

Assessing the Thermodynamic Feasibility of the Conversion of Methane Hydrate into Carbon Dioxide Hydrate in Porous Media

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Abstract

Concerns about the potential effects of rising carbon dioxide levels in the atmosphere have stimulated interest in a number of carbon dioxide sequestration studies. One suggestion is the sequestration of carbon dioxide as clathrate hydrates by injection of carbon dioxide into methane hydrate. Energy-supply research estimates indicate that natural gas hydrates in arctic and sub-seafloor formations contain more energy than all other fossil fuel deposits combined. The simultaneous sequestration of carbon dioxide and the production of methane by injection of carbon dioxide into deposits of natural gas hydrates, if possible, represents a potentially efficient and cost effective option for the sequestration of carbon dioxide.

Data in the literature show that the conversion of bulk methane hydrate into carbon dioxide hydrate is thermodynamically favored. These results are not directly applicable to naturally occurring hydrates, because the hydrates in these locations are embedded in sediments. The thermodynamics of any potential conversion of CH_4 hydrate to CO_2 hydrate will therefore be affected by the size of the pores in which the conversion of CH_4 hydrate to CO_2 hydrate would take place. We have developed a model that is able to explain and predict equilibria in porous media for any pore size distribution. This model can be used to calculate the heats of dissociation for these hydrates in porous media as a function of pore size and temperature. These results allow for an assessment of the thermodynamic feasibility of converting CH_4 hydrate to CO_2 hydrate in porous media involving various size pores. We have used this model to derive a simple, explicit relation for the hydrate formation conditions in porous media, as well as the enthalpy of dissociation for these hydrates.

Introduction

The build up of carbon dioxide in the atmosphere due to anthropogenic emissions has become of great scientific and popular interest due to the potential of this gas to play an important role in greenhouse effects, and its reported potential to induce global warming on the order of 2 – 5 K over the next century (Ravkin, 1992). As a result of these concerns, various researchers have suggested the sequestration of CO₂ to remove it from the atmosphere. One set of potential sequestration scenarios involves the injection of CO₂ into the earth's oceans. One obvious drawback to these scenarios is that due to its solubility in water the injected CO₂ will dissolve, with unknown ecological effects. This potential dissolution of CO₂ could be reduced/prolonged by some extent if the conditions were such that CO₂ hydrates could be formed and were stable. Gas hydrates are crystalline structures, belonging to a group of solids known as clathrates, which involve a lattice made up of hydrogen-bonded water molecules containing cavities occupied by guest gas molecules. Gas hydrates form under low temperature – high pressure conditions, both above and below the freezing point of water. Under proper conditions, the lattice is stabilized by van der Waals forces through the occupation of specific cavities within the lattice by certain types of guest molecules. The type of guest molecule(s) present determines which of three known crystal structures the lattice assumes (Sloan, 1997).

It has been suggested (Komai et al., 1997) that the injection of CO₂ into methane hydrate could result in the simultaneous sequestration of the CO₂ and the liberation of methane (which could be used as a clean fuel). Since much of the world's naturally occurring methane hydrates are in sediments below the ocean floors or in permafrost regions, it is necessary to consider the effects of porous media on the formation of these hydrates separately, as well as for mixtures. In this work we examine empirical relations based on experimental data for bulk hydrates that have been presented in the literature (Holder et al., 1988; Kamath, 1983; Sloan, 1997). It is demonstrated that such relations can be derived from the standard thermodynamic models that have been applied to predict hydrate formation conditions. In addition, a simple relation is presented that allows for the prediction of the equilibrium conditions in porous media and,

subsequently, the enthalpy of dissociation of these hydrates. In this work we shall only consider hydrate equilibria above 273.15 K (where the equilibria involve liquid water), though similar relations can be derived for temperatures below the water ice-point.

