

Comparative Study of Hydrogen, Argon, and Xenon Uptake into a Propane Hydrate

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The rate of absorption of hydrogen, argon, and xenon into a Type II propane clathrate hydrate has been studied. The propane hydrate is synthesized from 250- μm ice grains, is estimated to have a porosity of 65% and has roughly the consistency of chalk. Hydrogen is rapidly absorbed by the hydrate sample and approaches the equilibrium vapor pressure in an hour before a very slow residual absorption process ensues. For an initial hydrogen pressure of 1.5 MPa, about 4.5% of the available 5^{12} cages are occupied by hydrogen after 1 h, and 4.9% after 18 h. In contrast, for both argon and xenon significantly more gas is absorbed by the hydrate but at a much slower rate: about 5% as fast for xenon and 1% as fast for argon. We conclude that hydrogen readily diffuses through the propane hydrate microcrystal structure, while argon and xenon are probably absorbed by growing new double hydrate while consuming the propane hydrate. Although considerably higher pressures would be required to store significant quantities of hydrogen in propane hydrate, it appears that the crystal can be loaded and emptied in relatively short times. © 2010 American Institute of Chemical Engineers AICHE J, 56: 2734–2741, 2010

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Introduction

The possible development of hydrogen as a commercial energy source has inspired a large number of proposals for new methods for storing and transporting hydrogen. Hydrogen gas storage and transport is limited by both safety and leakage considerations. Among the alternative storage media that have been suggested are solid metals, nanoporous materials, and clathrate hydrates.^{1–3} Clathrate hydrates are solid structures in which water molecules form cages that can trap various small gas molecules. As such, they provide an attractive possibility for storing hydrogen since water is cheap and abundant when compared with other proposed storage media.^{4–10}

Pure structure Type II hydrogen clathrate hydrate was first observed by Dyadin¹¹ and characterized by Mao et al. using diffraction methods.^{12,13} Pure hydrogen hydrate will prob-

ably continue to have the best possible mass percent hydrogen of any gas hydrate system, estimated to be 5.3 wt % by Mao et al. Loshkin et al. has since revised the mass fraction of hydrogen in the clathrate to 3.8%.⁹ However, the extreme pressure needed for synthesis, 180–220 MPa, almost certainly limits the practical application of this substance. This led several groups to investigate whether a mixed or binary tetrahydrofuran (THF) and H₂ hydrate would be a more practical hydrogen storage medium. THF and water yields a Type II pure hydrate structure at temperatures up to 277 K. The Type II hydrate structure consists of two cages, denoted as 5^{12} and $5^{12}6^4$, in a 2:1 ratio. The 5^{12} cages have 20 water molecules arranged into 12 pentagonal faces, with an oxygen atom at each vertex and a hydrogen atom on each edge. The $5^{12}6^4$ cages are slightly larger with 28 water molecules arranged into 12 pentagonal faces and 4 hexagonal faces. There are sixteen 5^{12} cages, eight $5^{12}6^4$ cages, and 136 water molecules in a face-centered cubic unit cell.

In 2004, Florusse et al. found that a stable Type II binary THF/H₂ hydrate can be formed at pressures of 5 MPa at 279.6 K, significantly lower than 300 MPa at 280 K for a

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pure H₂ hydrate.¹⁴ As the THF induces a Type II clathrate hydrate by almost completely filling the large cages, only the small cages are available for H₂ storage. They found that an average of 0.5–1 hydrogen molecule occupied each small cage. In 2005, Lee et al. discovered that by decreasing the amount of THF in the THF/H₂ composition, they could increase the H₂ storage capacity in the binary hydrate. Hydrogen replaces the THF in some of the large cages while filling the small cages which leads to a storage capacity of about 4.0 wt % at 12 MPa hydrogen and 277.3 K. However, they noted that synthesis of the THF/H₂ clathrate hydrate is too slow to be a practical storage/transportation medium.¹⁵ It should be noted that following the work of Mao, Florusse, and Lee et al., conflicting reports have been made in the literature regarding the hydrogen occupancy of the small cavities in both the pure and binary hydrates.^{10,16–21} Strobel and Hester et al.^{15,18} used high-resolution neutron diffraction experiments to show that the hydrogen molecules singly occupied the small dodecahedral (5¹²) cavities only. They also conducted hydrogen uptake into preformed THF clathrate experiments and determined from clathrate decomposition that the maximum amount of hydrogen stored in the binary was about 1.0 wt % at moderate pressure (<60 MPa). This hydrogen concentration corresponds to one hydrogen molecule in each of the 5¹² cages and one THF molecule in each of the 5¹²6⁴ cavities. Mulder et al.²¹ used experimental and theoretical methods to conclude that the pressure dependence of hydrogen occupation (at $T = 274$ K) in small cages of the THF hydrate does not show any signs of saturation at pressures below 10 MPa. They also observed that hydrogen does not stabilize the THF clathrate when reducing the THF content below the stoichiometric amount. Alavi et al. performed molecular dynamic simulations of binary structure II H₂/THF clathrates¹⁷ and H₂/D₂ structure II clathrates¹⁸ to determine cage occupancies at various pressures and temperatures. They concluded that lattice free energy and configurational energy differences are small for different combinations of cage occupancies in the binary THF/H₂ and pure H₂/D₂ clathrate structures at given pressure and temperature. Therefore, one must expect various combinations of cage occupancies in the bulk clathrate samples.¹⁸ The binary system has greater flexibility for accommodating different occupancies than the pure H₂ clathrate and the actual loading of the binary clathrate may be controlled by a combination of temperature, pressure, and kinetic conditions.¹⁷

