly reduced by accommodating tetrahydrofuran (THF).^{13–17} This is advantageous to its use as hydrogen storage because a moderate pressure such as 15 MPa suffices

^{a)}Electronic mail: htanaka@cc.okayama-u.ac.jp.

TABLE I. Geometries and parameters of intermolecular interactions for water, acetone, and hydrogen. The interactions are described by charge (q), LJ size (σ), and energy (ϵ) parameters. The coordinates are those of the sites with the origin of the center of gravity.

Potential	Site	$\sigma/0.1$ nm	$\epsilon/\text{kJ mol}^{-1}$	q/e	$x/0.1$ nm	$y/0.1$ nm	$z/0.1$ nm
TIP5P	O	3.12	0.669	0	0	0	0.0651
	H			0.241	0	± 0.7570	0.5859
	Charge			-0.241	± 0.572	0	0.404
Acetone	C	3.75	0.4396	0.300	0	0.0893	0
	O	2.96	0.8793	-0.424	0	1.3112	0
	CH ₃	3.91	0.6699	0.062	± 1.2864	-0.696	0
Hydrogen	H			0.4932	0	± 0.3707	0
	Center	3.038	0.2852	-0.9864	0	0	0

for its stabilization.^{13–17} However, it accompanies a serious disadvantage. That is, occupation by a second guest necessarily reduces the occupancy of hydrogen. Thus, there must be a kind of tradeoff between reduction in the dissociation pressure and its efficiency. There have been several attempts to seek promoter species and to determine optimal occupancy by the promoter that achieves a low dissociation pressure and high occupancy by hydrogen.^{18–20}

It is highly desirable to establish a relation between reduction of the dissociation pressure and the efficiency as hydrogen storage in a wide range of pressure with varying composition of a promoter species. To this end, we should find a simple way to evaluate the thermodynamic stability of clathrate hydrates and its cage occupancy from intermolecular interactions currently available under a fixed occupancy of a promoter guest. Instead of THF, we choose acetone as a promoter. Acetone seems to be a little harder to be engaged in structure II clathrate hydrate.²¹ However, the resultant stability does not depend on the promoter species as far as it is engaged. We first extend the vdWP theory to a fixed number of promoter molecules, without taking account of an equilibrium of a promoter with that outside explicitly. This condition is justified by the fact that acetone is much more preferentially engaged than hydrogen. It is also helpful to perform GCMC simulations at high pressures where multiple occupancy is expected.

We propose a method to estimate the stability of hydrogen-acetone binary clathrate hydrates by the extended vdWP theory combined with GC/NPT MC simulations. This seems to be the only way to implement numerical evaluation of the free energy for multiple cage occupancy since that for triple or quadruple is actually impossible to calculate. Various cage occupancies are obtained from GC/NPT MC simulations in the presence of acetone. Once a certain amount of promoter species is encapsulated, its stability is dependent on its occupancy but is irrelevant to the choice of it in neglecting the guest-guest interaction. Thus, the thermodynamic stability is evaluated with the chemical potential values of the empty hydrate and ice in equilibrium with the hydrate.

The present paper is organized as follows. Models and simulation methods used in the present study are described in Sec. II. The cage occupancies for hydrogen clathrate at various temperatures and pressures are shown and a relation be-

tween the vdWP theory and the GC/NPT hybrid ensemble MC simulation is discussed in Sec. III. The conclusion is given in Sec. IV.

II. SIMULATION METHOD

The choice of intermolecular interactions and the methods of calculating the chemical potential of hydrogen fluid, generating the crystalline structure of hydrate II, and implementing GC/NPT MC simulations, are briefly outlined here; the details were described elsewhere.¹⁰ The methods for calculating various free energies are also described.

A. Intermolecular interactions and structure of clathrate hydrate II

The thermodynamic stability and the cage occupancy of clathrate hydrate are evaluated with intermolecular potentials which are reliable but as simple as possible. In the present study, all interactions are assumed to be pairwise additive. The water-water intermolecular interaction is described by the TIP5P potential.²² This potential has often been used in the study of water. It is believed to be the most reliable within the framework of pair potential in reproducing phase behavior of pure water.²³ The TIP5P model consists of five interaction sites; a positive charge, q , on each proton, two negative charge ($-q$) sites extended from the oxygen toward the remaining tetrahedral directions, also a Lennard-Jones (LJ) potential between oxygen nuclei. Choice of the water-water interaction, however, does not make a significant difference in cage occupancy under moderate compression, which does not lead to collapse of the original clathrate hydrate structure or to significant hydrogen bond cleavage. An acetone molecule is treated as a rigid rotor with four interaction sites, two methyl groups, a carbonyl carbon, and an oxygen atom.²⁴ The individual sites interact with each other via LJ and Coulombic potentials. A hydrogen molecule is modeled by a rigid rotor with two sites, 0.074 14 nm apart, having a positive charge and one site, at the midpoint, having an LJ potential center and a negative charge.²⁵ For all the unlike site-site interactions, the Lorentz–Berthelot rule is applied. The parameters on the interaction potentials and the molecular geometries are tabulated in Table I. The interaction potentials for all pairs of molecules are truncated smoothly at 0.8655 nm.²⁶ The correction term arising from

the truncation of all the LJ interactions is taken into account in calculating the free energy of hydrogen fluid and the occupancy in clathrate hydrate.

