Determination of the Gibbs Free Energy of Gas Replacement in SI Clathrate Hydrates by Molecular Simulation

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The thermodynamic feasibility of extracting CH_4 gas from its hydrate clathrate by CO_2 replacement is analyzed by molecular dynamics simulation. The approach to this investigation is the proof-of-principles and the development of the molecular tools to study the replacement equilibrium process. The effect of the water (model) description on the free energy of the replacement process is discussed and some relevant implications regarding the real process are addressed.

I. Introduction

The steady increase in atmospheric concentration of carbon dioxide, typically 30% of global anthropogenic emissions, is being considered as the chief cause of global warming by the greenhouse effect.[1,2] One possible way to restrain this increase is to separate the carbon dioxide from the discharge sources and then to sequester it for a long-term storage [3]. Interestingly, there are two complementary sides to this story. On one hand, there is Marchetti's[4] suggestion for ocean sequestration of carbon dioxide as a possible route to alleviate this situation. This idea has become both a promising and a controversial alternative for controlling and/or capturing this greenhouse gas.[5−7] On the other hand, there have been counter suggestions that the sequestration of CO_2 could take place through the exploitation of naturally occurring methane gas hydrates (whereby replacement of CH_4 by CO_2 gas that would create a scenario in which the CO_2 could provide the hydration energy necessary to decompose the CH_4 hydrates[8,9] and at the same time leave the unwanted CO_2 in a stable, long-term stored state).

In principle, it is expected that oceans can take large quantities of carbon dioxide in the form of gas clathrate.[10,11] Subsequent work indicated the need for deep-sea injection of the gas to avoid possible outgassing into the atmosphere.[12] Moreover, more recent studies[13] suggested that shallow injection might also be an alternative as long as a denser solution is produced, a condition that would allow the sinking of the dissolved gas to greater depths.[14]

Natural gas deposits in the form of hydrates occur in the subterranean Arctic regions (permafrost) and the sea bottom,[15] where methane is the main constituent, and thus, they become a large source of fossil fuel as a potentially attractive clean energy resource.[16] Several methods for the exploitation of natural gas from hydrate deposits have been proposed, including thermal stimulation with steam or hot water injection, depressurization, and injection of hydrate inhibitors.[17] Any of these techniques will become energetically feasible if the energy required to decompose the hydrates is significantly smaller than the thermal energy recovered from the gas; economic feasibility is, of course, a separate issue.

The novelty of the gas replacement approach is the added benefit of CO_2 mitigation, by long-term sequestration as a gas hydrate, and simultaneous extraction of CH_4 gas from the CH_4 hydrate deposits. To test the feasibility of CH_4 displacement by CO_2 in the clathrate matrix (into the goal of its fixation in the deep ocean floor), we first need to determine the relative stability between CH_4 and CO_2 hydrates.

In this work, we report on the simulation methodology that can establish the thermodynamic feasibility of such a scenario; that is, CH_4 displacement by CO_2 will be thermodynamically feasible if the change in Gibbs free energy for this process is negative. In section II, we describe the coupling parameter-based method used in this investigation to determine efficiently the change of Gibbs free energy in the guest's mutation process. In section III, we present the intermolecular models, describe the simulation methodology, and discuss the simulation results. Finally, in section IV, we summarize the main findings and discuss the corresponding free energy of gas-replacement as well as the relevant implications.

II. Free Energy Approach

Let us first begin by defining an idealized process where a fully occupied methane gas sI clathrate hydrate will be transformed at constant temperature T and pressure P into a fully occupied sI carbon dioxide gas hydrate, where the free energy involved in this mutation process is denoted as $\Delta G^{CH_4 \rightarrow CO_2}$. Instead of attempting to define a simulation where the CH_4 guest molecules are explicitly transformed into CO_2 molecules (which would require a rather complex coupling parameter process to

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describe the conversion between CH_4's tetrahedral and CO_2's linear geometry), we apply a computationally simpler two-step thermodynamic cycle between our desired end states (the fully occupied CH_4 and CO_2 hydrates) and a common spherical reference particle, X. The net free energy change of our virtual molecular mutation, from CH_4 guest molecules to CO_2 molecules, then simply becomes equal to the appropriate difference in free energy between the two steps:

$$\Delta G^{CH_4 \rightarrow CO_2} = \Delta G^{CH_4 \rightarrow X} - \Delta G^{CO_2 \rightarrow X} \tag{1}$$

In addition, the Gibbs free energy of CH_4 and CO_2 mutation into the intermediate species X, can be further broken down into the change of the ideal gas and the corresponding residual contributions, i.e.:

$$\Delta G^{CH_4 \rightarrow X} = \Delta G^{CH_4 \rightarrow X}_{\text{ideal gas}} + \Delta G^{CH_4 \rightarrow X}_{\text{residual}} \tag{2}$$

$$\Delta G^{CO_2 \rightarrow X} = \Delta G^{CO_2 \rightarrow X}_{\text{ideal gas}} + \Delta G^{CO_2 \rightarrow X}_{\text{residual}} \tag{3}$$

The ideal gas contributions in eqs 2 and 3 can be determined exactly using standard statistical mechanical techniques as described in detail in the Appendix. The evaluation of the corresponding residual free energy terms, however, is considerably more complicated because they contain the free energy contributions associated with the transformation of the guest-solvent intermolecular interactions.