Empirical Fits to Bulk Hydrate Data

Kamath (1983) has noted that the equilibrium pressures for single component hydrates are well fit by simple relations of the form

$$\ln(P_{eq}) = \frac{a}{T} + b. \quad (1)$$

This simple form is often referred to as an Antoine equation (Reid and Sherwood, 1966), and is analogous to the vapor-pressure equations derived from the Clapeyron equation

$$\frac{d(\ln P_{vp})}{d(1/T)} = \frac{-\Delta H_v}{R\Delta Z_v}, \quad (2)$$

where ΔH_v is the enthalpy of vaporization, and ΔZ_v is the difference between the gas and liquid compressibility factors. Reduction of eq (2) to a form analogous to eq. (1) results from the assumption that the ratio $\Delta H_v/\Delta Z_v$ is constant. The analogy between hydrate equilibrium pressures and vapor pressures is certainly not perfect, though the seeming agreement between experimental data and linear fits of this type are suggestive that this relation should be derivable from the statistical thermodynamic equations used to predict hydrate formation. Figure 1 shows graphical representations of the correlations given in Table 1 for methane and carbon dioxide hydrates using eq. (1). While this relation has been remarked on by several authors (see for example Sloan, 1997; and Holder, 1988), no explanation for its validity based on a statistical thermodynamic model has been presented in the literature.

Table 1: Correlations for fitting experimental equilibrium pressures for methane and CO₂ hydrates to $\ln(P_{eq}) \approx \frac{a}{T} + b$ where P_{eq} is in atm and T (> 273.15) is in K.

	a	b
Methane	-8995	36.09
Carbon Dioxide	-10091	39.39

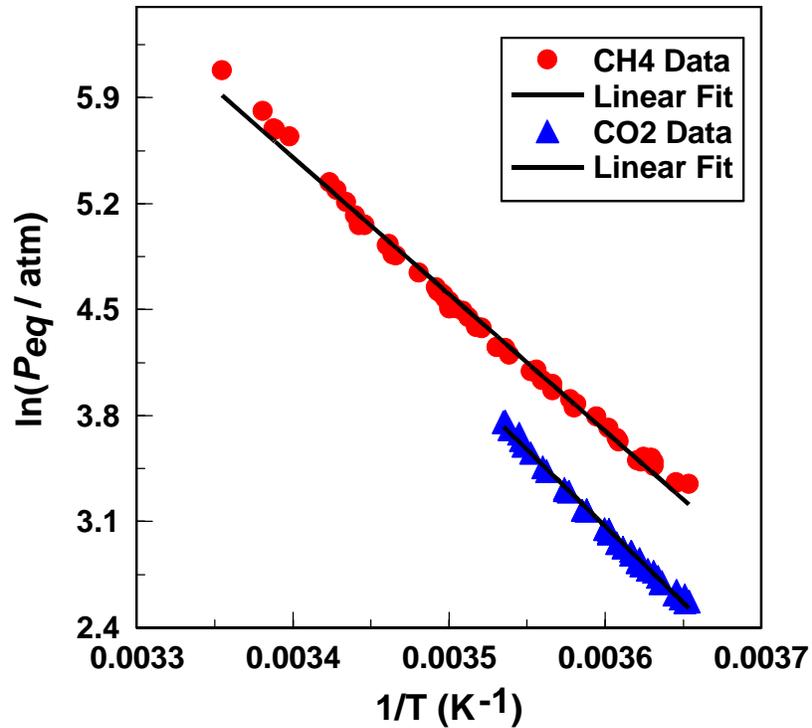


Figure 1: Shown are experimental equilibrium pressures for methane (●) and carbon dioxide (▲) hydrate formation, as well as linear correlations using eq. (1) and the parameters given in Table 1.

Modeling Hydrate Formation in the Bulk

Munck et al. (1988) presented a single equation involving T_f and P_f (the temperature and pressure under which the hydrate forms) that can be used to predict hydrate formation conditions. In the case of hydrates formed from single component gases, this equation takes the form

$$\frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{RT} dP - \ln(\gamma_w X_w) + \sum_i \eta_i \ln(1 - Y_i) = 0 \quad (3)$$

