

# Thermodynamic Modeling of CO<sub>2</sub>+THF sII hydrate phase equilibria: Implication for hydrate-based CO<sub>2</sub> sequestration<sup>#</sup>

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## ABSTRACT

Hydrate-based CO<sub>2</sub> sequestration has emerged as one of the possible methods for the long-term storage of CO<sub>2</sub> as hydrates within the geological media, notably under marine sediments. In this direction, a thermodynamic model for the phase equilibria of CO<sub>2</sub> hydrates in pure water and THF solutions ( $\leq 5.56$  mol%), based on the fugacity approach is employed to predict the three-phase (LHV) equilibrium pressures and the fractional occupancy of CO<sub>2</sub> and THF molecules in small and large cages. The hydrate, vapor, and liquid phases are modeled using the van der Waals-Platteeuw solid solution theory, Peng-Robinson-Stryjek-Vera equation of state, and the modified UNIFAC method, respectively. The model-predicted equilibrium pressures are in excellent agreement with experimental data with an AAD of 1.55%. The presence of THF has greatly reduced the CO<sub>2</sub> hydrate equilibrium pressures. The cage occupancy results revealed the reduction in small cage occupancy of CO<sub>2</sub> at ( $\geq$ ) 1.296 mol% THF and a continuous substantial decrease in large cage occupancy of CO<sub>2</sub> with increased THF concentration. However, the overall hydrate stability is ensured by the large cage occupancy of the large molecule THF in larger fractions. This study is an important precursor for future hydrate-based CO<sub>2</sub> sequestration.

**Keywords:** gas hydrates, CO<sub>2</sub> sequestration, mitigation technologies, thermodynamic modeling, THF, cage occupancy.

## NONMENCLATURE

### Abbreviations

LHV	liquid-hydrate-vapor
UNIFAC	Universal quasi-chemical Functional Group Activity Coefficients
%AAD	Percent absolute average deviation
THF	Tetrahydrofuran

$M$	Type of cavity (small or large)
$i, j$	Number of guest components
$n$	Total number of data points

## 1. INTRODUCTION

The continued increase in atmospheric greenhouse gases especially the increased CO<sub>2</sub> level is a serious threat to the global environment [1–3]. However, for a sustainable future, long-term CO<sub>2</sub> mitigation is essential and this is one of the urgent and a pressing issue that needs immediate attention to be addressed. Several CO<sub>2</sub> sequestration technologies have been proposed and tried; however, safe, long-term, cost-effective, stable, and high storage capacity are still issues that need to be considered seriously before the actual commercialization of any CO<sub>2</sub> sequestration process [2,3]. More recently, hydrate-based CO<sub>2</sub> sequestration has been regarded as an effective way to bring carbon neutrality, in which, CO<sub>2</sub> as a guest substance can be stored in the network of hydrogen-bonded water cavities that forms non-stoichiometric, crystalline solid hydrate at a certain temperature and pressure condition [1–3].

Gas hydrates have been studied extensively since Davy discovered hydrate formed from chlorine for the first time in 1810. Ever since then, these compounds have been the subject of curiosity all over the world to industry and academia due to their other potential importance such as in the flow assurance industry for their unwanted formation in pipelines, for their presence as natural gas hydrates that are considered as a source of energy, in storage and transportation of gases as hydrates, separation, desalination, refrigeration, and carbon sequestration [1,4–6]. Depending on the size of the guest molecule that is trapped inside the hydrate cages, either structure I/II/H is formed. All three hydrate structures have 5<sup>12</sup> as a common small cage that is formed by the combination of 12 pentagonal faces. Similarly, a 5<sup>12</sup>6<sup>2</sup> and 5<sup>12</sup>6<sup>4</sup> are the large cage types in sl

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and sII hydrate structure, respectively. A sH hydrate contains medium  $4^35^66^3$  and large  $5^{12}6^8$  cage type. A unit cell of sI hydrate has 2 small and 6 large cages, a sII hydrate has 16 small and 8 large cages, and sH hydrate has 1 small, 2 medium and 1 large cage per unit cell [1,4–6].