Typically, the change of residual free energy in a mutation process can be accurately determined by molecular simulation through the coupling parameter technique, commonly known as thermodynamic integration (TI). During a TI simulation, a coupling parameter, λ, is introduced into the system's Hamiltonian, H, such that $H(\lambda = 0)$ and $H(\lambda = 1)$ denote the two end states of the transformation process. The free energy change for the transformation can then be expressed by the integral[18]

$$\Delta G^{0 \rightarrow 1} = \int_0^1 \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{\lambda NPT} d\lambda \tag{4}$$

where the $\langle \partial H/\partial \lambda \rangle_{\lambda NPT}$ represents the isothermal–isobaric time averages determined directly from a simulation as a function of λ. Because we have explicitly separated the free energy of each of our transformations into the ideal gas and the residual components, eqs 2 and 3, we need only the configurational portion of the Hamiltonian to be a function of λ.

To calculate properly the free energy of mutation, we will need to define a Hamiltonian whereby the intermolecular interactions of the O in CO_2 and the H in CH_4 are removed, whereas the C interactions are converted into X interactions in a continuous fashion. For that purpose, we have used the following intermolecular potentials. For the reference species X, we have chosen the simple 12–6 Lennard-Jones model of argon ($\epsilon = 0.996$ kJ/mol, $\sigma = 3.41$ Å).[19] To be consistent with our previous work,[20] we describe CO_2 as the three-site model developed by Harris and Yung[21] and CH_4 according to the set VII of Williams' parametrization.[22] For the solvent, two different models of water were chosen, the SPC/E [23] and TIP5P.[24] All cross interactions were determined using the standard Lorentz–Berthelot combining rules, unless otherwise noted in Table 1.

Returning to the problem of designing our virtual mutation process, we can now define our simulation Hamiltonians for the calculations of eqs 2 and 3 as follows. For the CH_4 hydrate, the intermolecular interactions of the methane guest molecules were taken to be

$$\begin{aligned} U_{CH_4}(\lambda) = {} & \sum_{i=C<j=C} 4[\lambda\epsilon_C + (1-\lambda)\epsilon_{Ar}] \times \\ & \left[\left(\frac{\lambda\sigma_C + (1-\lambda)\sigma_{Ar}}{r_{i,j}}\right)^{12} - \left(\frac{\lambda\sigma_C + (1-\lambda)\sigma_{Ar}}{r_{i,j}}\right)^{6}\right] + \\ & \sum_{i\neq C<j\neq C} 4\lambda\epsilon_{i,j}\left[\left(\frac{1}{[\alpha(1-\lambda)^2 + (r/\sigma_{i,j})^6]^2}\right) - \right. \\ & \left.\left(\frac{1}{[\alpha(1-\lambda)^2 + (r/\sigma_{i,j})^6]}\right)\right] + \\ & \sum_{i\neq C<k} 4\lambda\epsilon_{i,k}\left[\left(\frac{1}{[\alpha(1-\lambda)^2 + (r/\sigma_{i,k})^6]^2}\right) - \right. \\ & \left.\left(\frac{1}{[\alpha(1-\lambda)^2 + (r/\sigma_{i,k})^6]}\right)\right] \end{aligned} \tag{5}$$

where σ and ϵ are the Lennard-Jones parameters and r is the site–site interaction distance. The summation indexes i and j refer to atoms in different guest molecules, whereas the index k refers to atoms in the host molecules (water).

The coupling parameter λ varies from 0 to 1 such that $\lambda = 0$ represents the intermolecular interactions in a pure Ar hydrate and $\lambda = 1$ represents the intermolecular interactions for a pure CH_4 hydrate. The quantity α is an arbitrary parameter (chosen to be equal to 0.5) introduced in order to remove well-documented singularities that can occur at $\lambda = 0$.[25] Likewise, for the CO_2 mutation to Ar, we used a similar representation to that of eq 5, with an additional coupling parameter to remove the partial charges of the Harris–Yung model prior to the mutation of the corresponding Lennard-Jones interactions. This additional step in the TI procedure was required in order to avoid poor configuration sampling due to the strong attraction between the partial charged sites as the Lennard-Jones' repulsive interactions were removed. As such, the interaction energy of a CO_2 hydrate was then defined as

$$U^{COUL}_{CO_2}(\lambda_1) = \frac{\lambda_1^2}{4\pi\epsilon_0}\sum_{i<j}\left(\frac{q_i q_j}{r_{i,j}}\right) + \frac{\lambda_1}{4\pi\epsilon_0}\sum_{i<k}\left(\frac{q_i q_k}{r_{i,k}}\right)$$