The formation of the binary H₂-THF clathrate hydrate from THF hydrate was kinetically modeled by Nagai et al.²² The H₂-THF phase that is formed is a two-step process, hydrogen adsorption onto the particle surface, and then subsequent migration into the particle. These two formation steps, adsorption and diffusion, are driven by the difference in hydrogen fugacity at the bulk and equilibrium conditions. They concluded that the rate of hydrogen consumption and hydrogen occupancy in the S-cages depends on temperature, initial pressure, and particle size of the THF hydrate. From the model, Nagai et al. estimated that the activation energy of adsorption was -5.9 kJ/mol, the activation energy of diffusion was 78.7 kJ/mol and the diffusion coefficient was on the order of 10^{-12} m²/s. Alavi and Ripmeester²³ used electronic-structure calculations with fixed cage configuration to estimate the energy barriers to the escape of the H₂ guest

molecules from the pentagonal and hexagonal faces of the pure sII clathrate hydrate cages. They calculated the energy required for a hydrogen molecule to migrate through a hexagonal face at 21–25 kJ/mol. The energy barrier to migration through the smaller pentagonal faces of the small cages is much larger, ranging from 105 to 121 kJ/mol. The rate constants for H₂ migration from the large cages are roughly two orders of magnitude larger than those for migration from the small cages. The diffusion coefficients, D , of the H₂ guests in the large cages are comparable with those measured for H₂ molecules in zeolites, 10^{-8} m²/s, and diffusion coefficients for H₂ through the pentagonal face of the small cage is of the order of 10^{-11} m²/s at $T > 250$ K. These calculated diffusion coefficients are lower limits to the true values and the H₂ molecules were considered to be rigid. Mulder et al. noted that the pentagonal windows connecting the small cages have an opening ~ 1.2 Å in size. As the kinetic diameter of the hydrogen molecule (2.89 Å) is significantly larger, they assume that transient defects in the cage structure facilitate molecular hydrogen diffusion. This leads to a value of the diffusion coefficient, D , that lies between 10^{-16} and 10^{-14} m²/s depending on which type of defect dominates.²¹

Our investigation began with the query: does a Type II hydrate former exist at near-ambient conditions that can absorb and release hydrogen by manipulating the pressure. If a preformed hydrate can absorb and deliver hydrogen quickly and in sufficient quantities, then perhaps a system can be developed for a practical storage/transport medium. We selected propane as the Type II hydrate former because propane is relatively inexpensive. Also, the propane hydrate is stable up to propane pressure of 0.56 MPa at 279 K,²⁴ which are commercially viable conditions for a storage medium. So far, there have been no studies to determine how adding hydrogen to a propane hydrate affects its stability range. The sorption of hydrogen in preformed propane clathrate and pure water ice-grains at various pressures and temperatures are presented in this report. Uptake experiments were also conducted with argon (Ar) and xenon (Xe) gases and results presented for comparative purposes.

Experimental

As the study reported here was intended to point toward a practical storage/delivery system, we chose to investigate relatively low hydrogen pressures in the order of 0.67 and 1.5 MPa at a moderate temperature of 263 K. We started with sieved ice grains for propane hydrate production. Also, we wanted the overall sample size to be large enough so that a finite amount of hydrogen would be absorbed. To this end, porous hydrate plugs 2.2 cm in diameter by 9 cm long composed of 250 μm particles and weighing 50 g were exposed to hydrogen at a pressure of 0.67 or 1.5 MPa while maintaining a constant bath temperature of 263 K. The extent and rate of hydrogen uptake were measured by monitoring the pressure-drop over time. For comparison, the adsorption of hydrogen onto a similar plug of pure water-ice particles was measured. The results for hydrogen uptake were also compared with analogous experiments for Ar and Xe uptake. The equipment was designed to hold up to 50 g of ice grains. This was decreased to 10 g for the Xe uptake experiments because of the cost of Xe. The experiments start with

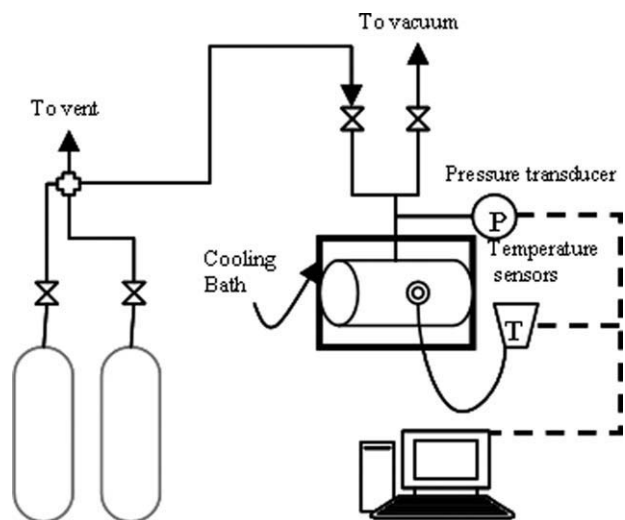


Figure 1. Schematic of experimental setup for the synthesis of propane hydrate and subsequent gas uptake.

propane hydrate production in the clathrate cell and then the hydrate is exposed to the sorbate gas at constant temperature. The cell pressure is monitored over time and the uptake rate is evaluated from the collected data.