These solid compounds are highly compact as they release nearly  $184 \text{ m}^3$  of  $\text{CO}_2$  gas from a  $1 \text{ m}^3$  of  $\text{CO}_2$  hydrate at STP conditions [1]. Also, natural gas hydrates have existed in nature under deep marine sediments for millions of years; hence, the technology of  $\text{CO}_2$  sequestration as hydrates in deep marine sediments is quite possible. However, it is essential to confirm the structural stability and high storage capacity of  $\text{CO}_2$  hydrate forming at moderate conditions. A promoter such as THF is very well known to shift the thermodynamic condition of any hydrate and also influences guest occupancy in hydrate cages [7].

Therefore, in this direction, we have developed a fugacity-based thermodynamic model to predict the equilibrium pressures for  $\text{CO}_2$  hydrate in three-phase LHV equilibria. Here, the hydrate phase is modeled using the van der Waals-Platteeuw (vdWP) solid solution theory. The fugacity of gas molecules in the vapor phase has been computed from the Peng-Robinson-Stryjek-Vera equation of state. Liquid phase activity coefficients are determined from the modified UNIFAC method for both the pure water system and the system involving the THF solution. In addition to the hydrate equilibrium pressure predictions, we have also predicted the guest occupancies in the hydrate cages through the developed model, which helped determine how much fraction of the hydrate cages are filled with  $\text{CO}_2$  and THF. The following sections describe the thermodynamic model developed, the results and discussions, and then the conclusions at the end.

## 2. THERMODYNAMIC MODEL

The proposed thermodynamic model for three-phase LHV equilibria of gas hydrates is based on the fugacity approach where the fugacity of water ( $f_w$ ) in the hydrate phase ( $H$ ) is equated to the fugacity of water in the coexisting liquid phase ( $L$ ) [8]:

$$f_w^H = f_w^L \quad (1)$$

We have investigated the Peng-Robinson-Stryjek-Vera (PRSV) equation of state to estimate the fugacity of the gaseous component  $\text{CO}_2$  in the vapor phase. The liquid phase activity coefficients have been estimated from the modified UNIFAC method (for both pure water and THF solutions) whereas the hydrate phase has been modeled

using the vdWP theory. The change in equilibrium condition due to the presence of THF has been taken into account through the changes in the reference hydrate vapor pressure and the Langmuir constant values.

The occupancy of guest molecules in small and large cages that helps in determining the fraction of  $\text{CO}_2$  and THF getting occupied in the hydrate cages is dependent on the product of the Langmuir constant ( $C$ : describes the guest-water interaction inside the cavity) and fugacity ( $f$ ) and is given by Eq. (2).

$$\theta_{ml} = \frac{C_{ml} f_l}{1 + \sum_i C_{mj} f_j} \quad (2)$$

The Langmuir constant is a function of temperature and is being estimated from the expression and the required parameters as given in Kluada and Sandler's work [8].

$$\% \text{AAD} = \frac{100}{n} \sum_{i=1}^n \left| \frac{P_i^{\text{exp}} - P_i^{\text{model}}}{P_i^{\text{exp}}} \right| \quad (3)$$

At equilibrium, the fugacity of water in the hydrate phase and the liquid phase will become equal and the equilibrium pressure will be predicted for the given temperature. The accuracy of the model is confirmed by finding the absolute deviation between the model predicted pressure ( $P^{\text{model}}$ ) and experimental pressure ( $P^{\text{exp}}$ ) at each point. The %AAD over the 'n' number of data points is calculated using the eq. (3).

## 3. RESULTS AND DISCUSSIONS

The developed model is being used to predict the equilibrium pressure for  $\text{CO}_2$  hydrate in LHV equilibria. In addition, we have predicted the cage occupancies of  $\text{CO}_2$  and THF in small and large cages of the hydrate accurately.