$$\begin{aligned} U^{VDW}_{CO_2}(\lambda_2) = {} & \sum_{i=C<j=C} 4[\lambda_2\epsilon_C + (1-\lambda_2)\epsilon_{Ar}] \times \\ & \left[\left(\frac{\lambda_2\sigma_C + (1-\lambda_2)\sigma_{Ar}}{r_{i,j}}\right)^{12} - \left(\frac{\lambda_2\sigma_C + (1-\lambda_2)\sigma_{Ar}}{r_{i,j}}\right)^{6}\right] + \\ & \sum_{i\neq C<j\neq C} 4\lambda_2\epsilon_{i,j}\left[\left(\frac{1}{[\alpha(1-\lambda_2)^2 + (r/\sigma_{i,j})^6]^2}\right) - \right. \\ & \left.\left(\frac{1}{[\alpha(1-\lambda_2)^2 + (r/\sigma_{i,j})^6]}\right)\right] + \\ & \sum_{i\neq C<k} 4\lambda_2\epsilon_{i,k}\left[\left(\frac{1}{[\alpha(1-\lambda_2)^2 + (r/\sigma_{i,k})^6]^2}\right) - \right. \\ & \left.\left(\frac{1}{[\alpha(1-\lambda_2)^2 + (r/\sigma_{i,k})^6]}\right)\right] \end{aligned} \tag{6}$$

such that, $U_{CO_2}(\lambda_1,\lambda_2) = U^{COUL}_{CO_2}(\lambda_1) + U^{VDW}_{CO_2}(\lambda_2)$.

To easily calculate the λ derivative of the Hamiltionian indicated in eq 4 during the course of our simulations, we have chosen to use the numeric differentiation

$$\frac{\partial H(\lambda)}{\partial \lambda} = \frac{U_{\text{Simulation}}(\lambda + \delta) - U_{\text{Simulation}}(\lambda - \delta)}{2\delta} \qquad (7)$$

where $U_{\text{simulation}}$ is the total configurational energy of the system at a given time step and the perturbation δ was set at 0.006025 and 0.005 for the Coulombic and van der Waals interactions, respectively. Although the calculation of the right-hand-side of eq 7 is quite straightforward for van der Waals interactions, the evaluation becomes slightly more complicated for Coulombic interactions. The simplest way to scale the Coulombic interactions effectively is to scale the magnitude of the solute partial charges while keeping the mutating molecule electroneutral. To these ends, the charges for the mutating CO_2 were defined as

$$\begin{aligned} q_{\text{C,Simulation}}(\lambda_1 \pm \delta) &= (\lambda_1 \pm \delta) q_{\text{C}} \\ q_{\text{O,Simulation}}(\lambda_1 \pm \delta) &= -\frac{1}{2}(\lambda_1 \pm \delta) q_{\text{C}} \end{aligned} \qquad (8)$$

where q_{C} on the right-hand-side of eq 8 denotes the full partial charge of the carbon site for the Harris−Yung CO_2 model. Through a simple inspection of eq 8, one can now see the reasoning behind our choice of the λ^2-coupling dependence for the guest−guest interactions and the linear λ coupling for the guest−host Coulombic interactions in eq 6.

According to eqs 4−8, the Gibbs free energy changes during in the mutation process of CH_4 into Ar and of CO_2 into Ar become

$$\Delta G_{\text{residual}}^{\text{CH}_4 \rightarrow \text{Ar}} = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\text{NTP},\lambda} \mathrm{d}\lambda \qquad (9)$$

$$\Delta G_{\text{residual}}^{\text{Ar} \rightarrow \text{CO}_2} = \int_0^1 \left\langle \frac{\partial U(\lambda_1,\lambda_2)}{\partial \lambda_1} \right\rangle_{\text{NPT},\lambda 1,\lambda_2 = 1} \mathrm{d}\lambda_1 + \int_0^1 \left\langle \frac{\partial U(\lambda_1,\lambda_2)}{\partial \lambda_2} \right\rangle_{\text{NPT},\lambda 1 = 0,\lambda_2} \mathrm{d}\lambda_2 \qquad (10)$$

where the $\langle \partial U/\partial \lambda_i \rangle_{\text{NPT},\lambda_i,\lambda_j}$ are the time averages determined directly from our NPT-MD simulations as a function of λ_i. Finally, the change of free energy for the mutation of CH_4 hydrate into CO_2 hydrate becomes

$$\Delta G_{\text{mutation}}^{\text{CH}_4 \rightarrow \text{CO}_2} = \Delta G_{\text{residual}}^{\text{CH}_4 \rightarrow \text{Ar}} - \Delta G_{\text{residual}}^{\text{CO}_2 \rightarrow \text{Ar}} + \Delta G_{\text{total}}^{\text{ideal}} \qquad (11)$$

where the expression for the analytical determination of $\Delta G_{\text{total}}^{\text{ideal}}$ is given in the Appendix.

