J. Chem. Thermodynamics 44 (2012) 5–12

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Molecular dynamics Gibbs free energy calculations for CO_2 capture and storage in structure I clathrate hydrates in the presence of SO_2, CH_4, N_2, and H_2S impurities ☆

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ARTICLE INFO

Article history:
Received 26 August 2011
Received in revised form 28 August 2011
Accepted 30 August 2011
Available online 7 September 2011

Keywords:
Clathrate hydrates
Molecular dynamics
Free energy calculations
Carbon dioxide sequestration
Thermodynamic integration
Carbon capture and storage
Sulfur dioxide
Flue gas

ABSTRACT

The capture of CO_2 from flue gas in coal, natural gas, and other fossil fuel burning power stations and storage of CO_2 in depleted gas reservoirs in the form of the solid clathrate hydrate have been suggested as methods of carbon capture and storage. These methods have the benefit of only needing water as the CO_2 capturing material. The flue gas contains impurities including SO_2, CH_4, N_2, and H_2S which can interfere with the CO_2 hydrate formation process. Some of these gases may also be found as residuals in depleted natural gas reservoirs. In this work, we use the molecular dynamics thermodynamic integration method to calculate the Gibbs free energy of the substitution reactions at conditions relevant to carbon capture ($T = 200$ K and 0.1 MPa and at 273 K and 1.0 MPa conditions),

$$\text{clathrate}[CO_2, p, T] + Y(\text{fluid}, p, T) \rightarrow \text{clathrate}[Y, p, T] + CO_2(\text{fluid}, p, T)$$

where Y is the impurity species in the flue. Knowledge of the Gibbs free energy for this reaction will allow us to determine whether the impurities need to be eliminated from the flue or can participate in the hydrate formation process as neutral species without affecting the stability of the desired CO_2 clathrate hydrate. For the thermodynamic integration, we use the nonlinear mixing scheme. In addition to calculating the ΔG for the above reaction, the contributions of different terms in the intermolecular potential of the guest molecules to the ΔG will be determined.

1. Introduction

World energy demands and the cost (real and perceived) associated with the start up of new technologies for energy production mean that fossil fuels will continue to be used for power generation and therefore CO_2 will continue to be emitted at high rates from flue stacks in combustion plants. Coal combustion for power generation alone produces 7 giga tonnes of anthropogenic CO_2 per year [1]. Although CO_2 is not considered a particularly potent greenhouse gas (GHG), its importance is due to the rate of increase of this gas in the atmosphere. Carbon capture and storage (CCS) represent a serious strategy to reduce the environmental impact of energy production by capturing CO_2 from the combustion gas and storing it permanently.

At the moment, the most significant barrier to large scale CCS from fuel burning power plants is that a low energy CO_2 scrubbing technology does not exist, although several methodologies are being explored and developed. One CO_2 scrubbing method in wide use is based on aqueous amines which are used to capture the CO_2 from the flue gas by chemisorption [2]. However, recovery of the sorbant after the gas capture process is very energy intensive due to the heating of the solution that is required. The liquid is also toxic and corrosive, making alternatives to this approach desirable. Another technology that has received wide attention is the use of nanoporous solids, such as metal organic frameworks (MOFs) to capture CO_2(g) in flue gas [3]. The combustion flue stream is composed of CO_2(g), O_2(g), H_2O(g), SO_2(g), and N_2(g) [4]. A problem with the MOF materials (other than their current high cost of production) is that they are susceptible to being poisoned by water [5]. Recently, it has been proposed to use the clathrate hydrate formation potential of CO_2(g) gas under pressure ((1.5 to 2.5) MPa at $T = 273$ K) as a means of CO_2(g) capture from model combustion flue streams [6,7]. There are two advantages of using clathrate hydrates instead of other novel technologies for CO_2(g) capture. The first is that the only material needed to capture the gas is water and no other hazardous or expensive materials are involved. The second, whereas other novel technologies are poisoned by water, which hinders there uptake capabilities, clathrate hydrates rely on water to capture the gas. Thus the abundant H_2O found in flue gas should not pose any problems to the operation.

