

Abstract

The current theoretical understanding of thermodynamics of clathrate hydrates is based on the van der Waals and Plattew (vdWP) theory developed using statistical thermodynamics approach. vdWP theory has been widely used to predict the phase equilibrium of clathrate hydrates over the decades. However, earlier studies have shown that this success could be due to the presence of a large number of parameters.

In this thesis, a systematic and a rigorous analysis of vdWP theory is performed with the help of Monte Carlo molecular simulations for methane hydrate. The analysis revealed that long range guest-water interactions and guest-guest interactions are important, Monte Carlo integration to is superior to the spherical shell approximation for the Langmuir constant calculation and even after inclusion of all the interactions and using Monte Carlo integration for Langmuir constant, the vdWP theory still fails to regress parameters correctly. This failure of vdWP theory is attributed to the rigid water lattice approximation.

To address the rigid water lattice approximation, a new method is proposed. In the proposed method, the Langmuir constant is computed in flexible water lattice, by considering the movement of water molecules. The occupancy values predicted using the proposed method are in excellent agreement with the values obtained from Monte Carlo molecular simulations for variety of hydrates, methane, ethane, carbon dioxide and tetrahydrofuran(THF) hydrates .

In addition to small guest molecules like methane, ethane etc. which are mod-

eled as rigid, the method is extended for large guest molecules like propane and isobutane, using configurational bias Monte Carlo method. The phase equilibrium and occupancy along the phase equilibrium predictions from vdWP theory are compared with the exact phase equilibrium computed from Monte Carlo molecular simulations. This comparison is done for a wide variety of hydrate systems, single hydrates, binary hydrates and quaternary hydrate. In all the cases, the vdWP theory with the flexible water lattice showed significant improvement over the rigid lattice model with significantly less absolute relative deviations in pressure.

Guest-cavity interactions for hydrates are calculated using *ab-initio* calculations. In general, these guest-cavity interaction from first principle calculations are used to develop classical force field parameters in alternative to Lorentz-Berthelot rule. In the study, comparison of guest-cavity interactions from MP2 and CCSD(T) methods revealed that less expensive MP2 method, which is generally used, is insufficient to capture the dispersion interactions accurately. These guest-cavity interactions using CCSD(T) method extrapolated to complete basis set are used to model the interaction parameters between cyclopropane and water. The potential parameters obtained from *ab-initio* calculations are used in the calculation of Langmuir constant using vdWP theory. Langmuir constant calculated using vdWP theory with flexible water lattice gave close agreement with the values obtained from experimental occupancy data.

In addition, simulation methodology to calculate ternary hydrate phase equilibrium is extended for binary hydrates. Simulations have been successful in the prediction of sI-sII and sII-sI structural transitions as observed in experiments. Predicted methane-ethane binary hydrate is also compared with the available experimental phase equilibrium data. The phase equilibrium obtained from simulations showed very good qualitative agreement with the experimental data.