One final small technical point worth noting is that the actual mass of the guest molecules need not be a function of the coupling parameter, λ, because we have explicitly separated the free energy change due to molecular mass into the analytic ideal gas term. As a result, we have chosen not to alter the guest molecule's molecular mass throughout the course of the growing-in process (i.e., the mass of the guest molecule at $\lambda = 0$ is either 16 or 44 g/mol, instead of the correct value of 40 g/mol for Ar). Because we are only interested the hydrate's thermodynamic properties, our decision to make the mass of the mutating guest molecule constant during the growing-in process will only affect the efficiency of our simulation sampling and not the averages of the simulated properties.

TABLE 1: Summary of Interaction Parameters[a]

	ϵ (kJ/mol)	σ (Å)	q (|e|)
	Water (SPC/E)		
O	0.6504	3.166	−0.8476
H			0.4238
	Water (TIP5P)		
O	0.6714	3.120	0
H			0.2410
LP			−0.2410
	Methane[b]		
C	0.4051	3.351	0
H	0.0564	2.868	0
	Carbon Dioxide		
C	0.2411	2.785	0.6646
O	0.6901	3.064	−0.3323
	Reference X		
Ar	0.996	3.41	0

[a] All cross interactions were determined using the Berthelot-Lorentz combining rules. [b] The cross methane C to methane H interactions used $\epsilon = 0.1709$ kJ/mol and $\sigma = 3.024$ Å instead of the standard Berthelot−Lorentz combining rules. This is because the Lennard-Jones interaction parameters have to be translated from Williams' original exp-6 potential form (see Appendix of ref 20 for details).

III. Intermolecular Potential Models, Simulation Method, and Results

The initial CH_4 and CO_2 hydrate configurations were taken from a previous study.[20] Each simulation box consisted of 368 water molecules [either SPC/E or TIP5P] and 64 guest molecules. Periodic boundary conditions and an Ewald summation were employed. The simulation was conducted using the DL_POLY software,[26] and the Ewald screening parameter and largest k vector were determined in order to ensure a 10^{-5} convergence in the electrostatic energy. A cutoff length of 10 Å was used for all Lennard-Jones interactions. Interactions beyond the cutoff length were corrected for using the standard assumption of a uniform density distribution. All of the simulations were conducted in the NPT ensemble, using a Nosé−Hoover thermostat [27] to control the temperature, and Andersen's barostat to control the pressure.[28] The temperature was set to 270 K and the pressure to 5 MPa. The translational and rotational equations of motion were integrated using a Verlet "leapfrog" algorithm, and the orientational degrees of freedom were described using quaternions.

It is worth mentioning that the coupling parameter formalism set forth in this section is independent of the type of water model. This provides us the unique opportunity to investigate the effects of the type of solvent model on our thermodynamic modeling of the hydrate gas extraction process. Two sets of simulations were performed in order to determine $\Delta G_{\text{residual}}^{\text{CH}_4 \rightarrow \text{CO}_2}$, one using the traditional planar SPC/E water model and the other using the five-site nonplanar TIP5P water model. Both water models were parametrized using thermodynamic properties at ambient conditions and both involve a single 12−6 Lennard-Jones sphere to describe the oxygen site, with embedded simple point charges (for more details see ref 20 and/or the appropriate references therein).

Three simulations were required in order to evaluate eq 11: one for the mutation of CH_4 into Ar, one for the removal of the point charges in CO_2, and one for the mutation of the "uncharged" CO_2 to Ar. The simulation results are presented in Tables 2 and 3 and graphically in Figures 1 and 2. For each integration, the number of the windows (values of λ) was adjusted to produce a smooth and well-behaved curve. Each window consisted of a 30 ps equilibration followed by a 70 ps

TABLE 2: Thermodynamic Integration Data for the Hydrate System with SPC/E Water as the Host Molecule at $T = 270$ K and $P = 5$ MPa

λ_1[a]	$\langle dU/d\lambda_1\rangle_{\lambda_1,\lambda_2=1}$ (kJ/mol)	λ_2[b]	$\langle dU/d\lambda_2\rangle_{\lambda_1=0,\lambda_2}$ (kJ/mol)	λ[c]	$\langle dU/d\lambda\rangle$ (kJ/mol)
1.00	−4.715	1.00	−7.750	1.00	−0.680
0.90	−4.270	0.80	−1.500	0.80	2.310
0.80	−3.843	0.60	3.878	0.60	4.216
0.70	−3.410	0.40	6.134	0.40	2.650
0.60	−2.933	0.30	4.541	0.30	0.061
0.50	−2.633	0.25	1.504	0.25	−0.753
0.40	−2.206	0.20	−0.398	0.20	−1.939
0.30	−1.830	0.15	−3.378	0.15	−2.779
0.20	−1.488	0.10	−5.227	0.10	−3.444
0.10	−1.163	0.05	−7.394	0.05	−3.935
0.00	−0.813	0.00	−8.438	0.00	−4.148
$\int\langle\cdots\rangle\, d\lambda$	−2.65 kJ/mol (± 0.03)		0.08 kJ/mol (± 0.03)		0.89 kJ/mol (± 0.03)

[a] For the transition of CO_2 to CO_2 (no partial charge). [b] For the transition of CO_2 (no partial charge) to Ar. [c] For the transition of CH_4 to Ar.