A method to generate clathrate hydrate II structure was described previously.³ The unit cell of the hydrate II is cubic and experimental lattice parameters are used in the initial stage of GC/NPT MC simulation; $a=b=c=1.731$ nm with $\alpha=\beta=\gamma=\pi/2$.¹ We generate 32 different structures, each of which is of proton-disordered form and has nearly zero net dipole moment. The basic cell in the present MC simulations is composed of 8 unit cells of clathrate hydrate II, in which 1088 water molecules are placed on the lattice sites.

B. GC/NPT Monte Carlo simulations

Accommodation of a guest molecule can be regarded as an adsorption in each cavity. Thus, the number of guest molecules at a given pressure (at a given chemical potential of guest species in its fluid phase) can be evaluated in the same fashion as usual adsorption process by GCMC simulation. This simulation is carried out with the fixed parameters of the temperature, the volume of the clathrate hydrate, V , and the chemical potential of the guest species, μ_h (or μ_a). The chemical potential of the guest molecule is calculated from the equation of state as shown below. We assume that the hydrostatic pressure, P , on the hydrate is equal to that of the hydrogen fluid. The pressure covered in this study ranges from 1 to 200 MPa, which may lead to alternation of the cell dimension. Then, there is a more appropriate way to calculate the cage occupancy at a given temperature and pressure as a function of the pressure of hydrogen in equilibrium with the clathrate hydrate in question. That is, a standard MC technique with a constant pressure is applied with the fixed numbers of water and guest molecules. This meets the Gibbs phase rule. A system is treated as an isothermal-isobaric (NPT) ensemble with respect to water and guest at a given instant and the volume change is attempted according to NPT MC simulation scheme in addition to the grand canonical procedures. Thus, our simulation is a hybrid one, called GC/NPT MC simulation. The volume is dependent on the hydrostatic pressure. A guest hydrogen molecule is inserted or deleted according to the standard technique of GCMC simulation at a given temperature T and pressure P . A trial insertion is made at an arbitrary position with random distributions of polar and azimuthal angles. Such an insertion accompanied by the interaction energy w with all other molecules including N_h hydrogen molecules in a volume, V , is accepted for a polar angle θ with a probability

$$\min\left\{1, \frac{Vz \sin \theta}{(N_h + 1)} \exp(-\beta w)\right\}, \quad (1)$$

where z stands for the fugacity of guest molecule, and β is $1/k_B T$ with the Boltzmann constant k_B ; z is calculated with the thermal de Broglie wavelength Λ as

$$\ln z = \beta(\mu_h - \mu_{\text{rot}}^{\text{id}}) + \ln \Lambda^3, \quad (2)$$

where μ_h and $\mu_{\text{rot}}^{\text{id}}$ are the chemical potential of hydrogen and its ideal rotor part, respectively. A deletion of an arbitrarily

chosen molecule out of N_h guests in the system is attempted. The trial is accepted with a probability

$$\min\left\{1, \frac{N_h}{Vz \sin \theta} \exp(\beta w')\right\}, \quad (3)$$

where w' is the interaction energy of the chosen guest with all other molecules. The intermolecular interaction is truncated smoothly as in GCMC simulations, but its correction to the pressure is taken into consideration with an assumption that molecular distribution is uniform beyond the truncation.

In the present GC/NPT MC simulations, a single MC step consists of either a trial creation or annihilation (with the equal probability) followed by five trial moves of molecules, and a subsequent volume change. Each MC simulation at given temperature and pressure includes 4×10^7 steps.

C. Chemical potential for hydrogen fluid

The equation of state for the model hydrogen fluid whose constituent molecules interact with the prescribed potential is unknown. We thus calculate the pressure-density isotherms from NVT MC simulations and then obtain the chemical potential as a function of pressure for each temperature. The number of molecules used in the simulation is taken to be in a range between 128 and 512, depending on the density, so that the volume falls into a certain range. The density ranges from 0.2 to 64 mol L⁻¹, which is enough for the present purpose. The chemical potential of the imperfect gas (fluid) for a linear rigid rotor is calculated as follows. At a given temperature, we perform NVT MC simulations of pure hydrogen with various volumes (number densities, ρ). The long-range interaction is again taken into account in the calculation of the pressure. Thus, we obtain an isotherm of the pressure.

The free energy per molecule, a_h , at T and ρ for hydrogen with the mass, m , and the moment of inertia, I , is given by sum of the ideal and the nonideal parts as

$$a_h = k_B T \left[\ln \rho \left(\frac{\beta h^2}{2\pi m} \right)^{3/2} - 1 + \ln \left(\frac{\beta h^2}{4\pi^2 I} \right) \right] + \int_0^{\rho} \frac{p - \rho k_B T}{\rho^2} d\rho, \quad (4)$$

where h is the Planck constant. Since we deal with a one-component bulk fluid system, the chemical potential, μ_h , is simply given by

$$\mu_h = a_h + P\rho^{-1}, \quad (5)$$

where ρ at a given pressure P is calculated from the interpolation of the isotherm.