In eq (3), $\bar{T} = (T_0 + T) / 2$, T_0 is the temperature of the standard reference state ($T = 273.15$ K, $P = 0$), $\Delta\mu_w^0$ is the chemical potential difference for the reference state, η_i is the ratio of the number of cavities of type i to the number of water molecules in the hydrate lattice, and Y_i denotes the probability of a cavity of type i being occupied by the guest molecule, and is given in terms of the fugacity of the hydrate guest in the gaseous state (f_i) and the Langmuir adsorption constant (C_i) by $Y_i = \frac{C_i f_i}{1 + C_i f_i}$. Additionally,

$\Delta H_w = \Delta H_w^0 + \int_{T_0}^T \Delta C_p(T') dT'$, where ΔH_w^0 is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature, $\Delta C_p(T')$ is assumed constant and equal to ΔC_p^0 (the reference heat capacity difference), and ΔV_w is the volume difference between the empty hydrate and pure liquid water (at T_0), and is assumed constant. In the present model the temperature dependence of the Langmuir constants is accounted for by using the form presented by Munck et al (1988),

$$C_i = \frac{A_i}{T} \exp(B_i / T), \text{ where } A_i \text{ and } B_i \text{ are experimentally fit parameters, and are}$$

dependent on which guest molecule is present. The analysis we will describe below could be applied to any of the various forms of this model (all of which are based on that presented by van der Waals and Platteeau (1959)), but the one given above has several advantageous characteristics that facilitate the objectives of this work. As noted earlier,

we shall only consider equilibria involving liquid water, though the analysis that will be presented can also be applied to equilibria involving ice.

While eq. (3) can be solved numerically for the equilibrium pressure (given any choice of temperature) by an iterative procedure, it is not possible to solve for the pressure as a function of temperature, explicitly. Our goal is to find an accurate approximation of the true solution that allows such an explicit form to be determined. We begin by a consideration of the terms involving either the pressure or fugacity of the gas. The first such term on the left-hand side of eq. (3) is due to the affect of the volume difference between the empty hydrate lattice and the normal state of the water, namely

$$\int_0^{P_f} \frac{\Delta V_w}{RT} dP = \frac{\Delta V_w}{RT} P_f .$$

Due to the relatively small volume change when hydrates form

from water, the magnitude of this term is small compared to others in eq. (3). As a result of this, we consider $\ln f$ to be given by $\ln f \approx \ln f^0 + \ln f^1$ where the second contribution (assumed small) is due to this term, and $\ln f^0$ can be found by ignoring this term in eq. (3). The other terms involving the pressure are those related to the cage occupancies

$$\sum_i \eta_i \ln(1 - Y_i) = \eta_s \ln(1 - Y_s) + \eta_l \ln(1 - Y_l), \quad (4)$$

where on the right hand side we have used a subscript “s” to denote quantities for the “small” cages, and “l” for those in “large” cages. Using the form for Y_i given above, each term of eq. (4) can be rewritten using

$$\begin{aligned} \eta_i \ln(1 - Y_i) &= -\eta_i \ln(1 + C_i f) \\ &= -\eta_i \ln \left[C_i f \left(1 + \frac{1}{C_i f} \right) \right] \\ &= -\eta_i \left\{ \ln(C_i f) + \ln \left(1 + \frac{1}{C_i f} \right) \right\} \end{aligned} \quad (5)$$

Clearly, if $C_i f$ is large enough, $\ln(1 + C_i f) \approx \ln(C_i f)$. If this approximation is not adequate but $C_i f$ is still larger than unity, one can use a Taylor series expansion of the second logarithm in the last line of eq. (5) to arrive at

$$\eta_i \ln(1 - Y_i) \approx -\eta_i \left\{ \ln(C_i f) + \frac{1}{C_i f} - \frac{1}{2} \left(\frac{1}{C_i f} \right)^2 + \dots \right\}. \quad (6)$$

To demonstrate the validity of using $\ln(1 + C_i f) \approx \ln(C_i f)$, we shall consider its application to methane hydrates. The experimental temperatures and pressures found in Sloan (1997), as well as the second virial coefficient (used to convert these pressures to fugacities) have been used to construct Figure 2 where the percent error in approximating $\ln(1 + C_i f)$ as $\ln(C_i f)$ for both the small and large cages over the temperature range from 273.7 K to 298.1 K is shown. Clearly, this approximation is extremely good for the large