### 3.1 Phase equilibrium plot of $\text{CO}_2$ hydrate in pure water and THF solutions ( $\leq 5.56 \text{ mol}\%$ )

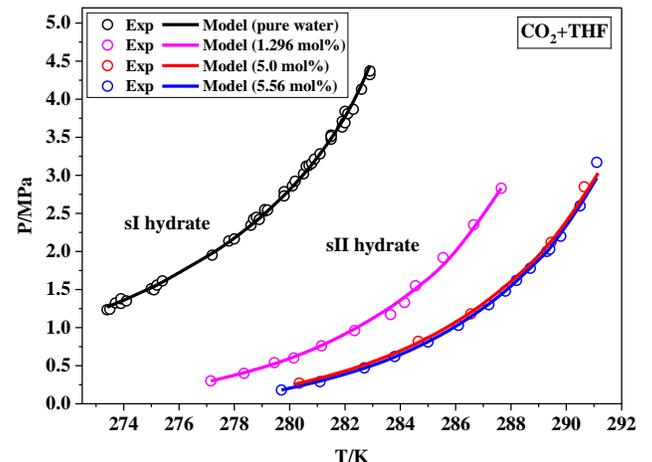


Fig. 1 Phase diagram ( $P$  vs.  $T$ ) for  $\text{CO}_2$  hydrate in pure water and in the presence of 1.296, 5.0, and 5.56 mol% THF solution [1,9–11].

Fig. 1 represents the phase equilibrium plot for  $\text{CO}_2$  hydrate formed in pure water (sI structure) and in the presence of varying THF concentrations such as 1.296, 5.0, and 5.56 mol% (sII structure). As seen in Fig. 1, the pressure required to form a stable  $\text{CO}_2$  hydrate in the presence of pure water at any given temperature is high compared to what it is required in the presence of THF. THF being a large molecule cannot fit into the large cage of sI hydrate; hence, a sII structure is formed in the presence of THF at any given concentration during the  $\text{CO}_2$  hydrate formation. A large molecule like THF has a very strong interaction with the large cage, and this ultimately reduces the overall hydrate equilibrium pressure and promotes the formation of a stable  $\text{CO}_2$  hydrate. As in Fig. 1, the equilibrium pressure keeps decreasing with the increase in THF concentration and reaches saturation at the stoichiometric THF concentration of 5.56 mol%. This confirms the fact that the hydrate can be stored under moderate conditions.

### 3.2 Cage occupancy of $\text{CO}_2$ /THF

#### 3.2.1 Small cage occupancy of $\text{CO}_2$

The cage occupancy details are of great importance as they give an idea of how much fraction of the hydrate cages are filled with  $\text{CO}_2$  and THF; and how THF affects the  $\text{CO}_2$  occupancy.

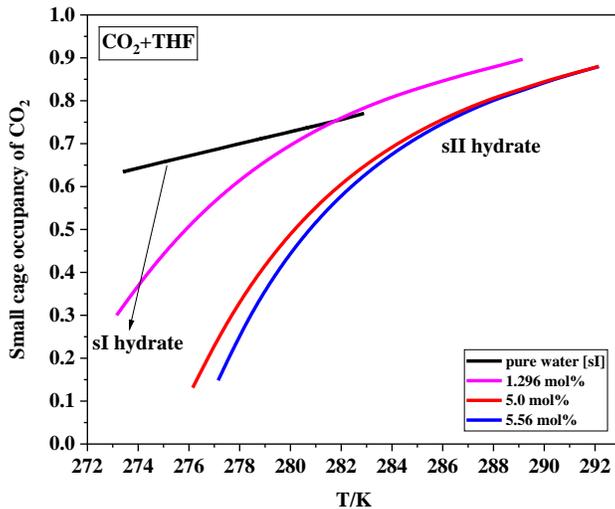


Fig. 2 Small cage occupancy of  $\text{CO}_2$  vs. temperature plot in the presence of 1.296, 5.0, and 5.56 mol% THF solution.

