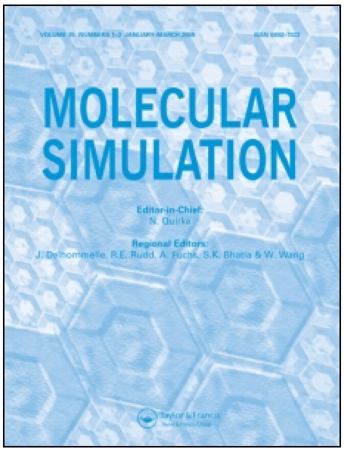

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The Stability of Clathrate Hydrates: Temperature Dependence of Dissociation Pressure in Xe and Ar Hydrate

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THE STABILITY OF CLATHRATE HYDRATES: TEMPERATURE DEPENDENCE OF DISSOCIATION PRESSURE IN Xe AND Ar HYDRATE

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The thermodynamic stability of clathrate hydrates I and II encaging xenon or argon has been investigated by examining the temperature dependence of the dissociation pressure. The evaluation of the stability is made based on the generalized van der Waals and Platteeuw theory developed by Tanaka and Kiyohara [J. Chem. Phys. **98**, 4098 (1993)]. In the new treatment, the free energy of formation of hydrates in equilibrium with ice is calculated by taking the coupling of the host lattice vibrations with guests into consideration. The predicted dissociation pressures of Xe and Ar hydrates agree well with experiments in higher temperature range. A poor agreement between experiment and calculation for Ar clathrate hydrate at low temperature is improved by the use of a quantum mechanical partition function for a harmonic oscillator in evaluating the free energy difference between ice and empty hydrate.

KEY WORDS: Clathrate hydrate, thermodynamic stability, generalized vdWP theory

1 INTRODUCTION

Gas hydrate is a nonstoichiometric compound consisting of host water lattice and various kinds of guest molecules encaged in the cavities in the host lattice. The host lattice is made up by planar cyclic pentamers and hexamers. All of water molecules have four neighbors firmly hydrogen bonded. No clathrate hydrate is stable in the absence of guest molecules. Generally, two types of clathrate hydrates are known to be formed [1]. On one hand, the type I hydrate structure consists of 46 water molecules, 6 larger cages and 2 smaller cages in the unit cell. The larger and smaller cages are tetrakaidecahedron and pentagonal dodecahedron. The radii of the cages are 4.33 Å and 3.91 Å, respectively. On the other hand, the type II hydrate structure is composed of 136 water molecules, 8 larger cages and 16 smaller cages in the unit cell. Those cages are hexakaidecahedron and dodecahedron. The radii of the larger and the smaller cages are 4.68 Å and 3.90 Å, respectively.

Most of the guest species are nonpolar or only weakly polarized. When those guest molecules are dissolved in liquid water, the hydration is dominated by the (excess) entropy, which is referred to as hydrophobic hydration [2]. Structural similarity between the water molecules surrounding the solute and the clathrate hydrate has often been emphasized. In computer simulation studies, the structure

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similar to the hydrate was indeed observed [3]. Therefore, an investigation of clathrate hydrates serves to understand the origin of the hydrophobic hydration.

Clathrate hydrates have not attracted attention until the discovery of the fact that they are responsible for the blockage of natural gas pipelines. In addition, gas hydrates have been used for gas storage reservoirs, separation of gases, resources of natural gas, and desalination of water [4]. Therefore, it is very important to investigate the thermodynamic stability as well as the mechanism of their formation and melting processes.

The thermodynamic stability of these clathrate hydrates has long been accounted for based on the van der Waals and Platteeuw (vdWP) theory [5]. We generalized the original vdWP theory for various hydrates in order to predict the phase behaviors of clathrate hydrates more accurately [6–8]. Some of the assumptions on the original vdWP theory could be eliminated in the generalized form; the coupling of the guest with host molecules was taken into account in evaluating the free energy of the hydrate formation. It was demonstrated that this modification is very important and accounts for the discrepancy between the original vdWP theory and the experiment.