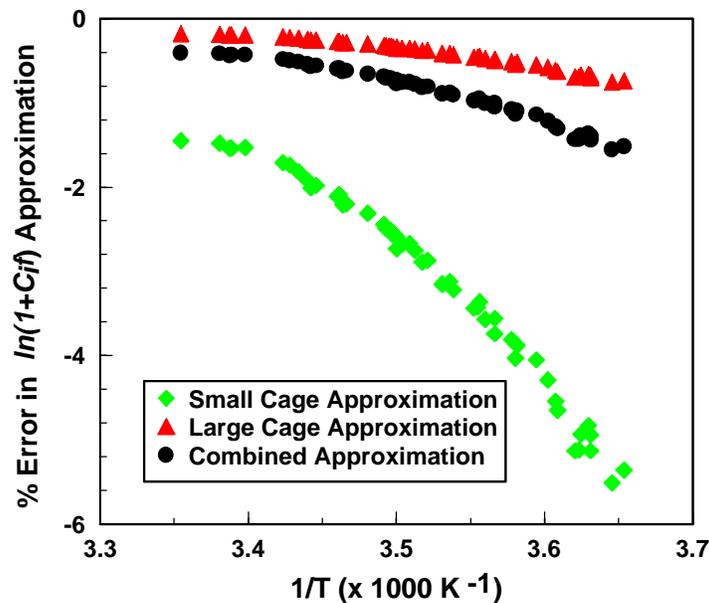


Figure 2: Shown are the percent errors in approximating $\ln(1 + C_i f)$ as $\ln(C_i f)$ in both the large (\blacktriangle) and small (\blacklozenge) cages in methane hydrates, as well as the error (\bullet) in using these approximations to compute the sum of the terms as appears in eq. (7).

cages, and has a maximum error of 5.5 % for the small. Applying this approximation for both terms in (3) yields

$$\eta_s \ln(1 - Y_s) + \eta_l \ln(1 - Y_l) \approx (\eta_s + \eta_l) \ln f + \eta_s \ln C_s + \eta_l \ln C_l. \quad (7)$$

The error resulting from using the approximations for both cages (as in eq. (7)) is also shown in Figure 2, and is less than 1.6%. Using (7) in (3) leads to

$$\begin{aligned} \ln f &\approx \frac{1}{\eta_s + \eta_l} \left\{ \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{RT} dP - \eta_s \ln C_s - \eta_l \ln C_l - \ln(\gamma_w X_w) \right\} \\ &\approx \frac{1}{\eta_s + \eta_l} \left\{ \frac{\Delta\mu_w^0}{RT_0} + \left(\frac{\Delta H_w^0 - T_0 \Delta C_P^0}{R} \right) \left(\frac{1}{T_f} - \frac{1}{T_0} \right) - \frac{\Delta C_P^0}{R} \ln \left(\frac{T_f}{T_0} \right) + \frac{\Delta V_w}{RT} P_f \right. \\ &\quad \left. - \eta_s \ln C_s - \eta_l \ln C_l - \ln(\gamma_w X_w) \right\} \end{aligned} \quad (8)$$

The second equality in eq. (8) follows from carrying out the indicated integrations. For hydrocarbons such as methane (where the gas solubility in water is very small), the last term on the right hand side of eq. (8) can be neglected (Munck, 1988). As mentioned above, we compute $\ln f$ as $\ln f \approx \ln f^0 + \ln f^1$, where the second term is small compared to the first, and is due to the affect of the term involving P_f on the RHS of (8). Neglecting this term, the zeroeth order term of $\ln f$ for a gas hydrate such as that involving methane is found to be

$$\begin{aligned} \ln f^0 &\approx \frac{1}{\eta_s + \eta_l} \left\{ \frac{\Delta\mu_w^0}{RT_0} + \left(\frac{\Delta H_w^0 - T_0 \Delta C_P^0}{R} \right) \left(\frac{1}{T_f} - \frac{1}{T_0} \right) - \frac{\Delta C_P^0}{R} \ln \left(\frac{T_f}{T_0} \right) - \eta_s \ln C_s - \eta_l \ln C_l \right\} \\ &\approx \frac{1}{\eta_s + \eta_l} \left\{ \left(\frac{\Delta H_w^0}{R} - \eta_s (T_0 + B_s) - \eta_l (T_0 + B_l) \right) \frac{1}{T_f} + \right. \\ &\quad \left. \left(\frac{\Delta\mu_w^0 - \Delta H_w^0}{RT_0} - \eta_s [\ln(A_s/T_0) - 1] - \eta_l [\ln(A_l/T_0) - 1] \right) \right\} \quad (9) \\ &\approx \frac{\alpha}{T_f} + \beta \end{aligned}$$