D. Calculation of free energy of solid and liquid states and free energy of cage occupation

The free energy of ice is calculated by its individual components, the interaction energy at 0 K, $U_q(V)$, the harmonic free energy, $F_h(T, V)$, the anharmonic free energy, $F_a(T, V)$, and the residual entropy term, S_c , as

$$A(T, V) = U_q(V) + F_h(T, V) + F_a(T, V) - TS_c. \quad (6)$$

It should be noted that the interaction energy at 0 K is a function of volume alone, which is obtained from conventional NPT MC simulations. The harmonic vibrational energy is calculated from a set of the normal frequencies, ν as

$$F_h(T, V) = k_B T \sum_i \ln(\beta h \nu_i). \quad (7)$$

The anharmonic free energy is calculated as

$$\frac{F_a(T, V)}{T} = - \int_0^T \frac{U_a}{T^2} dT, \quad (8)$$

where U_a is the anharmonic energy given by

$$U_a = U - U_q - U_h, \quad (9)$$

with $U_h = 3(N_w - 1/2)k_B T$ for N_w water molecules. The residual entropy term is given by $N_w k_B \ln(3/2)$ for both ice and empty clathrate and does not actually contribute to the chemical potential difference. The Gibbs free energy affected by pressure is evaluated by

$$G = A + PV. \quad (10)$$

All these properties depend on the volume, and thus the pressure. However, their pressure dependences are, here, expected to be small in the pressure range examined. It is assumed that the compressibilities for ice and clathrate are similar to each other and the pressure dependence of the chemical potential *difference* between ice and clathrate arising from the compressibility difference can be neglected.

The free energy difference of a fluid with a potential energy function Φ_N from the corresponding ideal gas state A^{id} at the same density is calculated by thermodynamic integration,

$$\begin{aligned} \Delta A &= A - A^{\text{id}} = \int_0^1 \frac{dA(\lambda)}{d\lambda} d\lambda \\ &= \int_0^1 \left\langle \frac{\partial \Phi'_N(\lambda)}{\partial \lambda} \right\rangle_{N, T, V, \lambda} d\lambda \\ &\approx \sum_k \left\langle \frac{\partial \Phi'_N(\lambda_k)}{\partial \lambda} \right\rangle_{N, T, V, \lambda_k} \Delta \lambda, \end{aligned} \quad (11)$$

where the perturbation potential is given by $\Phi'_N(\lambda) = \lambda^k \Phi_N$ with k set to 8. In numerical calculation, the increment in λ is chosen to be 0.02. The ideal free energy is given by

$$\begin{aligned} A^{\text{id}} &= Nk_B T \left(\ln \rho \left(\frac{\beta h^2}{2\pi m} \right)^{3/2} - 1 \right. \\ &\quad \left. - \ln \left[\frac{\pi^{1/2}}{\sigma} \prod_j \left(\frac{8\pi^2 I_j}{\beta h^2} \right)^{1/2} \right] \right), \end{aligned} \quad (12)$$

where σ is the symmetry number and I_j stands for j th diagonalized component of the inertia tensor. In the actual calculation, NPT MC simulations for $N=300$ are performed with the steps of 3×10^6 (1 MC step= N trial move +1 volume change) to determine the equilibrium volume, which are followed by NVT MC simulations at each λ value with

3×10^6 MC steps (1 MC step= N trial move) for equilibration and 3×10^6 MC steps for averaging. This method is applied to liquid acetone.

The free energy of cage occupation is calculated by a simple integration on coordinates and orientations of an acetone inside a larger cage as

$$\begin{aligned} f_a &= -k_B T \ln \left\{ \sigma^{-1} \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \prod_{j=1}^l \left(\frac{2\pi I_j}{\beta h^2} \right)^{1/2} \right. \\ &\quad \left. \times \int_v \int_{\Omega} \exp[-\beta \phi(\mathbf{r}, \mathbf{\Omega})] d\mathbf{r} d\mathbf{\Omega} \right\}, \end{aligned} \quad (13)$$

where $\phi(\mathbf{r}, \mathbf{\Omega})$ is the interaction potential of an acetone with the surrounding molecules. This method is applicable only to a single occupancy of a nonlinear rigid molecule at the present stage. In calculating the above quantity, it is found that the interaction between water and acetone in the present model is not so strong as to form a hydrogen bond breaking a hydrogen bond between water molecules; the lowest value of $\phi(\mathbf{r}, \mathbf{\Omega})$ is found to be around -47 kJ mol $^{-1}$, the magnitude of which is less than the half of the magnitude of the corresponding energy for water.