It was revealed that the original vdWP theory is sufficient to describe the thermodynamic stability of clathrate hydrates for a very small guest and that the host-guest coupling is important as the guest diameter approaches to the limiting value of the cage size [8]. It was also argued why a very small guest species such as Ar forms not the structure I clathrate but the structure II clathrate more preferentially [9]. In order to examine the applicability of the generalized vdWP theory in more detail for the prediction of the thermodynamic stability of clathrate hydrates, we apply this theory, in the present study, to the Xe and Ar hydrates over a wide range of temperature.

2 THEORY AND METHOD

In the present calculation, we postulate pairwise-additivity of all the interactions. The water-water intermolecular interaction is described by the TIP4P potential [10]. This potential has often been used in the study of water and is believed to be the most reliable, at least in reproducing important properties of pure water. The Xe-Xe and the Ar-Ar interactions are described by Lennard-Jones (LJ) potential. The size and energy parameters for Xe and Ar atoms are 4.047 Å and 1.9205 $\mathrm{kJ\,mol^{-1}}$ and 3.405 Å and 0.9960 $\mathrm{kJ\,mol^{-1}}$, respectively [11, 12]. For the water-guest interaction, a usual combining rule is adopted to the water-guest interaction in which the LJ parameters for oxygen atom of water molecule are set equal to those of TIP4P water.

The unit cells of the type I and the type II clathrate hydrates are cubic and the experimental lattice parameters $a(=b=c)$ are 12.03 Å and 17.31 Å, respectively [1]. Six hydrate structures of the type I, four structures of the type II and four ice Ic structures generated previously are used [7, 8]. The structures are of proton-disordered form and have zero net dipole moment. A minimizing process of the potential energy is required for the specific intermolecular interactions, since each generated structure corresponds only roughly to the minimum energy structure. The crystalline configurations of the minimum potential energy are obtained by applying the steepest descent method in a similar way as used in the analysis of water [13].

The interaction potentials for all pairs of molecules are truncated smoothly at 8.655 Å in the same way as made in the previous calculations [6-8, 13].

Here, the essential part of the generalized vdWP theory will be presented, which is appropriate for the clathrate hydrates encaging Xe and Ar. Consider a system which consists of n_w unit cells, and is in equilibrium with a gas phase of the guest species. Each unit cell has $m_w = 46$ or $m_w = 136$ water molecules and a maximum of 8 or 24 guest molecules in the structure I or II hydrate, respectively. The number of water molecules is $N_w = m_w n_w$. The total number of smaller cages N_s is $2n_w$ and that of larger cages N_l is $6n_w$ for the structure I hydrate. The total number of smaller cages N_s is $16n_w$, and that of larger cages N_l is $8n_w$ for the structure II hydrate. Then, the relevant canonical partition function Z_{j_s,j_l}, when j_s smaller cages and j_l larger cages are occupied, is given by

$$Z_{j_s,j_l} = \binom{N_s}{j_s}\binom{N_l}{j_l}\exp(-\beta n_w A_w^0)\exp[-\beta(j_s f_s + j_l f_l)], \tag{1}$$

where A_w^0 denotes the free energy of a single unit cell of the empty clathrate hydrate, $\beta = 1/kT$, k stands for Boltzmann's constant, and T is the temperature of the system. Here, f_s and f_l are the free energy changes due to the occupancy of the smaller and the larger cage by a guest molecule. The canonical ensemble is transformed to the grandcanonical ensemble with respect to guest molecules using the chemical potential of the guest species μ. The grand partition function Ξ is written as

$$\Xi = \exp(-\beta n_w A_w^0)\{1 + \exp[\beta(\mu - f_s)]\}^{N_s}\{1 + \exp[\beta(\mu - f_l)]\}^{N_l}. \tag{2}$$

The mean occupation number $\langle N \rangle$ is given by

$$\begin{aligned}\langle N \rangle &= kT\partial \ln\Xi/\partial\mu \\ &= N_s\exp\{\beta(\mu - f_s)\}[1 + \exp\{\beta(\mu - f_s)\}]^{-1} \\ &+ N_l\exp\{\beta(\mu - f_l)\}[1 + \exp\{\beta(\mu - f_l)\}]^{-1}.\end{aligned} \tag{3}$$

The chemical potential of water is calculated from

$$\begin{aligned}\mu_w &= -kT\partial \ln\Xi/\partial N_w \\ &= \mu_w^0 - \frac{m_s kT}{m_w}\ln[1 + \exp\{\beta(\mu - f_s)\}] - \frac{m_l kT}{m_w}\ln[1 + \exp\{\beta(\mu - f_l)\}],\end{aligned} \tag{4}$$

where μ_w^0 is the chemical potential of water in empty clathrate hydrate.