TABLE 3: Thermodynamic Integration Data for the Hydrate with TIP5P Water as the Host Molecule at $T = 270$ K and $P = 5$ MPa

λ_1[a]	$\langle dU/d\lambda_1\rangle_{\lambda_1,\lambda_2=1}$ (kJ/mol)	λ_2[b]	$\langle dU/d\lambda_2\rangle_{\lambda_1=0,\lambda_2}$ (kJ/mol)	λ[c]	$\langle dU/d\lambda\rangle_\lambda$ (kJ/mol)
1.00	−3.736	1.00	−5.642	1.00	−0.6914
0.90		0.80	−1.429	0.80	2.995
0.80	−3.015	0.60	3.326	0.60	4.097
0.70		0.40	6.624	0.40	2.181
0.60	−2.201	0.30	4.413	0.30	0.0914
0.50		0.25	1.985	0.25	−0.6645
0.40	−1.497	0.20	−1.023	0.20	−2.013
0.30		0.15	−3.121	0.15	−2.539
0.20	−0.9284	0.10	−5.498	0.10	−3.480
0.10		0.05	−7.766	0.05	−3.719
0.00	−0.2867	0.00	−8.712	0.00	−4.204
$\int\langle\cdots\rangle\, d\lambda$	−1.93 kJ/mol (± 0.03)		0.23 kJ/mol (± 0.03)		1.0 kJ/mol (± 0.03)

[a] For the transition of CO_2 to CO_2 (no partial charge). [b] For the transition of CO_2 (no partial charge) to Ar. [c] For the transition of CH_4 to Ar.

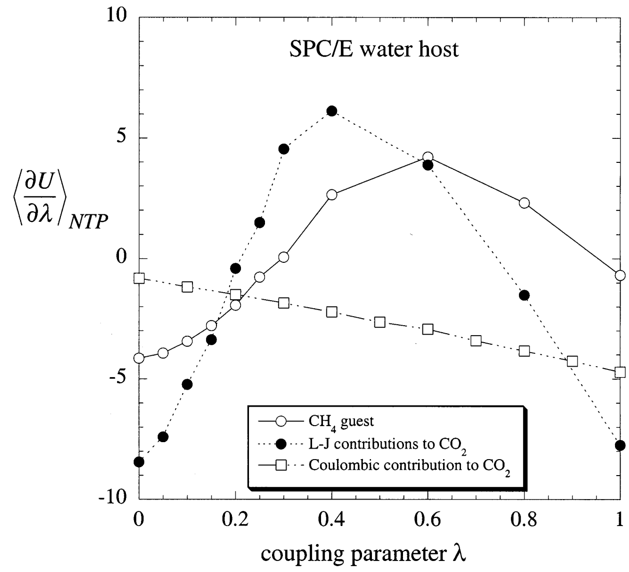

Figure 1. Coupling parameter dependence of the integrands in eqs 9 and 10 for SPC/E water host.

averaging period. At each window, the radial distribution functions for each species were examined, and the basic hydrate structure was found to remain intact during the entire mutation. Because we start from well equilibrated sI clathrate structures generated in our previous work[20] and each window represents a perturbation of the preceding fully equilibrated system, we found that this simulation length per window provided an adequate sampling for the system configuration.

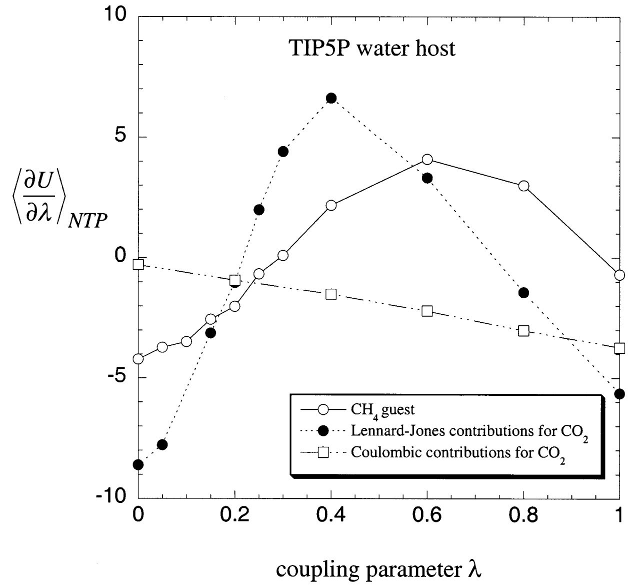

Figure 2. Coupling parameter dependence of the integrands in eqs 9 and 10 for TIP5P water host.