E. Grand canonical MC simulation for acetone clathrate hydrate

In order to perform GCMC simulation for a large molecule such as acetone, a different kind of GCMC simulation method has been proposed and applied to propane.⁵ This method is briefly outlined here. The GCMC simulation is carried out by choosing one of the cages that can accommodate a guest molecule. If it is empty, a creation trial is attempted by designating position and orientation where a weighting function, χ , is multiplied to facilitate convergence and then accept-reject scheme is applied; a creation is accepted with a probability,

$$\min\{1, z v_c \sin \theta \exp(-\beta w) \chi^{-1}\}, \quad (14)$$

where v_c is the volume of each cage but does not appear in a practical GCMC simulation. The weighting function is chosen to be

$$\chi(\mathbf{r}, \mathbf{\Omega}) = v_c (\beta \kappa / 2\pi)^{3/2} \exp\left(-\beta \kappa \frac{\mathbf{r}^2}{2}\right). \quad (15)$$

The parameter κ is introduced to sample the central region of a cage more preferentially and is set to $2\pi k_B T$, where \mathbf{r} is in 0.1 nm. If a chosen cage is occupied, a deletion trial is accepted with a probability,

$$\min\{1, \exp(\beta w) \chi / z v_c \sin \theta\}. \quad (16)$$

III. THEORY, SIMULATION RESULTS, AND DISCUSSION

We extend the vdWP theory to binary systems where the number of promoter molecules is either allowed to alter or fixed to a constant. Combined with GC/NPT MC simulations, the phase equilibrium for the binary clathrate hydrate is examined on the basis of the theory developed.

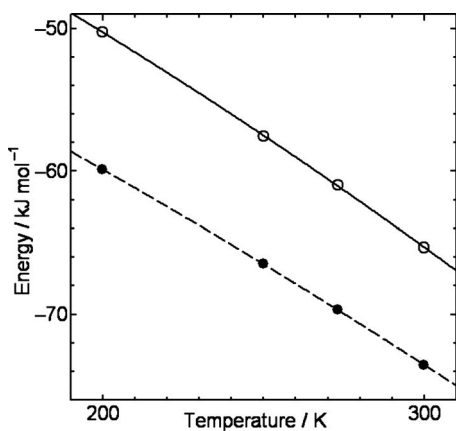


FIG. 1. Temperature dependences of the chemical potential of acetone (open circle) and the free energy of cage occupation (filled circle) at pressure 0.1 MPa.

A. Free energy of cage occupation and chemical potential of ice and empty hydrate

The free energy of acetone in its pure liquid is calculated at several temperatures and pressures, which is converted to the chemical potential. The free energy of the larger-cage occupation by acetone is calculated by the numerical integration at several temperatures. Its temperature dependence is plotted in Fig. 1 along with the chemical potential at 0.1 MPa. It indicates that the chemical potential is considerably higher than that of the free energy. This indicates that a great number of the larger cages is occupied by acetone molecules, which leads to stability of the acetone clathrate hydrate. (Its spontaneous formation is not confirmed from only this estimation but it must be done by comparison of the chemical potentials of water in two phases.) Pressure dependence of the chemical potential of acetone at 273 K is plotted in Fig. 2. It is evident from the slope of the curve that the volume of pure acetone is almost constant over the pressure range from 0 to 100 MPa.

The free energies of ice Ih and empty clathrate hydrate structure II are calculated at 273 K and 10 MPa. The individual components are listed in Table II. The chemical potential of ice Ih is lower than that of the empty clathrate, which ensures that structure II empty clathrate hydrate is less

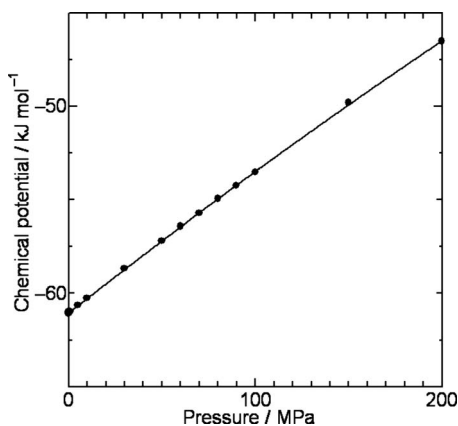


FIG. 2. Pressure dependence of the chemical potential of acetone at temperature 273 K.

TABLE II. Free energy components of hexagonal ice and empty clathrate II and chemical potential in kJ mol^{-1} .

	U_q	F_a	F_h	A	PV	μ
Ice	-57.4958	-1.7918	8.9552	-51.2609	0.1843	-51.0766
Clathrate	-56.5531	-1.7302	8.7946	-50.4173	0.2158	-50.2014
Difference						-0.8752

stable than ice Ih. The obtained difference, $\Delta\mu = \mu_i - \mu_c^0 = -0.88 \text{ kJ mol}^{-1}$, is similar to that obtained previously for a different water model.⁵ Its temperature dependence is roughly estimated from the entropy difference $\Delta s = (\Delta h - \Delta\mu)/T$, where Δh is the enthalpy difference obtained by the conventional NPT MC simulation. A similar estimation is made for pressure dependence using the volume difference Δv .

