Title: Thermal Dissociation Behavior and Dissociation Enthalpies of Methane–Carbon Dioxide Mixed Hydrates

Authors: Tae-Hyuk Kwon[1], Timothy J. Kneafsey[2], and Emily V. L. Rees[3]

Affiliations:

[1] Corresponding Author, Earth Sciences Division,
Lawrence Berkeley National Laboratory, 1 Cyclotron Rd. Berkeley, CA 94720, U.S.A.
Tel: 1-510-486-4201 Fax: 1-510-486-5686
Email: thkwon@lbl.gov

[2] Earth Sciences Division,
Lawrence Berkeley National Laboratory, 1 Cyclotron Rd. Berkeley, CA 94720, U.S.A.
Tel: 1-510-486-4414 Fax: 1-510-486-5686
Email: tjkneafsey@lbl.gov

[3] Earth Sciences Division,
Lawrence Berkeley National Laboratory, 1 Cyclotron Rd. Berkeley, CA 94720, U.S.A.
Tel: 1-510-486-4096 Fax: 1-510-486-5686
Email: evrees@lbl.gov

Corresponding Author: Tae-Hyuk Kwon

Abstract

Replacement of methane with carbon dioxide in hydrate has been proposed as a strategy for geologic sequestration of carbon dioxide (CO_2) and/or production of methane (CH_4) from natural hydrate deposits. This replacement strategy requires a better understanding of the thermodynamic characteristics of binary mixtures of CH_4 and CO_2 hydrate (CH_4-CO_2 mixed hydrates), as well as thermophysical property changes during gas exchange. This study explores the thermal dissociation behavior and dissociation enthalpies of CH_4-CO_2 mixed hydrates. We prepared CH_4-CO_2 mixed hydrate samples from two different, well-defined gas mixtures. During thermal dissociation of a CH_4-CO_2 mixed hydrate sample, gas samples from the head space were periodically collected and analyzed using gas chromatography. The changes in CH_4-CO_2 compositions in both the vapor phase and hydrate phase during dissociation were estimated based on the gas chromatography measurements. It was found that the CO_2 concentration in the vapor phase became richer during dissociation because the initial hydrate composition contained relatively more CO_2 than the vapor phase. The composition change in the vapor phase during hydrate dissociation affected the dissociation pressure and temperature—the richer CO_2 in the vapor phase led to lower dissociation pressure. Furthermore, the increase in CO_2 concentration in the vapor phase enriched the hydrate in CO_2. The dissociation enthalpy of the CH_4-CO_2 mixed hydrate was computed by fitting the Clausius-Clapeyron equation to the pressure-temperature (PT) trace of a dissociation test. It was observed that the dissociation enthalpy of the CH_4-CO_2 mixed hydrate lay between the limiting values of pure CH_4 hydrate and CO_2 hydrate, increasing with the CO_2 fraction in the hydrate phase.

1. INTRODUCTION

Gas hydrates are ice-like crystalline solid compounds composed of cages formed from hydrogen-bonded water molecules that encapsulate guest molecules, such as light hydrocarbons and carbon dioxide. Since the occurrences of natural gas hydrates in permafrost regions and in deep oceanic sediment formations have been reported, gas hydrates, primarily methane (CH_4) hydrate, have aroused interest in terms of it being a potential new energy resource, a potential geohazard, and contributor to global warming. Considerable interest is also growing in carbon dioxide (CO_2) hydrate, since natural CO_2 hydrate deposits have been found,[1] and the possibility of geologic carbon storage using CO_2 hydrate has been proposed.[2,3]

Methane hydrate and carbon dioxide hydrate contain many structural similarities. Both form structure I hydrates, since the gas molecules of CH_4 and CO_2 are approximately the same size (4.36 and 5.12 Å, respectively). These structural similarities between methane hydrate (CH_4 hydrate) and carbon dioxide hydrate (CO_2 hydrate) suggest that CO_2 sequestration could be used simultaneously as a method for methane recovery, via the replacement of methane by CO_2 in natural hydrate deposits.[4-6] Such use would potentially aid in the mitigation of global warming, by providing long-term sequestration of CO_2 in hydrate form. In particular, when CH_4 hydrate is surrounded by gaseous or liquid CO_2 under water-limited conditions (i.e., all the water is in the form of hydrogen-bonded water cages, and no free water is available to form new clathrate hydrates), it has been reported that CO_2 hydrate forms by releasing CH_4 molecules from the hydrate and encapsulating CO_2 in its place.[5,7] This is referred to as CH_4-CO_2 replacement.

However, using CH_4-CO_2 replacement for the purpose of geologic CO_2 storage in, and methane gas recovery from, natural methane hydrate deposits requires a better understanding of the thermodynamic characteristics and thermophysical properties of the binary mixtures of CH_4 and CO_2 hydrate (hereafter, CH_4-CO_2 mixed hydrates). Understanding the dissociation behavior of CH_4-CO_2 mixed hydrates will be particularly essential in developing an accurate model for predicting the consequences of CO_2 injection into CH_4 hydrate deposits, and for simulating CH_4-CO_2 replacement. In addition, the dissociation enthalpy of CH_4-CO_2 mixed hydrates is a key parameter in predicting these processes on a reservoir scale because of the considerable latent heat that is expected to be generated or absorbed during the formation/dissociation/replacement processes of a mixed gas hydrate system.

This study explores the thermal dissociation behavior of CH_4-CO_2 mixed hydrates. CH_4-CO_2 mixed hydrate samples were formed from well-defined CH_4-CO_2 gas mixtures, and then dissociation behavior of the samples was monitored. Changes in the CH_4-CO_2 compositions in both the vapor phase and hydrate phase during dissociation were analyzed based on gas chromatography measurements. Dissociation enthalpies of CH_4-CO_2 mixed hydrates were estimated using the experiment data and the Clausius-Clapeyron equation, and these were compared to published data on dissociation enthalpies of pure CH_4 hydrate, pure CO_2 hydrate, and mixed hydrates.

2. EXPERIMENT PROGRAM

2.1. Sample Preparation

All experiments in this study were conducted in a rigid-walled high pressure reaction vessel (aluminum alloy, internal volume = 38.6 cm^3, internal diameter = 25.4 mm, height = 76.2 mm). Both end caps for the vessel had a single feed-through (inlet and outlet end), allowing for injection and flow of gas through the sample. The vessel was instrumented with one thermocouple (T-type; Omega Engineering, Stamford CT) and one pressure transducer (CEC Instrument Division, IMO Delaval Inc.) to monitor the temperature and pressure during the formation and dissociation processes (see Figure S1 in the Supporting Information). The temperature of the reaction vessel was controlled by circulating temperature-controlled fluids from a refrigerating circulator through a jacket surrounding the reaction vessel. The pressure of the system was controlled by the regulator on compressed gas cylinders.

Two different CH_4-CO_2 gas mixtures—one 67% CH_4, 33% CO_2 (mole fraction) and the other 33% CH_4, 67% CO_2—were used as gas hydrate formers (see Table 1). Distilled water was used to form CH_4-CO_2 mixed hydrate samples without the addition of an electrolyte.

