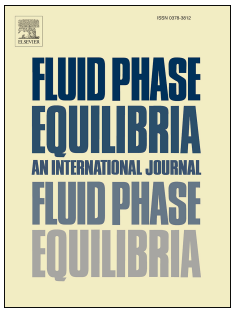

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PII: S0378-3812(16)30584-2

DOI: 10.1016/j.fluid.2016.11.030

Reference: FLUID 11340

To appear in: *Fluid Phase Equilibria*

Received Date: 18 August 2016

Revised Date: 27 November 2016

Accepted Date: 28 November 2016

Please cite this article as: R.K. Zhdanov, K.V. Gets, R.V. Belosludov, O.S. Subbotin, Y.Y. Bozhko, V.R. Belosludov, Theoretical modeling of the thermodynamic properties and the phase diagram of binary gas hydrates of argon and hydrogen, *Fluid Phase Equilibria* (2016), doi: 10.1016/j.fluid.2016.11.030.

Theoretical modeling of the thermodynamic properties and the phase diagram of binary gas hydrates of argon and hydrogen

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Abstract

Theoretical calculation of the thermodynamic properties and determining of equilibrium hydrate composition of binary argon + hydrogen hydrates has been performed with taking into account the concurrent cage occupation by different guest types. For this purpose the original previously developed approach has been used that allows to take into account multiple cage occupancy and the possibility of mixed clusters inside the cages as well as the influence of guest molecules on the host lattice. Separately, argon and hydrogen form cubic structure II (*sII*) hydrates. Therefore, in this work we considered only *sII* gas hydrates formation. It is shown that thermodynamic stability of binary argon + hydrogen hydrates strongly depends on the presence of argon in the gas phase as the heavier component. Thus, with increasing argon content in the system the hydrate stability field extends to low pressures with increase of argon fraction in the small cavities.

Keywords: Clathrate hydrate, Binary hydrate, Hydrogen storage, Statistical thermodynamic, Equation of state

1. Introduction

Clathrate hydrates are crystalline solids that consist of water molecules forming crystal lattice and guest molecules of one or more types placed in cavities created within the water framework. Inclusion of guest molecules increases stability of the hydrate structure. Most of the known gas hydrates have one of three different structures: cubic structure I (*sI*), cubic structure II (*sII*) and hexagonal structure (*sH*). In the unit cell of the structure I there are two types of cavities: 2 small 5^{12} (**D**) and 6 large $5^{12}6^2$ (**T**) cavities. The unit cell of the structure II includes 16 small 5^{12} (**D**) and 8 large $5^{12}6^4$ (**H**) cavities. Unlike these two structures, hexagonal structure has cavities of three different types: small cavity 5^{12} (**D**), medium cavity $4^3 5^6 6^3$ (**D'**) and large cavity $5^{12}6^8$ (**E**).

After discovering that hydrogen is able to form the hydrates of structure II [1] and hydrogen content in this hydrate can reach ∼5 wt% many researchers started to consider hydrogen hydrates as a promising medium for hydrogen storage [2–4]. This hydrate had been formed from the liquid water cooled in presence of hydrogen to temperature 234 K at pressure 220 MPa. The value of ∼5 wt% hydrogen content in this hydrate was determined assuming fourfold occupation of large cavities and double occupation of small cavities by hydrogen molecules in *sII* hydrate [5].

Hydrogen hydrates are not the only possible water phases in high pressure range in the system "hydrogen – water." The other possibilities are hydrogen-filled ice II or ice Ic [6], but the phase diagram of H_2 + H_2O system is not completely investigated now.

Binary hydrates with hydrogen and second heavier component (help gas) can be formed at lower pressures than

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