The experimental apparatus for the synthesis of propane hydrate and gas uptake is presented in Figure 1. The clathrate cell has a 2.55 cm internal radius and is 11.0 cm long. The temperature of the cell and contents is maintained with an ethylene glycol bath controlled by a Neslab 740 programmable chiller. Chemically pure propane (99%), zero grade hydrogen (99.995%), UHP Ar (99.999%), and research grade Xe (99.995%) are used in the experiment and nano-pure water (18.0 M Ω cm) is used to make the hydrate. The cell pressure is monitored with an omega pressure transducer that is accurate to ± 0.003 MPa. The internal cell temperature is monitored with low voltage temperature sensors that are accurate to ± 0.5 K. Pressure and temperature values are acquired over time with an Omega data acquisition system and Labview VI software program.

Propane hydrate production is the first phase of the experiment. Nanopure water pellets are ground and sieved through a 250- μ m mesh. The clathrate cell is loaded with about 50 g (or 10 g) of ice grains and pressurized with propane. The cell temperature and pressure is maintained at 272.2 K (-1.0°C) and 0.38 MPa (55 psia), double the propane hydrate vapor pressure. The cell contents were annealed for 3 days while cycling the bath temperature between 269 and 275 K to maximize hydrate production. Gas uptake and decomposition measurements indicate that the above procedure yields $\sim 67\%$ theoretical yield of propane enclathration. Because our goal was to test a fairly simple procedure for storing hydrogen, we did not try either extensive temperature cycling or active mixing methods to increase the propane hydrate yield. Given that the volume of the ice plug created by this procedure was on average 160 cm³ and weighed 50.0 g, the average density of the plug (ice and voids) is 0.31 g/cm³ and the density of ice is 0.91 g/cm³. So, the approximate porosity of the plug is 65%. A photo of the

propane clathrate plug produced by this procedure is shown in Figure 2. It has a reasonably uniform consistency, with no large voids or imperfections near the surface. Breaking up a similar sample indicated that the same consistency extended to the middle of the plug, although there were small regions where the consistency was more powdery.

Once the propane clathrate was prepared, uptake measurements proceeded as follows. The cell temperature was dropped to 263 or 272 K and the propane pressure was lowered to 0.12 MPa (17 psia) or 0.17 MPa (25 psia), the propane hydrate vapor pressure at the cell temperature. The cell was then pressurized with the sorbate gas to a total cell pressure of 0.32 MPa (46 psia), 0.67 MPa (99 psia), or 1.5 MPa (215 psia). Therefore, the partial pressure of the sorbate gas in the cell at 263 K was 0.20, 0.55, or 1.38 MPa; and the partial pressure of the sorbate gas at 272 K was 0.15, 0.50, or 1.33 MPa, respectively. The cell contents were allowed to sit for 2–4 days while pressure and temperature measurements were recorded as time proceeded. Uptake experiments were also performed with the clathrate cell filled with pure water-ice grains (no propane hydrate in the cell) for comparison. Pressure was converted to moles of propane gas using the Peng-Robinson equation of state, since propane compressibility is significantly less than one for the experimental conditions.^{25,26} However, in experiments involving more than one gas, it was not possible to determine the relative uptake of the two gasses. We assumed that most of the addition uptake was of hydrogen, Ar, or Xe, depending on the experiment, and the Ideal Gas Law was used for molar calculations of the sorbate gases, whose compressibilities are nearly one at near-ambient conditions.²⁷ This introduces a small amount of error in the analysis of the Xe data. In the most extreme case, the Xe compressibility factor would be about 0.96 at a reduced temperature of 0.91 and a reduced pressure of 0.12. We decided that accounting for this



Figure 2. The clathrate cell filled with propane hydrate.

The picture was taken at the end of an experimental run that started with 50 g ice grains and propane gas. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

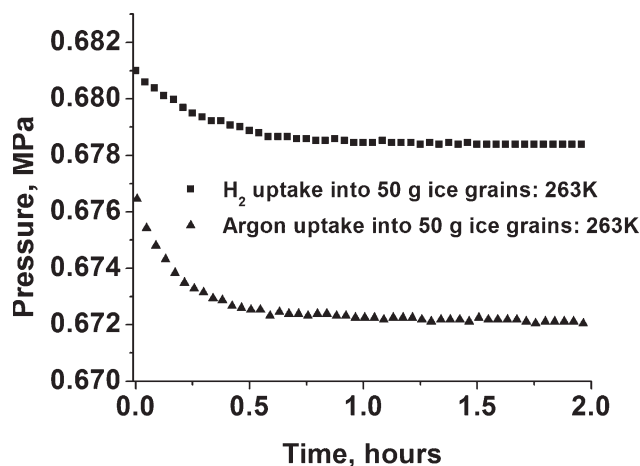


Figure 3. Hydrogen and argon uptake into pure water-ice particles.

compressibility was not justified due to the other uncertainties in the data.