☆ Paper for gas hydrate initiative

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doi:10.1016/j.jct.2011.08.025

Understanding how impurities present in the flue gas may influence the formation of CO_2 clathrate hydrates is important to using these materials for both carbon capture and storage. For example, Beeskow and coworkers recently studied the effects of 1% SO_2 and NO_2 impurities on the CO_2 hydrate formation process [8]. They found an enrichment of SO_2 in the hydrate phase compared to the gas concentration, which suggests that clathrate hydrate formation also removes these unwanted contaminants from the flue. In the arena of permanent storage, clathrate hydrates may also play a role depending on how the CO_2 is stored. For example, permanent storage under deep ocean sediments [9] and depleted oil and gas fields [10] has been proposed, where clathrate hydrate formation prevents the dispersal and leakage of the CO_2 back into the ocean water. Injection of CO_2 into sediment layers in colder northern climates or under lakes and ocean beds where conditions may be appropriate for hydrate formation has been suggested as a route for carbon storage [11–13]. In all of these processes, the impurities in the flue gas that are captured and injected with the CO_2 or existing gases in the injection site, such as methane may interfere with the CO_2 storage process.

Under pressure, cubic structure I (sI) is the stable phase of the $CO_2(g)$ clathrate hydrate which makes it a prime candidate for testing flue gas capture performance [6,7]. The latter's unit cell consists of two "small" (s) 12-sided cages with pentagonal faces [5^{12}] and six "large" (l) 14-sided cages composed of twelve pentagonal and two hexagonal sides [$5^{12}6^2$] giving the sI unit cell a formula of $S_2L_6{\cdot}46H_2O$. The structure of the small and large sI clathrate hydrate cages are shown in figure 1. Each cage can theoretically hold one CO_2 molecule.

Clathrate stabilities and gas substitution thermodynamics have been previously studied via molecular dynamics simulations. The Gibbs free energy associated with different guest loadings for various gasses (Ne, Ar, Xe and CH_4) was calculated to determine the optimal capacity for storage in these clathrates under different pressure conditions [14,15]. More recently we [16,17] have used, MD Gibbs free energy calculations to examine CO_2 clathrate hydrates under conditions relevant to permanent deep sea storage of CO_2 [9].

In this work, we examine the substitution thermodynamics of CO_2 clathrate hydrates with common combustion gases under conditions relevant for CO_2 capture, storage, and related gas purification applications. Flue gas has a weight composition of 65.96% $CO_2(g)$, 8.29% $N_2(g)$ and Ar(g), 1.28% $O_2(g)$, 0.80% $SO_2(g)$ and other gases forming fractions of the output [4]. To evaluate the potential of these other gases to disrupt the $CO_2(g)$ clathrate hydrate formation, we perform a series of molecular dynamics Gibbs free energy calculations based on thermodynamic integration to determine the relative thermodynamic stability of the different clathrates under the conditions of flue gas. The free energies of substituting $CO_2(g)$ with other guests or combinations of other guests will give us insight into the efficiency and practicality of clathrate hydrates as carbon dioxide capture tools in flue stacks. Furthermore this work studies the substitution of CO_2 from both large and small clathrate hydrate cages to determine which ones are the favoured sites for substitution with different guests. This study examines the free energies of substituting $CO_2(g)$ with $SO_2(g)$, $H_2S(g)$, $N_2(g)$ and $CH_4(g)$ gases found in industrial flue streams. Finally, we determine the separate contributions of the van der Waals and electrostatic parts of the intermolecular potential energy to the total Gibbs free energy of CO_2 substitution to get further insight on the major factors which contribute to clathrate stability and selectivity.

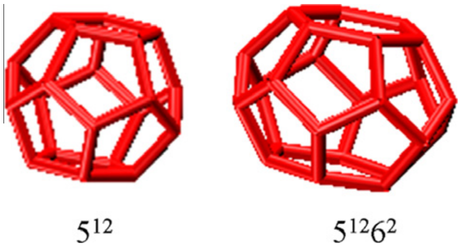

FIGURE 1. The structure of the small (5^{12}) and large ($5^{12}6^2$) cages of the sI clathrate hydrate. The effective diameter of the small cage is 0.484 nm and the major and minor axes of the large cage are 0.612 and 0.507 nm, respectively.