B. Phase equilibrium and the van der Waals and Platteuw theory for binary clathrates

In the present study, occupancies of hydrogen and the promoter acetone are examined. That is, we consider the equilibria among three phases ($p=3$) in the binary clathrate hydrate with the components of water, hydrogen, and acetone (the number of components, $c=3$). The clathrate hydrate is in equilibrium with either aqueous solution or ice coexisting with hydrogen fluid. It is known that the larger cage accommodates maximally four hydrogen molecules ($m=4$) or at most one acetone molecule and the smaller one contains zero or one hydrogen molecule. If both guest species are variable being subject to constant chemical potential values according to the original vdWP theory, the grand partition function with the free energy of the empty clathrate A_w^0 is given by

$$\Xi = \exp(-\beta A_w^0) \sum_{n_a=0}^{N_l} \binom{N_l}{n_a} \exp[\beta n_a (\mu_a - f_a)] \times \left\{ \prod_{j=1}^m \sum_{n_j} \binom{N_l - n_a - \sum_{k=1}^{j-1} n_k}{n_j} \right\} \times \exp[\beta n_j (j\mu_h - f_j)] \left\{ \sum_{n_s=0}^{N_s} \binom{N_s}{n_s} \exp[\beta n_s (\mu_h - f_s)] \right\}, \quad (17)$$

where N_l and N_s stand for the numbers of the larger and smaller cages in the clathrate hydrates and the free energies of cage occupancy by acetone and by j hydrogen molecules in a larger cage, and that by a hydrogen molecule in a smaller cage are denoted by f_a , f_j , and f_s , respectively. Finally a simple form is obtained as

$$\Xi = \exp(-\beta A_w^0) \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{N_l} \{1 + \exp[\beta(\mu_h - f_s)]\}^{N_s}. \quad (18)$$

One of the independent variables, V , is changed to the pressure P applied on the clathrate hydrate as

$$Y = \frac{1}{v_0} \int_0^\infty \Xi \exp(-\beta PV) dV, \quad (19)$$

where v_0 is the unit volume.

The mean numbers of hydrogen and acetone molecules are expressed as

$$\begin{aligned} \langle n_h \rangle &= \frac{\partial \ln Y}{\partial(\beta\mu_h)} \\ &= N_l \left\{ \sum_{j=1}^m j \exp[\beta(j\mu_h - f_j)] \right\} \\ &\quad \times \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{-1} \\ &\quad + N_s \exp[\beta(\mu_h - f_s)] \{1 + \exp[\beta(\mu_h - f_s)]\}^{-1} \end{aligned} \quad (20)$$

and

$$\begin{aligned} \langle n_a \rangle &= \frac{\partial \ln Y}{\partial(\beta\mu_a)} \\ &= N_l \exp[\beta(\mu_a - f_a)] \\ &\quad \times \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{-1}. \end{aligned} \quad (21)$$

Since the clathrate hydrate is treated as an NPT ensemble with respect to water, the chemical potential of water is calculated as

$$\begin{aligned} \beta\mu_c &= -\frac{\partial \ln Y}{\partial N_w} \\ &= \beta\mu_c^0 - \alpha_l \ln \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\} \\ &\quad - \alpha_s \ln \{1 + \exp[\beta(\mu_h - f_s)]\}. \end{aligned} \quad (22)$$

The larger-cage occupancy (fraction) x_j by j hydrogen molecules, the corresponding occupancy x_a by an acetone

molecule, and the smaller-cage occupancy x_s by a single hydrogen molecule are given, respectively, as

$$x_j = \exp[\beta(j\mu_h - f_j)] \times \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{-1},$$

$$x_a = \exp[\beta(\mu_a - f_a)] \times \left\{ 1 + \exp[\beta(\mu_a - f_a)] + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{-1}, \quad (23)$$

$$x_s = \exp[\beta(\mu_h - f_s)] \{1 + \exp[\beta(\mu_h - f_s)]\}^{-1}.$$

The occupancies, x , are inserted in the above equation to find the equilibrium chemical potential of water given by

$$\mu_c = \mu_c^0 + \alpha_l k_B T \ln \left(1 - x_a - \sum_{j=1}^m x_j \right) + \alpha_s k_B T \ln(1 - x_s). \quad (24)$$

We first examine an equilibrium among the clathrate, the aqueous solution, and the hydrogen fluid, although the equilibrium will not be treated explicitly in the present paper. Since there are three phases ($p=3$) and three components ($c=3$; water, acetone, and hydrogen), the number of independent thermodynamic variables is given as $f=c+2-p=2$ according to the phase rule. Here they are taken to be T and P . The aqueous solution is assumed, hereafter, to be ideal for the sake of simplicity (its extension to nonideal solution is straightforward introducing the activity). The chemical potentials of the aqueous solution and of the clathrate hydrate are then described, respectively, by

$$\mu_w(T, P) = \mu_w^0(T, P) + k_B T \ln(1 - y_a), \quad (25)$$

$$\mu_a(T, P) = \mu_a^0(T, P) + k_B T \ln y_a, \quad (26)$$

under the condition $\mu_w < \mu_i$, where y_a is the mole fraction of acetone in aqueous solution. The occupancies at equilibrium are obtained by solving the equation $\mu_c(T, P) = \mu_w(T, P)$ combined with Eq. (23) assuming the chemical potential of hydrogen is equal to the pure fluid as $\mu_h(T, P) \approx \mu_h^0(T, P)$.