Results and Discussion

The pressure decrease over time for each experiment was plotted and analyzed for uptake rate and final occupancy of the given sorbate into both pure water-ice grains and propane hydrate. Figure 3 is a plot of hydrogen and Ar uptake into 50 g of pure water-ice grains as a reference for the hydrate study. The pressure decrease for hydrogen uptake into 50 g of ice grains is 0.0026 MPa or 0.30 mmol after 2 h, and most of the uptake occurred in the first 30 min. The ice grains absorb 0.52 mmol of Ar (0.0045 MPa pressure drop) in 2 h, and, again, most of this occurred in the first thirty minutes. The greater adsorption of Ar compared to hydrogen is as expected since it is the more polarizable gas.

Figure 4 shows the uptake of hydrogen by the propane clathrate as a function of time. Plot 4a shows the first 2 h of uptake and, 4b, the extended data. The uptake of hydrogen by the propane hydrate was 0.039 MPa or 3.8 mmol after 30 min, and 0.045 MPa or 4.3 mmol in 2 h, 20 times more than for the pure ice grains. Over 2 days, the total uptake increased to 0.055 MPa, or 5.3 mmol. The two sample runs gave similar, but not identical results. This is due to the fact that it is difficult to prepare identical clathrate samples. Most of the hydrogen is absorbed relatively quickly, in less than 30 min, but there is residual uptake over a long period of time. The data for ice grain uptake is shown at the top of the graph for comparison; note that, in this case, there is negligible long-term absorption.

Figure 5 shows hydrogen uptake for an initial pressure of 1.5 MPa. Again, most of the absorption occurs during the first 30 min, the pressure drop is 0.077 MPa, or 7.4 mmol are absorbed. The pressure drop after 2 h is 0.087 MPa, or 8.4 mmol absorbed and the pressure decreased by 0.0936 MPa over 18 h, which is equivalent to 9.0 mmol absorbed. The initial partial pressure of hydrogen for the two experiments was 0.52 and 1.4 MPa, while the uptake after 30 min was 3.8 and 7.4 mmol.

As discussed earlier, the yield for propane hydrate for the initial 50 g of ice was 67%. We assume that this defines the number of cages available and that for each propane molecule enclathrated there are two cages available to store hydrogen molecules. Occupancies, given in Table 1, for hydrogen are calculated by defining one hydrogen molecule per cage as the theoretical limit. The cage occupancy after 22 h was 2.1% for 0.68 MPa initial pressure and 4.7% for 1.5 MPa initial pressure. These correspond to theoretical weight percentages of 0.02 and 0.04, respectively. For comparison, Strobel et al. obtained 0.35 and 1 wt %, respectively, for hydrogen formation pressures of 6 and 60 MPa.¹⁶ The THF clathrate was exposed to hydrogen for 7 days while the bath temperature was cycled between 270 and 278 K every 8–12 h. So, the initial results here indicate that hydrogen storage close to the theoretical limit for a given pressure can be reached reasonably quickly by adding the hydrogen to the preformed propane clathrate. Again, note

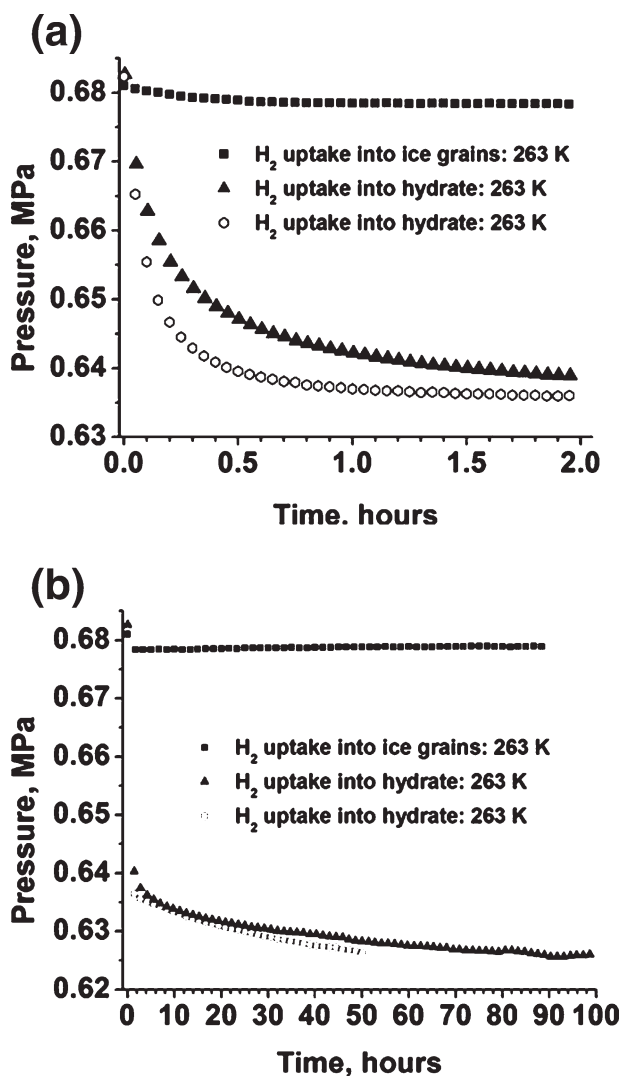


Figure 4. H₂ uptake data plotted as pressure (MPa) vs. time (h)

(a) The plot showing the first 2 h of the experiment and (b) the plot for the overall experimental run.