The hydrate was formed inside a porous medium, made from F110 sand (100% silica sand with 120 μm mean grain size). The material was pre-wetted with distilled water, then compacted into the pressure vessel (average porosity = 0.35, water saturation = 0.38). There was no significant capillary effect on phase equilibrium boundary during dissociation,[8] thus the pressure-temperature (PT) phase behavior of mixed hydrates in sands is presumed to be identical to that in the bulk

condition. No additional water was added to the samples prior to hydrate formation. The gas mixture was injected into the sample through the inlet end of the vessel and pressurized to about 4.0 MPa for Gas Mixture 1 and about 3.4 MPa for Gas Mixture 2 while at room temperature. Then, the system was cooled to and maintained at ~1.5ºC until hydrate formation took place as indicated by an increased temperature in the sample from the exothermic hydrate formation. During hydrate formation, a constant fresh gas feed was maintained through the sample by bleeding gas from the outlet end of the vessel at a flow rate of 20 cm^3/min under atmospheric conditions. More than 24 hours were given for the samples to form hydrate at their respective pressures and temperatures, and for both gas mixtures the same procedure was applied to prepare hydrate samples. The volume of water added for hydrate formation was 5.14 cm^3, leaving the volume of head space filled with gas to be 8.49 cm^3. After hydrate formation, assuming 100% phase transformation of water to hydrate and the hydration number of 6, the hydrate saturation in the porous media (defined as the hydrate volume divided by the total pore volume) was expected to be approximately 47–48%, leaving the head space to be about 7.1–7.2 cm^3.

2.2. Dissociation Procedure

Before commencing thermal dissociation, the pressure of a hydrate sample was stepwise reduced using a constant-volume gas sampler (~2.64 cm^3) until the first indication of hydrate dissociation (i.e., pressure re-bound) was observed. Then, hydrate samples were thermally dissociated by stepwise heating 1.5ºC per increment under constant volume conditions (isochoric condition with no mass flux). Once the temperature had stabilized after every temperature step (50–60 mins), a constant-volume of gas (~2.64 cm^3) was collected for gas chromatography (GC) analysis by opening the valve between the pressure vessel and the pre-evacuated gas sampler, and filling the gas sampler with gas (see Figure S1 in the Supporting Information). After isolating the sampled gas by closing the valve, the gas contained in the sampler was bled to a gas sample bag. 200 μL of the gas was withdrawn from the gas-filled bag by a syringe, and then it was injected to a gas chromatograph (SHIMADZU GC-8A, thermal conductivity detector) to determine gas composition. For each gas sample in a bag, GC analysis was repeated three times. Composition of the gas samples, i.e., the mole fractions of CH_4 and CO_2 gases, was determined by averaging the obtained results. Each time gas was sampled, a pressure drop occurred inside the vessel, causing additional hydrate dissociation.

After sampling, gas released from this additional hydrate dissociation increased the pressure to the equilibrium condition once again. Stepwise heating and sampling was continued until no pressure increase was observed after gas sampling, indicating that all hydrate had been dissociated from the sample. The same procedure of thermal dissociation was applied for both gas mixtures.

3. RESULTS AND DISCUSSION

3.1. Thermal Dissociation of CH_4-CO_2 Mixed Hydrates

As the temperature increases under constant volume, a binary mixture of hydrate releases mixed gas and water, resulting in an increase in fluid pressure that hinders further dissociation and facilitates the re-formation of gas hydrate, re-establishing another equilibrium condition. Pressure increases along the gas-water-hydrate equilibrium of the binary mixture during the thermally driven dissociation. This behavior continues until either the PT state reaches the second quadruple point or all hydrate dissociates. The pressure and temperature responses of CH_4-CO_2 mixed hydrates formed from Gas Mixture 1 (CH_4: CO_2 = 0.67:0.33) during thermal dissociation are shown in Figure 1. Hydrate dissociation started when the pressure and temperature reached the hydrate equilibrium boundary for Gas Mixture 1. Dissociation ended at approximately 4.5 MPa and 8.5ºC when all the hydrate dissociated.

As thermal dissociation proceeded, the CH_4/CO_2 molar ratio in the vapor phase decreased from 2.03 to 1.54, as shown in Figure 1b. This indicates that more CO_2 than CH_4 was released from the hydrate phase during thermal dissociation, as the CO_2 mole fraction in the vapor phase increased by ~19.5% over the hydrate dissociation. This is because the hydrate phase concentrated CO_2 compared to the gas feed composition. This enrichment of the hydrate phase with CO_2 also suggests that more CO_2 was encaged in the hydrate phase over CH_4 when forming hydrate from a mixture of the two gases. From GC results, it is estimated that the CO_2 fraction occupied in hydrate cages before commencing dissociation was approximately 38% (see Section 3.2 for details). Therefore, during dissociation, CO_2-rich gas, i.e., composed of 62% methane and 38% CO_2, was added to the vapor phase, decreasing the observed CH_4/CO_2 molar ratio from the original gas mixture.

The pressure of the sample increased with the temperature increase along the phase boundary of the

mixed hydrate. This boundary was calculated using the CSMGem software, as shown in Figure 1c.[9] It was observed that the PT trace showed a slight shift toward lower pressure (or higher temperature) when compared to the phase boundary calculated by the CSMGem software. This observation suggests that an increase in CO_2 concentration in the vapor phase during dissociation gradually lowers the equilibrium pressure (or dissociation pressure) at a given temperature compared to the initial equilibrium curve. It is found that the change in vapor composition leads to a change in the partial pressures (or fugacities) of both CH_4 and CO_2 gases, and governs the equilibrium of the three-phase system (i.e., hydrate, water, vapor). Moreover, a distinctive PT trace during dissociation was observed while equilibrating the temperature after the 6th gas sampling (see Point A in Figure 1c). It revealed that the hydrate dissociated along a different phase boundary, corresponding to the final gas composition of 60.7% CH_4 and 39.3% CO_2, deviating from the original phase boundary. This is presumed to be due to the CO_2-rich hydrate forming simultaneously from dissociated gas, but the evidence of this reformation of hydrate (e.g., exothermic heat signal) was not detected in the region of interest.

For Gas Mixture 2 (CH_4 : CO_2 = 0.33 : 0.67), hydrate dissociation started when the pressure reached ~1.8 MPa at about 1.4ºC, and ended at ~3.4 MPa and 7.5ºC (Figure 2). The CH_4/CO_2 molar ratio in the vapor phase decreased from 0.555 to 0.414, as shown in Figure 2b, while the CO_2 mole fraction in the vapor phase increased from 0.643 to 0.707. The initial CO_2 fraction occupied in hydrate cages is estimated to be ~70% by the inverse calculation based on the GC results (described below). However, the CH_4/CO_2 composition of the first sampling (i.e., ~0.555 at ~100 min in Figure 2b) was higher than that of the gas feed (i.e., 0.49) because more CO_2 than CH_4 from the gas feed was consumed during hydrate formation. This implies that the bleeding rate (20 cm^3/min) was not fast enough to ensure no feed gas composition change during hydrate formation. The phenomenon of relative decreasing dissociation pressure with increasing temperature was also observed, as shown in Figure 2c.

3.2. Change in Hydrate Composition during Dissociation

Hydrate composition during thermal dissociation was derived based on the GC results at a given pressure and temperature. It was assumed that all the water had formed hydrate before commencing

dissociation. Due to a lack of reliable data, a weighted mean based on the hydrate composition of CH_4 and CO_2 was taken for the density of a mixed hydrate, assuming that the hydration number is 6 (e.g., the density of CH_4 hydrate is ~0.91 g/cm^3; the density of CO_2 hydrate is ~1.1g/cm^3). During dissociation, the quantity of dissolved gas in the aqueous phase is assumed to be negligible compared to the amount of free gas released. The moles of the gas mixture were calculated by using the Redlich-Kwong equation[10], and the moles of CH_4 gas or CO_2 gas in the vapor phase were estimated using the van der Waals mixing rule.[11] Throughout these calculations, the molar quantity of a gas mixture sampled by our constant volume sampler (2.64 cm^3) at each step was taken into consideration.

The calculated hydrate compositions are superimposed with the thermodynamic calculations by the CSMGem in Figure 3. The GC results for PT conditions along the three-phase equilibrium curve (where water, hydrate and free gas co-exist) were chosen to compute hydrate composition. The initial fraction of CO_2 in the hydrate for Gas Mixture 1 was estimated to be approximately 38.1%. As the temperature increased, the CO_2 fraction in the hydrate phase increased to a maximum of 41.6% at 8.6ºC where the hydrate dissociation was completed (Figure 3a). As the CO_2 concentration in the vapor phase changed from 32.9% to 37.2%, the CO_2 fraction in the hydrate phase changed from 38.1% to 41.6%. The hydrate became richer in CO_2 due to the increased levels of CO_2 in the vapor phase. CO_2 was therefore preserved in the hydrate phase to establish the equilibrium composition of CH_4-CO_2 hydrate mixtures.

