THERMODYNAMIC STABILITY AND KINETIC ASPECTS OF CH_4 - CO_2 HYDRATE EXCHANGE

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EXTENDED ABSTRACT

Hydrates are ice-like, crystalline structures, occurring at high pressures and temperatures around 5°C, in which gas molecules are trapped in water-cages[1]. Research on hydrate formation has become increasingly popular since it became evident that large reserves of naturally occurring methane hydrates exist. As the total amount of methane trapped in hydrates exceeds the collected amount of conventionally available gas, research on harvesting of methane hydrates becomes imperative.

By exchanging CH_4 with CO_2, two things can be accomplished. We harvest natural gas for energy production, and we store a greenhouse gas. We thus have an elegant solution to two problems of paramount importance.

In previous work, the thermodynamic properties of an sI hydrate filled with CO_2, CH_4, and a mixture of the two has been studied[2] using semi-Grand Canonical Monte Carlo simulations. An empty hydrate lattice, with a specified amount of water molecules, was filled with CO_2 and CH_4 while maintaining constant volume and temperature. The Helmholtz energy difference between an occupied hydrate and an empty hydrate with isolated gas molecules was computed. Thus, a potential thermodynamic pathway for exchanging CH_4 for CO_2 hydrates was found. In that work, calculations for the Helmholtz energy associated with the formation of the empty hydrate structure were not reported. Now, we will present precisely those results[3]. In addition, we will report values for the Gibbs energy associated with this process. Those values are relevant for applications where one operates at a constant pressure, rather than at a constant volume.

The kinetic aspects of the CO_2 - CH_4 exchange are also important. In order to establish a model of guest molecules swapping cages, we first investigate H_2 molecules diffusing into empty cages in an sII hydrate. We expect the H_2 molecules to have an easier time swapping cages, due to their smaller size. It will be necessary to introduce flaws in the hydrate lattice, by removing some water molecules[4]. A fraction of the hydrate is filled with H_2, such that a gradient of the filling fraction arises along one of the axes. By artificially maintaining this gradient, we will obtain a flow along the direction of the gradient. By calculating the average flow for different gradients, we can thus establish the diffusion constant for one total fractional filling.

With the model for cage swapping established, we consider pure CO_2 and CH_4 diffusing in an otherwise empty lattice. We then consider a mixture of CO_2 and CH_4. Results from these simulations will be presented.

REFERENCES

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