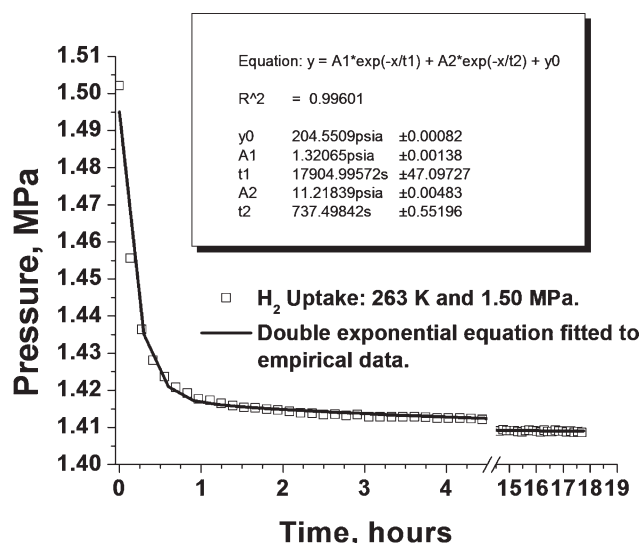


Figure 5. H₂ uptake data plotted as pressure (MPa) vs. time (h) for initial pressure of 1.50 MPa at 263 K.

The characteristic time, t_i seconds, is related to the rate constant by $k_i = 1/t_i, s^{-1}$.

that most of the hydrogen uptake occurred in the first 30 min.

The Ar uptake data is presented in Figure 6. Again, the details of the uptake are not exactly reproducible but the general trends are clear. During the first 20 min, the uptake of Ar by the propane clathrate is not significantly higher than that of pure ice grains. This is an important result because it indicates that the surface area available for adsorbing gas was not significantly higher for the propane hydrate than for the pure water ice grains. Thus, the much larger uptake of hydrogen by the propane hydrate than by the pure ice grains is almost certainly due to diffusion into the solid, rather than to surface adsorption. However, while the uptake of Ar onto the ice grains levels off after 30 min, uptake by the propane hydrate continues for the entire 90 h of data collection, and is still far from equilibrium at the end of the run. The Ar uptake was 0.33 wt % and 2.0 % occupancy after 22 h, and 0.50 and 3.0% occupancy at the end of the 90-h run. So, much more hydrogen than Ar is absorbed in the first hour, about the same amount of the two gasses is absorbed over 22 h, but Ar absorption continues over the 90-h run. Even after 90 h, the 0.50 wt % and 3.0% occupancy of the small cages by Ar is considerably less than

Table 1. Total Uptake (Wt %) and Occupancy (%) for Hydrogen and Argon into a Propane Clathrate

Gas	Parameters	Uptake (Wt %)	Occupancy Yield (%)
H ₂	0.68 MPa, 50 g, 263 K	0.02	2.1
	1.5 MPa, 50 g, 263 K	0.04	4.9
Argon	0.68 MPa, 50 g, 263 K	0.33	2.0
	0.68 MPa, 10 g, 263 K	0.46	2.8
	0.68 MPa, 10 g, 272 K	0.68	4.2
	0.33 MPa, 10 g, 272 K	0.34	2.1

expected for equilibrium. Maekawa²⁸ showed that the Ar + C₃H₈ system forms SII hydrates with equilibrium pressures that increase proportionally as the mole fraction of C₃H₈ decreases, ranging from 0.18 to 0.65 MPa at 273.5 K. The equilibrium Ar occupancy for the binary Ar/propane clathrate was predicted by Anderson²⁹ to be about 36% of the available small cages at an equilibrium pressure of 0.51 MPa at 273.5 K. The Ar uptake rate for the hydrate indicates that not only is Ar diffusion into the preformed propane hydrate slow with adsorption the limiting stage but also new binary hydrate formation on the excess ice in the cell is minimal. So, although in the thermodynamic limit propane hydrate will absorb much more Ar than hydrogen, the absorption kinetics is at least two orders of magnitude slower for Ar than for hydrogen.

Rate constants were evaluated for the uptake experiments by fitting first-order exponential decay curves to the experimental data, pressure vs. time. For hydrogen, the data is clearly not first order over the entire range of time, and the data was fitted to a double exponential function:

$$P = y_0 + A_1 \times \exp(-t \times k_1) + A_2 \times \exp(-t \times k_2);$$

where P is the pressure, MPa; t is time, seconds; k_1 and k_2 are rate constants, s^{-1} ; and y_0 , A_1 , and A_2 are the fitted parameters. The resulting fit was excellent with a $R^2 = 0.996$. The Ar data was fitted to a single exponential function, $A_2 = 0$, which was adequate to reproduce the data over the entire time range of measurement, 90 h, with an $R^2 = 0.985$. Equations fitted to Ar data over 20–22 h exhibited R^2 values of 0.99 and greater. The double exponential fit for the hydrogen uptake indicates two different rate-controlling mechanisms are important, one at short time and one at long times. Given the extent of hydrogen uptake at short times, we conclude that diffusion into the preformed small cages of the Type II propane hydrate matrix must dominate the uptake. No other sorption effect could account for the amount of uptake. At longer times, the kinetics are almost certainly more complicated. We suspect that this data is dominated by additional hydrate formation analogous to the cases of Ar and Xe discussed below. However, any

