12826 J. Am. Chem. Soc. **2001,** *123,* 12826−12831

Time-Resolved in Situ Neutron Diffraction Studies of Gas Hydrate: Transformation of Structure II (sII) to Structure I (sI)

Yuval Halpern,*,† Vu Thieu,† Robert W. Henning,‡ Xiaoping Wang,‡ and Arthur J. Schultz*,‡

Contribution from the Energy Systems Division, Argonne National Laboratory, Argonne, Illinois 60439, and Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois 60439

Received January 31, 2001

Abstract: We report the in situ observation from diffraction data of the conversion of a gas hydrate with the structure II (sII) lattice to one with the structure I (sI) lattice. Initially, the in situ formation, dissociation, and reactivity of argon gas clathrate hydrate was investigated by time-of-flight neutron powder diffraction at temperatures ranging from 230 to 263 K and pressures up to 5000 psi (34.5 MPa). These samples were prepared from deuterated ice crystals and transformed to hydrate by pressurizing the system with argon gas. Complete transformation from D_2O ice to sII Ar hydrate was observed as the sample temperature was slowly increased through the D_2O ice melting point. The transformation of sII argon hydrate to sI hydrate was achieved by removing excess Ar gas and exposing the hydrate to liquid CO_2 by pressurizing the Ar hydrate with CO_2. Results suggest the sI hydrate formed from CO_2 exchange in argon sII hydrate is a mixed Ar/CO_2 hydrate. The proposed exchange mechanism is consistent with clathrate hydrate being an equilibrium system in which guest molecules are exchanging between encapsulated molecules in the solid hydrate and free molecules in the surrounding gas or liquid phase.

Introduction

Clathrate hydrates are a general class of compounds composed of water and gas molecules.[1] They usually form at high pressures and low temperatures although a few are stable at ambient pressure. The natural occurrence of gas hydrates, as well as environmental concerns over the increase of carbon dioxide in the atmosphere, have led to speculation that CO_2 could be stored in hydrate form on the ocean floor.[2−4] This could be achieved by sequestering the excess CO_2 within a hydrate framework. Moreover, it may be possible to simultaneously extract the methane from methane hydrate reserves on the ocean floor and replace the guest molecule with carbon dioxide.[5]

At temperatures and pressures found a kilometer or more in depth in the ocean, carbon dioxide is a liquid. In experiments in which CO_2 is transported to the ocean floor, it is shown to pool as a liquid and react with the seawater to produce CO_2 hydrate.[6] However, it could also interact with other existing hydrates. Because of this, the environmental and safety issues, and possible potential benefits, of direct exposure of hydrates on the ocean floor to liquid carbon dioxide need to be examined. The literature contains many experimental reports in which different ratios of two or more gases are premixed and then typically reacted with water to map the pressure−temperature phase diagram and to investigate which of two or three structure types formed.[7−10] However, the experimental results described in this paper are different from others in the literature since they involve immersing a prepared sample of one hydrate (Ar hydrate) with one type of hydrate structure (sII) in liquid CO_2, which is a hydrate former of another structure type (sI).

Gas hydrates typically form one of two structures, labeled structure I (sI) and structure II (sII), although a third lattice named structure H (sH) is known.[1,11] Structure type I has primitive cubic unit cell with contents denoted as $6X{\cdot}2Y{\cdot}48H_2O$, where X and Y represent the large, 14-hedra, and small, 12-hedra, cavities which can accommodate a guest atom or molecule. Structure type II is face-centered cubic with contents of $8X{\cdot}16Y{\cdot}136H_2O$, where X and Y represent 12-hedra and 16-hedra cavities, respectively. For a particular gas or guest molecule, the structure type formed appears to be dependent on the size of the guest molecule, as well as how easily it can be accommodated by the cavities of the crystal lattices.[1,11] Carbon dioxide is known to form sI, whereas argon forms sII. In this contribution, we report the observation of the conversion of a sII hydrate to sI by immersing the sII Ar hydrate in liquid CO_2 (a structure I former) under pressure. It should be noted that although methane hydrate forms structure I, natural gas

---

* Corresponding authors.

† Energy Systems Division.

‡ Intense Pulsed Neutron Source.

[1] Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

[2] Herzog, H.; Golomb, D.; Zemba, S. *Environ. Prog.* **1991**, *10*, 64−74.

[3] Nishikawa, N.; Morishita, M.; Uchiyama, M.; Yamaguchi, F.; Ohtsubo, K.; Kimuro, H.; Hiraoka, R. *Energy Convers. Manage.* **1992**, *33*, 651−657.