Fig. 2 represents the occupancy of  $\text{CO}_2$  in small cages of sI and sII hydrates with temperature. From Fig. 2, it is clear that the small cage occupancy of  $\text{CO}_2$  when hydrate forms sI structure is higher than the  $\text{CO}_2$

occupancy when hydrate forms sII structure in the presence of THF with a concentration of  $\leq 1.296$  mol%. However, the  $\text{CO}_2$  occupancy in small cages of sII hydrate structure at certain temperatures in THF solutions (especially at higher temperatures) is higher than  $\text{CO}_2$  occupancy in small cage sI hydrate structure. As mentioned in eq. (2) that the occupancy is a product between the Langmuir constant values and the fugacity values. The interactions between the guest and host molecule in small and large cages of sI and sII structure vary and this causes changes in the occupancies of the  $\text{CO}_2$  molecule in small cages of sII hydrate. However, in general, the occupancy of  $\text{CO}_2$  in small cages of sII hydrate seems to be affected by the presence of THF in large cages of sII hydrate.

#### 3.2.2 Large cage occupancy of THF and $\text{CO}_2$

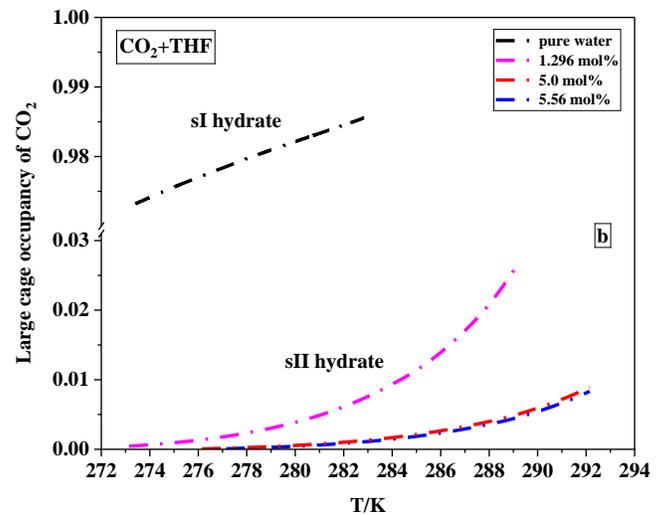
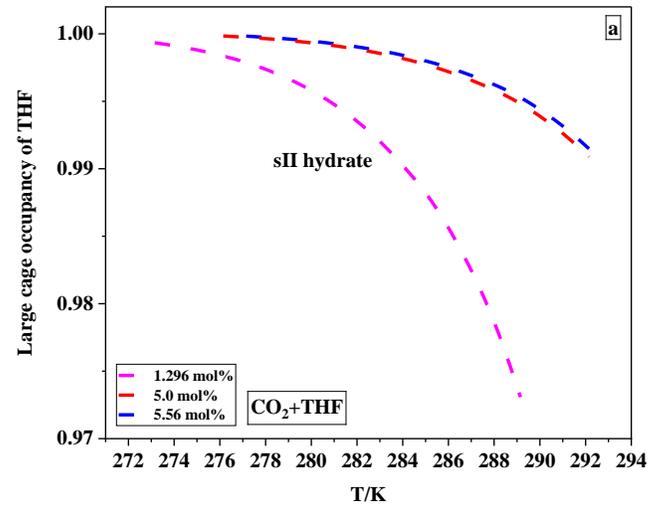


Fig. 3 Large cage occupancy vs. temperature plot for (a) THF (b)  $\text{CO}_2$ , in the presence of 1.296, 5.0, and 5.56 mol% THF solution.

The large THF molecule easily fits inside the large cage of sII hydrate, and hence, this leaves no place for the CO<sub>2</sub> molecules to get inside the larger cages of the sII hydrate. As seen in Fig. 3(a), the increase in THF concentration further increases the occupancy of THF molecules. Almost all the large cages are completely occupied by THF molecules at 5.56 mol% THF concentration. On the other hand, there is a possibility for a small fraction of CO<sub>2</sub> molecules to occupy large cages of sII hydrate; however, this is possible only at low concentration of THF such as 1.296 mol% (Fig. 3(b)). For higher THF concentrations such as 5.0 and 5.56 mol%, this value becomes insignificant. However, as in Fig. 3(b), compared to the CO<sub>2</sub> occupancy in large cages of sI hydrate, the occupancy of CO<sub>2</sub> in large cages of sII hydrate is completely affected only due to the presence of THF molecule. The increase in temperature decreases the occupancy of THF and increases the CO<sub>2</sub> occupancy in larger cages of sII hydrate.