It is assumed in the original vdWP theory that a guest molecule moves interacting with the fixed host water, which provides merely a potential field to encapsulate the guest, and that the cage occupancy does not produce any frequency shift in the vibration of the host lattice. The assumption on the vdWP theory can be eliminated by the following method. We assume that the free energy due to the guest molecule comparable with the cage size can be described by intermolecular vibrational motions, that is, the free energy f (either f_s or f_l), can be approximated by

$$f = \Delta g + u, \tag{5}$$

where u is the minimum value of the potential energy for the guest (with surrounding water molecules) and Δg denotes the vibrational free energy change due to the guest.

The vibrational motions are postulated to be a collection of harmonic oscillators. Thus, the free energy of vibration g (both for empty or occupied hydrate) is evaluated according to the classical mechanical partition function for an individual harmonic oscillator as

$$g = kT\int \ln(\beta\hbar\omega)h(\omega)d\omega, \tag{6}$$

where $h(\omega)$ is the density of state normalized to the (mean) number of degrees of freedom per molecule for each system, and $\hbar$ is the Planck's constant divided by 2π. Then, the difference in the vibrational free energy between empty and occupied hydrates Δg is calculated taking account of the number of degrees of freedom for each system. When an occupied cage is large compared with the size of the guest, the coupling of the guest with the host water is rather weak. Hence, the free energy is given by

$$f = -kT\ln b. \tag{7}$$

In equation (7), b is the partition function of the individual guest molecule. The partition function of cage occupancy is defined as

$$b = (mkT/2\pi\hbar^2)^{3/2}\int_{V_{cage}} \exp[-\beta w(\mathbf{r})]d\mathbf{r}, \tag{8}$$

where the integration spans the single cage, V_{cage}. m is the mass of a guest molecule, and $w(\mathbf{r})$ denotes the interaction potential between the guest and the surrounding water molecules.

The free energy of the system is given by the entropy arising from the occupancy of guest molecules and the free energy due to the motions of guests inside the cages either by the intermolecular vibrational motions or the single particle integration. It is assumed in our treatment that f_s and f_l are independent of the occupancy of other cages so as to avoid complicated but ineffective treatment. This is because the interaction between guest molecules is not so strong in those noble gas hydrates. Therefore, f_s and f_l are evaluated for the fully occupied hydrate I for guest Xe or hydrate II for guest Ar.

In order to obtain the density of state $h(\omega)$ for intermolecular vibrational motions, normal mode analysis is performed by diagonalizing the mass weighted force constant matrix $\mathbf{m}^{-1/2}\mathbf{V}\mathbf{m}^{-1/2}$, where $\mathbf{V}$ is the matrix representing the second derivatives of the potential and $\mathbf{m}$ is the appropriately defined mass tensor [7].

3 RESULTS AND DISCUSSION

The potential energy of the guest Xe with surrounding water molecules in the structure I is calculated, where the host water molecules are fixed at the lattice sites. The potential energy curves calculated along the three directions of Cartesian coordinate axes are depicted in Figure 1 as a function of the distance from the center of the cage. The potential energy surfaces for Xe in the smaller cage are well approximated to parabolic curves. On the other hand, the potential energy surfaces in the larger cage are twisted and are different for different directions, since the shape of the larger cage in the structure I hydrate is oblate. For that reason, the guest motion

