

Theoretical Modeling of Phase Diagram of Clathrate Hydrates toward Hydrogen Storage Applications

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ABSTRACT

Original approach accounting for multiple cage occupancy, host lattice relaxation, and the description of the quantum nature of guest behavior has been used for estimation the thermodynamic properties of pure hydrogen and binary X+H₂ hydrates with the possibility of multiple filling of cavities by guest molecules. The thermodynamic conditions of hydrate formation at equilibrium with ice phase have been determined. The hydrogen storage content in hydrates is estimated in wide range of *p-T* regions. This approach can be useful for understanding the thermodynamic properties of the binary hydrate and it can support the experimental exploration of novel hydrogen storage materials based on clathrate hydrates. The method is general and can apply to the various non-stoichiometric inclusion compounds with weak guest-host and guest-guest interactions.

Keywords: hydrogen storage, clathrate hydrate, phase diagram, binary systems, modeling

1 INTRODUCTION

Although fossil and nuclear sources will remain the most important energy provider for nearest future, the technological solutions that involve alternative possibilities of energy supply and storage are in urgent need of development. To meet the storage challenge, basic research is needed to identify new materials and to address a host of associated performance and system issues, such as operating pressure and temperature, the durability of the storage material, the hydrogen delivery pressure, overall safety and so on. No material available today comes close to meeting all the requirements for onboard storage of hydrogen for supplying a fuel cell/electric vehicle [1].

There are several candidate groups for storage materials; each with positive and negative attributes. The traditional hydrides have excellent H-volume storage capacity, good and tunable kinetics and reversibility, but poor H-storage by weight. Highly porous carbon and hybrid materials have capability of high mass storage capacity, but since adsorption is of molecular hydrogen, they can only work at cryogenic conditions. The light metal alloys have the required mass density, but poor kinetics and high

absorption temperatures/pressures. The complex hydrides undergo chemical reactions while desorbing/adsorbing, thus restricting kinetics and reversibility. Hence, research on adequate H-storage materials remains a challenge – in particular for the vehicle transportation sector [2].

The clathrate hydrate is another type of material, which has a potential application as hydrogen storage. This is a special class of inclusion compounds consisting of water and small guest molecules, which form a variety of hydrogen-bonded structures. These compounds are formed when water molecules arrange themselves in a cage-like structure around guest molecules. Recently, the interest in hydrogen clathrate hydrates as potential hydrogen storage materials has risen after a report that the clathrate hydrate of structure II (CS-II) can store around 4.96 wt % of hydrogen at 220 MPa and 234 K [3]. After that, the researchers have concentrated on accurate estimation of the hydrogen capacity of the CS-II clathrate hydrate and have focused on the formation of hydrogen hydrates at lower pressure since the extreme pressure required to stabilize pure hydrogen clathrate hydrates makes it impractical for commercial use [4, 5]. The possible formation of hydrogen hydrate with different structures by adding various guest molecules suggests the practical feasibility of the binary hydrate as a hydrogen storage candidate.

A significant reduction in the hydrate formation pressure, nearly 2 orders of magnitude, was found in the tetrahydrofuran (THF) – hydrogen – water system [5]. In this case the THF molecules can be included only in the large cages of host lattice that significantly reduces amount of hydrogen and hence makes such storage impractical. Moreover, it is already established that THF can be classified as an “irritant” compound with a low toxicity category and thus can be used only in modest amounts.

It will be interesting to consider the possible formation of hydrogen hydrates stabilized by other guest molecules which, for example, may also fill small cavities and see, whether hydrates formed from mixtures of these guests and H₂ can be used as a basis for hydrogen storage material. There are several types of gas hydrate structures with different cage shapes, and some of these hydrate structures can hypothetically store more hydrogen than the hydrate of structure CS-II.

For practical application of gas clathrates as hydrogen storage materials, it is important to know the region of

stability of these compounds as well as the hydrogen concentration at various pressures and temperatures. Thus, it is important to study the phase diagram of multi-component clathrate hydrates in detail which is still a challenging task due to their complexity [4]. Theoretical approaches can be useful for understanding the thermodynamic properties of the binary hydrate and they can support the experimental exploration of novel hydrogen storage materials based on clathrate hydrates.

In this work, we calculate the thermodynamic properties and the degree of filling of the large and small cavities for binary X+H₂ hydrates in various range of pressures and temperatures.