The second relation in (9) follows from using the above given form for the Langmuir constants and expanding the logarithm in the third term on the right of the first line of eq.

(9) in terms of a power series in T_f/T_0 and truncating after the first nonzero term. This last approximation is done only to show how the Antoine type relation comes about, and is not necessary to simplify the calculations. Figure 3 shows predictions using eq. (9) (with the parameter values given in Table 2) for methane hydrate (dotted trace), as well as the experimental data (Sloan, 1997). Even without including the correction for the volume change on hydrate formation the maximum error is less than 4%.

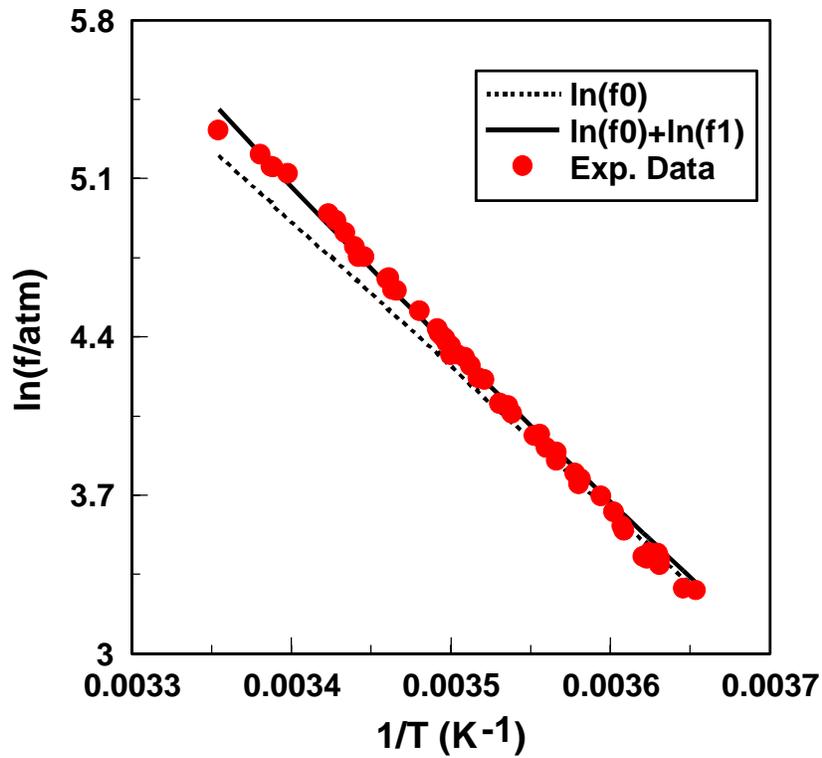


Figure 3: Shown are experimental data (•) for methane hydrate formation, as well as approximations using eq. (9) (···) and eq. (10) (—).

Table 2: Parameter values for bulk hydrate formation from liquid water

Property	Unit	Bulk Value for Methane	Bulk Value for CO ₂
$\Delta\mu_w^0$	J/mol	1264	1264
$(\Delta H_w^0)_{liq}$	J/mol	-4858	-4858
ΔC_p^0	J/mol·K	39.16	39.16
ΔV_w	cm ³ /mol	3.0	3.0
σ_{hw}	J/m ²	0.0267	0.0267
A_i	K/atm	0.0007228 (small cavity) 0.02335 (large cavity)	0.0002474 (small cavity) 0.04246 (large cavity)
B_i	K	3187 (small cavity) 2653 (large cavity)	3410 (small cavity) 2813 (large cavity)