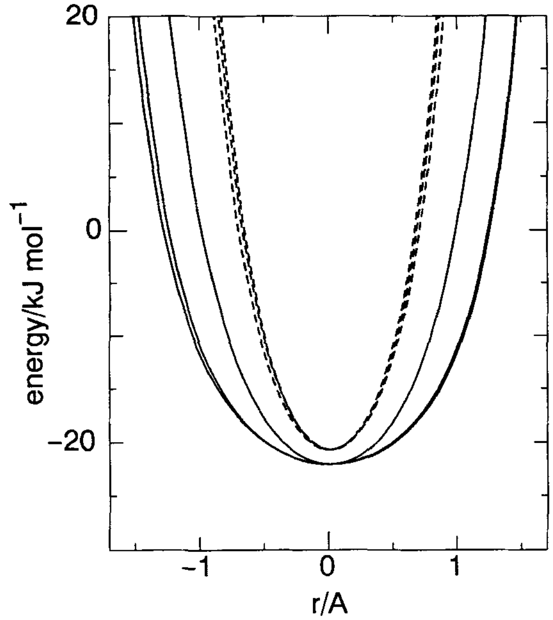

Figure 1 The potential energy of a guest molecule in a large cavity (solid line) of the clathrate hydrate I and in a smaller cage (dotted line) along three orthogonal axes. The guest is Xe and the unit of energy is kJ mol^{-1}.

in the larger cage cannot be approximated to harmonic oscillation. The potential energy curves of the guest Ar in the structure II hydrate are shown in Figure 2. Contrary to the structure I hydrate, the potential energy curves are not quadratic even in the smaller cage. In the larger cage, the potential energy curve has two minima along each coordinate axis.

It was shown in the previous study [8] that a guest molecule in a large cage is only weakly coupled with the host water molecules and that the guest motion is rather irrelevant to the condition as to whether the host water molecules are fixed or allowed to move. Therefore, we use either equation (5) or equation (7) in the practical application of the vdWP theory, depending on the guest and cage size. The harmonic approximation, equation (6) is valid only for occupancy of the smaller cage in the Xe hydrate. The free energy of occupancy is evaluated according to equation (8) for both types of cages in the Ar hydrate and for the larger cage in the Xe hydrate.

When the hydrate is in equilibrium with ice or liquid water and also with the guest in gas phase, the pressure of the guest species in gas phase is referred to as dissociation pressure. At dissociation pressure, the chemical potential difference between the occupied (real) hydrate and the empty (artificial) hydrate must be the same value as the chemical potential difference between pure water (either liquid water or ice) and the empty hydrate. The former chemical potential difference is evaluated according to equation (4). In addition, the latter chemical potential difference should be known. The chemical potential values of ice and empty hydrate are divided into the three contributions; (i) the entropy arising from the proton-disorder in configuration space, (ii) the free energy of intermolecular vibrations (via phonon density),

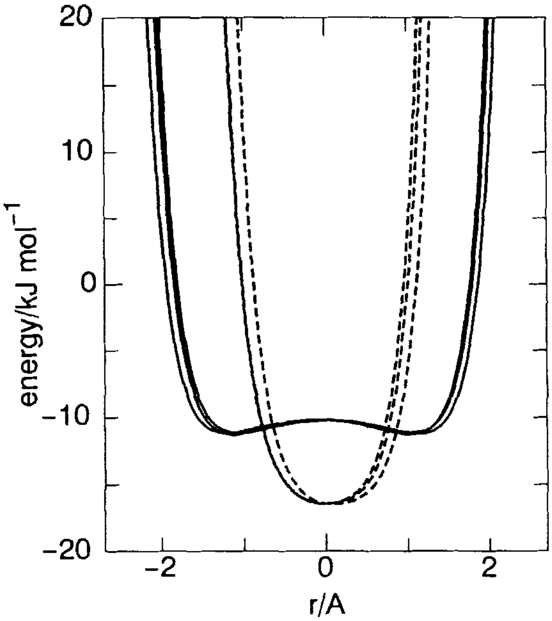

Figure 2 The potential energy of a guest molecule in a large cavity (solid line) of the clathrate hydrate II and in a smaller cage (dotted line) along three orthogonal axes. The guest is argon and the unit energy is kJ mol^{-1}.