The initial CO_2 hydrate composition for Gas Mixture 2 was estimated to be 70.6%. As the temperature increased, the CO_2 hydrate composition showed a very small increase to 71.2% at a temperature of 4.2ºC, then decreased to 70.7% at 8.5ºC when the hydrate dissociation was completed (see Figure 3b). While the CO_2 concentration in the vapor phase increased from 66.2% to 70.7%, the CO_2 hydrate fraction changed from 70.6% to a maximum of 71.2%. Contrary to the hydrate composition change in the case of Gas Mixture 1 (i.e., 38.1–41.6% CO_2), Gas Mixture 2 showed a smaller change in hydrate composition (i.e., 70.6–71.2% CO_2). In general, the guest fractions in the hydrate phase calculated along the three-phase equilibrium are in agreement with the CSMGem calculations; however, in the case of Gas Mixture 2, a difference of 5% was observed.

3.3. Dissociation Enthalpies of Methane-Carbon Dioxide Mixed Hydrates

Dissociation enthalpy of gas hydrate. The general reaction formula for dissociation of gas hydrate is written as $M\cdot nH_2O$ (*s*) = M (*g*) + nH_2O (*l*), where M is a hydrate-forming gas (or hydrate-forming gas mixture) and *n* is hydration number. Thus, molar dissociation enthalpy of gas hydrate is defined as the heat required to decompose hydrate and to release one mole of guest gas molecule.[12] While van der Waals forces are the only interactions between the guest and host molecules, the molar dissociation enthalpies of gas hydrate ΔH_d are determined by the following factors: (1) the number of hydrogen bonds per guest molecule and (2) the interaction between guest molecules and host water molecules. However, the number of hydrogen bonds per guest molecule is a complex feature of not only by the structural type of hydrate, but also cage occupancy; and they both are directly related to the relative size of the guest molecule and the cavity.

Structure I (sI) hydrate contains 46 water molecules per unit cell that is comprised of 2 small cavities (12 pentagonal faces, 5^{12}) and 6 large cavities (12 pentagonal faces and 2 hexagonal faces, $5^{12}6^2$). Structure II (sII) hydrate contains 136 water molecules per unit cell comprised of 16 small cavities (5^{12}) and 8 large cages ($5^{12}6^4$).[13] The numbers of water molecules per cavity are 5.75 for sI hydrate and 5.67 for sII hydrate. Therefore, when fully occupied, it could be misread that sI hydrates would require larger molar dissociation heat than sII hydrates. However, results have been reported to be opposite of this because sII hydrate-forming gases are generally too big to occupy small cages of sII hydrate.[12,13] For an example, propane (C_3H_8) occupies only large cages, forming sII hydrate with the hydration number *n* of 17. ΔH_d for $C_3H_8\cdot 17H_2O$ is 129.2 kJ/mol gas.[12] On the contrary, ethane (C_2H_6) hydrate (sI hydrate) was reported to have ΔH_d of 71.8 kJ/mol gas, though ethane (C_2H_6) occupies only large cages with an ideal hydration number *n* of 7.67.[12]

Since gas hydrates are non-stoichiometric solid crystals, it has been known that even pure hydrate can result in a range of dissociation heats due to the different cage occupancies with a given hydrate-forming species and a given hydrate structure. Strictly speaking, more cages occupied within a hydrate would lower the free energy of the water molecules making up the lattices, compared to the free energy of the water molecules in the empty lattice in the absence of guest molecule inside. However, according to the definition of the molar dissociation enthalpy (i.e., heat required to release one mole of guest molecule), a gas hydrate with a higher hydration number (more empty cages) usually results in larger molar enthalpy change during dissociation than the

same hydrate with a lower hydration number (less empty cages). For an instance, Anderson[14] reportedly calculated ΔH_d of CO_2 hydrate to be 63.6 kJ/mol gas for n = 6.6 at 273 K which is the first quadruple point and 57.6 kJ/mol gas for n = 5.6 at 283 K which is the second quadruple point.

Finally, the interaction between guest molecules and host water molecules is known to affect molar dissociation enthalpy of gas hydrate. In general, bigger guest size results in a higher enthalpy change,[15,16] e.g., ΔH_d for CH_4 hydrate = 52–57 kJ/mol gas, ΔH_d for CO_2 hydrate = 58–65 kJ/mol gas, and ΔH_d for C_2H_6 = 62.5 kJ/mol gas (see Table 2). However, the data shown in Table 2 may have different cage occupancies, and thus, different numbers of hydrogen bonds per guest molecule even though those gases form sI hydrate. It is still challenging to isolate and explore only the effect of guest molecule size on the molar dissociation enthalpy as the cage occupancies always vary depending on the species of guest molecule, size of guest molecules and type of hydrate structure.

The Clausius-Clapeyron equation prediction. The molar dissociation enthalpy of gas hydrates can be estimated from the univariant slope of the phase equilibrium boundary (ln P vs $1/T$) using the Clausius-Clapeyron equation:[13,17]

$$\frac{d\ln(P)}{d(1/T)} = -\frac{\Delta H_d}{z \cdot R}, \qquad (1)$$

where P is the pressure, T is the temperature, ΔH_d is the enthalpy of dissociation, z is the compressibility factor, and R is the universal gas constant. If the compressibility factor does not change significantly over the measured PT data range, the equation can be used to calculate the enthalpy of dissociation from measured PT data, assuming that ΔH_d does not change significantly over a narrow temperature range.[13]

However, after Skovborg and Rasmussen[18] and Anderson[14,19] challenged the use of the Clausius-Clapeyron equation, and after extensive discussions[13,14,18-24], the consensus for the valid use of Equation (1) was identified with these restrictions: (a) the gas composition and the fractional quantity of the guest molecules occupied in the hydrate cavities should not change appreciably, and (b) the condensed phase volume changes (solid to liquid in this case) should be negligible relative to the gas volume. In particular, Gupta et al[24] argues for limiting the use of the Clausius-Clapeyron equation under high pressure (e.g., higher than 4 MPa). The Clapeyron equation is also known to be

limited in that it is difficult to apply to multicomponent gas hydrate systems.[22,24]

The Clausius-Clapeyron prediction can therefore only be applied when the pressure is lower than 4 MPa, such that the gas compressibility is low enough to reasonably assume that the volume change during phase transformation is equal to the volume of gas released. The predictions for pure hydrates using the Clausius-Clapeyron equation by Sloan and Fleyfel[13] are within 2% of the measured values using a Calvet-type calorimeter by Handa[12] at low pressure. Consequently, the dissociation enthalpy of CH_4-CO_2 mixed hydrate can be reasonably determined by using the Clausius-Clapeyron prediction method, because the PT data measured in this study during thermal dissociation are within a range of low pressure (less than 3.4 MPa). Moreover, it was recently found that the dissociation enthalpy of pure CH_4 hydrate, either predicted by using the Clapeyron equation (e.g., Anderson[19]) or measured by using a differential scanning calorimeter (e.g., Gupta et al.[24]), remains constant over the three-phase co-existence region. Thus, the calculated results are presumed to be applicable over the conditions investigated here.

Calculated results. The pressure and temperature traces of the thermal dissociation tests (Figures 1c and 2c) were used to obtain the dissociation enthalpies. The compressibilities of the tested gas mixtures were determined using the Redlich-Kwong equation, and the values used are listed in Table 1. The gas compressibilities of Gas Mixture 1 and Gas Mixture 2 are assumed to remain constant over the pressure and temperature range that occurred during the test (the actual changes of those values are less than 3% as seen by the values in Table 1). It is also justifiable to assume that fractional compositions in both hydrate and gas phases do not change significantly (see Figure 3). Figure 4 shows the PT data and the linear fitting of the Clausius-Clapeyron equation. The linearity of two curves, as shown in Figure 4, reduces error and results in the same slopes within the selected PT range.

