

Phase Behavior of Different Forms of Ice Filled with Hydrogen Molecules

Lukman Hakim, Kenichiro Koga, and Hideki Tanaka

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima, Kitaku, Okayama 700-8530, Japan
(Received 27 November 2009; revised manuscript received 19 February 2010; published 16 March 2010)

A hybrid grand-canonical Monte Carlo simulation has been performed to investigate the hydrogen hydrate compounds in which hydrogen molecules are stored in ice II and ice I_c . A simple theoretical model, which can reproduce the simulation results, provides the phase diagrams of the two-component system in the pressure-composition plane. Stability enhancement of the two ice forms by hydrogen is quantified by the chemical potential calculation of water. The phase transitions among various phases including the two hydrogen hydrates are predicted as functions of pressure, hydrogen occupancy, and temperature.

DOI: 10.1103/PhysRevLett.104.115701

PACS numbers: 64.70.Ja

Hydrogen clathrate hydrates have been studied for their potential as a hydrogen storage material and also for their planetary and physical chemistry interest [1–5]. The hydrogen clathrate of classical structure II [6] whose occupancy is confirmed later by Monte Carlo (MC) simulations [7,8], implies that hydrogen molecules, despite their small size as guest species, can stabilize a variety of host lattices of water. It was also reported that hydrogen molecules can be engaged in the interstitial spaces of ice II and ice I_c , giving two stable clathrate hydrate compounds termed C_1 and C_2 [9]. Given a variety of hydrogen hydrates, it is of fundamental importance that the phase behavior of a water-hydrogen system be systematically studied in the P , T , and chemical-composition space. Unfortunately, the thermodynamic stability of C_1 and C_2 relative to other water-hydrogen composite phases in a wide range of thermodynamic conditions has been scarcely explored. In this Letter we report the phase behavior for realistic models of C_1 and C_2 in the pressure and hydrogen-mole-fraction plane at various temperatures.

The accommodation of hydrogen molecules inside ice II (C_1) and ice I_c (C_2), along with their stability under various thermodynamic states, is investigated using a hybrid type of grand-canonical (GC) and isothermal-isobaric (NPT) MC simulations. A hydrogen molecule is modeled as a linear rigid rotor with a single Lennard-Jones (LJ) potential site and a negative charge site both at the center of mass and two positive charges at the individual protons [10]. The water-water interaction is described by TIP4P potential [11]. The interaction between water and hydrogen is described by assuming the Lorentz-Berthelot rule. The interaction potentials for all pairs of molecules are truncated smoothly at 0.8655 nm [12] and the standard correction for LJ interactions is made. The simulation box for Ice II structure is taken to be a rectangular prism ($a = 25.97$ Å, $b = 22.49$ Å, $c = 25.01$ Å) containing 576 water molecules, while that for ice I_c is taken to be a cubic box ($a = 38.64$ Å) containing 216 unit cells or equivalently 1728 water molecules. The ice I_c configurations are

generated according to Bernal-Fowler rules [13] so as to have no net polarization. The pressure dependence of chemical potential for pure hydrogen is obtained from constant-volume MC simulations [7].

In the GC-NPT MC simulation, temperature T and the number of water molecules N_w are kept fixed in the whole process. An insertion or a deletion of hydrogen is attempted with the chemical potential of hydrogen (μ_h) and the instantaneous volume (V) fixed. The pressure P is set to a constant corresponding to the prescribed μ_h and T in the rest of the procedures. A trial insertion is made at an arbitrary position with randomly chosen polar θ and azimuthal ϕ angles. The insertion is accepted with probability

$$p_{\text{insert}} = \frac{\exp[\beta(\mu'_h - w)] \sin\theta(2\pi mk_B T/h^2)^{3/2} V}{(N_g + 1)} \quad (1)$$

where w is the interaction energy, N_g is the number of hydrogen molecules, m is the mass of a hydrogen molecule, h is Planck constant, μ'_h stands for the chemical potential of hydrogen that excludes the contribution from the free rotational motion, β is $1/k_B T$ with k_B Boltzmann constant. Trial deletion of a randomly chosen hydrogen molecule out of N_g is accepted with probability

$$p_{\text{delete}} = \frac{\exp[\beta(-\mu'_h + w)] N_g}{\sin\theta(2\pi mk_B T/h^2)^{3/2} V}. \quad (2)$$

The volume change is attempted according to the standard NPT MC simulation. In this GC-NPT MC simulation, a single step consists of a trial insertion or deletion with the same probability, followed by five trial moves of randomly chosen water or hydrogen molecules and trial volume change. Each MC simulation is carried out for at least 10^8 steps.