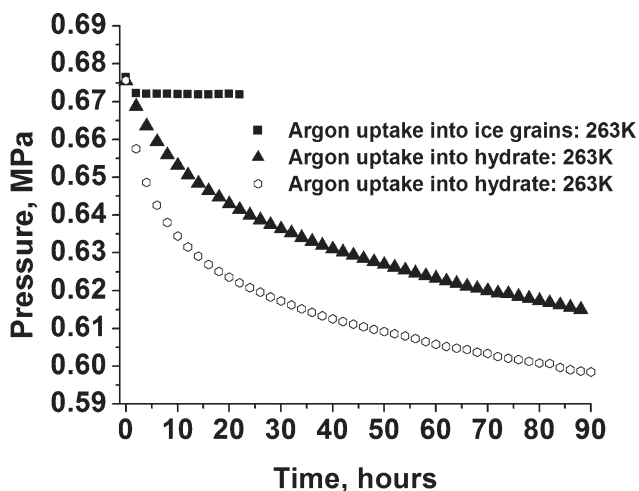


Figure 6. Argon uptake data plotted as pressure (MPa) vs. time (h).

Table 2. Rate Constants^a for Sorbate Uptake into a Preformed Propane Clathrate

Sample Size, Temperature, and Pressure	Hydrogen k_1 (s^{-1}) (Fitted Time)	Argon k_1 (s^{-1}) (Fitted Time)	Xenon k_1 (s^{-1}) (Fitted Time)
50 g, 263 K, 1.5 MPa	1.4×10^{-3} (18 h)		
50 g, 263 K, 0.68 MPa	1.9×10^{-3} (50 h)	1.0×10^{-5} (90 h)	
50 g, 263 K, 0.68 MPa		3.0×10^{-5} (22 h)	
10 g, 263 K, 0.68 MPa		1.1×10^{-5} (22 h)	1.5×10^{-5} (22 h)
10 g, 272 K, 0.68 MPa		1.1×10^{-5} (22 h)	1.4×10^{-5} (22 h)
10 g, 272 K, 0.33 MPa		1.3×10^{-5} (20 h)	3.6×10^{-5} (20 h)

^aHydrogen data was fitted with a double exponential decay curve, only the larger rate constant is reported, the second rate constant is much smaller. For instance, the values for the 1.5 MPa hydrogen run are: $y_0 = 1.4$ MPa, $A_1 = 0.009$ MPa, $A_2 = 0.077$ MPa, $k_1 = 5.6 \times 10^{-5} s^{-1}$, $k_2 = 1.4 \times 10^{-3} s^{-1}$, $R^2 = 0.996$.

conclusion regarding the long term uptake of hydrogen is quite speculative without further experiments to test this hypothesis. The rate constants for hydrogen and Ar uptake experiments (along with those for Xe to be discussed later) are presented in Table 2. An example of the quality of the fit is included in

Figure 5. The relative percent error associated with the rate constants from curve fitting varies from 0.065 to 0.15%.

Uptake experiments into propane hydrate were also conducted with Xe gas. The sample size was reduced from 50 to 10 g of ice grains because of the cost of Xe. The Xe experiments were conducted at 0.68 MPa, 272 K; 0.68 MPa, 263 K; and 0.32 MPa, 272 K. Ar uptakes by similar examples were studied for comparison. As discussed later, for these pressures and temperatures Xe would quickly react with pure ice grains to form Type I Xe hydrate. However, when the preformed propane hydrate is exposed to Xe, the uptake is relatively slow but faster than for Ar. The results are presented in Figure 7. Xe uptake during a 22-h period is 7.4 times greater than Ar uptake at an initial pressure of 0.68 MPa as shown in Figure 7a, and about 14.8 times greater at an initial pressure of 0.32 MPa as shown in Figure 7b. Although Xe uptake is considerably faster than that of Ar at the temperatures and pressures tested here, it is clearly still not at equilibrium at the end of the runs. Ar uptake increases with an increase in Ar partial pressure, the uptake in 22 h for 0.51 MPa initial Ar partial pressure is 2.0 mmol and 1.0 mmol at 0.16 MPa Ar partial pressure. However, the results for Xe are quite different; the Xe uptake in 22 h at 0.51 and 0.16 MPa was nearly constant at 14.6 and 14.8 mmol, respectively. The Xe uptake and occupancy values are presented in Table 3. We have recently reported²⁵ the ability of Xe to greatly accelerate the incorporation of propane into hydrate. We find that Xe is incorporated more slowly into the preformed propane clathrate than either the growth of pure Xe clathrate or the growth of Xe/propane double hydrate. (The double hydrate is formed by exposing ice particles to a gas mixture of Xe and propane).