The numerical integration of the results presented in Tables 2 and 3 yields a residual contribution to $\Delta G^{CH_4 \rightarrow CO_2}$ of −3.46 ± 0.04 and −2.70 ± 0.04 kJ/mol for the SPC/E and TIP5P hosts, respectively. Thus, the total change in the Gibbs free energy for the mutation process, after invoking the ideal gas contributions from the Appendix, becomes −12.11 ± 0.05 kJ/mol of guest molecules for the SPC/E host and −11.35 ± 0.05 kJ/mol of guest molecules for the TIP5P host. Thus, our simulation suggests that the fully loaded CO_2 hydrate is significantly more thermodynamically stable than the corresponding CH_4 hydrate at the state conditions studied here. Note, however, that the largest contribution to the change in free energy comes from the ideal gas contributions, i.e., 2.5−3 times larger than the corresponding residual contributions.

The difference in residual free energy between Ar and CO_2 hydrates was determined to be −2.57 ± 0.04 and −1.70 ± 0.04 kJ/mol for the SPC/E and TIP5P solvent models, respectively. The change in residual free energy for the mutation of Ar into CH_4 is 0.89 ± 0.03 and 1.00 ± 0.03 kJ/mol, respectively. Thus it appears that the Ar hydrate's residual free energy lies between those of CH_4 and CO_2. The more favorable residual free energy state of the CO_2 hydrate is due to its strong CO_2−CO_2 and CO_2−water electrostatic interactions, without which the residual free energy of the CO_2 hydrate would be either comparable or slightly higher than that of the Ar hydrate.

IV. Final Comments

In this work, we analyze the thermodynamic feasibility of extracting CH_4 gas from its original hydrate clathrate by CO_2 replacement at one state condition and guest load. The approach to this investigation is the proof-of-principles and the development of the molecular tools to study the replacement equilibrium process. Our simulation results indicate the following:

(1) The residual Gibbs free energy of the fully loaded gas hydrates decreases with the guest species as $CH_4 \rightarrow Ar \rightarrow CO_2$; thus, the replacement of CH_4 with CO_2 is thermodynamically feasible at the state condition examined.

(2) The details of the water model description have little effect on the calculated $\Delta G_{\text{mutation}}^{CH_4 \rightarrow CO_2}$; that is, the relative stability of the hydrates is dominated by the ideal gas contribution over the residual contributions to the total Gibbs free energy.

We should also note that our study has been carried out under some very special conditions. First, the hydrates were assumed to be "clean"; that is, not only the solvent but also the gases were pure. However, the actual hydrate systems are usually "dirty", in that solvated species are usually present (particularly electrolytes) that can affect the equilibrium conditions, a situation that emphasizes the need for a detailed analysis of the effects of those species on the relative system's free energy. Second, the replacement process was assumed to occur from a fully loaded (maximum host occupancy) CH_4 hydrate to a fully loaded CO_2 hydrate, whereas the most likely scenario to be encountered in nature will be one with only a partially loaded gas hydrate.

Moreover, although we determined the change of the Gibbs free energy in the hypothetical mutation process, it is useful to highlight the connection between this process and the actual engineering application of extracting methane via carbon dioxide sequestration.[9] In the earlier sections, we defined a hypothetical mutation reaction, i.e.

$$CH_4(\text{hydrate}) \Leftrightarrow CO_2(\text{hydrate}) \tag{12}$$

where a CH_4 hydrate was transformed into a CO_2 hydrate. Although this hypothetical scheme was useful in the development of our simulation methodologies, it does not represent the entire process, one in which aqueous CO_2 will push the CH_4 from its hydrate cage, to produce aqueous (and eventually gaseous) CH_4, i.e.

$$CO_2(\text{gas}) + CH_4(\text{hydrate}) \Leftrightarrow CH_4(\text{gas}) + CO_2(\text{hydrate}) \tag{13}$$

Certainly, the complete extraction scheme will involve (residual) Gibbs free energy contributions from the gas and/or aqueous phase, with approximately the same order of magnitude as the one for the mutation process in the hydrate matrix (this is based on simple estimations from Ohgaki's work[29]). However, we note that these contributions are just a small fraction of the corresponding ideal gas counterpart terms.

In terms of the sensitivity of the water models, the difference in the residual Gibbs free energy of replacement between the TIP5P and the SPC/E water is small (~0.8 ± 0.07 kJ/mol of guest), although still significant given an overall residual Gibbs free energy of −3.1 ± 0.07 kJ/mol (Table 2).

(3) The different descriptions of the water model might have a rather strong effect on the resulting $\Delta G^{\text{extraction}}$ (eq 13), due to the relatively small changes of residual Gibbs free energies in the corresponding mutation processes (note that the corresponding ideal gas counterparts will cancel out exactly).

A "back-of-the-envelope" calculation indicates that the extraction, in contrast to the mutation, process might become only slightly favorable, i.e., $\Delta G^{\text{extraction}} \approx -(1.0 - 1.5)RT$. This situation indicates that a more systematic feasibility study of the extraction process will require the calculation of the relative free energies of guest mutation between the solid (hydrate) and the fluid (aqueous) phases, following the methodology presented in section II. This kind of study might include the effect of gas and/or electrolyte concentrations, as well as the corresponding equilibrium between aqueous and hydrate phases. However, this is beyond the limited scope of this work, though it is part of our ongoing research effort on the subject.