[4] Saji, A.; Yoshida, H.; Sakai, M.; Tanii, T.; Kamata, T.; Kitamura, H. *Energy Convers. Manage.* **1992**, *33*, 643−649.

[5] Ohgaki, K.; Takano, K.; Sangawa, H.; Matsubara, T.; Nakano, S. *J. Chem. Eng. Jpn* **1996**, *29*, 478−483.

[6] Brewer, P. G.; Friederich, G.; Peltzer, E. T.; Franklin M. Orr, J. *Science* **1999**, *294*, 943−945.

[7] Saito, S.; Kobayashi, R. *AIChE J.* **1965**, *11*, 96−99.

[8] Handa, Y. P.; Ratcliffe, C. I.; Ripmeester, J. A.; Tse, J. S. *J. Phys. Chem.* **1990**, *94*, 4363−4365.

[9] Subramanian, S.; Kini, R. A.; Dec, S. F.; Sloan, E. D., Jr. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 873−886.

[10] Montano, P. A.; Linton, J.; Thieu, V.; Halpern, Y. *J. Synchrotron Rad.* **2001**, *8*, 972−974.

[11] Jeffrey, G. A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 135−190.

10.1021/ja010280y CCC: $20.00

(mixtures of hydrocarbons and other gases) hydrates found in the Gulf of Mexico and possibly other regions are structure II.[12] We have also examined the kinetics of the argon hydrate system. These experiments were carried out using the high-intensity powder diffractometer (HIPD) instrument at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory.

Experimental Procedures

Formation of Structure II Ar Hydrates. Powdered ice was prepared by freezing deuterated water (Aldrich, 99.9%) in liquid nitrogen and then crushing the ice in a mortar and pestle. Large ice particles were removed with a 250 μm sieve, and the powdered ice was placed in the pressure cell that was already cooled in liquid nitrogen. On the basis of the weight of the water at the end of the experiment, the amount of initial powdered ice in a fully loaded pressure cell was 1.50 ± 0.05 g. The apparatus has been described in more detail in an earlier publication.[13] The pressure cell was closed, mounted on the cold stage of a Displex closed-cycle helium refrigerator, and placed into the sample chamber on the HIPD diffractometer. The pressure cell was kept in liquid nitrogen throughout this process to prevent the ice from melting and to minimize condensation buildup on the outside of the cell. Before argon gas was introduced to the system, the sample was allowed to stabilize at the working temperature (230, 243, 253, or 263 K). The cell was then charged to 5000 psi (34.5 MPa) with argon gas. Neutron data were collected in intervals of 15 min to observe the transformation from ice to sII argon hydrate. Limited instrument time did not allow for the complete conversion to hydrate under these conditions, with conversion typically less than 50%.

Conversion of sII Ar Hydrates into sI Hydrates by Gas Exchange with CO_2. In these samples, the argon hydrate was formed at 263 K and 34.5 MPa in the manner described above. Complete conversion of ice to hydrate was then obtained by keeping the sample pressurized with 5000 psi (34.5 MPa) Ar and slowly warming it through the ice melting point. Since D_2O was used instead of H_2O, the melting point was 276.8 K (3.8 °C). The sample temperature was increased from 263 to 278 K (0.8 K/hour) to obtain complete conversion. When the conversion to hydrate was finished, the sample was cooled to a predetermined, working temperature (230, 243, 253, or 263 K).

Excess argon gas was then released by opening a valve used to isolate the sample from the atmosphere. This valve was kept open for several minutes to vent all of the excess argon gas. Complete gas removal was confirmed by closing the valve and noting the cell pressure stabilized around 1 atm. Next, carbon dioxide at a pressure of 900 psi (6.2 MPa) was quickly introduced to the sample at the same temperature. At these pressures and temperatures carbon dioxide is a liquid. Neutron diffraction data were collected in 15 min intervals during the initial, rapidly transforming stage, but were extended to 30 min intervals after approximately 24 h. Data were collected for up to 160 h depending on the temperature. At the end of this period, around 96% of the sII Ar hydrates were converted to the sI type.

The gases encaged in the hydrate samples at this point were collected for mass spectroscopy (MS) analysis. This was done for each of the four reaction temperatures. For this process, at 243 K excess CO_2 was first vented to 1 atm in the manner described above. At 243 K, excess CO_2 present in the pressure cell was in the liquid form, and the venting process took about 10 min, as the liquid had to boil off. The venting temperature of 243 K was used in all trials to avoid solid CO_2 formation (sublimation point of 194.5 K at 1 atm), and to minimize hydrate dissociation (~216 K for CO_2 hydrate decomposition temperature at 1 atm)[1] which proceeds slowly at 243 K. A 150-cm^3 evacuated gas collection bottle was then attached to the experimental setup. The sample was then heated from 243 to 298 K to dissociate the hydrate, and the evolving gases were collected in the bottle for mass spectroscopy (MS) analysis. The final pressure in the collection bottle was 30 psi (207 kPa). The mass spectrometer used was a Spectra Multi-Quad, model LMI, manufactured by Leda-Mass.

