Experiments are reported that show propane is incorporated into clathrate hydrate cages much more rapidly using propane–xenon mixtures than for pure propane gas. Uptake rates for pure propane type II clathrate hydrate, pure xenon type I clathrate hydrate, and propane and xenon binary type II clathrate were studied for several different synthesis procedures. Upon adding a 0.92 xenon:propane ratio gas mixture to ice particles, the time required for achieving 62% of the theoretical yield of propane enclathration is 20 min, versus 3 days for pure propane. Although the acceleration of clathrate formation decreases as xenon is depleted, enhancement continues even after the composition falls below 3% Xe. It appears that xenon serves to nucleate the dodecahedral 512 cages while propane nucleates the larger 51264 cages. The type II xenon–propane structure is not only more thermodynamically stable than either pure hydrate; it is also formed much more quickly than propane clathrate, nearly as fast as type I xenon clathrate.

Experimental Section

A typical experiment was performed as follows. First, ice pellets were formed by dripping nanopure water into liquid nitrogen. The ice pellets were then ground in a cold coffee grinder. After the powder was sieved through a 250 µm mesh screen, a 10 g sample was placed into a 260 cm³ cell, warmed to 272 K, and exposed to the absorbate gases. The gas was delivered to the cell through 6.4 mm tubing that is coiled and submerged in the cooling bath to avoid heating of the ice particles during gas addition. The cell pressure and temperature
were monitored and recorded over time throughout the experimental run, including clathrate formation and decomposition. Gas chromatography analysis was performed on the gas phase in the clathrate cell before and after clathrate decomposition. The quantity of ice particles converted to clathrate hydrate and the amount of propane and xenon incorporated into the clathrate hydrate were calculated from the cell pressure and gas-phase composition. All gas analysis was performed with the total pressure below the propane vapor pressure. The pressure data below is precise to ±1%, the temperature data to ±0.5 K, and the yield values to ±3%. However, the reproducibility of that data is limited to ±10%. The main source of variability is, we believe, due to variations in the particle size distribution from the ice grinding and sieving process.

Results

Pressure versus time data were plotted and analyzed for absorbate uptake into ice grains. Figure 1 shows three runs that illustrate qualitative trends for different gases. Plot A shows the pressure changes versus time when 10 g of ice particles is exposed to pure propane gas at 272 K. In this case, the propane was added as quickly as possible up to a pressure of 0.38 MPa. When the inlet valve was closed (t = 0.3 min), the propane pressure dropped slowly, 0.024 MPa in 20 min. At this pressure and temperature, the propane compressibility is 0.915; therefore, 0.0029 moles of propane were absorbed in 20 min, yielding an overall solid stoichiometry 0.083 C₃H₈:17 H₂O, for an 8.3% theoretical yield of propane clathrate hydrate. As shown in Figure 2, the uptake rate decreases from a slow initial rate, and even after 3 days the solid has only achieved 67% of the theoretical uptake, and has not yet reached the equilibrium vapor pressure, 0.17 MPa.

In contrast, when a similar experiment was performed with xenon gas, Figure 1, plot B, it is impossible to get the starting pressure up to 0.38 MPa before the onset of rapid xenon clathrate formation. The xenon was added more slowly to the cell to emphasize changes in the uptake kinetics with time. When the pressure reached about 0.33 MPa, clathrate hydrate formation rapidly accelerated resulting in a pressure drop, and the inlet valve was quickly closed. The xenon pressure then dropped to the hydrate vapor pressure of 0.15 MPa at 272 K within 1.5 min. During this short period of time, 0.021 moles of xenon were absorbed yielding a solid stoichiometry of 1.7 Xe:46 H₂O, or a 21% theoretical yield relative to a perfect type I hydrate. In contrast, a 0.92:1 Xe:C₃H₈ mixture achieves a 62% yield in 20 min, over 2 orders of magnitude faster.

Figure 1. Pressure vs time when xenon and/or propane is added to 10 g samples of ice grains. Plot A: For pure propane the pressure was quickly raised to 0.38 MPa. Uptake was very slow; equilibrium was not reached after 3 days. Plot B: For xenon, the pressure was raised to 0.33 MPa more slowly and, upon closing the inlet valve, equilibrium was reached in 2 min. Plot C: Xenon was first added to 0.14 MPa and then propane was added slowly. Gas uptake initiated when the combined pressure reached 0.23 MPa. In this case, the inlet valve was not closed, so it is not possible to state if equilibrium was reached.

In contrast to the case of propane for which 8.3% of the ice was converted to clathrate in 20 min, 21% of the ice is converted to xenon clathrate in only 1.5 min, and the reaction only stops because the xenon clathrate equilibrium vapor pressure is reached. If more xenon is added after the system reaches equilibrium, further uptake is slower, showing that the remaining ice surface is less exposed to the ambient gas because of clathrate crust formation, as expected.

Plot C in Figure 1 was obtained by sequentially exposing 10 g of ice particles first to xenon and then to propane. First, xenon was added to achieve a pressure of 0.14 MPa, low enough to avoid the formation of type I xenon hydrate. Next, propane was added slowly to the cell through a needle valve to yield a final pressure of 0.38 MPa in 10 min. After another 10 min of annealing, the needle valve was closed and the remaining gas was analyzed for composition. Finally, after quickly reducing the gas pressure in the cell to 0.14 MPa, the solid was decomposed and the gas phase was analyzed again. The reason for venting some of the head gas before decomposition is to avoid the production of liquid propane, which would compromise the stoichiometric analysis. Samples were never vented to pressures lower than the expected clathrate vapor pressure to avoid hydrate decomposition before the analysis period.