The dissociation enthalpy of gas hydrate Sample 1 (i.e., formed from Gas Mixture 1 and estimated to have approximately 60% methane and 40% CO_2 in hydrate) is calculated to be 57.23 kJ/mol gas, while that of gas hydrate Sample 2 (i.e., formed from Gas Mixture 2 and estimated to have approximately 29% methane and 71% CO_2 in hydrate) results in 62.82 kJ/mol gas, as shown in Table 1. The changes in hydrate compositions during thermal dissociation in the temperature range of interest were less than 2%—e.g., CO_2 fractions in hydrate increased from 38.6 to 40.4% for gas hydrate Sample 1 in the temperature range of 3–6^{o}C, and from 71.0 to 71.2% for gas hydrate

Sample 2 in the temperature range of 2–6°C. Thus, it is approximated that gas hydrate Sample 1 has ~40% of CO_2 fraction in hydrate phase and gas hydrate Sample 2 has ~71% of CO_2 fraction in hydrate phase. The calculated dissociation enthalpies of CH_4-CO_2 mixed hydrates are superimposed with published data in Figure 5. In addition, the estimated values based on the PT equilibrium boundaries predicted by CSMGem in a low temperature regime (1–7°C) are added for comparison in Figure 5. It is found that the values for CH_4-CO_2 mixed hydrates lie between the limiting values of pure CH_4 hydrate and CO_2 hydrate, and increase with CO_2 concentration in the hydrate phase. Therefore, our results support the hypothesis that the molar enthalpy of dissociation increases with an increasing number of the large guest molecules occupied in sI hydrate cages, and are consistent with the observations by Rydzy et al.[15] and Hachikubo et al.[16] It also reveals that the values estimated by CSMGem are larger than our results. This is because the predicted PT boundaries do not agree well with the PT traces of the test results, particularly in a low temperature regime.

4. Conclusions

In this study, two CH_4-CO_2 mixed hydrate samples were formed: (1) 60% CH_4 and 40% CO_2 in hydrate from a gas mixture of 67% CH_4 and 33% CO_2, and (2) 30% CH_4 and 70% CO_2 in hydrate from a gas mixture of 33% CH_4 and 67% CO_2. The thermal dissociation behavior of CH_4-CO_2 mixed hydrates was monitored, and the changes in CH_4/CO_2 compositions of both vapor phase and hydrate phase during dissociation were analyzed using gas chromatography. GC measurements showed that more CO_2 than CH_4 was encaged in the hydrate phase compared to the composition of the gas feed. Likewise, more CO_2 was released than CH_4 from the hydrate phase during thermal dissociation, which enriched the vapor phase in CO_2, because the initial CO_2 concentration in the hydrate phase was higher than that of the gas feed.

It was also found that an increase in CO_2 concentration in the vapor phase during dissociation of CH_4-CO_2 mixed hydrates gradually lowers dissociation pressure at a given temperature. This is because the vapor composition changes result in a change in the partial pressures (or fugacities) of both CH_4 and CO_2 gases, and govern the equilibrium of the three-phase system (hydrate, water, vapor). At the same time, it was observed that the increased levels of CO_2 in the vapor phase enriched the hydrate in CO_2 to establish the equilibrium composition of CH_4-CO_2 hydrate mixtures.

The molar dissociation enthalpies of CH_4-CO_2 mixed hydrates were estimated using the PT trace of the thermal dissociation data and the Clausius-Clapeyron equation. The dissociation enthalpy of CH_4-CO_2 mixed hydrates having a CO_2 fraction of 40% was calculated to be 57.23 kJ/mol gas while that of CH_4-CO_2 mixed hydrates containing a CO_2 fraction of 70% was calculated to be 62.82 kJ/mol gas. It was found that the values for CH_4-CO_2 mixed hydrates lie between the limiting values of pure CH_4 hydrate and CO_2 hydrate and increase with CO_2 fraction in the hydrate phase.

The composition of CH_4-CO_2 mixed hydrates produced and the resulting PT equilibrium conditions are therefore presumed to be determined by the CH_4/CO_2 vapor composition. This condition is expected where gaseous CO_2 is injected into a methane hydrate deposit containing free methane gas under water-limited conditions. Because mixed hydrate with more CO_2 has higher dissociation enthalpy, releasing CH_4 and trapping CO_2 in hydrate phase during CH_4-CO_2 replacement process is likely to be an exothermic reaction.

Acknowledgement

The authors are grateful to anonymous reviewers for valuable comments and suggestions. Support for this research was provided by ConocoPhillips under Agreement Number LB09005884 with LBNL, by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, and by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2009-352-D00299).

Supporting Information Available:

Test set-up for hydrate dissociation and gas sampling for GC analysis (Figure S1). This information is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Inagaki, F.; Kuypers, M. M. M.; Tsunogai, U.; Ishibashi, J.; Nakamura, K.; Treude, T.; Ohkubo,

S.; Nakaseama, M.; Gena, K.; Chiba, H.; Hirayama, H.; Nunoura, T.; Takai, K.; Jorgensen, B. B.; Horikoshi, K.; Boetius, A. *P. Natl. A. Sci. U.S.A.* **2006**, *103*, 14164.

(2) House, K. Z.; Schrag, D. P.; Harvey, C. F.; Lackner, K. S. *P. Natl. A. Sci. U.S.A.* **2006**, *103*, 14255.

(3) Tohidi, B.; Yang, J. H.; Salehabadi, M.; Anderson, R.; Chapoy, A. *Environ. Sci. Technol.* **2010**, *44*, 1509.

(4) Lee, H.; Seo, Y.; Seo, Y. T.; Moudrakovski, I. L.; Ripmeester, J. A. *Angew. Chemie. Int. Edit.* **2003**, *42*, 5048.

(5) Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, R. L.; Inomata, H. *Energ. Convers. Manage.* **2005**, *46*, 1680.

(6) Park, Y.; Kim, D. Y.; Lee, J. W.; Huh, D. G.; Park, K. P.; Lee, J.; Lee, H. *P. Natl. A. Sci. U.S.A.* **2006**, *103*, 12690-12694.

(7) Jung, J. W.; Espinoza, D. N.; Santamarina, J. C. *J. Geophys. Res.* **2010**, *115*.

(8) Kwon, T. H.; Kim, H. S.; Cho, G. C. *Environ. Sci. Technol.* **2008**, *42*, 8571.

(9) CSMGem. a free version of this software is available at http://hydrates.mines.edu/CHR/Software.html.

(10) Redlich, O.; Kwong, J. N. S. *Chem. Rev.* **1949**, *44*, 233.

(11) Kwak, T. Y.; Mansoori, G. A. *Chem. Eng. Sci.* **1986**, *41*, 1303.

(12) Handa, Y. P. *J. Chem. Thermodyn.* **1986**, *18*, 915.

(13) Sloan, E. D.; Fleyfel, F. *Fluid Phase Equilibr.* **1992**, *76*, 123.

(14) Anderson, G. K. *J. Chem. Thermodyn.* **2003**, *35*, 1171.

(15) Rydzy, M. B.; Schicks, J. M.; Naumann, R.; Erzinger, J. *J. Phys. Chem. B* **2007**, *111*, 9539.

(16) Hachikubo, A.; Nakagawa, R.; Kubota, D.; Hirotoshi, S.; Takahashi, N.; Shoji, H. "Dissociation heat of mixed-gas hydrate composed of methane and ethane"; The 6th International Conference on Gas Hydrates (ICGH 2008), 2008, Vancouver, Canada.