Figure 1 depicts C_1 and C_2 structures obtained from GC-NPT MC simulations. It is seen that the quasi-one-dimensional voids of ice II are filled with hydrogen molecules in the C_1 structure while in the C_2 structure a hydro-

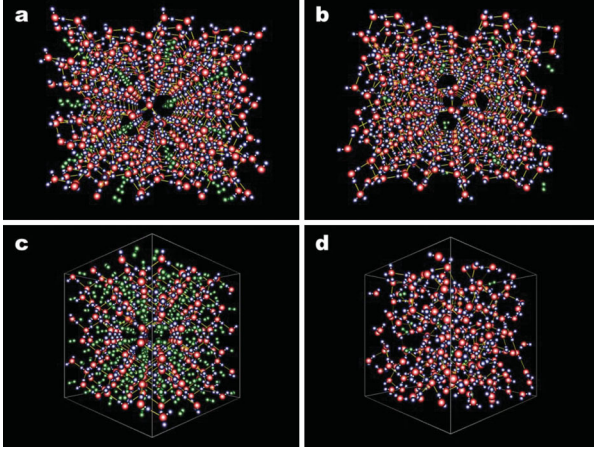


FIG. 1 (color). Structures of C_1 and C_2 in various hydrogen occupancy conditions obtained from simulation: (a) C_1 with maximum hydrogen occupancy; (b) C_1 with partial hydrogen occupancy; (c) C_2 with maximum hydrogen occupancy; (d) C_2 with partial hydrogen occupancy.

gen molecule locates in each interstice of ice I_c . The structure of C_1 is retained even when the voids of ice II are only partially occupied with hydrogen whereas the C_2 structure collapses when its voids are partially occupied.

The pressure dependence of hydrogen-to-water molecular ratio in C_1 is shown in Fig. 2. The ratio gradually increases as the compression proceeds, which is in sharp contrast to the behavior of common clathrate hydrates. This arises from the fact that ice II is a stable ice form even without hydrogen in a certain region of temperature-pressure plane while a usual clathrate is not stable in its empty state. The encaged hydrogen, however, further enhances the stability of the ice II structure and extends its stable region. The highest hydrogen-to-water molecular ratio is found to be 1:6 at all temperatures studied.

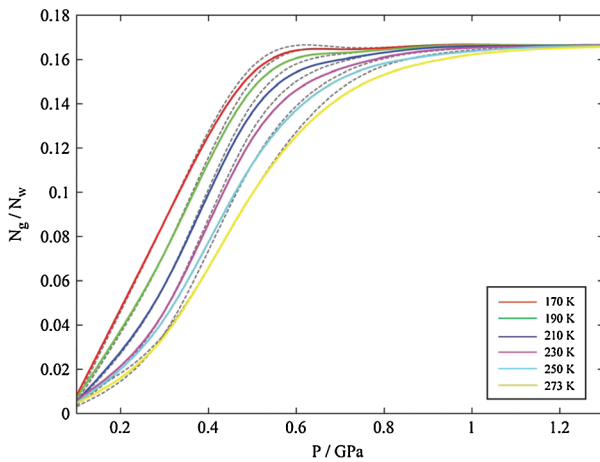


FIG. 2 (color). The molar ratio of hydrogen-to-water in C_1 under various pressure and temperatures obtained from simulation (solid line) and theoretical calculation (dashed line).

In the case of C_2 , as shown in Fig. 3, the hydrogen-to-water molecular ratio changes rapidly in a small range of pressure and, in particular, it does abruptly for high temperatures. When this ratio drops below a certain value, ice I_c structure is no longer intact and another ice morphology is substituted for ice I_c at high pressures [14]. The maximum molar ratio of water-hydrogen is found to be 1:1.

Giving the maximum molar ratio in C_2 , it is possible to regard ice I_c of N_w water molecules as a host lattice having N_w virtual cages, each of which allows at most one hydrogen. This is equivalent to the usual clathrate hydrate whose stability has been successfully estimated by van der Waals and Platteeuw (vdWP) theory [15,16]. Thus, the occupancy of hydrogen inside ice I_c can be estimated from a grand-canonical partition function. For the system with N_h virtual cages which is identical to N_w in C_2 , the partition function is given by

$$\Xi = \exp(-\beta A_w^0)(1 + \exp[\beta(\mu_h - f_h)])^{N_h}, \quad (3)$$

where A_w^0 is the free energy of empty ice and f_h the free energy of cage occupation. It is converted to the generalized partition function Y as

$$Y = \frac{1}{v_0} \int_0^\infty \Xi \exp(-\beta PV) dV, \quad (4)$$

where v_0 is the unit volume. The mean number of hydrogen molecules is expressed as

$$\langle N_g \rangle = \frac{\partial \ln Y}{\partial (\beta \mu_h)} \quad (5)$$

and the cage occupancy, x , defined as $\langle N_g \rangle / N_h$ is given by

$$x = \frac{\exp[\beta(\mu_h - f_h)]}{1 + \exp[\beta(\mu_h - f_h)]}, \quad (6)$$

where the free energy of cage occupancy f_h is evaluated by integration of potential interaction between a hydrogen