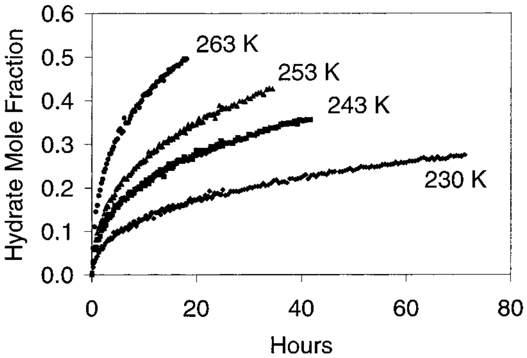

Figure 1. Conversion of deuterated ice to argon hydrate at 34.5 MPa (5000 psi) at various temperatures. Each data point represents the mole fraction of hydrate refined from a 15 min histogram.

Results and Discussion

Data Analysis. Neutron diffraction data were collected in 15 min intervals starting with the initial introduction of the gas into the system. The total length of the data collection depended on the initial starting temperature, with longer times required at lower temperatures. Time-of-flight neutron powder diffraction data were obtained using the 90° data bank on the HIPD. Data were analyzed using the GSAS program.[14]

The short data collection times and relatively low resolution of the HIPD instrument did not allow for a full Rietveld analysis of each data set. The lattice parameters of the phases observed in the spectrum (argon hydrate, CO_2 hydrate, ice, and aluminum) were refined in the initial stages but then fixed since the temperature and pressure of the sample did not change. The atomic positions and thermal parameters were determined in separate experiments for each temperature and were not varied during the refinements. In addition to four background parameters, the histogram scale factor, an absorption coefficient, and the phase fractions were allowed to refine. The weight fractions were extracted from each refinement and plotted in terms of mole fractions of hydrate.

Formation of sII Ar hydrates. The conversion of ice to argon hydrate (Figure 1) is a temperature-dependent process with ~25% conversion occurring in 51, 15, 9, and 3 h at 230, 243, 253, and 263 K, respectively, under 5000 psi (34.5 MPa) argon gas pressure. We have suggested[5] that after an initial period of fast conversion to hydrate on the ice particle surface, the formation process is then controlled by the diffusion rate of gas molecules through the accumulating hydrate layer. The following equation describes a conversion process of a particle from the outside to the inside during its diffusion-controlled stage at a constant temperature:[15]

$$(1-\alpha)^{1/3} = \left(\frac{-(2k)^{1/2}}{r_0}\right)(t-t^*)^{1/2} + (1-\alpha^*)^{1/3} \qquad (1)$$

where k and r_0 are the diffusion constant and the original radius of the particles, and α and α^* are degrees of reaction at times t and t^*. This equation has recently been used to fit the shrinking core model of the hydration of cement grains[16,17] and should also be applicable to the growing inward of a hydrate layer on

---

[12] Ripmeester, J. A. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 1−16.

[13] Henning, R. W.; Schultz, A. J.; Thieu, V.; Halpern, Y. *J. Phys. Chem. A* **2000**, *104*, 5066−5071.

[14] Larson, A. C.; Von Dreele, R. B. GSAS--General Structure Analysis System. Report No. LAUR 86-748, Los Alamos National Laboratory, Los Alamos, NM, 2000.

[15] Fujii, K.; Kondo, W. *J. Am. Ceram. Soc.* **1974**, *57*, 492−497.

[16] FitzGerald, S. A.; Neumann, D. A.; Rush, J. J.; Bentz, D. P.; Livingston, R. A. *Chem. Mater.* **1998**, *10*, 397−402.

[17] Berliner, R.; Popovici, M.; Herwig, K. W.; Berliner, M.; Jennings, H. M.; Thomas, J. J. *Cem. Concr. Res.* **1998**, *28*, 231−243.

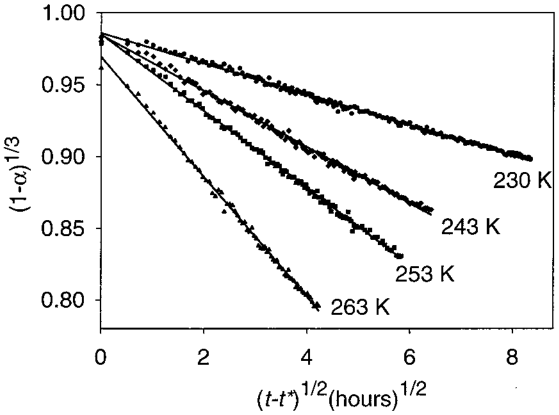

Figure 2. Plot of the experimental data of the conversion of deuterated ice to argon hydrate in terms of the shrinking core model.

