Stability of Mixed CO_2/CH_4 Hydrates

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The presence of vast deposits of methane hydrates on the seafloor has for some time been considered a viable source of non-renewable energy. Additionally, the methane guest molecules occupy the same hydrate structure, sI, as would carbon dioxide. It has therefore been suggested that one can harvest CH_4 , while at the same time depositing CO_2, leaving the hydrate structure intact. This could then fulfill a dual purpose of energy gathering and climate gas storage. However, for such an undertaking to be reasonable, one should make sure that the resulting hydrate remains thermodynamically stable at the reservoir conditions. To obtain an understanding of how the stability is affected by alterations to composition, we have calculated the Gibbs energy difference at reservoir conditions between a filled hydrate and a liquid water/guest molecule mixture, using Monte Carlo simulations. The Gibbs energy landscape as composition changes is then used to evaluate how stability is affected when CH_4 is replaced by CO_2 in the cages. Finally, we calculate the energy barriers associated with moving through cages, and use these to evaluate the speed at which an exchange, or a potential decomposition, might occur.