Finally, the reader should realize that because we are dealing with models as opposed to real systems we have complete control of the molecular details of the system. Consequently, molecular simulation offers us the unique opportunity to isolate specific details of the intermolecular interactions, to analyze their contribution to the replacement phenomenon under investigation, and to make unambiguous (cause-effect) connections between those details and the corresponding macroscopic response of the system which ultimately will allow a fundamentally based modeling of the process.[20]

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Appendix: Calculation of the Ideal Gas Contribution to the Free Energy of Mutation.

The ideal gas contribution for mutating a pure CH_4 hydrate into a pure CO_2 hydrate, $\Delta G_{\text{total}}^{\text{ideal}}$, can be written as the product of CO_2 and CH_4 guest molecule's molecular partition functions.[30] For the mutation $CH_4 \rightarrow CO_2$, the ideal gas free energy can be written as

$$\Delta G_{\text{total}}^{\text{ideal}} = kT \ln\left[\frac{q_{\text{trans}}^{CH_4}\, q_{\text{rot}}^{CH_4}\, q_{\text{vib}}^{CH_4}\, q_{\text{elec}}^{CH_4}}{q_{\text{trans}}^{CO_2}\, q_{\text{rot}}^{CO_2}\, q_{\text{vib}}^{CO_2}\, q_{\text{elec}}^{CO_2}}\right] \tag{A.1}$$

where k is the Boltzmann constant, T is the absolute temperature, and the subscripts refer to the translational, rotational, vibrational, and electronic partition functions. It is also noteworthy to point out that the expression in eq A.1 is independent of our particular choice of solvent model, because the solvent potential field remains unchanged throughout the course of the mutation. For both the Harris−Yung and Williams potential models of carbon dioxide and methane, respectively, $q_{\text{vib}} = q_{\text{elec}} = 1$, which allows us to deal with only the translational and rotational terms. It is then trivial to express the translational term of eq A.1 as

$$\begin{aligned}\Delta G_{\text{trans}} &= kT \ln\left[\frac{q_{\text{trans}}^{CH_4}}{q_{\text{trans}}^{CO_2}}\right] \\ &= -kT \ln\left(\frac{2\pi m_{CO_2} kT}{h^2}\right)^{3/2} V + kT \ln\left(\frac{2\pi m_{CH_4} kT}{h^2}\right)^{3/2} V \\ &= \frac{3}{2} kT \ln\left(\frac{m_{CH_4}}{m_{CO_2}}\right)\end{aligned} \tag{A.2}$$

where m is the mass of the guest molecule, h is Planck's constant, and V is the system's volume. The expression of the rotational free energy term can be derived in a similar manner. For a rigid rotating body, the partition functions for a tetrahedral (CH_4) and linear molecule (CO_2) are well-known and given by

$$q_{\text{rot}}^{CH_4} = \frac{\pi^{1/2}}{\sigma_{CH_4}}\left(\frac{8\pi^2 I_{CH_4} kT}{h^2}\right)^{3/2} \tag{A.3}$$

$$q_{\text{rot}}^{CO_2} = \frac{1}{\sigma_{CO_2}}\left(\frac{8\pi^2 I_{CO_2} kT}{h^2}\right) \tag{A.4}$$

where I is the moment of inertia and σ denotes the symmetry number of the guest molecule. The free energy change due to differences between the rotation of CO_2 and CH_4 guest molecules is then given by

$$\begin{aligned}\Delta G_{\mathrm{rot}} &= -kT\ln q_{\mathrm{rot}}^{\mathrm{CO_2}} + kT\ln q_{\mathrm{rot}}^{\mathrm{CH_4}} \\ &= kT\ln\left[\pi^{1/2}\left(\frac{\sigma_{\mathrm{CO_2}}}{\sigma_{\mathrm{CH_4}}}\right)\left(\frac{8\pi^2 I_{\mathrm{CH_4}}kT}{h^2}\right)^{3/2}\left(\frac{h^2}{8\pi^2 I_{\mathrm{CO_2}}kT}\right)\right] \\ &= kT\ln\left[\pi^{1/2}\left(\frac{\sigma_{\mathrm{CO_2}}}{\sigma_{\mathrm{CH_4}}}\right)\left(\frac{I_{\mathrm{CH_4}}{}^{3/2}}{I_{CO_2}}\right)\left(\frac{8\pi^2 kT}{h^2}\right)^{1/2}\right] \qquad \text{(A.5)}\end{aligned}$$

