Mixed H2-CH4 Hydrates as Materials for Hydrogen Storage

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1 Introduction

The present environmental factors and limited energy resources in future have led to a profound evolution of technical progress in the generation, storage and supply of energy. 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 request storage conditions, researches need to identify new materials and address a host of associated performance and system issues, such as operating pressure and temperature, the durability of the storage material, the reversibility of hydrogen uptake and release, the hydrogen delivery pressure, overall safety, toxicity, system-efficiency and cost [1].

The clathrate hydrate is material, which has a potential application as hydrogen storage. This is a special class of inclusion compounds consisting of water (red and white) and small guest (grey) molecules (see Figure 1), which form a variety of hydrogen-bonded structures.
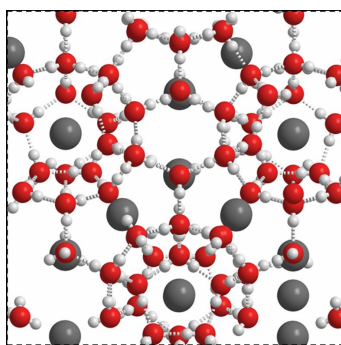

Figure 1: **Crystal structure CS-II clathrate hydrate.**

These compounds are formed when water molecules arrange themselves in a cage-like structure around guest molecules. As example, the methane in gas hydrates represents one of the largest sources of hydrocarbons on Earth. Interest in hydrogen clathrate hydrates as potential hydrogen storage materials has risen recently after a report that the clathrate hydrate of cubic structure II (CS-II) can store around 5.0 weight% of hydrogen at 220MPa and 234 K [2]. However, the extreme pressure required to stabilize this material makes it impractical. A significant reduction in the hydrate formation pressure, nearly 2 orders of magnitude, was found in the tetrahydrofuran (THF) – hydrogen – water system [3, 4]. 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.

Thus first, 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 H_2 can be used as a basis for hydrogen storage material. Second, 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. Therefore, 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.

In this work, we calculate the thermodynamic properties and the degree of filling of the large and small cavities for mixed propane+hydrogen and methane+hydrogen hydrates in various range of pressures and temperatures. For these binary hydrates, we also analyze the possibility to realize the "composition tuning mechanism" proposed earlier for THF+H_2 hydrate [4].

2   Computational Details

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:

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

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

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

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

$$F_{vib} = \frac{1}{2}\sum_{j\vec{q}}\hbar\omega_j(\vec{q}) + k_BT\sum_{j\vec{q}}\ln\left(1-\exp(-\hbar\omega_j(\vec{q})k_BT)\right),$$ (3)

where $\omega_j(\mathbf{q})$ is the j-th frequency of crystal vibration and $\mathbf{q}$ is the wave vector.

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 [5, 6].

3   Results and Discussions

The validity of the proposed approach was checked for pure CS-II hydrogen hydrates [6]. The calculated curve of the phase transformation between hexagonal ice and hydrogen hydrate agrees well with the available experiments. 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. At higher pressure the hydrogen storage capacity can increase up to 4 wt% (see Figure 2) 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 % [6].
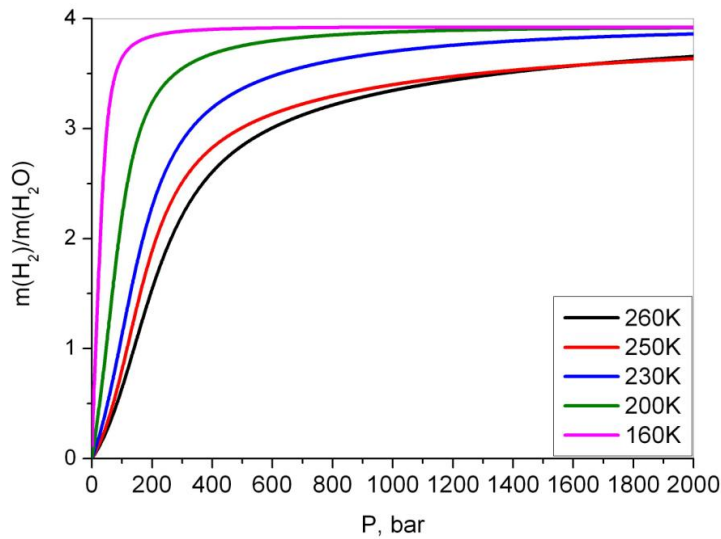