(iii) the potential energy of crystalline structure at temperature 0 K (at the local potential minimum structure). This is not, of course, applicable to liquid water. Therefore, we will treat equilibria between ice and hydrate exclusively; we are interested in an equilibrium between the low pressure ice (ice Ih or ice Ic) and the clathrate hydrates (structure I or II). All of those structures are of proton-disordered form obeying Bernal-Fowler-Pauling rule: The entropy contribution in hydrate from the proton-disorder is the same as in ice and the number of the configurations is approximately $(3/2)^{N_w}$ [14]. Since only the chemical potential difference is required, the second and the third terms should be evaluated in the present study. Here, we assume again that the free energy of vibrations is simply given by the free energy of harmonic oscillators and that the anharmonic contributions are negligible. We obtain the second and the third terms averaged over four ice Ic, six empty hydrate I and four empty hydrate II structures. The sum of the energy u^0 and the free energy of vibrations g^0 are shown in Figure 3. The averaged potential energies of ice Ic, the structure I hydrate and the structure II hydrate are -56.22 kJ mol^{-1}, -54.87 kJ mol^{-1} and -54.87 kJ mol^{-1}, respectively. Since the potential energies of two types of hydrates are almost the same, the difference arises solely from the difference in vibrational frequency distributions. This vibrational free energy is slightly lower in the structure II hydrate than in the structure I hydrate at 273.15 K. Its difference is becoming smaller with decreasing temperature.

The free energy of cage occupancy f is calculated according to either equation (5) or equation (7). Those free energy values at 273.15 K are given in the previous study [8]. All of those values increase with decreasing temperature as shown in

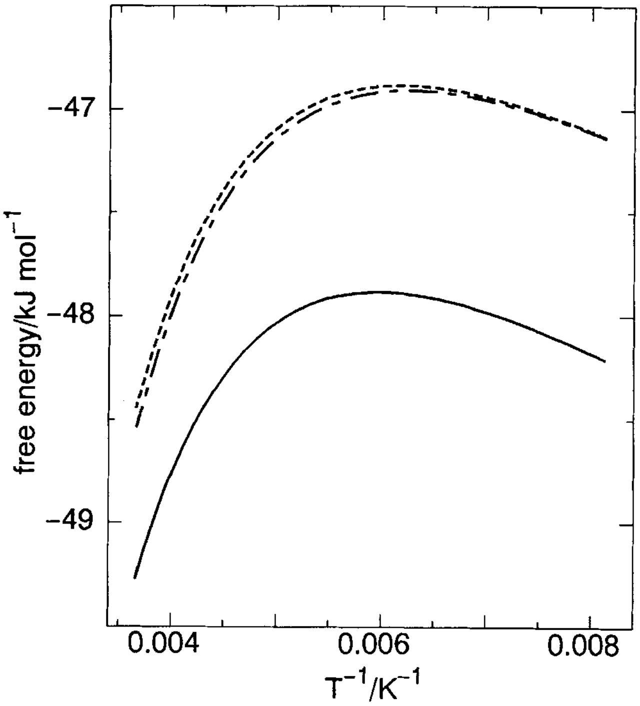

Figure 3 Sum of the vibrational free energy g^0 and the potential energy u^0 for ice Ic (solid line), structure I empty hydrate (dotted line) and structure II empty hydrate (dash-dot line) over a temperature range, 123.15 K to 273.15 K.

Figure 4. The potential energy u is the minimum energy value of $w(\mathbf{r})$ in equation (8). The potential energy values of Xe atom are $-28.29\,\mathrm{kJ\,mol^{-1}}$ in the smaller cage and $-29.83\,\mathrm{kJ\,mol^{-1}}$ in the larger cage of the structure I clathrate hydrate, respectively. The potential values of Ar atom are $-17.01\,\mathrm{kJ\,mol^{-1}}$ in the smaller cage and $-14.25\,\mathrm{kJ\,mol^{-1}}$ in the larger cage of the structure I, while those in the structure II are $-17.61\,\mathrm{kJ\,mol^{-1}}$ and $-11.43\,\mathrm{kJ\,mol^{-1}}$. The difference in the energy of the larger cage occupancy is larger than that of the smaller cage. The contribution from the intermolecular vibrations makes the total free energy more negative in all the cases.