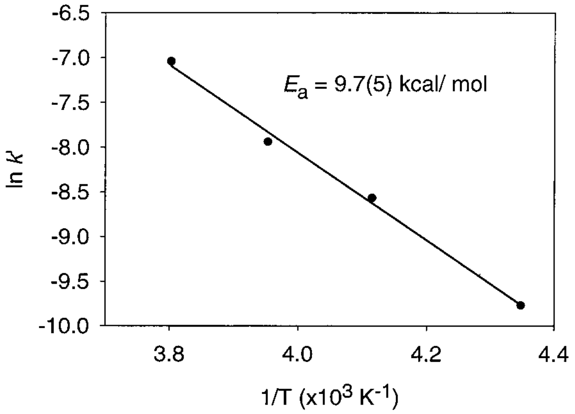

Figure 3. Plot of $\ln(k')$ as a function of $1/T$ (K^{-1}) for the conversion of deuterated ice to argon hydrate. An activation energy of the diffusion process to form argon hydrate was calculated from the slope of the straight line.

an ice particle.[13] For each temperature, obtaining a straight line by plotting $(1 - \alpha)^{1/3}$ as a function of $(t - t^*)^{1/2}$ indicates an agreement with eq 1. For a given particle size, the diffusion constant (k) can be calculated from the slope of the straight line.

The term t^* indicates the time where the conversion process is initially dominated by the diffusion of Ar molecules through the hydrate layer. In our experiments, we selected the t^* corresponding to ~5% conversion for each of the temperatures. This produced the best linear fit of eq 1 to the data. At times before or after 5% conversion, the fit greatly deviated from linearity, indicating that diffusion became the dominant factor in the reaction rate at t^* corresponding to ~5% conversion. Assuming an average ice particle size of 200 μm, 5% conversion corresponds to a hydrate layer with a thickness of approximately 1000 sII unit cells. Figure 2 shows a plot of the data in terms of eq 1 for each of the four temperatures.

The diffusion constants depend on the particle size and temperature, but for a given particle size distribution (r_0), the activation energy of the diffusion process is independent of these variables. The temperature dependence of a thermally dependent diffusion process should follow Arrhenius behavior described by $k = A \exp[-E_a/(RT)]$, where R is the gas constant. If k' is defined as k/r_0^2, k' can be calculated for each temperature from the slopes in Figure 2.

Figure 3 shows the straight line obtained by plotting $\ln(k')$ against $1/T$. An activation energy value of 9.7 kcal/mol was calculated from the slope of this line. This is less than the energy needed to break the hydrogen bonding in ice (12.7 kcal/mol)[18] but is greater than the energy needed to break the hydrogen bonding in liquid water (5 kcal/mol).[1] Analogous to the formation of CO_2 hydrate with an activation energy of 6.5 kcal/mol,[13] the argon hydrate-forming reaction is believed to occur between argon molecules and internal water in the quasi-liquid layer (QLL) rather than directly with ice molecules. The QLL is believed to be a thin mobile phase of water molecules with mobilities intermediate of those of liquid water and crystalline ice.[19]