The correction term that must be applied can be estimated by assuming that the pressure in $\frac{\Delta V_w}{RT} P_f$ can be approximated by f_0 . Since the overall magnitude of this term is less than 4% of the remaining terms, the error in approximating P_f by f_0 will be very small. Therefore, using α and β defined by eq. (9) we find that

$$\ln f \approx \frac{\alpha}{T_f} + \beta + \frac{\Delta V}{(\eta_s + \eta_l)RT} e^{\alpha/T_f + \beta}. \quad (10)$$

Eq. (10) is shown graphically in Figure 3 as the solid trace. This approximation has a maximum error on the order of 1% over the temperature range shown. As can be seen from the difference between the results of using eq. (9) and eq. (10) in Figure 3, the third term on the right hand side of eq. (10) essentially results in a change in the slope of $\ln f$. Unfortunately, because this term is not truly linear in $1/T$ but only appears so on the scale of $\ln f$, the dominant part of this correction can not be obtained from a Taylor series

expansion about the point $1/T_0$. It can, however be approximated by a straight line with only a small error, accounting for the high quality fit that can be attained using an Antoine type equation for methane hydrates. A similar equation can be derived for CO₂ hydrates, though the higher gas solubility and the need to include the other terms in eq. (6) result in the need for a slight modification of the methods used to arrive at the resulting equation. These equations will not be given here since they lend no new insight into this approximation and will not be used below.

Modeling Hydrate Formation in Porous Media

To consider hydrate formation in porous media, eq. (3) must be modified to include the effect of the relevant interface on the activity of the water. Making the necessary modifications, eq. (3) becomes (Henry et al, 1999; Clark et al, 1999)

$$\frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T_f} \frac{\Delta H_w}{RT^2} dT + \int_0^{P_f} \frac{\Delta V_w}{RT} dP - \ln(\gamma_w X_w) + \sum_i \eta_i \ln(1 - Y_i) + V_L \frac{2 \cos(\theta) \sigma_{hw}}{RT_f r} = 0. \quad (11)$$

In eq. (11), V_L is the molar volume of water in the pure water state, θ is the wetting angle between the pure water phase and the hydrate, σ_{hw} is the surface tension between the water and hydrate phases, and r is the radius of the pores in the porous medium. If the same analysis is performed on this equation as that described above, we arrive at (for methane and similar hydrates)

$$\ln f^0 \approx \frac{1}{\eta_s + \eta_l} \left\{ \left[\left(\frac{\Delta H_w^0}{R} - \eta_s (T_0 + B_s) - \eta_l (T_0 + B_l) \right) \frac{1}{T_f} + \left(\frac{2V_L \cos(\theta) \sigma_{hw}}{R} \right) \frac{1}{T_f r} \right] \right. \\ \left. \left(\frac{\Delta\mu_w^0 - \Delta H_w^0}{RT_0} - \eta_s [\ln(A_s/T_0) - 1] - \eta_l [\ln(A_l/T_0) - 1] \right) \right\}. \quad (12)$$

$$\approx \frac{\alpha}{T_f} + \frac{\gamma}{T_f r} + \beta$$

Since at any given temperature the fugacity in a porous medium should be higher than that in the bulk, the magnitude of $C_i f$ will be larger, making the approximations used in

eq. (4) to compute $\ln f^0$ even more valid in the porous medium. Computing the correction due to the volume change and calculating the total fugacity we find

$$\ln f \approx \frac{\alpha}{T_f} + \frac{\gamma}{T_f r} + \beta + \frac{\Delta V e^{\alpha/T_f + \gamma/T_f r + \beta}}{(\eta_s + \eta_l) R \bar{T}}. \quad (13)$$

Since the last term in eq. (13) should be a small correction, eq. (12) suggests that the logarithm of the gas fugacity for simple hydrates in porous media should be very close to a bilinear function of $1/T$ and $1/r$. The form of (12) is called bilinear since for a fixed value of $1/T$ the function is linear in $1/r$, while for any fixed value of $1/r$ it is linear in $1/T$. The complete surface, however, does have a very small amount of curvature due to the overall nonlinearity of its functional form, though it is so small as to be difficult to see in Figure 4, where eq. (13) has been used to generate the surface for methane hydrate formation in porous media.