At dissociation pressure, the chemical potential of water in ice (μ_i^0) is the same value as in hydrate, which states $\mu_i^0 - \mu_w^0 = \mu_w - \mu_w^0$, as mentioned earlier. The difference between ice and empty hydrate is already calculated from the phonon density of state and the minimum potential energy. The difference between occupied and empty hydrates is calculated according to equation (4). The way in which the chemical potential difference ($\mu_w - \mu_w^0$) depends on the pressure is much more significant and straighforward than the difference ($\mu_i^0 - \mu_w^0$) [15]. Therefore, we neglect the pressure dependence of the latter, ($\mu_i^0 - \mu_w^0$). When both the curve for ($\mu_w - \mu_w^0$) and the horizontal line for ($u_i^0 - \mu_w^0$) against the pressure of the guest in gas phase are plotted, only one intersection is obtained at given temperature. This intersection corresponds to the dissociation pressure, which is depicted as a function

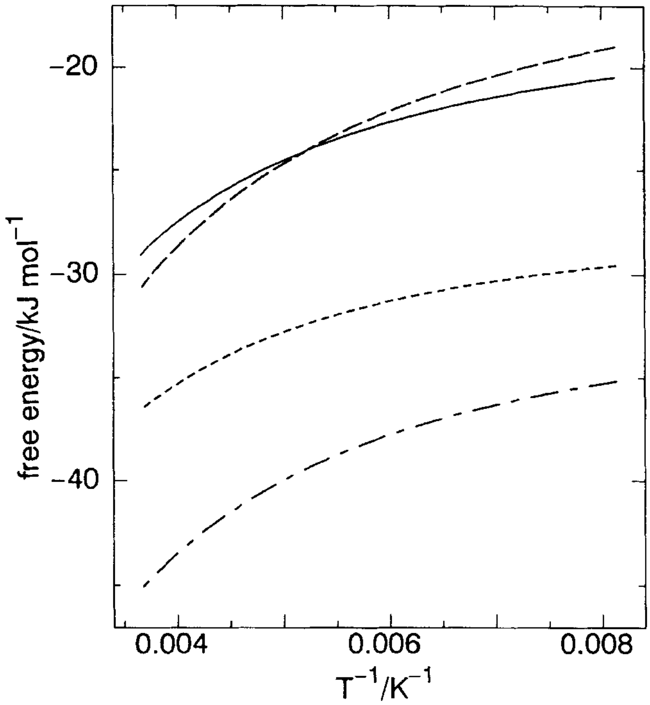

Figure 4 Temperature dependence of the free energy of cage occupancy, f. The guest molecule is either Xe or Ar. Solid line; in smaller cage of the Ar hydrate, dashed line; in larger cage of the Ar hydrate, dotted line; in smaller cage of the Xe hydrate, dash-dot line; in larger cage of the Xe hydrate.

of the (inverse) temperature in Figure 5. In the case of the Xe hydrate, the predicted pressure agrees well with the experiment [16]. The agreement is excellent at temperature 273.15 K but is rather poor for the Ar hydrate at low temperature [16]. This may indicate that our method based on classical mechanics is not appropriate in low temperature regime. If we use quantum mechanical partition functions for harmonic oscillators in evaluating the free energy difference between ice and empty hydrate given as

$$g = kT\int \ln[2\sinh(\beta\hbar\omega/2)]h(\omega)d\omega, \tag{9}$$

the agreement with the experiment is much better in low temperature region.

The average number of occupied cages is calculated according to equation (3). The occupancy rates for the Ar and Xe hydrates are plotted against the temperature in Figure 6. The occupancy rate decreases with increasing temperature and approaches to the asymptotic value of high temperature, 0.5. The occupancy rate is generally higher in Ar hydrate than in Xe hydrate reflecting the stronger interaction between water and Xe atom.