(17) Kang, S. P.; Lee, H.; Ryu, B. J. *J. Chem. Thermodyn.* **2001**, *33*, 513.

(18) Skovborg, P.; Rasmussen, P. *Fluid Phase Equilibr.* **1994**, *96*, 223.

(19) Anderson, G. K. *J. Chem. Thermodyn.* **2004**, *36*, 1119.

(20) Glew, D. N. *Nature* **1959**, *184*, 545.

(21) Barrer, R. M. *Nature* **1959**, *183*, 463.

(22) van der Waals, J. H.; Platteeuw, J. C. *Nature* **1959**, *183*, 462.

(23) Yamamuro, O.; Suga, H. *J. Therm. Anal. Calorim.* **1989**, *35*, 2025.

(24) Gupta, A.; Lachance, J.; Sloan, E. D.; Koh, C. A. *Chem. Eng. Sci.* **2008**, *63*, 5848.

(25) Nakagawa, R.; Hachikubo, A.; Shoji, H. "Dissociation and specific heats of gas hydrates under submarine and sublacustrine environments"; The 6th International Conference on Gas Hydrates (ICGH 2008), 2008, Vancouver, Canada.

(26) Yoon, J. H.; Yamamoto, Y.; Komai, T.; Haneda, H.; Kawamura, T. *Ind. Eng. Chem. Res.* **2003**, *42*, 1111.

List of Tables

Table 1. Compositions of the gas mixtures, mixed hydrates, and the dissociation enthalpies of the CH_4-CO_2 mixed hydrates

Table 2. Molar dissociation enthalpies of various gas hydrates

Table 1. Compositions of the gas mixtures, mixed hydrates, and the dissociation enthalpies of the CH_4-CO_2 mixed hydrates

	Gas Feed Composition [CH_4:CO_2 mole fraction]	Resulting Hydrate Composition [a] [CH_4:CO_2 mole fraction]	Gas Compressibility [b] [-]	Enthalpy of Dissociation [kJ/mol gas]	PT Range [c]
Gas Mixture 1	0.67:0.33	0.40:0.60	0.896 ± 0.014	57.23 ± 0.93	2.5 - 3.4 MPa 3 - 6ºC
Gas Mixture 2	0.33:0.67	0.29:0.71	0.893 ± 0.032	62.82 ± 2.26	1.5 - 2.8 MPa 2 - 6ºC

Note: [a] Hydrate composition resulting from the feed gas composition is estimated based on the GC results. [b] Gas compressibility is determined by using the Redlich-Kwong equation. [c] PT range describes the range of pressure and temperature which our experiment data and fitting curves cover.

Table 2. Molar dissociation enthalpies of various gas hydrates [a]

Material	Dissociation Enthalpy [kJ/mol gas]	Reference
CH_4 hydrate ($h \rightarrow l + g$)	54.44	Gupta et al. (2008)[24]
	54.19	Handa (1986)[12]
	56.9	Sloan and Fleyfel (1992)[13]
	56.84	Kang et al. (2001)[17]
	55.3	Nakagawa et al. (2008)[25]
	51.6	Rydzy et al. (2007)[15]
	52.9	Anderson (2004)[19]
	53.81	Yoon et al. (2003)[26]
Ethane hydrate ($h \rightarrow l + g$)	71.8	Handa (1986)[12]
	71.1	Nakagawa et al. (2008)[25]
CO_2 hydrate ($h \rightarrow l + g$)	57.7 - 63.6	Anderson (2003)[14]
	65.22	Kang et al. (2001)[17]
	57.66	Yoon et al. (2003)[26]
85% CH_4 + 15% CO_2 hydrate	53.4	Rydzy et al. (2007)[15]
70% CH_4 + 30% CO_2 hydrate	53	Rydzy et al. (2007)[15]
60% CH_4 + 40% CO_2 hydrate	57.23	This study
29% CH_4 + 71% CO_2 hydrate	62.82	This study

Note: [a] Molar dissociation enthalpies are for the reaction, $M \cdot nH_2O\ (s) = M\ (g) + nH_2O\ (l)$, where M is a hydrate-forming gas (or hydrate-forming gas mixture) and n is hydration number. Thus, molar dissociation enthalpy of gas hydrate is defined as the heat required to decompose hydrate into liquid and gas and to release one mole of guest gas molecule.

List of Figures

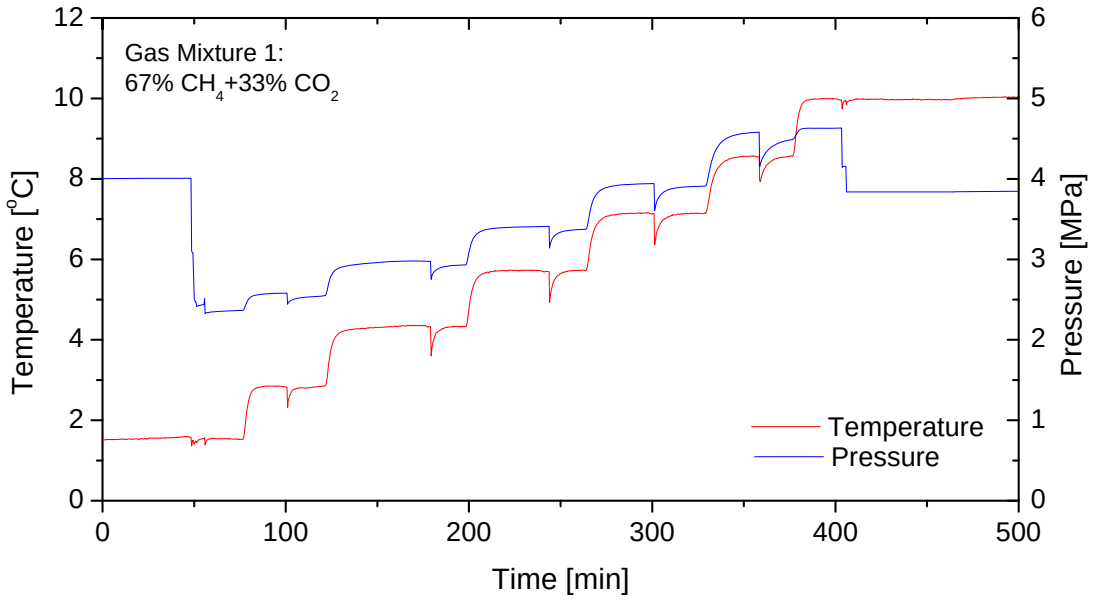
Figure 1. Thermal dissociation of CH_4-CO_2 mixed gas hydrate formed using Gas Mixture 1: (a) temperature and pressure change; (b) gas composition change; and (c) PT trace during thermal dissociation. The phase boundary PB computed with the CSMGem software corresponds to the gas mixture of 67% CH_4 and 33% CO_2.

Figure 2. Thermal dissociation of CH_4-CO_2 mixed gas hydrate formed using Gas Mixture 2: (a) temperature and pressure change; (b) gas composition change; and (c) PT trace during thermal dissociation. The phase boundary PB computed with the CSMGem software corresponds to the gas mixture of 33% CH_4 and 67% CO_2.