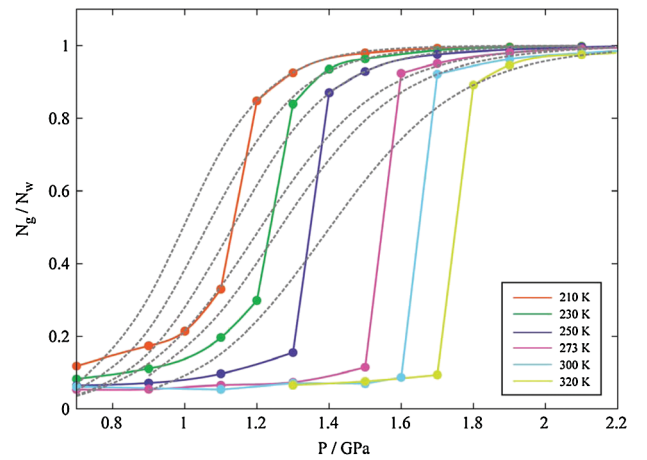


FIG. 3 (color). The molar ratio of hydrogen-to-water in C_2 under various pressure and temperatures obtained from simulation (solid line) and theoretical calculation (dashed line).

molecule with the surrounding water molecules inside ice void as

$$\exp(-\beta f_h) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \left(\frac{2\pi I k_B T}{h^2}\right) \times \iint \exp(-\beta w(\mathbf{r}, \boldsymbol{\Omega})) d\mathbf{r} d\boldsymbol{\Omega}, \quad (7)$$

where I stands for the moment of inertia of a hydrogen molecule. The estimated hydrogen occupancy inside ice I_c is also plotted in Fig. 3. The result agrees well with that from the simulation in high occupancy region but deviates significantly in low occupancy. The discrepancy is due to the assumption in theoretical calculation that the host structure (ice I_c) is stable in the absence of hydrogen at any pressures, which then leads to the possibility of partial occupancy. However, this is valid for the case of C_1 , hence a similar method can be applied to C_1 by dividing each cylindrical-channel into cells, each of which contains only a single guest molecule. The obtained result as given in Fig. 2 agrees well with the MC simulation over the entire pressure and temperature range studied. The successful predictions by this theoretical calculation indicate that an underlying mechanism in the accommodation of hydrogen is simple: It is determined by the free energy of cage occupation which is in turn dominated by the vacant space for a hydrogen molecule to be engaged.

The C_1 and C_2 phases occupy neighboring regions in the phase diagram but the phase boundaries are not fully established. It is important to evaluate their thermodynamic stability in terms of the chemical potential, for then the phase boundaries are predicted. The chemical potential of water in C_1 and C_2 is calculated as

$$\frac{\partial Y}{\partial N_w} = \mu_c = \mu_c^0 + \alpha k_B T \ln(1-x) \quad (8)$$

where $\alpha = N_h/N_w$ is the cage-to-water ratio and

$$\mu_c^0 = (A_c^0 + PV)/N_w \quad (9)$$

is the chemical potential of the empty ice. The Helmholtz free energy of ice, A_c^0 , containing no hydrogen molecule is approximated by the sum of the potential energy at its minimum structure, the harmonic free energy, and the residual entropy term (in the case of ice I_c and VII). The harmonic free energy of water is calculated from normal mode analysis [12,17].

Since the occupancy in C_2 is approximately unity at high pressure and the lattice vibrations are possibly shifted to higher frequencies, the harmonic free energy should be evaluated in the presence of hydrogen, and thus the chemical potential is replaced by the corresponding μ_c^l which includes the modulation of intermolecular vibrational frequency [18]. Equation (8) is rewritten in a more convenient form as

$$\mu_c = \mu_c^l + \alpha(f_h - \mu_h + k_B T \ln x). \quad (10)$$

This is an essential manipulation in the case of C_2 since otherwise ice I_c collapses at high pressure.

