



Influence of guest molecule properties and gas phase composition on hydrate stability

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The stability of a certain gas hydrate phase is usually provided by mechanical, thermal and chemical equilibrium with the coexisting phases: Only if all three conditions of equilibrium are reached the hydrate phase remains stable. Thermal and mechanical equilibrium conditions strongly depend on the composition of the coexisting phases such as vapour phase (feed gas) and liquid phase:

1.) Assuring a chemical equilibrium state between all phases, the stability of the hydrate phase can be estimated from the ratio of the host cavity size compared to the size of the included guest molecule, the guest-to-cavity-ratio. As the enclathrated guest molecules prevent the water cavities from collapsing, a small guest molecule encased into a large hydrate cage may be less stabilizing compared to a well suited guest molecule hindering the water molecules to interact in the way of building new hydrogen bonds. On the other hand, a guest molecule which is as large as the cavity may induce distortions of the cavity structure which also may have destabilizing effects. This hypothesis will be verified by results from systematic experiments concerning the interaction of the guest molecule with the host lattice and the stability limits of the corresponding gas hydrate.

2.) In case of changes of the chemical potential of the coexisting phases, the reestablishment of the chemical equilibrium state is the driving force of all subsequent processes. Even if pressure and temperature conditions are in the stability field of a certain hydrate phase, dissolution, structural transitions and swapping processes regarding the enclathrated guest molecules can be observed. This will be demonstrated with results from experiments on exchange reactions of simple and mixed gas hydrates with CO₂. The experiments include microscopic observation, in situ Raman spectroscopy, in situ X-ray diffraction and differential scanning calorimetry.

With a better understanding of equilibrium conditions and the guest-host interactions on a molecular level, the impact of destabilizing factors on hydrates in nature will be more predictable.