Figure 2:   The amount of stored hydrogen in the pure CS-II hydrogen hydrate.

The phase diagrams of propane+hydrogen hydrate with structure II have been constructed and they are in agreement with available experimental data. 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 [6]. 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.* [4]. 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 as shown in Figure 3.
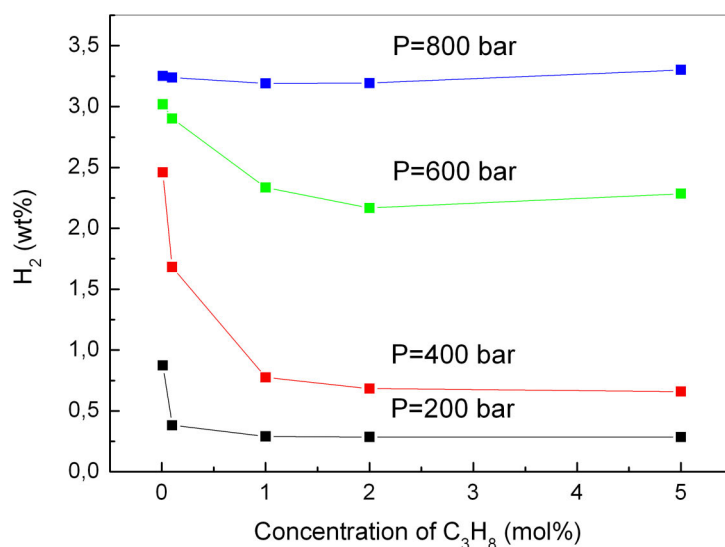

Figure 3:   **The amount of stored hydrogen in the mixed propane+hydrogen CS-II hydrate.**

It has been also estimated that the pure hydrogen hydrate of CS-I structure can store more hydrogen but this structure is thermodynamically unstable as comparable with CS-II structure and hexagonal ice. Therefore, the mixed methane+hydrogen hydrates of CS-I and CS-II structures have been investigated with different methane and H_2 concentrations. 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 was found to be lower in comparison with the pressure of pure hydrogen hydrate formation. 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 "composition tuning mechanism" has been also observed for the methane+hydrogen CS-II hydrate as in the case of propane+hydrogen one. The introduction of methane as a second guest component in the binary hydrogen CS-II hydrate does not only

reduce the formation pressure but also reproduces the hydrogen storage ability of the pure clathrate hydrate. The calculations showed that the stabilization of CS-I hydrate can be also realized for H_2-methane-H_2O systems with relative large concentration of methane in the gas phase. However, in this case, the amount of storage hydrogen in CS-I structure reduced during increasing pressure. In contrast to CS-II structure, the methane filling of large cages increase with increasing pressure and in the high pressure region the hydrogen molecules are gradually expelled by methane molecules. By variation of methane concentration in gas phase, the mass percentage of hydrogen in mixed methane+hydrogen CS-I hydrate can reach amount 2 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. Therefore, it is important to determine the optimal balance between storage capacity and formation conditions for the practical feasibility of the binary hydrate as a hydrogen storage candidate. There are significant difficulties in experimental investigation and treatment of phase diagrams of multi-component clathrate hydrates that could result in a loss of important information related to the guest content in storage media. We believe that the proposed approach could support experimentalists in the practical realization of hydrogen storage material based on clathrate hydrate.

Acknowledgement

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