GENERAL RESEARCH

A Fugacity Model for Gas Hydrate Phase Equilibria

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A classical thermodynamic model for the equilibrium pressures of different guests of structure I and II gas hydrates is proposed that removes the need for reference energy parameters used in the van der Waals and Platteeuw (vdWP) type models. The assumption of a constant crystal lattice for different guests within a structure, which is not in agreement with quantum chemistry calculations, is removed. This model uses published Kihara cell potential parameters determined from viscosity and second virial coefficient data, unlike previous models that fit these parameters to hydrate data. Quantum mechanical calculations were used to reduce the number of fitted parameters in the new model. This model greatly improves upon the accuracy of previous models and is applicable over a wide temperature range. Percent absolute average deviations in the predicted equilibrium pressures is 3.27% with two or three guest-hydrate specific parameters compared to more than 11% with three adjustable parameters in the vdWP type models and 8.55% using a recent thermodynamic model that uses five guest-hydrate parameters.

Introduction

Gas hydrates or clathrates are crystalline solids consisting of a guest(s) component(s) and water. Each guest is trapped in a cage-like water structure that forms a crystalline lattice. Hydrates can form at conditions above the normal freezing point of water. The guests of main interest here are methane, carbon dioxide, and other hydrophobic components that are present in the environment.

There has been considerable interest in gas hydrates over the past 100 years, especially in the petroleum industry. Large hydrated masses occurring in natural gas pipelines, for example, in the Arctic regions and in the sea, can slow or completely obstruct flow. Also there has been a recent resurgence in developing methods to harvest the huge amounts of methane present in natural gas hydrates. A recent estimate of the amount of methane trapped in hydrates is as much as 300 times the normal freezing point of water. The guests of main interest here are methane, carbon dioxide, and other hydrophobic components that are present in the environment.

In the past, gas hydrates were often discussed in the context of their potential as a source of natural gas. However, more recently, there has been increased interest in the potential of gas hydrates as a means of sequestering carbon dioxide and other greenhouse gases.

Hydrate Structure

There are three known hydrate crystal structures. Structures I and II form with relatively small guests, e.g., methane, nitrogen, ethane, etc. Structure I (sI) is a body-centered-cubic (bcc) structure with a lattice parameter of 12.03 Å with ethylene oxide as a guest. The cubic cell contains 46 H2O molecules, 2 dodecahedra (512), and 6 large voids (51262), where 512 is used to indicate that the polyhedron contains 12 five-membered ring faces. Structure II (sII) is a bcc structure with a lattice parameter of 17.31 Å for a double hydrate with tetrahydrofuran and hydrogen sulfide as guests. Each cubic cell contains 136 water molecules, 8 large voids (51264), and 16 dodecahedra. Structure H is only known to form with at least one small guest (i.e., methane) and one large guest, e.g., cyclooctane, methylcyclohexane, etc. The structure H (sH) unit cell contains 34 water molecules, 1 large void (51262), 3 dodecahedra, and 2 43562 cavities.

The primary focus of this study is structure I and II hydrate formers. The radii of the different cavities in structures I and II are listed in Table 1. There has been a disagreement in the literature as to which set of cavity radii should be used. The cavity radii used in this study were taken directly from crystallography measurements by averaging the distance of all oxygens in the water molecules from the mass-weighted center of a cage. The radii used by Sloan are close to the crystallography measurements but are adjusted slightly to provide a better representation of the cell potential in his model. John et al. used a different set of radii which best characterized their simulation results of the guest-host interactions in a specific cavity. Other researchers have determined that radii from crystallography measurements should be used, because those best represent the actual cavity size.

Van der Waals and Platteeuw Type Models

The classic model for determining hydrate equilibrium pressures and temperatures was developed by van der Waals and Platteeuw. This model was later extended by Parrish and Prausnitz to account for...