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# Clathrate hydrates for energy storage and transportation

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Abstract. Formation pressure of mixed hydrogen + methane, hydrogen + ethane and hydrogen + propane hydrates can be controlled by the gas phase composition allowing these hydrates to be considered as promising hydrogen storage containers. At low methane (ethane) concentration in the gas phase, the hydrate of the cubic structure II is formed, and at the methane concentration exceeding 6 mol.% (1 mol.% for ethane) the cubic structure I is formed. The mass percentage of hydrogen in the hydrate phase depends on the second gas concentration in the gas phase as well as on the thermodynamic conditions of hydrate formation. At a low concentration of methane (ethane) in the gas phase, the mass percentage of hydrogen in the hydrate can reach 2.5 wt% at 250 K. The curves of the monovariant equilibrium "gas-hydrate-ice Ih" for double hydrates are calculated and found to be in agreement with the available experimental data. Thermodynamic properties of mentioned mixed hydrates allow to considering mixed hydrates as appropriate materials for hydrogen storage.

#### 1. Introduction

Dyadin et al.[1,2] found the anomalous behavior of the  $H_2O-H_2$  system at hydrogen pressures of 100– 360 MPa and temperatures of 263-283 K, and hypothesized that a clathrate phase of hydrogen hydrate was formed at these conditions. Later Mao et al. [3] confirmed the formation of the hydrogen clathrate hydrate with cubic structure II (CS-II) at 220 MPa and 234 K, and indicated the hydrogen content was 50 g/liter, which corresponds to 5.3 wt% [4]. Hydrogen hydrates are stable at ambient pressures and temperatures T=77 K and decompose with hydrogen emission when heated to 140 K [3], and hence may be used for hydrogen storage. But the extreme pressure is required for the pure hydrogen clathrate hydrates formation and the low temperature that is required for hydrogen storage, makes it impractical for commercial use. A significant reduction in tetrahydrofuran (THF)-hydrogen CS-II hydrate formation pressure (forming at 120 bar and 270 K) by nearly two orders of magnitude was found in the THF-

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hydrogen-water system [5, 6]. It was shown [7-10] that small cavities are occupied by hydrogen, and large cavities are occupied by hydrogen and THF molecules. Occupation of large cavities by THF molecules leads to the stabilization of the hydrate at low pressures, but prevents the occupation of these cavities with hydrogen that significantly reduces the amount of hydrogen that can be stored.

Other clathrate structures can be realized for the binary hydrate of hydrogen in which the second gas component, such as carbon dioxide CO<sub>2</sub> [11–16], methane CH<sub>4</sub>, [16, 17], ethane C<sub>2</sub>H<sub>6</sub> [18-20], propane C<sub>3</sub>H<sub>8</sub> [20, 21], cyclopropane C<sub>3</sub>H<sub>6</sub> [22], tetra-n-butylammonium bromide C<sub>16</sub>H<sub>36</sub>BrN and tetra-n-butylammonium fluoride C<sub>16</sub>H<sub>36</sub>FN [23], methylcyclohexane C<sub>7</sub>H<sub>14</sub>, and methyl tert-butyl ether C<sub>5</sub>H<sub>12</sub>O [24] plays the role of promoter for hydrate formation at lower pressure. However, adding the second gas reduces the amount of hydrogen storage, which is already low for practical application as an onboard hydrogen storage system.

In this paper, we present the study performed by methods of theoretical physics. Thermodynamic functions were obtained in a wide range of temperature and pressure [25] - [28] within the framework of the theory of clathrate hydrates, and at the thermodynamic conditions required for the possible practical application of double clathrate hydrates containing hydrogen for the development of energy storage and transportation technology.

#### 2. Methods

In order to accurately estimate the thermodynamic properties of hydrogen clathrate hydrates, we developed a method based on the solid solution theory of van der Waals and Platteeuw. This model allows one to take into account the influence of guest molecules on the host lattice and guest-guest interactions — especially when more than one guest molecule occupies a cage. The free energies, equations of state, and chemical potentials of mixed hydrates, namely hydrogen + methane, hydrogen + ethane and hydrogen + propane, with different cage fillings have been estimated using this approach. The detailed description of the method is presented in [27].

The  $H_2$ - $H_2$  interaction potential parameters [28] were taken as follows: the long-distance dispersion interaction part was taken from [29], and the short-range repulsion part was estimated with a density functional calculation using the Tohoku Mixed-Basis Orbitals (TOMBO) method.

The gas phases were considered [25] as a mixture of non-ideal gases. All guest molecules were considered as spherically symmetric Lennard-Jones particles which interact by the (6-12) potential with the Lorentz–Berthelot combination rules for cross parameters [30,31]. The parameters of intermolecular interactions and molar composition of gas phase are collected for all the components in table 1.

composition of gas phases.					
Component	σ (Å)	ε (kJ mol <sup>-1</sup> )	Ref.		
$CH_4$	3.73	1.2305	[32]		
$C_2H_6$	3.954	2.02	[33]		
$C_3H_8$	5.637	2.0129	[34]		

Table	1.	Intermolecular	interactions	parameters	and	molar
compos	sitio	n of gas phases.				