Combining eqs A.2 and A.5 then gives us the expression for the total ideal gas free energy contribution for the $CH_4 \rightarrow CO_2$ mutation:

$$\begin{aligned}\Delta G_{\mathrm{total}}^{\mathrm{ideal}} &= \Delta G_{\mathrm{trans}} + \Delta G_{\mathrm{rot}} \\ &= \frac{3}{2}kT\ln\left(\frac{m_{\mathrm{CH_4}}}{m_{\mathrm{CO_2}}}\right) + kT\ln\left[\pi^{1/2}\left(\frac{\sigma_{\mathrm{CO_2}}}{\sigma_{CH_4}}\right)\left(\frac{I_{\mathrm{CH_4}}^{3/2}}{I_{\mathrm{CO_2}}}\right)\left(\frac{8\pi^2 kT}{h^2}\right)^{1/2}\right] \qquad \text{(A.6)}\end{aligned}$$

For our chosen model of CH_4, $\sigma = 12$ and the rotational frequency is given by $B = 172.17$ GHz, where $I = h/(8\pi^2 B)$. For Harris−Yung's CO_2 model, it is quite easy to show that $\sigma = 2$ and $B = 11.68$ GHz. Thus, at $T = 273.15$ K, $\Delta G_{\mathrm{trans}} = -3.743$ kJ/mol, $\Delta G_{\mathrm{rot}} = -4.907$ kJ/mol, and $\Delta G_{\mathrm{total}}^{\mathrm{ideal}} = -8.65$ kJ/mol.

References and Notes

(1) Schwalm, C. R.; Ek, A. R. *Forest Ecol. Mgmt.* **2001**, *150*, 241.

(2) Meyer, R.; Joos, F.; Esser, G.; Heimann, M.; Hooss, G.; Kohlmaier, G.; Sauf, W.; Voss, R.; Wittenberg, U. *Global Biogeochem. Cycl.* **1999**, *13*, 785.

(3) Hitchon, B.; Gunter, W. D.; Gentzis, T.; Bailey, R. T. *Energy Convers. Mgmt.* **1999**, *40*, 825.

(4) Marchetti, C. *Climate Change* **1977**, *1*, 59.

(5) Inoue, Y.; Ohgaki, K.; Hirata, Y.; Kunugita, E. *J. Chem. Eng. Jpn.* **1996**, *29*, 648.

(6) Uchida, T.; Takagi, A.; Mae, S.; Kawabata, J. *Energy Convers. Mgmt.* **1997**, *38*, S307.

(7) Saito, T.; Kosugi, S.; Kajishima, T.; Tsuchiya, K. *Energy Fuels* **2001**, *15*, 285.

(8) Ohgaki, K.; Takano, K.; Moritoki, M. *Kagaku Kogaku Ronbunshu* **1994**, *20*, 121.

(9) Ohgaki, K.; Takano, K.; Sangawa, H.; Matsubara, T.; Nakano, S. *J. Chem. Eng. Jpn.* **1996**, *29*, 478.

(10) Spencer, D. F.; North, W. J. *Energy Convers. Mgmt.* **1997**, *38*, S265.

(11) Brewer, P. G.; Orr, F. M.; Friederich, G.; Kvenvolden, K. A.; Orange, D. L. *Energy Fuel* **1998**, *12*, 183.

(12) Hoffer, M. J.; Wey, Y.-C.; Callegari, A. J.; Broecker, W. S. *Climate Change* **1979**, *2*, 53.

(13) Haugan, P. M.; Drange, H. *Nature* **1992**, *357*, 318.

(14) Saji, A.; Noda, H.; Takamura, Y.; Tanii, T.; Takata, T.; Kitamura, H.; Kamata, T. *Energy Convers. Mgmt.* **1995**, *36*, 493.

(15) Kvenvolden, K. A. *Chem. Geol.* **1988**, *71*, 41.

(16) MacDonald, G. J. *Annu. Rev. Energy* **1990**, *15*, 53.

(17) Holder, G. D.; Kamath, V. A.; Godbole, S. P. *Annu. Rev. Energy* **1984**, *9*, 427.

(18) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press: London, 1990.

(19) Maitland, G. C.; Rigby, M.; Smith, E. B.; Wakeham, W. *Intermolecular Forces: Their Origin and Determination*; Oxford University Press: New York, 1981.

(20) Chialvo, A. A.; Houssa, M.; Cummings, P. T. *J. Phys. Chem. B* **2002**, *106*, 442.

(21) Harris, J. G.; Yung, K. H. *J. Phys. Chem.* **1995**, *99*, 12021.

(22) Williams, D. E. *J. Chem. Phys.* **1967**, *47*, 4680.

(23) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(24) Mahoney, M. W.; Jorgensen, W. L. *J. Chem. Phys.* **2000**, *112*, 8910.

(25) Beutler, T. C.; Mark, A. E.; van Schnaik, R. C.; Gerber, P. R.; van Gunsteren, W. F. *Chem. Phys. Lett.* **1994**, *222*, 529.

(26) Forester, T. R.; Smith, W. DL_POLY_2.0; Daresbury Laboratory: Warrington, 1995.

(27) Nosé, S. *Mol. Phys.* **1984**, *52*, 255.

(28) Andersen, H. C. *J. Chem. Phys.* **1980**, *72*, 2384.

(29) Sugahara, T. Personal communication, 2002

(30) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1976.