Theoretical study of stability zones of mixed H\textsubscript{2} + CO\textsubscript{2} gas hydrates CS-I and CS-II

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Abstract. Using the original approach that utilizes statistical thermodynamic theory that has been developed in our group the phase p-T diagram and hydrate phase composition have been calculated for “CO\textsubscript{2} + H\textsubscript{2} + H\textsubscript{2}O”. Depending on the CO\textsubscript{2} content in the gas phase two hydrates types can be formed: CS-I and CS-II. It has been found that increasing CO\textsubscript{2} content in the gas phase drastically reduces hydrate formation pressure and in the same time reduces hydrogen uptake by the hydrate. While pure H\textsubscript{2} hydrates have CS-II structure, addition of more than 2 mol.% of CO\textsubscript{2} into the gas phase makes CS-I hydrate structure more stable, that displays worse maximum hydrogen content. These results could be helpful for practical use of hydrates for efficient CO\textsubscript{2} utilization and H\textsubscript{2} transportation.

1. Introduction

The use of hydrogen as an environmentally friendly fuel (so-called “hydrogen economy”) is considered as part of "low-carbon economy" trend that should replace the "hydrocarbon economy" in the future. Along with the search for technology for economically viable hydrogen gas production, there is the problem of finding an efficient way to store it. Currently, various solutions are being investigated: they involve low temperatures (liquid hydrogen), high pressures (compressed hydrogen), as well as various compounds that can enclose and reversibly release hydrogen molecules upon decomposition. Such compounds are metal and non-metal hydrides, compounds based on carbon (including nanotubes and carbohydrates) and nitrogen, ionic liquids, metal-organic frameworks, as well as clathrate hydrates. Clathrate hydrates are inclusion compounds formed by the host lattice (water molecules) and guest molecules placed in it. Like hydrogen itself, clathrate hydrates are the most environmentally friendly way to store and transport hydrogen.

Pure hydrogen hydrate is formed at pressures of above 1 kbar in the temperature range 263-283K [1] or at ambient pressure at 145K [2]. Later it was possible to significantly reduce the pressure of hydrate formation to 50 bar at ~280 K by adding THF to the gas mixture [3].

The high pressure (or low temperature) of hydrogen hydrate formation has opened the way for industrial gas separation under conditions where the hydrate formation of pure hydrogen or hydrogen-containing mixture is impossible. For example, it is possible to carry out the separation of carbon dioxide by this method. In the process of gasification (the oxidation of oil, coal, peat, fuel oil and tar in an atmosphere of oxygen, air, water vapor, carbon dioxide at a temperature of 1000-2000 °C and
pressure up to 10 MPa) up to 80% of the organic part of the fuel passes into the gas phase. The gasification process is accompanied by the release of energy and $H_2 + CO_2$ gas mixture (during Fischer-Tropsch process). This mixture is the main source of hydrogen. Clathrate hydrates are used to separate $H_2 + CO_2$ mixture into its components [4,5]. Upon decompression the double $H_2 + CO_2$ hydrate releases the $H_2$, which can be used in fuel cells or gas turbines further, whereas the remaining $CO_2$ in hydrate form can be utilized [6] or used in the formation of hydrocarbons.

Pure hydrogen forms hydrate of cubic structure II (CS-II), while pure carbon dioxide leads to the formation of cubic structure I (CS-I) hydrate. The structure of the mixed hydrate depends both on the thermodynamic conditions and the composition of the gas mixture. The aims of this work are to determine the structure of the double hydrate depending on thermodynamic conditions and gas phase composition, as well as to build the phase diagram “ice Ih – $H_2 + CO_2$ hydrate CS-I – $H_2 + CO_2$ hydrate CS-II – gas mixture” using the molecular and lattice dynamics methods.

2. Computational details
In our previous research works we successfully used our theoretical statistical thermodynamic model to describe physical properties of mixed hydrogen contained gas hydrates as hydrogen + methane [7], hydrogen + ethane [8], hydrogen + argon [9]. This model is based on classical van der Waals and Platteuw model but with lesser number of restrictions [10]. In the current work we used the same approach to describe mixed hydrogen + carbon dioxide hydrates. Additionally, it should be said that depending on the carbon dioxide content in the gas phase, formation of CS-I or CS-II hydrates is expected.