Next, equilibrium among ice, clathrate, and hydrogen fluid phases is considered. The number of components and the number of phases are the same as in the previous equilibrium and so is the number of independent variables $f=2$. Those are again taken to be T and P . The chemical potential of water in aqueous solution is substituted for that of ice. The occupancies of hydrogen and acetone (x_h and x_a) are obtained from

$$\mu_i(T, P) = \mu_c(T, P), \quad (27)$$

with $\mu_h(T, P) \approx \mu_h^0(T, P)$ under $\mu_i < \mu_w$. The relation of the chemical potential between ice and water in aqueous solution may impose a restriction on the range of x_a .

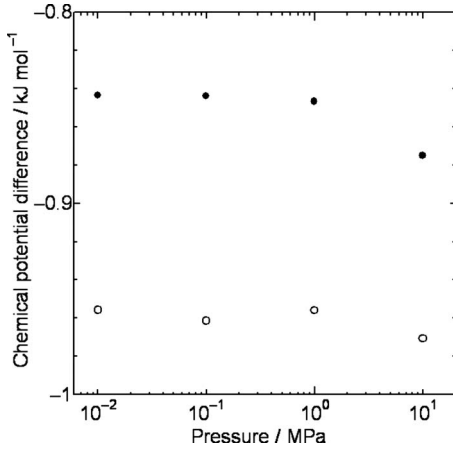


FIG. 3. Chemical potential difference between ice and clathrate at 273 K and various pressures. Filled circle: calculated from the free energy [left hand side of Eq. (28)]. Open circle: calculated from the occupancy (right hand side).

C. GCMC simulations of acetone clathrate hydrates

GCMC simulations of acetone clathrate hydrates serve to examine whether these potentials of water and acetone are appropriate to model the clathrate hydrates. This is actually made by calculating the mean occupancy at several pressures tentatively using the chemical potential of pure liquid acetone at a given temperature and pressure. (This condition is an artificial one since the high concentration of acetone inhibits formation of the clathrate.) The occupancy, x_a , is related to the chemical potential difference between ice and the empty clathrate hydrate as

$$\mu_i(T, P) - \mu_c^0(T, P) = \alpha_l k_B T \ln(1 - x_a). \quad (28)$$

Both sides of the above equation are plotted in Fig. 3 at 273.15 K and several pressures. It is shown that the right hand side is always lower. Since the concentration of acetone has an upper limit, this result simply indicates an acetone clathrate is more stable than ice. However, the most stable phase can be an aqueous solution where the chemical potential of water is lower than that in clathrate. Therefore, this leads to a conclusion that the combination of the intermolecular interactions suffice to reproduce acetone clathrate formation.

D. Phase equilibrium and the van der Waals and Platteeuw theory for restricted binary clathrates

If the number of acetone molecules in the larger cages is fixed to n_a , the relevant grand partition function, the occupancy of hydrogen, and the chemical potential of water in the clathrate hydrate are given by

$$\begin{aligned} \Xi &= \exp(-\beta A_w^0) \binom{N_l}{n_a} \exp(-\beta n_a f_a) \\ &\times \left\{ 1 + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{N_l - n_a} \\ &\times \{1 + \exp[\beta(\mu_h - f_s)]\}^{N_s}, \end{aligned} \quad (29)$$

$$\begin{aligned} \langle n_h \rangle &= \frac{\partial \ln Y}{\partial(\beta\mu_h)} \\ &= (N_l - n_a) \left\{ \sum_{j=1}^m j \exp[\beta(j\mu_h - f_j)] \right\} \\ &\times \left\{ 1 + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\}^{-1} \\ &+ N_s \exp[\beta(\mu_h - f_s)] \{1 + \exp[\beta(\mu_h - f_s)]\}^{-1}, \end{aligned} \quad (30)$$

$$\begin{aligned} \beta\mu_c &= -\frac{\partial \ln Y}{\partial N_w} \\ &= \beta\mu_c^0 + \alpha_l \ln(1 - x_a) \\ &- \alpha_l \ln \left\{ 1 + \sum_{j=1}^m \exp[\beta(j\mu_h - f_j)] \right\} \\ &- \alpha_s \ln \{1 + \exp[\beta(\mu_h - f_s)]\} \\ &= \beta\mu_c^0 + \alpha_l \ln \left(1 - x_a - \sum_{j=1}^m x_j \right) + \alpha_s \ln(1 - x_s), \end{aligned} \quad (31)$$

with

$$x_j = \frac{(1 - x_a) \exp[\beta(j\mu_h - f_j)]}{\sum_{k=0} \exp[\beta(k\mu_h - f_k)]}. \quad (32)$$

Even when the number of acetone molecules is fixed to a constant, the chemical potential of water can be expressed apparently by the same equation. In case of an equilibrium between hydrate and ice, there are three phases ($p=3$; clathrate, ice, and hydrogen fluid) with the components of two species ($c=2$; water and hydrogen). From the phase rule, $f = c + 2 - p = 1$, and T can be an independent thermodynamic variable while the occupancy $x_a (=n_a/N_l)$ is kept fixed and is regarded as a parameter. The equilibrium between ice and clathrate for a given x_a is obtained by solving

$$\begin{aligned} \mu_i(T, P) &= \mu_c^0(T, P) + \alpha_l k_B T \ln \left(1 - x_a - \sum_{j=1}^m x_j \right) \\ &+ \alpha_s k_B T \ln(1 - x_s). \end{aligned} \quad (33)$$

This equation is used for evaluation of stability of clathrate by GC/NPT MC simulations with a fixed number of acetone molecules. It is evident from Eq. (32) that the smaller x_a gives rise to partial decomposition of the clathrate hydrate into ice.