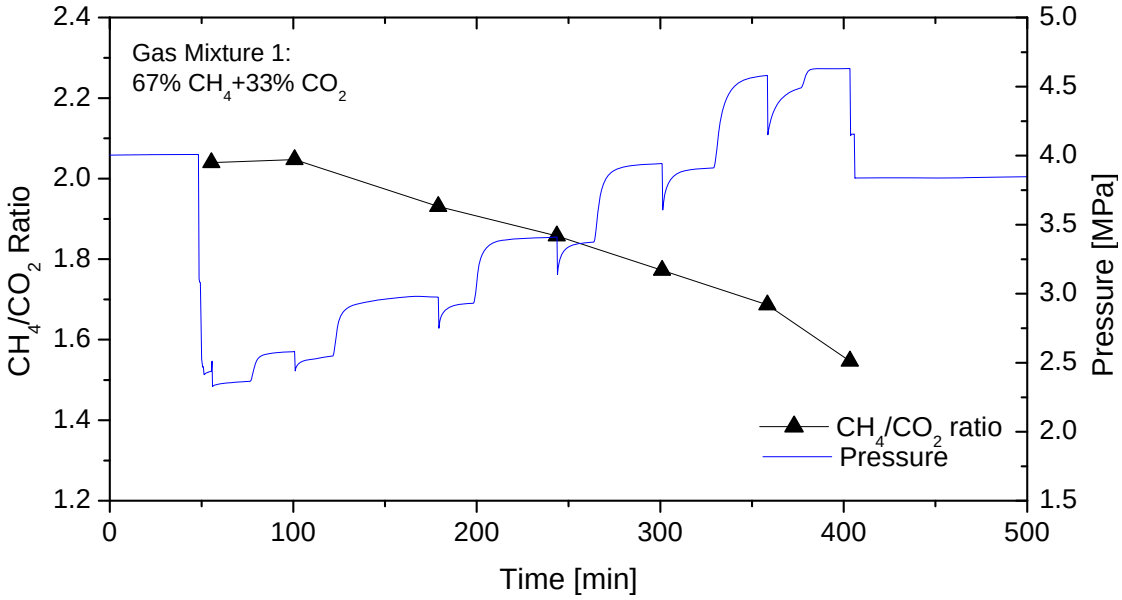
Figure 3. Change in the composition of CH_4-CO_2 mixed hydrates made from (a) Gas Mixture 1 and (b) Gas Mixture 2 during thermal dissociation along the three-phase equilibrium boundary.

Figure 4. Thermal dissociation data of CH_4-CO_2 mixed gas hydrates used in calculation of the enthalpy of dissociation.

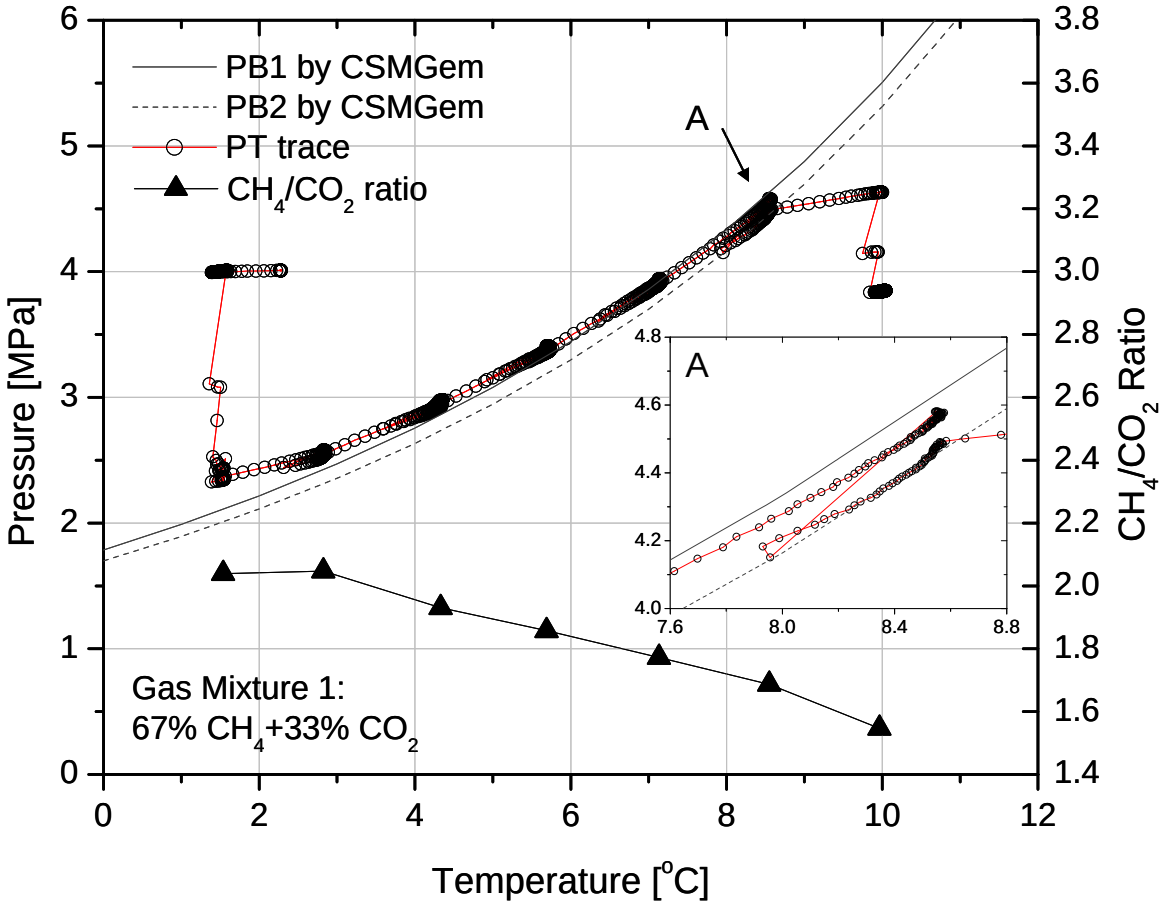
Figure 5. Dissociation enthalpies of CH_4-CO_2 mixed gas hydrates with respect to CO_2 fraction in hydrate phase.


Gas Mixture 1:
67% CH4+33% CO2
Temperature [°C]
Pressure [MPa]
Time [min]
Temperature
Pressure

(a)

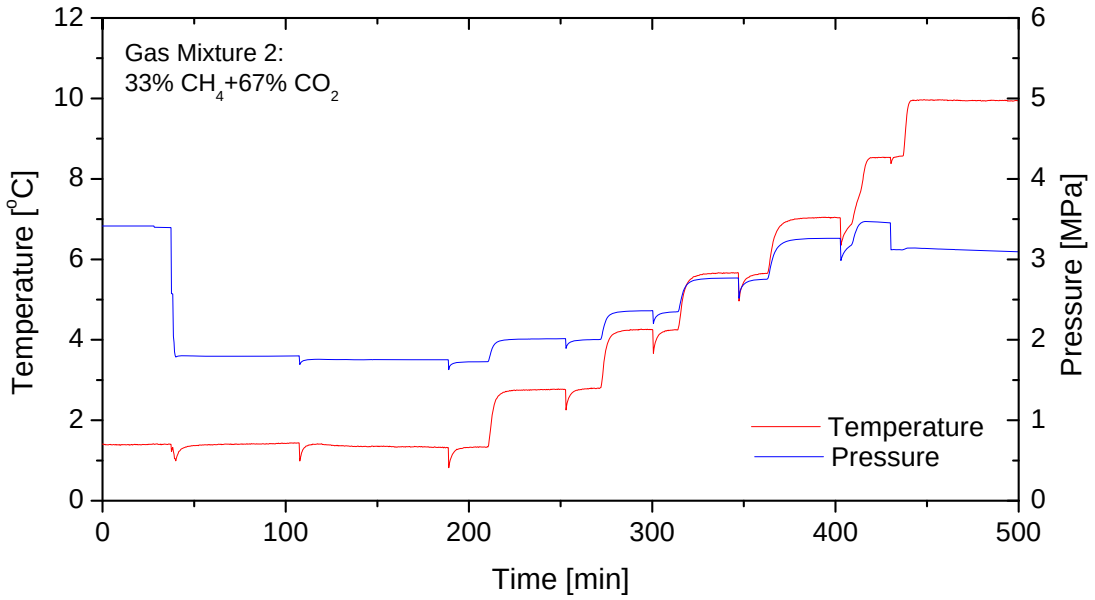

Gas Mixture 1:
67% CH4+33% CO2
CH4/CO2 Ratio
Pressure [MPa]
Time [min]
CH4/CO2 ratio
Pressure