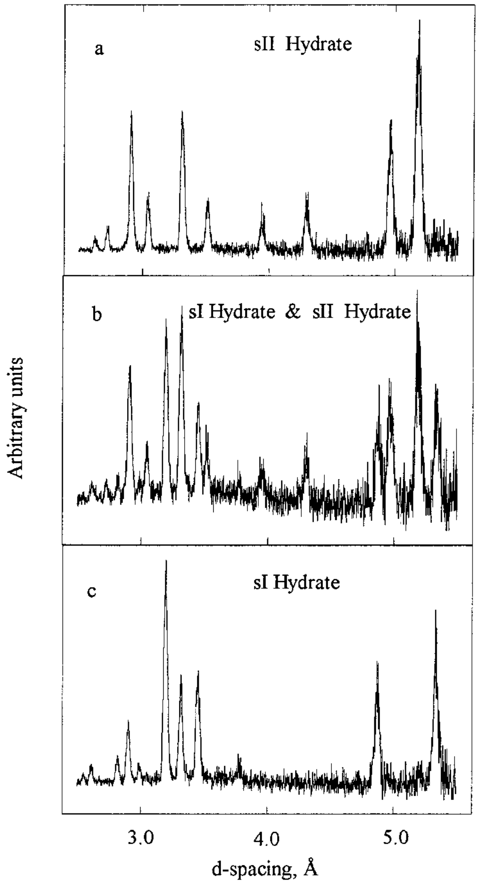

Figure 4. Neutron scattering patterns of sII Ar hydrate changes into sI hydrate at 243 K after excess Ar was vented and exchanged with CO_2 at 6.21 MPa: (a) Initial sII Ar hydrates at 243 K and 34.5 MPa of Ar; (b) approximately 50% of the sII hydrates converted to sI hydrates within 2 days after the excess Ar was replaced with 6.21 MPa CO_2 at 243 K; (c) 95% of the sII hydrates converted to sI hydrates within 4 days after the gas exchange.

Conversion of sII Ar Hydrate into sI Hydrate by Gas Exchange with CO_2. Neutron diffraction data in Figure 4 show the transformation, at 243 K, of the sII Ar hydrate to sI hydrate after the excess argon was replaced with CO_2. Figure 4a shows the sample of sII Ar hydrate at 243 K and 34.5 MPa. The hydrate sample, 2 days after the gas exchange from Ar to CO_2, is shown in Figure 4b. Diffraction peaks indicate the presence of both sI and sII hydrates. This sample was kept at 243 K for about 4 days in an effort to convert all sII hydrate to sI hydrate. After the 4-day period, neutron diffraction data indicated about 4% of the sample was sII hydrate and 96% sI hydrate (Figure 4c). MS results from these trials are discussed in the next section. The rate of conversion of sII Ar hydrate to the sI hydrate at various temperatures is shown in Figure 5. The decomposition

---

(18) Itagaki, K. *J. Phys. Soc. Jpn* **1967**, *22*, 427−431.

(19) Mizuno, Y.; Hanafusa, N. *J. Phys., Colloq. C1 Suppl.* **1987**, *48*, 511−517.

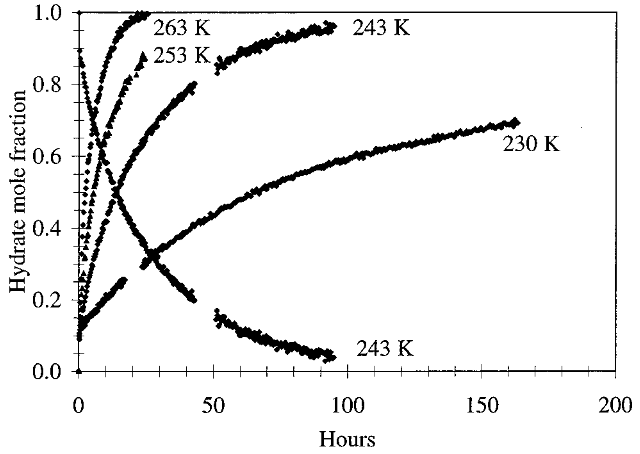

Figure 5. Conversion of sII Ar hydrate to sI hydrate after CO_2 gas exchange at various temperatures. Upward sloping curves indicate the sI hydrate formation, whereas the downward sloping curve (for 243 K trial) indicates the sII Ar hydrate decomposition.

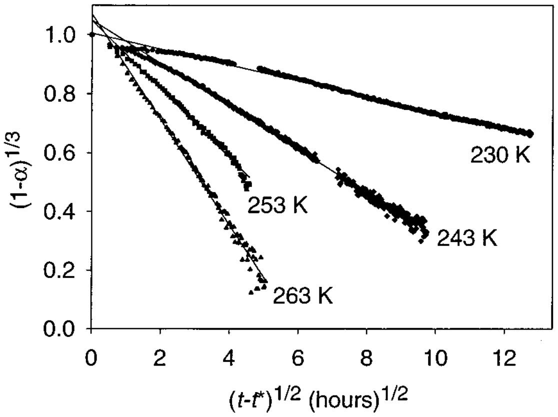

Figure 6. A plot of the experimental data of the conversion of Ar hydrate (sII) to Ar/CO_2 hydrate (sI) in terms of the shrinking core model.

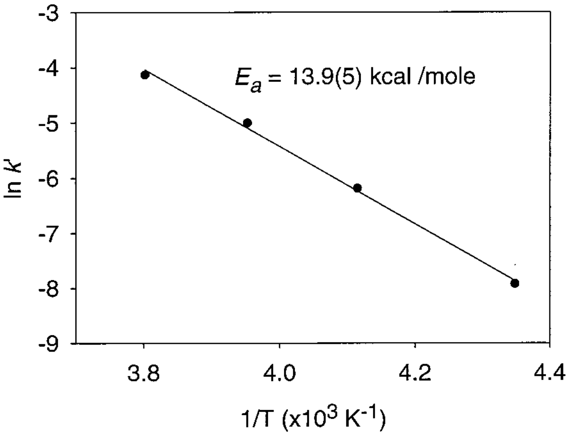

Figure 7. A plot of ln(k') as a function of $1/T$ (K^{-1}) for the conversion of Ar hydrate (sII) to Ar/CO_2 hydrate (sI).