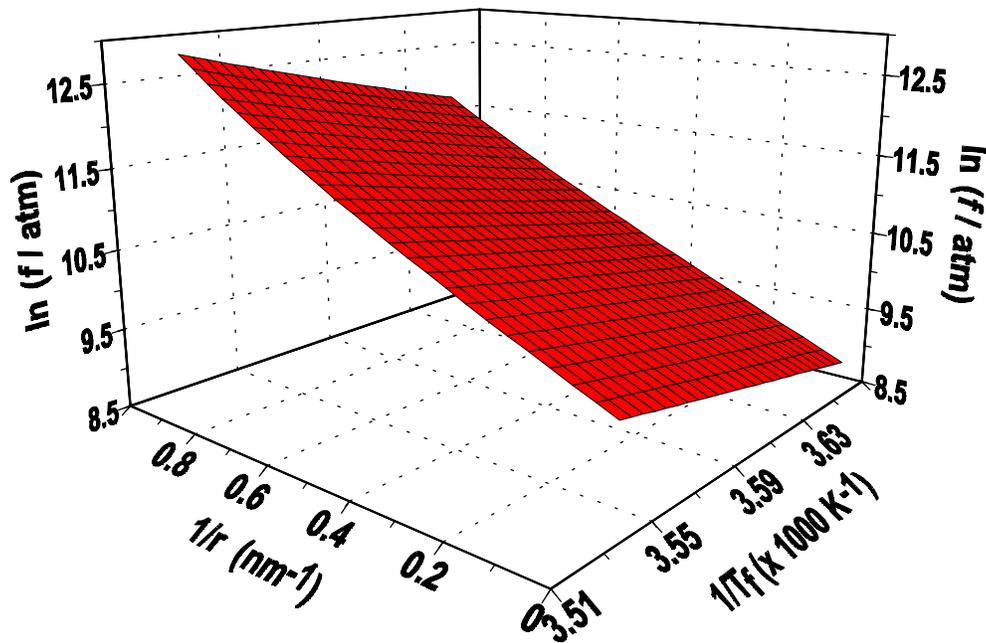


Figure 4: Shown is the surface representing predicted methane hydrate formation conditions in porous media using eq. (13).

Of primary interest to this work is the effect of the porous medium on the enthalpy of dissociation of the hydrates. While it has been shown that the sequestration of CO₂ by injection of CO₂ into methane hydrate is thermodynamically favored in the bulk (Komai et al., 1997), it has not been established that this holds for porous media. Using eq. (13) and the Clausius-Clapeyron equation

$$\frac{d(\ln(f))}{d(1/T)} = -\frac{\Delta H}{R}, \quad (14)$$

it is possible to estimate the change in enthalpy due to the porous media. Using eq. (13) in eq. (14) yields

$$\Delta H \approx -R \left\{ \alpha + \frac{\gamma}{r} + \frac{2\Delta V}{R(\eta_s + \eta_l)} \left[\left(\frac{T_f}{T_0 + T_f} \right)^2 + \alpha + \frac{\gamma}{r} \right] e^{\alpha/T_f + \gamma/T_f r + \beta} \right\}. \quad (15)$$

Since γ only depends on the hydrate lattice structure (and not on the gas species occupying the cages), it is the same for both methane and carbon dioxide hydrates which both form Structure I hydrates. As a result, it can be calculated based on well established quantities, and one only needs values of α and β (which are different for each gas) to estimate the dissociation enthalpies for various hydrates. While these can be calculated using relations similar to eq. (9), they can also be found by fitting (10) to the experimental data for the formation of bulk hydrates. This has been done for methane and CO₂ hydrates, with the results given in Table 3. The slight difference (approximately 4%) between the optimal values for methane shown in Table 3 obtained from fitting the data and the ones obtained using eq. (9) with the model parameters given in Table 2 is due to not having optimal values of the model parameters. The large R² values shown in Table 3 for both methane and carbon dioxide indicate the quality of the fits obtained with the functional form given in (10).