(b)

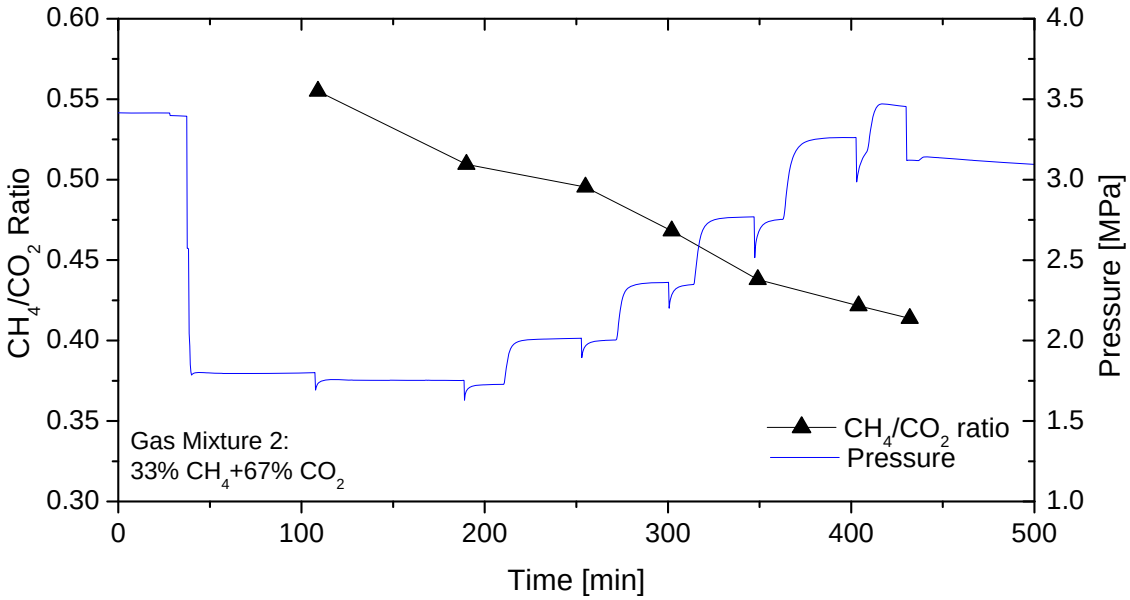


(c)

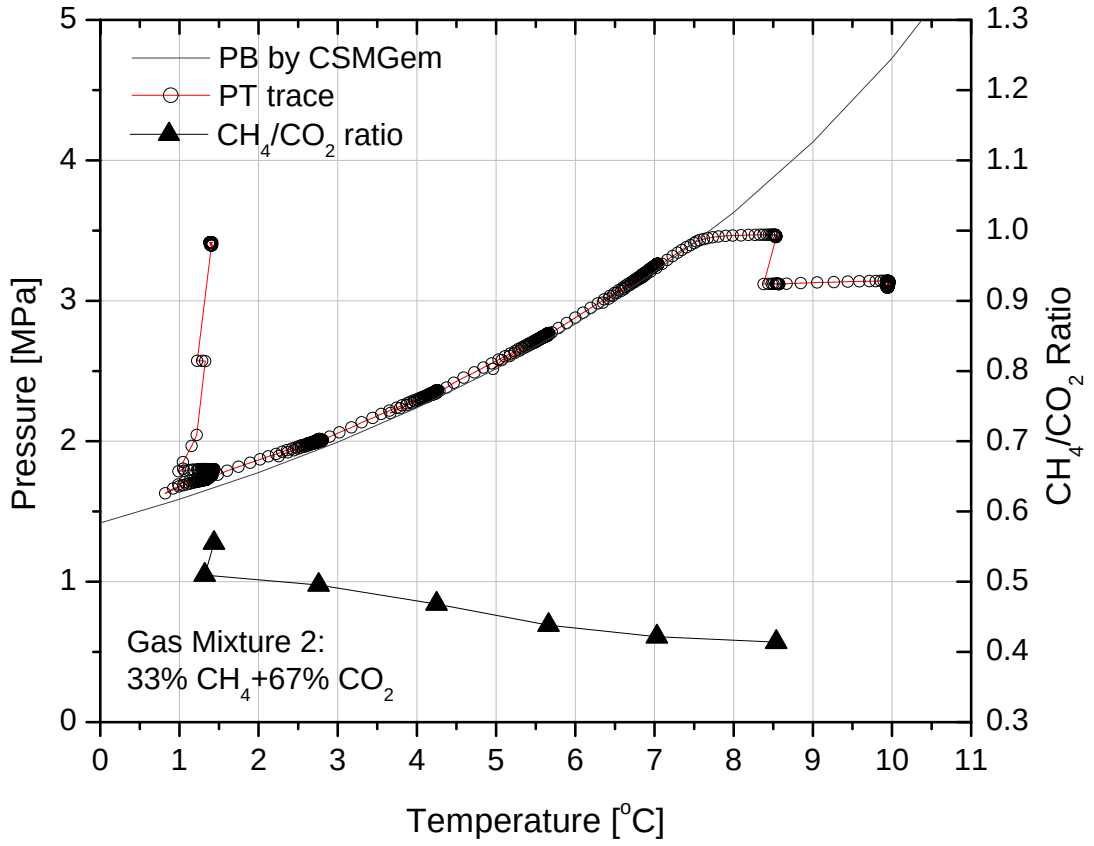
Figure 1. Thermal dissociation of CH_4-CO_2 mixed gas hydrate formed using Gas Mixture 1: (a) temperature and pressure change; (b) gas composition change; and (c) PT trace during thermal dissociation. The phase boundaries (PB) were computed with the CSMGem software. PB1 corresponds to the gas mixture of 67% CH_4 and 33% CO_2 and PB2 corresponds to the gas mixture of 60.7% CH_4 and 39.3% CO_2.


Gas Mixture 2:
33% CH4+67% CO2
Temperature [°C]
Pressure [MPa]
Time [min]
Temperature
Pressure
0
2
4
6
8
10
12
0
1
2
3
4
5
6
0
100
200
300
400
500

(a)

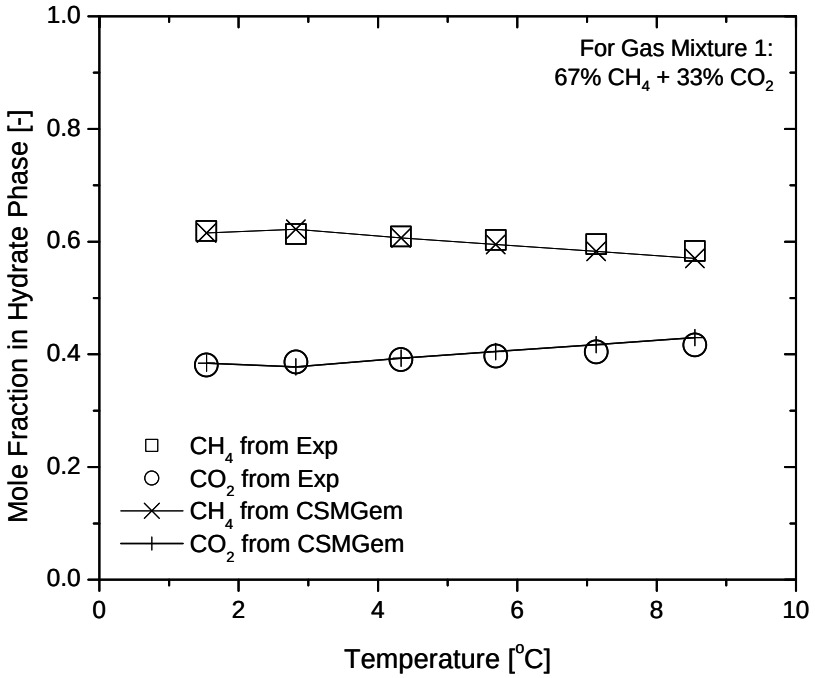

CH4/CO2 Ratio
Pressure [MPa]
Time [min]
Gas Mixture 2:
33% CH4+67% CO2
CH4/CO2 ratio
Pressure
0.30
0.35
0.40
0.45
0.50
0.55
0.60
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
100
200
300
400
500