Table 1. Results from Mass Spectrometry (MS) Analysis[a]

	mol % CO_2	mol % Ar	total
230 K (70% conversion)	41.4	58.6	100
243 K (96% conversion)	53.2	46.8	100
243 K (96% conversion)	54.7	45.3	100
253 K (96% conversion)	56.1	43.9	100
263 K (96% conversion)	66.2	33.8	100
gas composition (average of 243 K trials)	54.0 ± 0.8	46.0 ± 0.8	100
calculated mol of gas (243 K trials)	0.0069 mol	0.0059 mol	0.0128 mol

[a] Limited neutron beam time did not allow the 230 K experiment to reach ~96% conversion.

Table 2. Ratios of Guest Molecular Diameters to Cavity Diameters[1]

guest molecule	hydrate structure formed	Guest-to-Cavity Diameter Ratio			
		for guest in 5^{12} of sI	for guest in $5^{12}6^2$ of sI	for guest in 5^{12} of sII	for guest in $5^{12}6^4$ of sII
CO_2	sI	1.003	0.874	1.020	0.769
Ar	sII	0.745	0.648	0.757	0.571

rate of Ar hydrate (243 K trial) is also shown in the figure. Similar calculations using eq 1 and a t^* corresponding to conversion of 0% gives an activation energy of 13.9 kcal/mol for the structure change process (Figures 6 and 7). This value is higher than the energy needed to break hydrogen bonding in either water (5 kcal/mol) or ice (12.7 kcal/mol).

It is of interest to compare the t^* value of zero for the sII to sI hydrate conversion to the nonzero t^* values of 5% for ice to Ar hydrate and 20% for ice to CO_2 hydrate[13] conversions. In the latter two cases the conversion process is not diffusion-controlled until the ice particles are covered by a hydrate layer. As mentioned above, we estimate 5% conversion corresponds to a hydrate layer of about 1000 unit cells. In the conversion of sII to sI hydrate, the initial phase is already a gas hydrate such that a diffusion-controlled process through hydrate exists from the very beginning, which is consistent with t^* of zero. However, we wish to emphasize that the values of t^* are not obtained with high precision, and therefore any inferences based on these values should not be considered conclusive.

Composition and Occupancy of the sI Hydrates. From mass spectrometry (MS) analysis of the gases collected from the dissociating hydrate sample, the relative amounts of CO_2 and Ar in the final mixture of hydrates at 243 K were 54.0 ± 0.8 and 46.0 ± 0.8 mol %, respectively. Table 1 lists these results and shows a trend of increasing CO_2 mol % with increasing temperature, presumably because at any given pressure CO_2 hydrate is more stable than Ar hydrate. The values used in subsequent calculations were obtained from the average of two gas exchange experiments at 243 K. On the basis of the MS results and using the ideal gas equation, ($PV = nRT$, where $P = 207$ kPa, $V = 155$ cm^3, $T = 298$ K, and R is the universal gas constant) the amounts of CO_2 and Ar collected in the collection bottle were calculated to be 0.0069 and 0.0059 mol, respectively.

Neutron diffraction data indicated about 4% of the sample was sII hydrate and 96% sI hydrate. Assuming that the sII hydrate sample does not contain any CO_2, the amount of argon forming the 4 mol % of argon sII hydrate is 0.0005 mol. This amount is more than 1 order of magnitude less than the 0.0059 mol Ar determined from MS analysis. It is clear that the residual 4 mol % of the sII hydrate cannot account for the ~45 mol % of argon gas in the sample. The presence of the relatively large quantity of argon in the hydrate sample indicates that the sI hydrate formed by the introduction of CO_2 is not pure CO_2 hydrate, but mixed Ar/CO_2 hydrate of the type sI lattice.