In passing, it can be shown that a set of x_a and y_a should satisfy in order for a clathrate to be in equilibrium with aqueous solution,

$$\begin{aligned} \mu_c^0(T, P) + \alpha_l k_B T \ln \left(1 - x_a - \sum_{j=1}^m x_j \right) + \alpha_s k_B T \ln(1 - x_s) \\ = \mu_w^0(T, P) + k_B T \ln(1 - y_a), \end{aligned} \quad (34)$$

subject to the condition

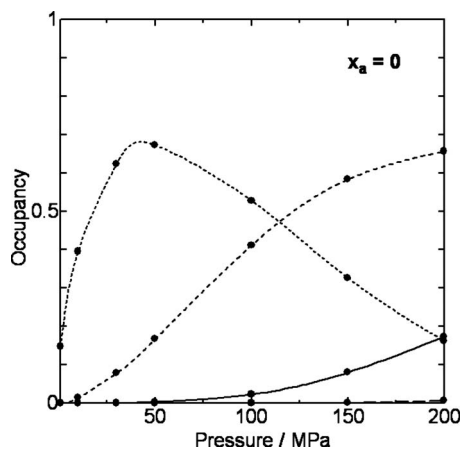


FIG. 4. Pressure dependence of various types of hydrogen occupancies at 250 K in the larger cage without acetone. Dotted: single. Dashed: double. Solid: triple. Dot-dash: quadruple.

$$f_a(T, P) + k_B T \ln x_a - k_B T \ln \left(1 - x_a - \sum_{j=1}^m x_j \right) = \mu_a^0(T, P) + k_B T \ln y_a, \quad (35)$$

the left hand side of which is derived from $\mu_a = -k_B T (\partial \ln Y / \partial n_a)$. There are possibly two intersections in the chemical potentials, which limit the stable concentration y_a since the chemical potential of water decreases with increasing acetone concentration. This also poses the upper and lower limits on x_a ; the stable phase in the region between the two limits is the clathrate hydrate alone. Thus, an acetone concentration in an initial aqueous solution to prepare a clathrate hydrate cannot be too high for a clathrate hydrate to be the only stable phase.

E. Occupancy of hydrogen with fixed number of acetone molecules

Occupation by acetone prevents hydrogen molecules from entering the larger cages, which thus undermines its efficiency. Utilization of a binary clathrate hydrate as a hydrogen storage is solely dependent on the balance between

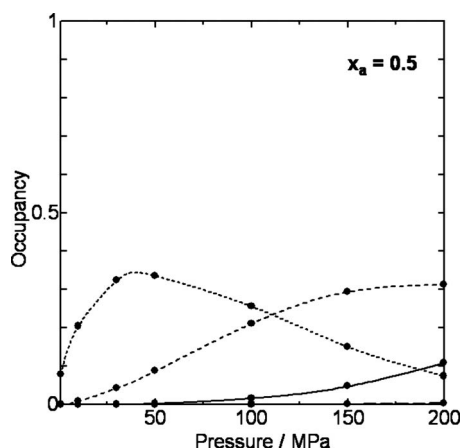


FIG. 5. Pressure dependence of various types of hydrogen occupancies at 250 K in the larger cage with half the larger cages occupied by acetone. Dotted: single. Dashed: double. Solid: triple. Dot-dash: quadruple.

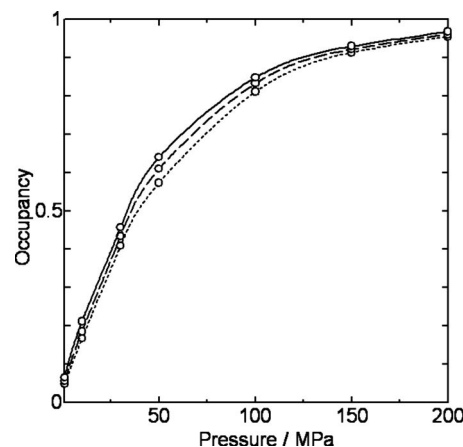


FIG. 6. Pressure dependence of occupancies of hydrogen at 250 K in the smaller cages with acetone occupancy of 0 (dotted), 0.5 (dashed), and 1 (solid).