2 THEORETICAL MODEL

In order to accurately estimate the thermodynamic properties of hydrogen hydrates, we developed a method based on the solid solution theory of van der Waals and Platteeuw (vdW-P) with some modifications that include multiple occupancies, host relaxation, and the description of the quantum nature of hydrogen behavior in the cavities. The following development of the model is based only on one of the assumptions of vdW-P theory: the contribution of guest molecules to the free energy is independent of mode of occupation of the cavities at a designated number of guest molecules. This assumption allows us to separate the entropy part of free energy:

$$F = F_1(V, T, y_{11}^1, \dots, y_{nm}^k) + kT \sum_{i=1}^m N_i \left[\left(1 - \sum_{l=1}^n \sum_{i=1}^k y_l^i \right) \ln \left(1 - \sum_{l=1}^n \sum_{i=1}^k y_l^i \right) + \sum_{l=1}^n \sum_{i=1}^k y_l^i \ln \frac{y_l^i}{i!} \right] \quad (1)$$

For a given arrangement $\{y_{11}^1, \dots, y_{nm}^k\}$ of the guest molecules in the cavities the free energy $F_1(V, T, y_{11}^1, \dots, y_{nm}^k)$ of the crystal can be calculated within the framework of a lattice dynamics approach in the quasiharmonic approximation as

$$F_1(V, T, y_{11}^1, \dots, y_{nm}^k) = U + F_{vib}, \quad (2)$$

where U is the potential energy, F_{vib} is the vibrational contribution:

$$F_{vib} = \frac{1}{2} \sum_{j\bar{q}} \hbar \omega_j(\bar{q}) + k_B T \sum_{j\bar{q}} \ln \left(1 - \exp(-\hbar \omega_j(\bar{q}) / k_B T) \right), \quad (3)$$

where $\omega_j(\mathbf{q})$ is the j -th frequency of crystal vibration and \mathbf{q} is the wave vector. This approach is taken into account the quantum effects in energy and entropy calculations. These effects are significant in water ice at low temperatures and no procedure to correct molecular dynamics calculations for these effects have been established [6].

If the free energy F is known then the equation of state and the Gibbs free energy $\Phi(P, T, \{y\})$ expressed in terms of chemical potentials of host and guest molecules can be

found and the corresponding equations are presented elsewhere [7-9].

3 RESULTS AND DISCUSSION

Using this approach, the phase diagram of the pure hydrogen CS-II hydrate has been constructed [8]. The calculated curve of the phase transformation between hexagonal ice and hydrogen hydrate agrees well with the available experiments [10,11]. The hydrogen content continues to increase due to multiple filling of the large cages. At low temperature the mass percentage of hydrogen in the CS-II hydrogen hydrate can reach amount up to 3.8 wt % for pressures of 160-180 bar. This value corresponds to configuration of four hydrogen molecules in the large cavities and one molecule in the small cages of the CS-II hydrate structure in agreement with experimental measurements [12]. At higher pressure the hydrogen storage capacity can increase up to 4 wt % indicating the changes from one to twofold filling for a limited number of small cavities. Increasing the temperature up to 260 K significantly reduces the amount of stored hydrogen. The maximum amount of hydrogen stored at this temperature and high pressures is about 3.5 wt % [8].

Instead of THF, the propane has been selected as a second guest component because of the binary CS-II propane+hydrogen hydrate has already been synthesized. It was shown that the propane as THF occupies only the large cavities of the CS-II hydrate and the formation of this hydrate is very similar to the situation observed in the THF-hydrogen-water system [13]. The formation pressure can be significantly reduced in the presence of propane as a second guest in the binary hydrogen hydrate. At a low propane concentration of 0.1 % in the gas phase, the binary hydrate becomes stable at a pressure around 380 bar which is about four times lower than that needed to form the pure hydrogen clathrate in the same temperature region [8]. By analogy with THF, propane brings the hydrate formation conditions closer to ambient conditions and it is undoubtedly favorable for a hydrogen storage material. The filling of the large cages by hydrogen molecules increases consecutively from one to four hydrogen molecules with increasing pressure. In contrast to hydrogen, the propane filling decreases with increasing pressure and in the high pressure region the propane molecules are gradually expelled by hydrogen molecules. The tuning of large cage occupancy can be attributed to the "composition tuning mechanism" proposed by Lee *et al.* [14]. The mass percentage of hydrogen in the mixed CS-II propane+hydrogen hydrate can amount up to 3.5 wt% at T=260 K and lower concentrations of propane in the gas phase and a pressure of 1000 bar. This value is comparable with the hydrogen content (3.5 wt %) estimated for pure hydrogen hydrate at the same temperature [8].