Figure 7a shows that both Ar and Xe are absorbed more quickly at the higher temperature. Hydrogen uptake is still two orders of magnitude faster than either Xe or Ar uptake as seen in Table 2. The errors in the measured and calculated variables were assumed to have normal distribution and to be statistically independent, so that the errors in the dependent variables were analyzed based on techniques

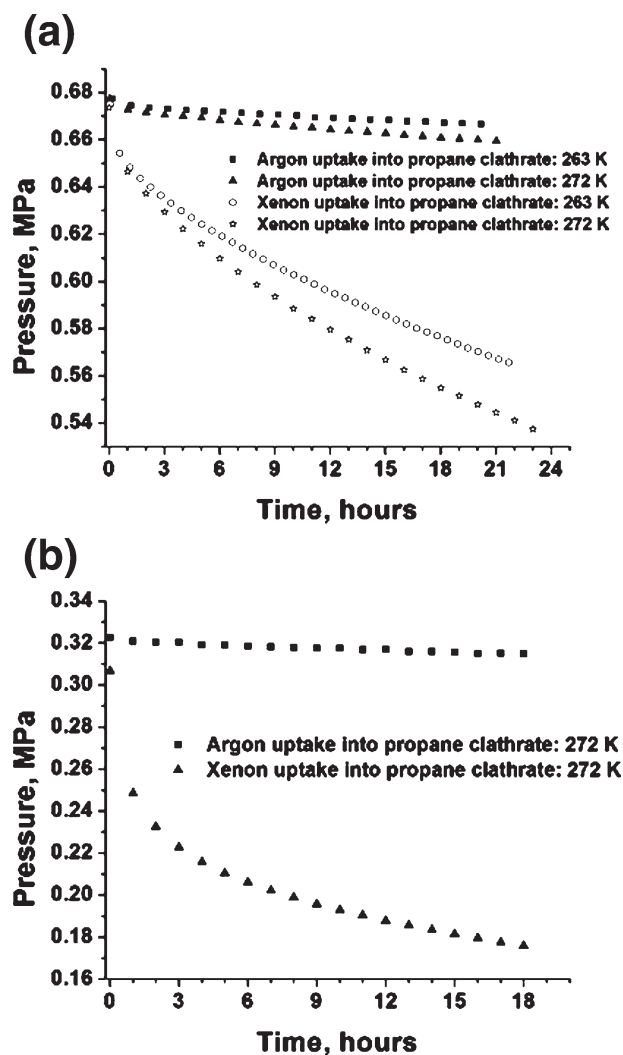


Figure 7. Xenon and argon uptake into a propane hydrate starting with 10 g ice grain samples.

(a) Data plotted for uptake starting at 0.67 MPa, 263 and 272 K. (b) Data plotted for uptake starting at 0.32 MPa and 272 K.

Table 3. Total Uptake (Wt %) and Occupancy (%) for Xenon into a Propane Clathrate

Gas	Conditions	Uptake (Wt %)	Occupancy Yield (%)
Xenon	0.68 MPa, 10 g, 263 K	10.5	24.8
	0.68 MPa, 10 g, 272 K	14.6	36.1
	0.33 MPa, 10 g, 272 K	14.8	43.4

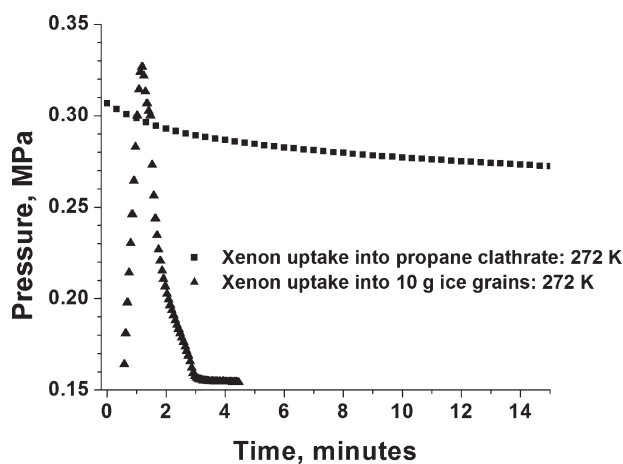


Figure 8. Xenon uptake into a propane clathrate made from 10 g ice grain sample and into 10 g of pure water.

presented in *Measurement Systems: Application and Design* by Doebelin.³⁰ The uptake values for hydrogen, Ar, and Xe exhibit a $\pm 1\%$ error and the occupancy yields show a $\pm 2\%$ error.

It is interesting to compare Xe uptake by propane clathrate to the growth of Type I Xe hydrate from pure-water ice grains. Figure 8 shows data for Xe quickly added to a propane hydrate sample and slightly more slowly to an ice grain sample. Note that in Figure 8, as well as in Figures 7a, b, it is possible to add considerable Xe to the cell with propane hydrate and the uptake that ensues is quite slow. In contrast, when the Xe pressure over ice grains reaches 0.33 MPa, rapid formation of Type I Xe hydrate commences, and, upon closing the inlet valve, the pressure drops to the Xe hydrate vapor pressure in less than 2 min. The small fraction of fast reaction suggests to us that the Xe is not exposed to a significant amount of fresh ice surface, suggesting that the remaining ice is protected from the gas by a layer of hydrate. Instead, the slower Xe uptake in propane hydrate is most likely a result of two processes: (1) Type II binary propane/Xe formation in the excess ice, especially since the reaction surface is exposed to the mixed gas and (2) Xe adsorption/diffusion into the existing propane hydrate. The propane clathrate formed for the Xe uptake in Figures 7 and 8 was allowed to anneal for 22 h. In an experiment in which the propane hydrate annealed for 3 days, the Xe uptake was even slower.