In this work carbon dioxide molecules were considered as one point particles with van der Waals potential described by the Lennard-Jones potential with parameters taken from work [11].

3. Results and discussion
Unlike previously studied cases like methane or argon, carbon dioxide case displays high solubility in water, therefore, phase equilibrium of hydrate with water phase should be studied carefully. At the first step we tried to reproduce phase diagram of $H_2O + CO_2$ system (Fig. 1). In this calculation we assumed that $CO_2$ is presented as a gas phase, and didn’t consider another possible carbon dioxide phases. At temperature lower than ice melting point (273 K) the calculated data match experimental values with high accuracy, especially at temperature over 230 K. But the behaviour of the calculated

![Figure 1. Hydrate phase diagram for CO2 gas hydrates. Blue line with solid dots is calculated values, circles [12], crosses [13], and squares [14] are experimental data.](image-url)
equilibrium line “CO$_2$ – water – hydrate” doesn’t follow the experimental data and the divergence from the experimental data increases with increasing temperature. As has been told before carbon dioxide has high solubility in water that strongly affects chemical potential of water molecules and introduces an error into the hydrate model. Because of this fact we decided to proceed calculations for water + CO$_2$ + H$_2$ system only for temperatures less than 273 K. The similar line for H$_2$ hydrate case has been already presented in our previous paper [15], in this paper we have increased the number of points on the temperature (see Fig. 3) in comparison with work [15].

Carbon dioxide gas and hydrogen gas separately form hydrates of CS-I and CS-II, respectively. For CO$_2$ + H$_2$ gas phase the hydrate structure depends on the gas phase composition. Fig. 2 presented formation pressure dependence of CS-I and CS-II CO$_2$ + H$_2$ hydrates on the gas phase composition at a fixed temperature of 250 K. It can be seen that the increasing carbon dioxide content strongly influences the formation pressure of CS-I hydrate and reduces it ~10 times at 10 mol.% of CO$_2$. At the same time an increase in CO$_2$ content also reduces CS-II hydrate formation pressure, but not as much as for CS-I case: at 10 mol.% formation pressure drops ~2 times. The intersection of CS-I and CS-II formation pressure lines gives the CO$_2$ content in the gas phase where phase transition between CS-I and CS-II occurs. At 250 K transition point is ~2.5 mol.% of CO$_2$. According to our calculations at different temperatures the transition point remains almost the same. In our earlier works we calculated the same transition conditions for CH$_4$ + H$_2$ and C$_2$H$_6$ + H$_2$ gas hydrates. It has been found that the CS-I to CS-II transition for the methane case occurs at ~5.5 mol.% [7], for ethane case at ~0.5 mol.% [8], that makes carbon dioxide influence intermediate. Such behaviour correlates with the increase of the C$_2$H$_6$, CO$_2$, and CH$_4$ hydrates formation pressure.

As it was mentioned earlier, the introduction of carbon dioxide causes reduction of gas hydrate formation. Fig. 3 presents the calculated monovariant “hydrate – gas – ice” equilibrium lines. Even very low carbon dioxide concentration in the gas phase can significantly reduce gas hydrate formation. For example at 2.5 mol.% of CO$_2$ formation pressure decreases ~2 times. Further increase of CO$_2$ content also drastically reduces hydrate formation pressure. Since at the highest carbon dioxide concentration in the gas phase the structure CS-I is more preferable the hydrogen content in this structure is very low, because only small cavities are available for hydrogen to occupy.
Figure 3. Hydrate – gas – ice equilibrium lines for carbon dioxide (blue line with closed circles), hydrogen (black line with crosses), and mixed CO$_2$+H$_2$ hydrates (green line with open circles) formed from gas phase with 2.5 mol.% CO$_2$ in the gas phase.

Conclusions
In this work we used the statistical thermodynamic model developed in our group to calculate thermodynamic properties of mixed carbon dioxide + hydrogen gas hydrates. The phase transition lines of CO$_2$ + H$_2$ hydrate CS-I and CS-II have been calculated and compared with the known experimental data. At temperature less than 273 K our results are in a good agreement with the experiment. The influence of CO$_2$ content in the gas phase on the hydrate formation pressure and the hydrate structure is crucial.

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