(b)

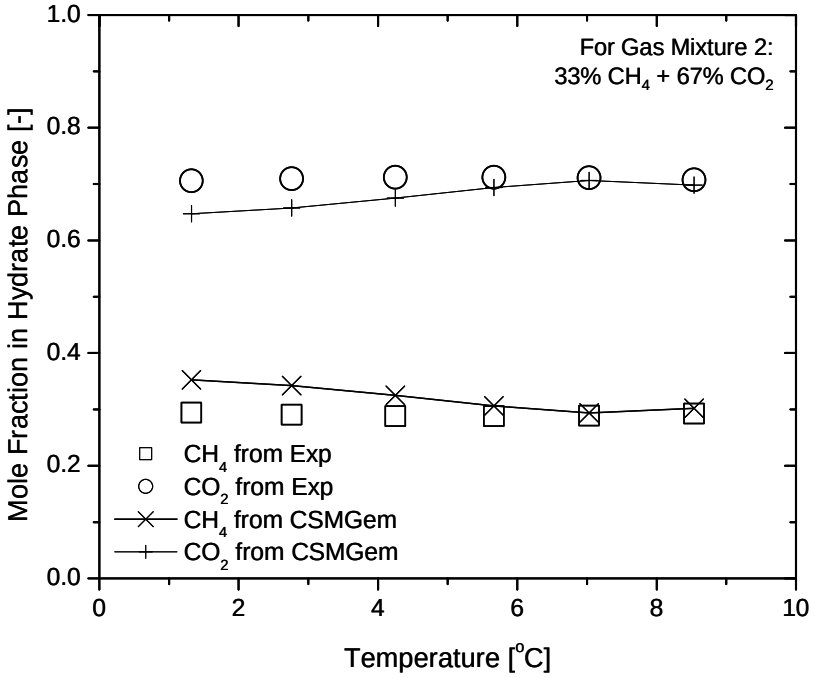


(c)

Figure 2. Thermal dissociation of CH_4-CO_2 mixed gas hydrate formed using Gas Mixture 2: (a) temperature and pressure change; (b) gas composition change; and (c) PT trace during thermal dissociation. The phase boundary (PB) computed with the CSMGem software corresponds to the gas mixture of 33% CH_4 and 67% CO_2.



(a)



(b)

Figure 3. Change in the composition of CH_4-CO_2 mixed hydrates made from (a) Gas Mixture 1 and (b) Gas Mixture 2 during thermal dissociation along the three-phase equilibrium boundary.

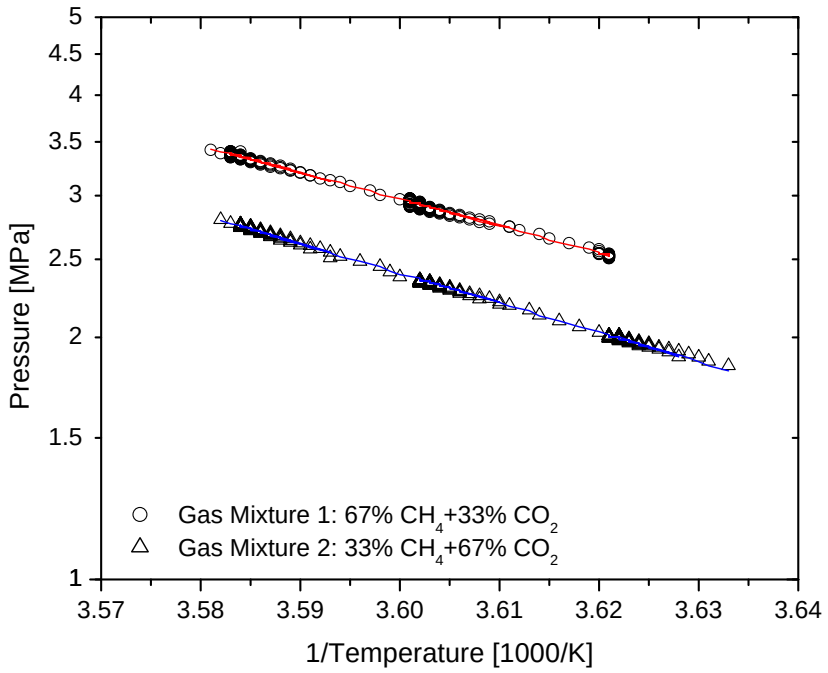


Figure 4. Thermal dissociation data of CH_4-CO_2 mixed gas hydrates used in calculation of the enthalpy of dissociation.

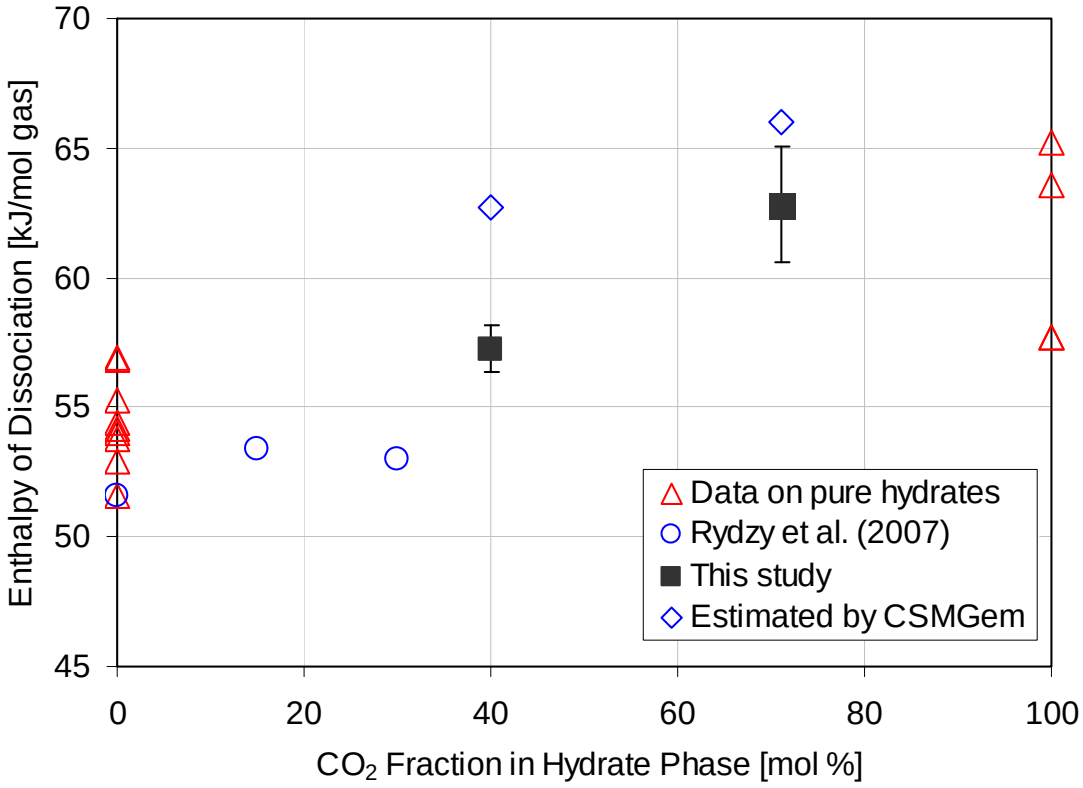


Figure 5. Dissociation enthalpies of CH_4-CO_2 mixed gas hydrates with respect to CO_2 fraction in hydrate phase.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.