the extent of depression of the dissociation pressure and the change in the occupancy of hydrogen. One of the goals in the present study is to evaluate the stability of hydrogen clathrate hydrate as a function of the fraction of acetone in the larger cages at various pressures, thereby making it possible to predict, via intermolecular interactions alone, whether it is formed at given conditions. To this end, calculation of the free energy for multiple cage occupancy is required. It is, however, impossible or impractical to calculate f_3 and f_4 , for this involves a considerable numerical integration task. To circumvent this difficulty, we take advantage of the fact that evaluation of the chemical potential of water in the clathrate hydrate requires only the various types of cage occupancies. The latter quantities can be obtained from GC/NPT MC simulations with the fixed number of acetone molecules. The larger-cage occupancies of various types for $x_a=0$ and 0.5 are given in Figs. 4 and 5, and the smaller-cage occupancies for $x_a=0, 0.5$, and 1 are shown in Fig. 6. The occupancy in the larger cage decreases monotonically with the occupancy of acetone. A detailed comparison shows that the relative occupancies of hydrogen to the available larger cages other than those encapsulating acetone remain almost constant irrelevant to the occupancy of acetone. However, a small en-

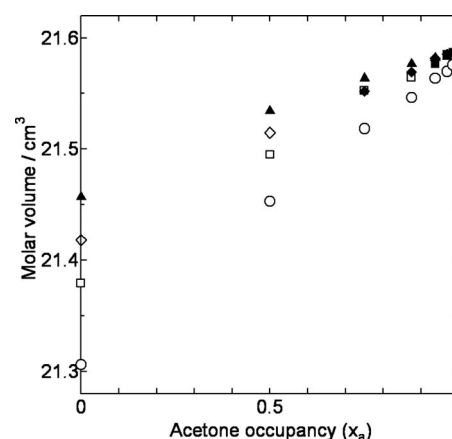


FIG. 7. Volume of the hydrogen clathrate at 1 MPa (circle), 100 MPa (square), 150 MPa (diamond), and 200 MPa (triangle) and at 250 K. Filled symbols indicate clathrate is more stable than ice.

TABLE III. Hydrogen occupation ratio to water (H_2/H_2O) in hydrogen clathrate hydrate with acetone at 250 K and at various pressures and acetone occupancies. No occupation ratio is given to an unstable state.

x_a	P/MPa					
	1	10	50	100	150	200
0	0.231
1/2	0.174
3/4	0.144
7/8	0.129
15/16	0.115	0.121
31/32	0.113	0.117
63/64	0.111	0.115
1	0.008	0.025	0.075	0.100	0.109	0.113

hancement in occupancy of hydrogen by promoter acetone is observed in the smaller cage. This seems to stem from the fact that incorporation of acetone expands the volume (Fig. 7) and also makes the amplitudes of the thermal vibrational motions in the host lattice smaller, which prevents the cages from being deformed. This leads to easier incorporation of hydrogen molecules although the increase in the occupancy is small.

It is possible to evaluate the stability of the clathrate hydrate at a given pressure with a fixed occupancy of acetone from the chemical potential difference between ice and empty clathrate hydrate, Eq. (33). This evaluation is made with the various types of hydrogen occupancies. Its stability relative to ice at 250 K is examined. Table III tabulates the mean hydrogen ratio to water for the stable clathrate at a given pressure. Unless there is a special correlation between hydrogen and acetone occupations, it is obvious from Eq. (32) that the larger x_a decreases x_j at an equilibrium. A stable binary clathrate hydrate must have a larger x_a under a low pressure of hydrogen. Thus, a clathrate containing a small amount of acetone under high pressure of hydrogen becomes unstable when it is decompressed. It is decomposed into ice and clathrate with a larger x_a .

IV. CONCLUDING REMARKS

Augmented stability of hydrogen clathrate hydrates by a promoter species has been investigated by an extension of the vdWP theory. Phase equilibria of hydrogen clathrates with either ice Ih or an aqueous solution are discussed. Acetone is chosen in the present study as a molecule to stabilize hydrogen clathrates but our theoretical treatment can be applied to any kind of binary clathrate hydrates with promoter molecules including THF. First, it is shown that acetone is indeed encaged to form clathrate hydrate by GCMC simulation and the free energy of cage occupation. New GC/NPT MC simulations are carried out with a fixed number of acetone molecules and a fixed chemical potential of guest hydrogen molecules. Various types of the cage occupancies in hydrogen clathrate hydrate have been obtained by these GCMC simulations in a wide range of hydrogen pressure since the triple and quadruple occupancies are otherwise impossible to evaluate. These occupancies enable to calculate the chemical potential of water in clathrate hydrate. Thus, we can discuss augmented thermodynamic stability of hydrogen

clathrates with the existence of a promoter guest species. It is rigorously shown that the augmented stability is due to the occupation of cages by the promoter molecules and that apparent weak and indirect attraction between acetone and hydrogen in the smaller cage is observed, which seems to be caused by stabilization of the cage structure. The present method is advantageous in establishing the efficiency-stability relation with the simple intermolecular interactions.

We show a condition that a clathrate hydrate with a fixed number of promoter molecules becomes stable. The partial occupancy of the larger cage is indeed effective to reduce the dissociation pressure. Since the occupancy depends solely on the affinity of promoter molecules to a clathrate, it is worthwhile discussing the stability of such a clathrate made of water and the promoter species in terms of the property in its aqueous solution.

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