In the P - x_H (mole fraction of H_2) plane where T is fixed, a one-phase state (C_1 or C_2) and a two-phase equilibrium state (ice VII + C_1 , VII + C_2 , C_1 + C_2 , C_1 + H_2 , or C_2 + H_2) form finite areas as shown in Fig. 4 while a three-phase equilibrium state or a triple point (ice VII + C_1 + C_2 or C_1 + C_2 + H_2) appears as a line of constant pressure, where H_2 stands for the hydrogen fluid phase. From now on, α denotes exclusively the cage-to-water ratio for C_1 ($=1/6$) and that for C_2 ($=1$) is not shown explicitly. The triple-point pressure P_0 for the C_1 + C_2 + H_2 coexistence (which is a line in the complete phase diagram including T) is obtained from the condition that the chemical potentials of water are the same in C_1 and C_2 phases as

$$\mu_{C1} = \mu_{C2} \quad \text{and} \quad \mu_h = \mu_h^0(T, P) \quad (11)$$

where $\mu_{C1} = \mu_{C1}^0 + \alpha k_B T \ln(1-x_1)$ and $\mu_{C2} = \mu_{C2}^0 + k_B T \ln(1-x_2)$ with

$$x_1 = \frac{\exp[\beta(\mu_h - f_{h1})]}{1 + \exp[\beta(\mu_h - f_{h1})]} \quad (12)$$

and $x_2 = \frac{\exp[\beta(\mu_h - f_{h2})]}{1 + \exp[\beta(\mu_h - f_{h2})]}.$

Here x_1 and x_2 stand for the occupancies in C_1 and C_2 , f_{h1} and f_{h2} for the corresponding free energies of cage occupation in C_1 and C_2 , and $\mu_h^0(T, P)$ for the chemical potential of pure hydrogen fluid. The above condition determines the pressure P_0 and the occupancies x_1^0 and x_2^0 at the triple point.

The phase boundary between the C_2 phase and the C_2 + H_2 coexistence (the right boundary of C_2 in the inset of Fig. 4) is obtained from the occupancy in C_2 , which is

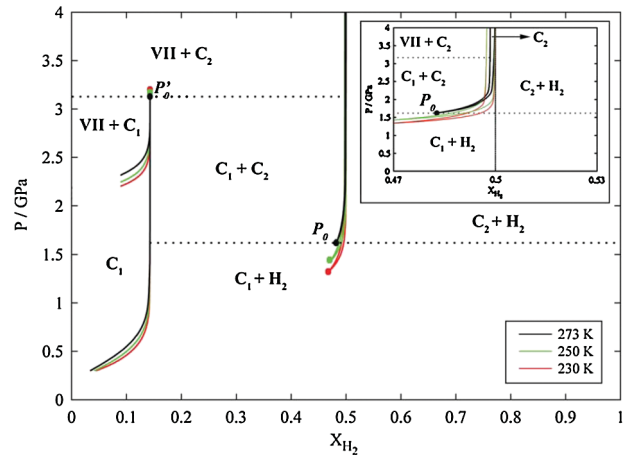


FIG. 4 (color). Phase diagram of C_1 and C_2 in pressure and hydrogen-mole-fraction plane. P'_0 indicates the pressure where the three-phase point of ice VII, C_1 , and C_2 is observed. P_0 indicates the pressure where the three-phase point of C_1 , C_2 , and fluid hydrogen is observed. The inset shows the magnified area around C_2 phase line.

$$x_2 = \frac{\exp[\beta(\mu_h - f_{h2})]}{1 + \exp[\beta(\mu_h - f_{h2})]} \quad \text{with} \quad \mu_h = \mu_h^0(T, P). \quad (13)$$

A similar condition determines the phase boundary between the C_1 phase and the $C_1 + \text{H}_2$ coexistence.

The other phase boundaries to be found are the one between the C_2 phase and the $C_1 + C_2$ coexistence (the left boundary of C_2 in the inset of Fig. 4) and between the C_1 phase and the $C_1 + C_2$ coexistence (the right boundary of C_1 in Fig. 4). These are again determined by the condition for the equivalence of the chemical potentials of water and hydrogen in C_1 and C_2 phases. It is determined by removing the unknown μ_h with the following condition combined with Eq. (11)

$$\mu_h = f_{h1} + k_B T \ln\left(\frac{x_1}{1 - x_1}\right) = f_{h2} + k_B T \ln\left(\frac{x_2}{1 - x_2}\right). \quad (14)$$

This leads, using the molecular volume v in each ice structure, to

$$x_2 - x_2^0 \approx (1 - x_2^0) \left\{ 1 - \exp\left[-\frac{\beta(\Delta P \Delta v)}{1 - \alpha}\right] \right\} \quad (15)$$

with $\Delta P = P - P_0$ and $\Delta v = v_2 - v_1$.