At the present time, most of the recognized gas hydrates have one of well-known three types of structures: the cubic I, cubic II and hexagonal structures (CS-I, CS-II

and sH, respectively). There is a pentagonal dodecahedron (a polyhedron with 12 pentagonal faces 5^{12}) in these hydrate structures as the basic small cavity. The basic 5^{12} cavities combine with $5^{12}6^2$ cavities form CS-I structure and with $5^{12}6^4$ cavities form CS-II one. The combination of dodecahedrons with $4^35^66^3$ and $5^{12}6^8$ cages gives sH structure. Assuming that the $5^{12}6^2$ and $5^{12}6^4$ cages can accumulate maximum 4 hydrogen molecules, the 5^{12} cavity up to 2 hydrogen molecules, the $4^35^66^3$ and $5^{12}6^8$ cages up to 1 and 5 hydrogen molecules, respectively, a theoretical limit mass of hydrogen storage can be determined. It has been found that the largest values of hydrogen mass (6.33 wt %) can be achieved for CS-I structure as comparable with hydrogen mass for CS-II (4.96 wt %) and sH (4.91 wt %) ones. Based on these results we select CS-I structures for further investigations.

It has been estimated that the pure hydrogen CS-I hydrate can store more hydrogen at $T=250$ K as shown in Figure 1.

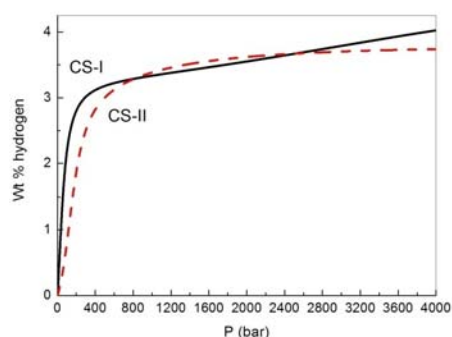


Figure 1: Hydrogen storage capacity of the CS-I (solid line) and CS-II (dashed line) hydrogen hydrates as a function of pressure at $T=250$ K.

It can be seen that at low pressure the CS-I structure can store up to 3.1 wt % and reach amount up to 4.0 wt % for pressures of 4 kbar. The analysis of filling degree of both cavities indicated that with increasing pressure the filling of the large cages increases consecutively from one to three hydrogen molecules and hence shows the similar behavior of filling the large cages as in the hydrogen CS-II hydrate. However, the degree of small cavity filling has achieved value of 0.9 indicating that hydrogen molecules occupied almost 90% of the small cavities in single form. This result differs from the small cage occupation in the case of CS-II structure. At high temperature, the filling degree of small cavity of CS-II hydrate has only achieved value of 0.6. This can be explained by the difference in order of small cavities in CS-I and CS-II structures. The structural features of CS-II hydrate increase the high hydrogen diffusion and migration at high temperatures that was observed experimentally [12].

The chemical potential curves of the water molecules in ice I_h and in pure hydrogen hydrate of CS-I and CS-II structures as a function of pressure at $T=250$ K are shown

in Figure 2. The intersection of the chemical potential curves of ice I_h and the CS-I hydrate has been found (around 1 kbar) that defines the formation pressure of the hydrogen hydrate at a given temperature. However, the CS-I structure is thermodynamically unstable as comparable with CS-II one. The hydrogen CS-II hydrate is also more stable than that of CS-I one in lower temperature region. These results can explain the experimental realization of hydrogen CS-II hydrate only.

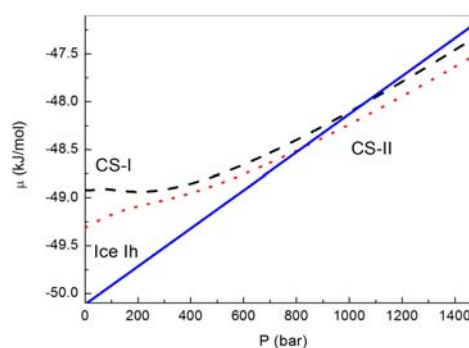


Figure 2: Pressure dependence of the chemical potentials of water molecules at $T=250$ K for I_h (solid line), hydrogen CS-I (dashed line) and CS-II (dotted line) hydrates.