We had expected that the uptake rate would be faster if we started with smaller ice grains. However, in a brief study, the rate actually slowed down when the ice grain screen was reduced from 250 to 180 μm . This somewhat surprising result is almost certainly due to the change in the sample morphology on conversion of the ice grains to propane hydrate as well as the ice loading technique and sample configuration employed in the experiment. As described earlier, on formation of propane hydrate the local morphology changes from ice powder to a sample that has the appearance and consistency of a piece of chalk due to hydrate growth at the surface of the ice grains and fusion of the neighboring grains. This has been discussed by Taykova

et al.³¹ and Stern et al.³² We start with a 50 g plug of ice grains that has a porosity of about 60–65%, which allows propane to access the inside of the plug. Propane hydrate formation results in a change in morphology, hence a change in porosity; however, the sample is still quite porous as shown by the rapid uptake of hydrogen, which can efficiently diffuse through the cracks and pores, as well as through the cage faces. An interesting question is how the effective surface area changes upon conversion of the ice grains to propane hydrate. Ostwald ripening at the surfaces most likely serves to reduce the effective surface. Ar uptake by propane hydrate is not faster than for pure ice grains, so there is certainly no increase of surface area on propane hydrate formation. The slow long-term uptake of hydrogen indicates that any diffusion is quite slow due to the large effective radius of the Ar. Similarly, for Xe a relatively small fraction of fast uptake is observed, indicating that surface adsorption plays a minor role. Of course, Xe would be expected to diffuse even more slowly than Ar. This leads us to conclude that the slow uptake of Xe is mainly due to Xe/propane double hydrate formation at the surface. The fact that propane clathrate hydrate quickly absorbs substantially more hydrogen than Ar and Xe, and that significantly more hydrogen was absorbed in the hydrate than the bare ice grains, is certainly due to hydrogen diffusion into the bulk.

As the propane clathrate is only about 67% of the theoretical yield when formed over 3 days, or about 48% theoretical yield when formed over 22 h,²⁶ either pockets of ice exist inside the clathrate sample or a large fraction of the remaining water is located on surfaces with a local morphology that inhibits further propane hydrate formation. Further investigation is required to determine the effect of ice grain particle size on sorbate uptake into the hydrate. For instance, it would be possible to grind and sieve the propane clathrate before exposure to gas. This was not performed in this study because we are more interested in a quick method for storing hydrogen in the hydrate.

We have not been able to perform measurements to determine how far into the solid the sorbates were able to penetrate. As at least an order of magnitude more hydrogen is absorbed by the hydrate than by the pure water-ice grains and since the final cage occupancy is not too different from what we would expect from high pressure experiments, it seems that the hydrogen must substantially penetrate into the hydrate. This hypothesis is bolstered by the empirical absorption rate. The initial hydrogen uptake is quite rapid, and then suddenly levels off. This is in contrast to the Ar and Xe data for which the absorption rate gradually slows with time. The long-time Ar and Xe uptake is possibly a result of slow annealing of the sample because of the low pressure applied in our experiments.

Summary and conclusions

Propane clathrate hydrate produced by the methods employed in this study is capable of absorbing hydrogen quite quickly, and appears to come close to equilibrium after 30 min. Very slow absorption proceeds for longer times. It is not obvious what is responsible for this longer-term uptake of hydrogen. We hypothesize that new propane hydrate is formed upon the addition of hydrogen, but this is

certainly speculative. In the limit of a single crystal of Type II propane hydrate, with one hydrogen molecule in each of the 5¹² cages, this would yield a hydrogen density of 1.0 wt %. Strobel et al.¹⁶ achieved a hydrogen loading of 1.0 wt % in hydrogen/THF double hydrate at approximately 60 MPa, which corresponds to one hydrogen molecule in each 5¹² cage. Hester et al. corroborated these results with high resolution neutron diffraction.¹⁹ Given that both water and propane are quite cheap; propane hydrate may offer one of the less-expensive alternatives for storing and shipping hydrogen, at the expense of some contamination by propane. It would not be difficult to separate the two species. However, the high hydrogen pressures that would most likely be required to achieve sufficient cage filling in propane hydrate may well offset the advantage of having a relative cheap storage medium that could be employed at moderate temperatures.

In contrast to hydrogen, which diffuses readily through the propane hydrate, Ar, and Xe are absorbed much more slowly. Ar absorption is still far from equilibrium after 90 h. Xe is absorbed considerably faster than Ar, indicating that diffusion is not the rate-limiting step in these cases. We speculate that for large species that are not able to diffuse through the cage walls, new double hydrate grows at the expense of the original propane hydrate. It is particularly interesting that propane hydrate is converted into propane/Xe double hydrate much slower than ice particles are converted into Type I Xe hydrate. Equilibrium is reached in a few minutes in the latter case, and is not reached for many hours in the former case.

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