2. Thermodynamics of the guest substitution

We are interested in determining the Gibbs free energy associated with the transformations,

$$\begin{aligned}&\text{clathrate}[(n+x)\text{CO}_2]+x\text{Y(g)}\\&\quad\rightarrow\text{clathrate}[n\text{CO}_2+x\text{Y}]+x\text{CO}_2\text{(g)},\end{aligned}\tag{1}$$

where x molecules of gas Y (SO_2, CH_4, H_2S, N_2) at a temperature T and pressure p replace xCO_2 molecules from the structure I (sI) clathrate hydrate. The CO_2 molecules originally in the clathrate hydrate phase are released into the gas (fluid) phase. The Gibbs free energy of this reaction determines whether the CO_2 hydrate is thermodynamically stable when exposed to impurity Y in the flue stream.

For the $xCO_2(g)$ molecules in the gas phase at T and p, the Gibbs free energy is,

$$G^{\text{g}}_{\text{CO}_2}=xkT\ln\left(\frac{\rho_{\text{CO}_2}(\text{g};T,p)}{q_{\text{CO}_2}}\right)+x\mu_{res}[\text{CO}_2(\text{g};T,p)].\tag{2}$$

The $\rho_{\text{CO}_2}(\text{g};T,p)$ is the number density of the $CO_2(g)$ in the gas phase and $q_{\text{CO}_2}(T)$ is the ideal gas $CO_2(g)$ partition function. The residual chemical potential for $CO_2(g)$ in the gas phase is determined by the thermodynamic expression,

$$\mu_{res}[\text{CO}_2(\text{g};T,p)]=\int_1^p[V(p,T)-V^{\text{ig}}(p,T)]dp,\tag{3}$$

where the real gas molar volume for $CO_2(g)$, $V(p,T)$ can be determined from experimental measurements at T and p, or calculated from MD simulations. For xCO_2 molecules in the clathrate hydrate phase at T and p, the Gibbs free energy is,

$$G^{\text{clathrate}}_{\text{CO}_2}=xkT\ln\left(\frac{\rho_{\text{CO}_2}(\text{clathrate};T,p)}{q_{\text{CO}_2}}\right)+x\mu_{res}[\text{CO}_2(\text{clathrate})],\tag{4}$$

where $\rho_{\text{CO}_2}(\text{clathrate};T,p)$ is the number density of the xCO_2 molecules in the clathrate phase and the clathrate residual chemical potential, $x\mu_{res}[\text{CO}_2(\text{clathrate})]$ is calculated using molecular dynamics thermodynamic integration, see below. Similar expressions can be written for the Gibbs free energy of the xY guest molecules in the simulation cell.

Combining equations (2) and (4) and the corresponding relations for the free energies of the Y guest, we determine the expression for the total Gibbs free energy of equation (1),

$$\begin{aligned}\Delta G_{\text{total}}=xkT&\left[\ln\left(\frac{\rho_{\text{Y}}(\text{clathrate};T,p)}{\rho_{\text{CO}_2}(\text{clathrate};T,p)}\right)+\ln\left(\frac{\rho_{\text{CO}_2}(\text{g};T,p)}{\rho_{\text{Y}}(\text{g};T,p)}\right)\right]\\&+x\{\mu_{res}[\text{Y(clathrate)}]-\mu_{res}[\text{CO}_2(\text{clathrate})]\}\\&+x\{\mu_{res}[\text{CO}_2(\text{g})]-\mu_{res}[\text{Y(g)}]\}.\end{aligned}\tag{5}$$

If as a first approximation, we assume that $CO_2(g)$ and Y (g) behave as ideal gases under the conditions of the experiment which leads to $\rho_{\text{CO}_2}(\text{g};T,p)=\rho_{\text{Y}}(\text{g};T,p)$ and $\mu_{res}[\text{CO}_2(g)]=\mu_{res}[\text{Y(g)}]=0$. If