In order to reduce the hydrate formation and stabilize CS-I structure, the second guest component should be selected according the following conditions. The guest size should be comparable with size of dodecahedron cavity, in pure form it can able to form both CS-I and CS-II hydrates and CS-I hydrate with this guest is more stable than that of CS-II structure. Based on these assumptions, the mixed methane+hydrogen hydrates of CS-I and CS-II structures have been investigated with different methane and H_2 concentrations. Moreover, along with hydrogen, methane can be considered as an additional energy resource. The formation pressures of the binary H_2+CH_4 CS-I and CS-II hydrates depend on methane concentration in the gas phase and with increasing methane concentration in the gas phase is found to be lower in comparison with the pressure of pure hydrogen hydrate formation (see Figure 3). At low methane concentration (less than 1 %), the mixed methane+hydrogen CS-II hydrate is more thermodynamically stable than CS-I hydrate with same composition of guest molecules. The introduction of methane as a second guest component in the binary hydrogen CS-II hydrate does not only reduce the formation pressure but practically reproduces (3.0 wt %) the hydrogen storage ability of the pure clathrate hydrate (3.5 wt %) at $T=250$ K and a pressure of 1 kbar due to the complete filling of small cavities by methane molecules. The calculations showed that at low temperature the stabilization of CS-I hydrate can be also realized for H_2 -methane- H_2O systems with relative small concentration of methane in the gas

phase as shown in Figure 4. In this case, the amount of storage hydrogen in CS-I structure smaller as comparable with one in structure II. In contrast to CS-II structure, the methane filling of large cages decreases with increasing pressure and the methane molecules are gradually expelled by hydrogen molecules in higher pressure region.

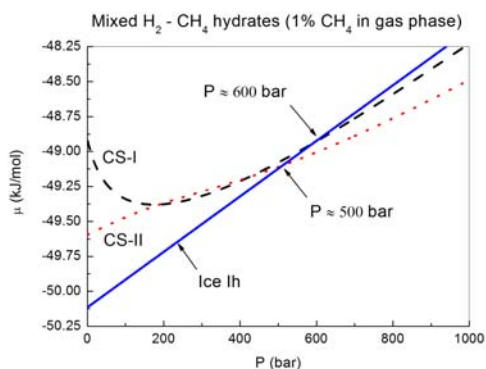


Figure 3: Pressure dependence of the chemical potentials of water molecules at $T=250$ K for I_h (solid line), hydrogen CS-I (dashed line) and CS-II (dotted line) hydrates at 1 % of methane concentration in the gas phase.

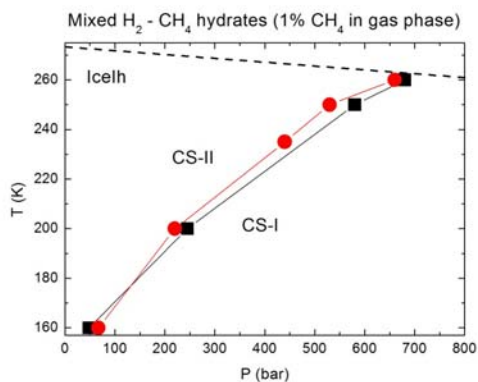


Figure 4: The calculated p - T diagram of H_2O - H_2 - CH_4 system. The equilibrium lines of I_h ice-CS-I (black squares) and I_h ice – CS-II (red cycles). The dotted line presents ice I_h -liquid water equilibrium phase transition.

By variation of methane concentration in gas phase, the mass percentage of hydrogen in mixed methane+hydrogen CS-I hydrate can reach amount 2.5 wt % at 250 K and 800 bar. However, the storage hydrogen amount depends on the methane concentration in the gas phase as well as thermodynamic conditions of hydrate formation.

4 CONCLUSIONS

We have presented a formalism for calculating the thermodynamic properties of clathrate hydrate with weak guest-host interactions. In distinction from the original vdW theory the suggested model accounted for the influence of guest molecules on the host lattice as well as guest-guest interaction. The present model allows one not only to calculate the hydrogen storage ability of known hydrogen hydrate but also predict this value for structures that have not yet been realized by experiment.

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