Similar procedures are applied to obtain the boundary between the $C_1 + \text{ice VII}$ coexistence and the C_1 phase (the left boundary of C_1 in Fig. 4), as well as the triple-point pressure P'_0 for the $C_1 + C_2 + \text{ice VII}$ coexistence.

The obtained phase diagram is shown in Fig. 4. When $P < P_0$ (1.6 GPa), for any value of x_{H} , the chemical potential of water in C_2 is higher than that in C_1 , and thus C_2 is not stable in this region. When $P > P_0$, the C_2 phase is in equilibrium with C_1 or with ice VII for $x_{\text{H}} < 0.5$ while it is in equilibrium with a hydrogen fluid for $x_{\text{H}} > 0.5$. In between, there is a narrow region (appearing as a line in Fig. 4 but visible as a region in the inset) where C_2 is the only stable phase. This region becomes wider as the temperature decreases, hence signifying higher stability of cubic ice structure at lower temperature. The theoretical prediction is in good agreement with the experimental observation that C_2 becomes more stable than C_1 when P is greater than a certain value while it coexists with the C_1 phase at lower pressures [9]. Furthermore, P_0 is shown to have a positive slope in the P - T plane while P'_0 has a negative slope. It should also be noted that the pressure where the ice I_c structure collapses in Fig. 3 is close to the triple-point pressure P_0 .

In summary, we calculate the occupancies of hydrogen from both GC-NPT MC simulation and a theoretical approach in ice II and ice I_c , the compounds of which are called C_1 and C_2 . The C_1 phase is stable under partial occupancy and gradually encages hydrogen with increasing pressure while C_2 is stable only when most of its

adsorption sites are occupied by hydrogen molecules. It is found that the theoretical calculation based on a modified vdWP theory for the present systems successfully reproduces the hydrogen occupancies obtained by MC simulations. Phase boundaries in the pressure-composition phase diagram are also estimated from the chemical potential calculation of water, and are found to be consistent with experimental observations [9]. Here it is evident that a certain hydrogen hydrate structure, in single form or mixtures, can be obtained by controlling the composition of water and hydrogen.

This work is supported by grant-in-aid by JSPS and MEXT, the Next Generation Super Computing Project, Nanoscience Program, MEXT, Japan and also Okayama Foundation for Science and Technology. The authors are grateful to Dr. H. Itoh for providing the ice II structure.

-
- [1] L. Schlapbach and A. Züttel, *Nature (London)* **414**, 353 (2001).
 - [2] V. V. Struzhkin, B. Militzer, W. L. Mao, H. Mao, and R. J. Hemley, *Chem. Rev.* **107**, 4133 (2007).
 - [3] H. Lee, J. W. Lee, D. Y. Kim, J. Park, Y. T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, and J. A. Ripmeester, *Nature (London)* **434**, 743 (2005).
 - [4] Y. H. Hu and E. Ruckenstein, *Angew. Chem., Int. Ed.* **45**, 2011 (2006).
 - [5] W. L. Mao and H. Mao, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 708 (2004).
 - [6] K. Lokhsin, Y. Zhao, D. He, W. L. Mao, H. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, *Phys. Rev. Lett.* **93**, 125503 (2004).
 - [7] K. Katsumasa, K. Koga, and H. Tanaka, *J. Chem. Phys.*, **127**, 044509 (2007).
 - [8] T. Nakayama, K. Koga, and H. Tanaka, *J. Chem. Phys.* **131**, 214506 (2009).
 - [9] W. L. Vos, L. W. Finger, R. J. Hemley, and H. Mao, *Phys. Rev. Lett.* **71**, 3150 (1993).
 - [10] I. F. Silvera and V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
 - [11] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
 - [12] I. Ohmine, H. Tanaka, and P. G. Wolynes, *J. Chem. Phys.* **89**, 5852 (1988).
 - [13] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
 - [14] T. Loerting, I. Kohl, W. Schustereder, K. Winkel, and E. Mayer, *Chem. Phys. Chem.* **7**, 1203 (2006).
 - [15] J. H. van der Waals and J. C. Platteeuw, *Adv. Chem. Phys.* **2**, 1 (1958).
 - [16] E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases* (CRC Press, Boca Raton, FL, USA, 2008), 3rd ed..
 - [17] A. Pohorille, L. R. Pratt, R. A. LaViolette, M. A. Wilson, and R. D. MacElroy, *J. Chem. Phys.* **87**, 6070 (1987).
 - [18] H. Tanaka and K. Kiyohara, *J. Chem. Phys.* **98**, 4098 (1993).