The most interesting aspect of Figure 1, plot C, is the downturn in pressure just past t = 1 min: rapid clathrate formation ensued and lasted for 1.5 min. The cell pressure dropped while the propane gas still flowed into the cell. We estimate that 12 mmol of gas are absorbed into the ice during this time. After 20 min the remaining gas-phase composition was 97% ± 2% propane and only 3% xenon. The cell pressure was then decreased to 0.14 MPa at 272 K and the solid phase was decomposed. After decomposition the pressure was 0.37 MPa at 293 K and the gas phase was composed of 65% ± 2% propane and 35% xenon. Analyzing these results shows that the stoichiometry of the solid was 0.40 Xe:0.28 C₃H₈:17 H₂O. After the initial fast uptake of 12 mM of gas, another 11.6 mM was absorbed during the next 18.5 min. For the ideal type II clathrate, with the small cages filled by Xe and the large cages filled with C₃H₈, the stoichiometric ratio would be 2 Xe:1 C₃H₈:17 H₂O. Propane uptake was at the expense of consuming...
with ice grains is not as dramatic as for the data in Figure 3. The overall uptake results are reported in Table 1 for all three mixtures. For the 0.92 Xe:propane mixture, more xenon than propane was absorbed by the ice. However, the propane absorption was 62% of the theoretical yield in only 20 min.

Table 2 summarizes the molar uptake, overall uptake rates, theoretical percent yields, and stoichiometry for the experiments described above, as well as propane type II and xenon type I clathrate hydrate formation experiments. Except for the case of pure Xe, uptake amounts are reported for a 20 min exposure. Clearly the 1.7 Xe:propane ratio mixture is the most efficient by this measure, but the 0.92 Xe:propane ratio mixture is nearly as efficient. Sequential addition of first xenon and then propane appears to use up the xenon rather inefficiently, even though the initial uptake rate is quite high. Although the leanest mixture gives the slowest propane uptake, it is still twice as fast as for pure propane.

### Discussion

Xenon clathrates form quickly but propane clathrates grow slowly. Under the conditions used here, pure xenon yields the type I unit cell with efficient filling of both types of cages for a typical stoichiometry of 1 Xe for 6.3 water molecules near 273 K, 1 atm.20,21 This implies that the 51262 cages are 97% occupied and the smaller 512 cages are 65% filled.21 Propane, on the other hand, resides only in the larger cages of the type II structure with an ideal stoichiometry of C6H14·(H2O)17. In the case of propane clathrate, 2/3 of the cells must form without the aid of a guest molecule to form a template. We suspect that the accelerated uptake kinetics for the Xe:propane mixture is due to xenon-induced nucleation of the small cages concomitant with propane nucleation of the large cages. Tse and Klug have performed22 molecular dynamics simulations of xenon interacting with an ice surface and find that the xenon becomes intercalated in less than a nanosecond and that protocages are already being formed during the simulation. This is consistent with the general idea that ice surfaces near the melting point are quite facile, almost liquidlike. The interaction of propane with the ice surface is also expected to be reasonably strong, so, when both molecules are present, each of the three cage types can be formed efficiently. Thermodynamics clearly favors the formation of the xenon/propane type II double hydrate, and the data presented above shows that this indeed is the predominant outcome because the final pressure is close to the double hydrate vapor pressure.23 The pressure at which rapid clathrate formation ensues is lower for the mixed gases, 0.17 MPa in Figure 3, than for pure xenon, 0.32 MPa in Figure 1, plot B. The xenon and propane work synergistically, filling both small and large cages, increasing the stability of the hydrate lattice and lowering the vapor pressure of the clathrate.

Although xenon clathrate formation goes to equilibrium in 3 min (Figure 1, plot B), while propane clathrate formation has
not obtained equilibrium in 3 days (Figure 2), the temperatures at which the two hydrates have 1 atm vapor pressure are quite similar: 262.8 K for Xe; 261.6 K for propane.\textsuperscript{(24)} By this criterion the stabilities of the two hydrates are similar and, on average, each propane molecule yields more lattice stabilization than a xenon atom. The difference in the rates of formation of the two pure clathrates is due more to local dynamics than to thermodynamics. Also, because Xe clathrate formation quickly goes to equilibrium under the conditions employed here shows that any crust layer formed over the ice surface does not significantly retard Xe incorporation into the hydrate. This may be due to the relatively high temperature of these experiments.

Uptake for the premixed 1.7:1 Xe:C\textsubscript{3}H\textsubscript{8} mixture exhibited the highest yield of propane enclathration, 66\% in 20 min, with about three-quarters of the propane enclathrated in the first 10 min as the cell was being filled (Figure 3). Although more xenon than propane was enclathrated, xenon enclathration was a lower fraction of the theoretical yield than was that of propane. The uptake of xenon and propane was nearly proportional to the pressure of xenon, onset of gas uptake occurred at about the same pressure as for the richer mixture, but the uptake rates were slower. For the 0.92 xenon/propane mixture, observable uptake of xenon and propane was faster than propane was enclathrated, xenon enclathration was a lower fraction of the theoretical yield than was that of propane. The important practical applications for rapidly growing large quantities of clathrate justify further study of this problem.

**References and Notes**

18. Gas chromatography analysis was performed using a Shimadzu GC-2014 gas chromatograph and an SE-30 column. 100 \( \mu \)L samples were taken from the sample cell and injected into the gas chromatograph using a gas syringe. Peak areas were calibrated against known gas mixtures. Retention times were 87 s for propane and 106 s for Xe, and the peaks were well separated.