The modified SPC/E water model was used [35] for the description of the ice and clathrate hydrate phases. Short-range interaction parameters between the oxygen atoms of the Lennard-Jones potential are  $\sigma$  = 3.1556 Å and the energy parameter  $\varepsilon$  = 0.65063 kJ/mol. The charges of hydrogen (q<sub>H</sub>=+0.4238lel) and oxygen (q<sub>O</sub>=-0.8476lel) were obtained to describe the long-range Coulomb interaction. The protons have been placed to satisfy the Bernal–Fowler rule and the water molecules have been placed so that total dipole moments of the unit cells of ice Ih and hydrates were equal to zero. The long-range electrostatic

interactions have been calculated by the Ewald method. Lattice dynamics calculations were performed on a supercell of ice Ih that contains 128 water molecules: the simulation cell of the CS-I hydrate consisted of 46 water molecules with 6 large and 2 small cages filled by guest molecules.

#### 3. Results

At the low concentration of methane (ethane) in the gas phase, a stable phase of the cubic structure II (CS-II) hydrate is formed, and at the methane (ethane) concentration exceeding 6 mol.% (ethane 1 mol.%) the cubic structure I (CS-I) is formed. The mass percentage of hydrogen in the hydrate phase depends on the second gas concentration in the gas phase as well as on the thermodynamic conditions of hydrate formation. Figure 1 shows the dependence of the formation pressure of the CS-II hydrates of  $H_2+C_4$ ,  $H_2+C_3H_8$  and CS-I hydrate of  $H_2+C_2H_6$  on the second gas concentration in the gas phase at 250 K.



**Figure 1.** The dependence of the formation pressure (P, MPa) of  $H_2+CH_4$ ,  $H_2+C_2H_6$ , and  $H_2+C_3H_8$  hydrates on the concentration (X, %) of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> in the gas phase.

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As the methane concentration increases to 6% in the gas phase, the pressure of  $H_2+CH_4$  hydrate formation decreases from 78.7 to 47.3 MPa. Formation pressure of  $H_2+C_2H_6$  hydrate decreases from 98.5 to 5.9 MPa as the ethane concentration increases to 5%. Formation pressure of  $H_2+C_3H_8$  hydrate decreases from 78.7 to 10 MPa with an increase in the concentration of propane to 1%.

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**Figure 2.** The dependence of the hydrogen content (wt%) in  $H_2+CH_4$ ,  $H_2+C_2H_6$ , and  $H_2+C_3H_8$  hydrates on the concentration (X, %) of  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$  in the gas phase.

Figure 2 shows the dependence of the hydrogen content in double hydrates on the concentration of the second gas in the gas phase. As the methane concentration is increased to 6% in the gas phase, the mass percentage of hydrogen decreases from 3.3 to 1.95 wt%. For  $H_2+C_2H_6$  hydrates mass percentage of hydrogen decreases from 3.33 to 0.04 wt%. For  $H_2+C_3H_8$  hydrates the mass percentage of hydrogen decreases from 3.51 to 0.21 wt% as the propane concentration increases to 1% in the gas phase.

Figure 3 shows the dependence of the mass percent of hydrogen contained in  $H_2+CH_4$ ,  $H_2+C_3H_8$  CS-II hydrates and  $H_2+C_2H_6$  CS-I hydrates on their formation pressure.



**Figure 3.** The dependence of the mass percentage (wt%) of hydrogen contained in  $H_2$ +CH<sub>4</sub>,  $H_2$ +C<sub>2</sub>H<sub>6</sub>, and  $H_2$ +C<sub>3</sub>H<sub>8</sub> hydrates on their formation pressure (P, MPa).

When the formation pressure of  $H_2+CH_4$  hydrate increases from 40 to 78.7 MPa the mass percentage of hydrogen increases from 1.25 to 3 wt%. Mass percentage of hydrogen in  $H_2+C_2H_6$  hydrate increases from 0.04 to 3.33 wt% with increasing the formation pressure from 5.9 to 98.5 MPa. Mass percentage of hydrogen in  $H_2+C_3H_8$  hydrate increases from 0.21 to 3.51 wt% with increasing formation pressure from

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10 to 78.7 MPa. Presented calculations are in agreement with the experimental data on mixed hydrogen + methane [17,36,37], hydrogen + ethane [19] and hydrogen + propane [20] hydrates.

#### 4. Conclusions

The curves of the monovariant equilibrium in "gas-hydrate-ice Ih" system for hydrogen + methane, hydrogen + ethane and hydrogen+propane double hydrates are calculated and well agree with the available experimental data. When the second gas concentration in the gas phase increases, the pressure of hydrate formation decreases significantly (figure 1) and at the same time the mass percentage of hydrogen in the hydrate decreases (figure 2). However, at sufficiently high mass percentage of hydrogen 2 wt% at T = 250 K the formation pressure is lower than the hydrogen hydrate formation pressure (figure 3). Mass percentage of hydrogen in the formed hydrates can be increased by increasing the pressure in the gas phase. It allows considering the mixed hydrates as advanced materials for hydrogen storage.

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