The results of using (15) to calculate values of the enthalpies of formation for methane and CO₂ hydrates in porous media are shown in Figure 5. The values of α and β from Table 3 for each gas have been used, along with the value of γ calculated using the parameters in Table 2, to construct these surfaces. We note that the calculated bulk

Table 3: Correlations for fitting experimental equilibrium fugacities for methane and CO₂ hydrates to $\ln f \approx \frac{\alpha}{T_f} + \beta + \frac{\Delta V}{RT} e^{\alpha/T_f + \beta}$ where f is in atm and T is in K.

	α	β	R^2
Methane	-6705	27.73	0.9972
Carbon Dioxide	-8482	33.43	0.9978

Enthalpies are in good agreement with values reported in the literature. For example, the experimental value for the enthalpy of dissociation of bulk methane hydrate to liquid water has been reported by Handa (1986) to be 54.19 KJ/mol, while that obtained from eq. (15) is 57.38 KJ/mol, a difference of less than 6%. As can be seen in Figure 5, there is a significant decrease in the difference between the enthalpies of dissociation for methane and CO₂ hydrates as $1/r$ increases (corresponding to smaller pore sizes in the sediment).

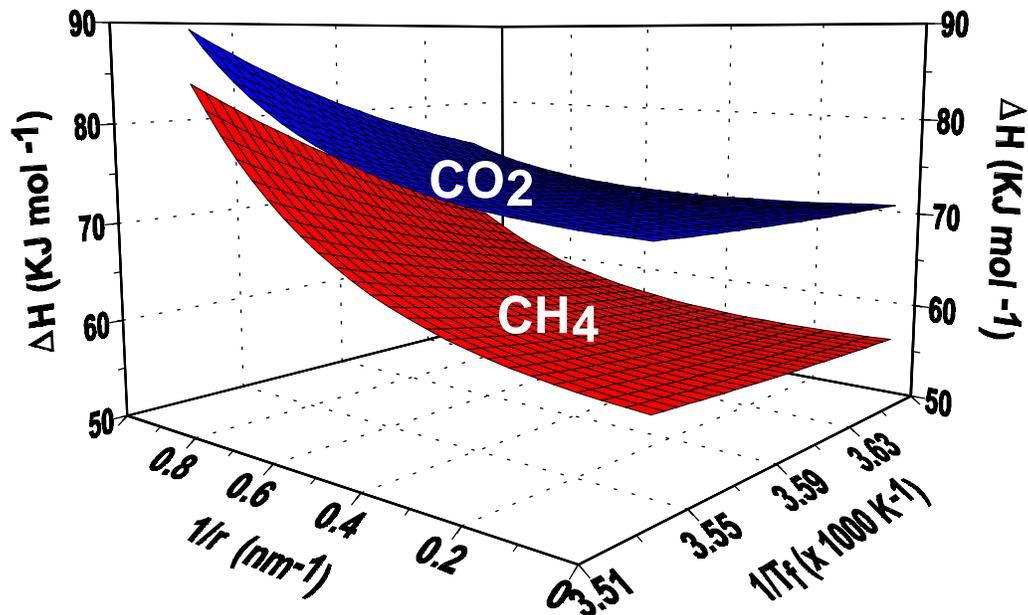


Figure 5: Shown are surfaces representing predicted enthalpies of dissociation for methane and CO₂ hydrates in porous media using eq. (15).

This decrease indicates that the replacement of methane by CO₂ in the hydrate lattice is less thermodynamically favored as the value of $1/r$ increases. This change may be experimentally detectable for sediments with very small pore sizes such as clays, and may manifest by taking a longer time for the displacement to take place in porous media as opposed to the bulk.

Future Activities

This work has considered the effect of porous media on the equilibrium of single component hydrates. We have shown that a relatively simple functional form allows for the estimation of both the equilibrium fugacity and the enthalpy of dissociation of the gas hydrates. If actual experimental replacement studies involving the injection of CO₂ into methane hydrate deposits are done in porous media, the gas involved in the equilibrium with the hydrate will not be made up of one component, but will be a mixture of carbon dioxide and methane. Future work will address such mixtures and the prediction of the resulting formation enthalpies.

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