The case where the sII argon hydrate sample had converted to 96% sI hydrate is considered below:

The ideal unit cell formulas for the two hydrate structures are: structure I [$2X{\cdot}6Y{\cdot}46D_2O$] and structure II [$16X{\cdot}8Y{\cdot}136D_2O$]; where X and Y are the small and large cavities in the structures, respectively. Table 2 lists the guest-to-cavity-size ratios for Ar and CO_2 in the different cavities of sI and sII

Table 3. Moles of Cavities Available for Gas Occupancy Based on 1.5 g D_2O (0.075 Mol) Converted into a Mixture of 96% sI and 4% sII Hydrate

molecule or cavity	structure I (96%) [2X.6Y.46D_2O]	structure II (4%) [16X.8Y.136D_2O]	total
D_2O in structure	0.072	0.003	0.075
cavities (total)	0.0125	0.0005	0.0130
small cavities	0.0031	0.00033	0.00343
large cavities	0.0094	0.00017	0.00957

hydrates. The guest-to-cavity-size ratio can be viewed as a measure of the fit of the gas in the cavities, as well as a measure of the extent of cavity stabilization by the guest. Guest-to-cavity-size ratios between 0.75 and 1.0 are typical, with a ratio larger than 1.0 implying that the guest is probably too large to stabilize the cavity.[1]

For the case of the 243 K experiments (see Tables 1 and 3), nearly 100% of the cavities (0.0130 mol) are filled with either Ar or CO_2 (0.0128 mol). Carbon dioxide is known to occupy both types of cages in structure sI. However, the fit of CO_2 in the $5^{12}6^2$ cage is better, due to size limitations of the molecule in the 5^{12} cage, as seen with a guest-to-small cavity-size ratio of slightly greater than 1. If all of the CO_2 (0.0069 mol) and 0.0023 mol of argon were to occupy the large cavities of sI hydrate, giving a cage occupancy of 98%, then the small cavities of sI could be completely occupied by the remaining argon gas (0.0031 mol). Argon is known to form sII hydrate, even though it can easily be accommodated by the 5^{12} cavities of either hydrate structure, which are of roughly the same size (see ratio in Table 2). However, it is more likely that there is a mixture of both gases in both cavities.

Probable Mechanism for Transformation of sII Ar Hydrate to Mixed Ar/CO_2 sI Hydrate. Two possible mechanisms can be envisioned for the transformation of the sII Ar hydrate to the mixed Ar/CO_2 type sI hydrate at temperatures below the ice point: *(1) ice as an intermediate:* decomposition of the sII Ar hydrate (at 6.21 MPa and 243 K) to form ice, followed by the conversion of the ice to the mixed gases product, and *(2) direct conversion:* the sII Ar hydrate converts directly, with no ice intermediate, into the mixed Ar/CO_2 type sI hydrate. However, this does not rule out the possibility of the involvement of a quasi-liquid layer in the conversion mechanism.

Experiments conducted with Ar hydrate at 243 K and 5.86 MPa (850 psi) of Ar showed the hydrates were stable under these P−T conditions (Figure 8a). Additionally, experiments were conducted with Ar hydrate in which excess Ar gas was replaced with He, a nonhydrate-forming gas, at 243 K at a total pressure of 900 psi (6.21 MPa, the same as the CO_2 pressure in the exchange experiments). As depicted in Figure 8b, only ∼17% decomposition (of the hydrate to form ice) occurs during the first 10 h after the exchange. Less than an additional ∼11% decomposition took place in the following 10 h. In contrast, the conversion of the sII Ar hydrates to the sI Ar/CO_2 mixed hydrates under 900 psi of CO_2 proceeds at a significantly faster rate under these pressure and temperature conditions (Figure 8c). Approximately 40% conversion occurs within the first 10 h, with additional 20% during the following 10 h. Figure 7d shows the rapid decomposition of Ar hydrate under atmospheric pressure to form ice. The slower rate of decomposition (under pressure of a nonhydrate-forming gas) than the rate of converting to mixed Ar/CO_2 sI hydrate (under the same pressure of CO_2) strongly suggests a direct conversion mechanism in which the sII Ar hydrate converts into the sI Ar/CO_2 mixed hydrate without first decomposing into ice. The absence of ice peaks in the neutron scattering pattern supports this proposed mechanism. In addition, the empirically observed value of zero for the time *t** where the sII-to-sI conversion is dominated by diffusion (vide supra) also supports a one-step process. Although we cannot entirely rule out the existence of an undetectable intermediate phase, such as a quasi-liquid layer, with an activation energy of 13.9 kcal/mol for the sII-to-sI transformation, an intermediate phase with weaker hydrogen-bonding energies is no longer required for the conversion to occur.