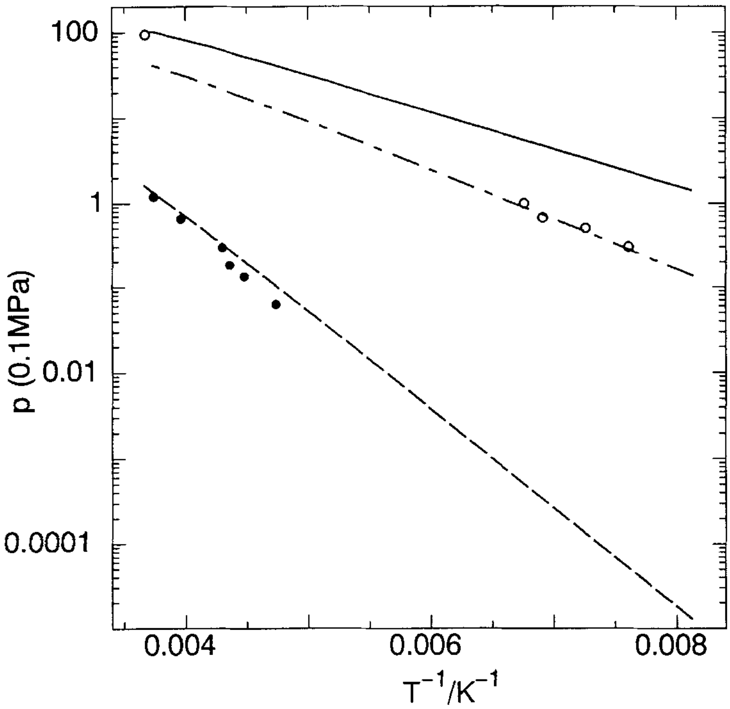

Figure 5 Dissociation pressure over a temperature range 123.15 K to 273.15 K. Solid and dashed lines show the calculated dissociation pressure for the Ar and Xe clathrates, respectively, where the chemical potential difference between ice and empty clathrate is evaluated according to classical mechanical partition function of harmonic oscillators. Dash-dot line shows the dissociation pressure for the Ar clathrate, evaluating the chemical potential difference according to quantum mechanical partition function. Both open and black circles show the experimental results for Ar and Xe clathrate hydrates, respectively.

4 CONCLUSION

The thermodynamic stability of clathrate hydrates I and II encaging Xe and Ar has been investigated by examining the temperature dependence of the dissociation pressure over a temperature range, 123.15–273.15 K. The evaluation of the stability is made based on the generalized vdWP theory. The free energy of formation of hydrates being in equilibrium with ice is calculated by taking the coupling of the host lattice vibrations with guests into consideration in the case of occupancy of the smaller cage by Xe atom. The coupling of the host water with guests is neglected and the single particle integration is used in all other cases when the free energy of cage occupancy is evaluated. The predicted dissociation pressure of the Xe and Ar hydrates agrees reasonably well with experiments in high temperature range. The discrepancy between the prediction and the experiment for the Ar hydrate at low temperature is much more smaller if a quantum mechanical partition function for a harmonic oscillator is used.

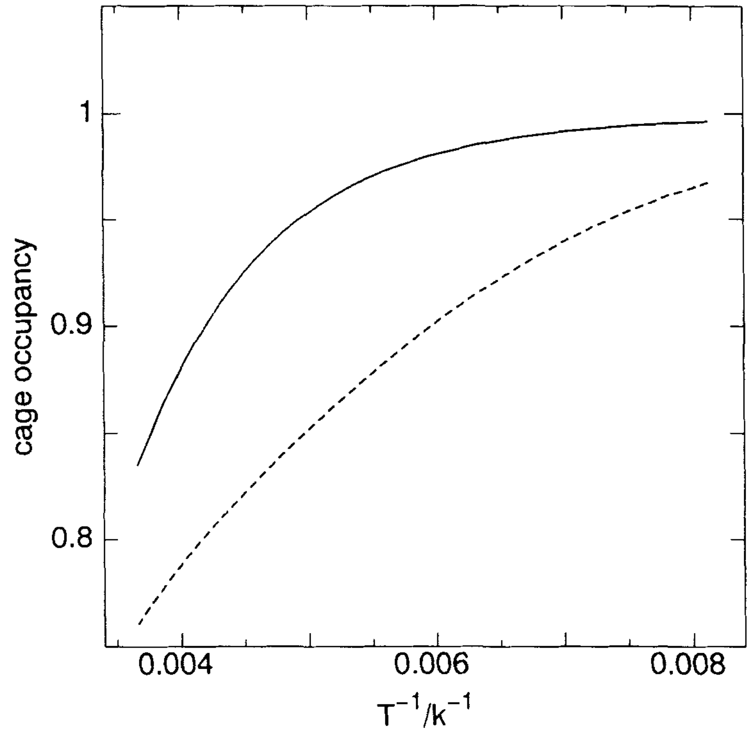

Figure 6 Temperature dependence of occupancy rate normalized to unity. Solid line; Ar hydrate, dashed line; Xe hydrate.

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