### 3.2.3 Fractional occupancy of THF and CO<sub>2</sub> in the hydrate phase

Fig. 4 represents the fractional occupancy of CO<sub>2</sub> and THF in the hydrate phase. The fractional occupancy of CO<sub>2</sub> in pure water is 100% as there will be only CO<sub>2</sub> as a guest molecule during the hydrate formation. However, in the presence of THF in the solution, a mixed hydrate will be formed and this will lead to the occupancy of CO<sub>2</sub> and THF divide in the hydrate phase in different fractions depending upon the THF concentration.

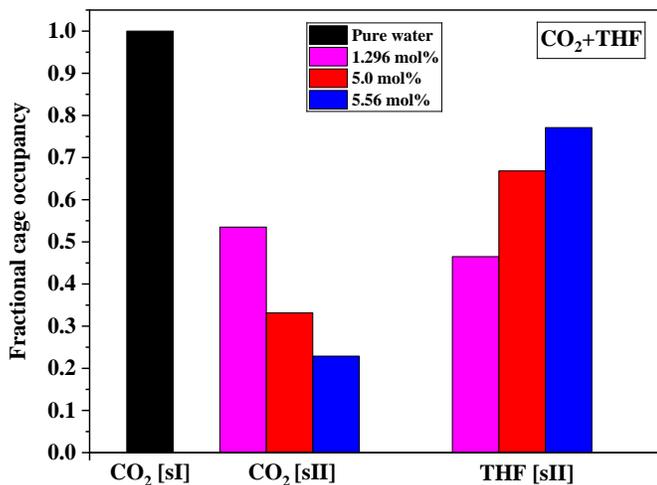


Fig. 4 Fractional occupancy of CO<sub>2</sub> and THF molecule in pure water and in the presence of 1.296, 5.0, and 5.56 mol% THF solution at 277.15 K.

As seen in Fig. 4, the fractional occupancy of CO<sub>2</sub> in the hydrate phase at 1.296 mol% THF concentration is higher than the THF fraction; however, the THF fraction

in the hydrate phase seems to be higher than the CO<sub>2</sub> fraction for THF concentrations at 5.0 and 5.56 mol%. This confirms the fact that the THF concentration plays a crucial role in deciding the storage capacity of the CO<sub>2</sub> in the hydrate phase.

## 4. CONCLUSIONS

In this work, a fugacity-based thermodynamic model is developed that predicts the equilibrium pressures for CO<sub>2</sub> hydrate formed in pure water and in THF solutions (1.296, 5.0, and 5.56 mol%) precisely with an AAD of 1.55%. The CO<sub>2</sub> hydrate equilibrium pressures in the presence of THF are drastically reduced up to 5.56 mol% concentration compared to the equilibrium pressures of CO<sub>2</sub> hydrate formed in pure water presenting the strong promotion effect of THF. The small cage occupancy of CO<sub>2</sub> molecules in sII hydrate for any THF concentration (except at certain higher temperatures) are found to be lower than the values of CO<sub>2</sub> occupancy in small cages of sI hydrate structure, confirming the impact of THF even on the small cage occupancy of CO<sub>2</sub>. The large cages are mostly occupied by THF molecules due to their large size and this makes it difficult for the CO<sub>2</sub> molecules to occupy in large cages of sII hydrate. However, at low THF concentration (1.296 mol%), a small fraction of CO<sub>2</sub> molecules occupied the large cages of sII hydrate and this value kept increasing with the increase in temperature. The fraction of CO<sub>2</sub> in the hydrate phase at a low concentration of THF (1.296 mol%) is higher than the THF fraction. However, at 5.0 and 5.56 mol% THF, the fraction of THF in the hydrate phase is observed to be higher than the CO<sub>2</sub> fraction. The THF concentration plays an important role in deciding the overall fraction of CO<sub>2</sub> to be stored in the hydrate phase. This overall study is an important contribution towards a better understanding of the phase equilibria and the cage occupancies of CO<sub>2</sub> and THF in the hydrate phase and helps in the advancement of CO<sub>2</sub> sequestration as hydrates in the marine environment and for CO<sub>2</sub> storage applications.

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