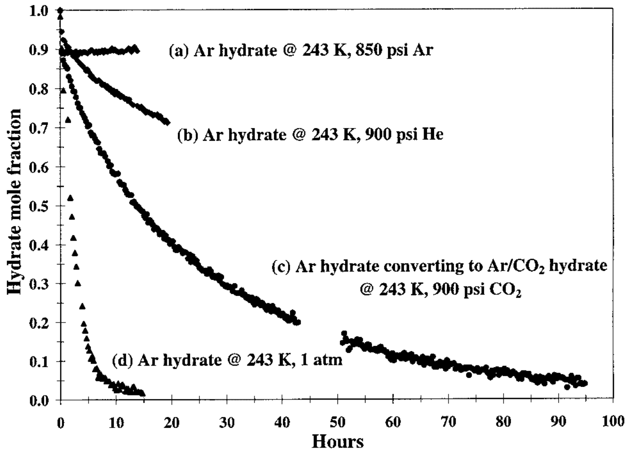

Figure 8. Effect of type of gas and its pressure on the rate of decomposition of sII Ar hydrate at 243 K. (a) Hydrate is stable under 5.86 MPa (850 psi) of Ar. (b) sII Ar hydrate decomposes slowly under 6.21 MPa (900 psi) of He. (c) sII Ar hydrate decomposes at a moderate rate under 6.21 MPa of CO_2 to form sI Ar/CO_2 mixed hydrate. (d) sII Ar hydrate decomposes rapidly under atmospheric pressure to form ice.

Hence, we suggest that gas hydrate is not a stagnant system, but rather an equilibrium assemblage in which hydrogen bonds open and close constantly and cavities are continually breaking and reassembling. During the time that the cavity is open, the guest molecule is free to leave the open cavity. A molecule of the same gas or of a different gas might become the next guest. The nature of the new guest determines the structure that results from the exchange. If the gas is removed from the system at such a rate that no other guest is available to stabilize the cavity (such as in cases where the pressure in the system is reduced) the cavity will not be reassembled. This destruction of the structure will continue until enough pressure of a hydrate-forming gas is rebuilt (e.g., if gas removal is stopped or a different hydrate-forming gas is introduced) to force guests back into damaged cavities and reassemble them. If the removal of gas is continued, the cavities will continue to break until the whole structure collapses. The rates of these breaking/reassembling processes are temperature-dependent. Hence, exchange or decomposition rates can be controlled significantly by changing the temperature of the gas hydrate system.

It should be emphasized that there are many reported studies of mixed-gas hydrates in which the dependence of the formation of either sI or sII has been investigated. For instance, mixtures of Xe (sI former) and Kr (sII former) were shown to form sII with an initial gas composition of less than 5 mol % of Xe, and sI with greater than 5 mol % of Xe.[8] The formation of either sI or sII from mixtures of methane with other hydrocarbons has also been studied extensively.[9,20] These previous studies all began with an initial composition of gases which were then reacted with ice or liquid water to form hydrate, which was then analyzed to determine its structure type. There are also several studies examining the kinetics of hydrate formation from

---

(20) Holder, G. D.; Hand, J. H. *AIChE J.* **1982**, *28*, 440−447.

either liquid water or ice.[13,21,22] However, to the best of our knowledge, the study in this paper is the first to examine the in situ transformation of one hydrate structure type to another by exposing the hydrate to a second gas hydrate former.

Conclusions

As pointed out previously,[1,8] small guests, such as argon, are sII formers because the relative number of small cavities is higher, with a ratio of 2:1 of small-to-large cavities. In the case of sI, the ratio of small-to-large cavities is 1:3, which favors larger guests that stabilize the larger cavities, such as carbon dioxide. In this paper we have described the observation by neutron diffraction of the conversion of a gas hydrate from structure type sII to sI. Initially, pure argon hydrate is formed with structure sII and is transformed to mixed argon/CO_2 hydrate with structure sI as shown by neutron powder diffraction. Once an initial layer of sI hydrate forms around the sII hydrate particles, the reaction kinetics are dominated by the diffusion of CO_2 through the outer sI hydrate layer. On the basis of mass spectroscopic data, the sI hydrate contains a mixture of argon and CO_2. We previously observed that CO_2 hydrate is stable under an applied pressure of helim gase which does not form a hydrate.[13] Argon hydrate under an applied pressure of helium gas dissociates at a slower rate than it reacts with CO_2 at the same pressure and temperature. These results are consistent with an equilibrium exchange between encapsulated guest molecules in the solid hydrate and free molecules in the surrounding gas or liquid phase.

Acknowledgment. The work at Argonne National Laboratory was supported by the U.S. Department of Energy, Basic Energy Sciences-Material Sciences, under Contract No. W-31-109-ENG-38.

JA010280Y

---

(21) Koh, C. A.; Savidge, J. L.; Tang, C. C. *J. Phys. Chem.* **1996**, *100*, 6412−6414.

(22) Takeya, S.; Hondoh, T.; Uchida, T. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 973−982.