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The self-preservation effect in CO₂ clathrate hydrates at low driving forces

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Clathrate hydrates of CO₂ are crystalline inclusion compounds composed of CO₂ and water. They are expected to occur in vast amounts on comets, icy moons, and the Martian ice caps, where they play a significant role in the planetology. On earth, they are considered for usage in carbon capture and storage technologies due to their high mass density of CO₂ [1,2].

Particularly, in the case of carbon storage good knowledge of stability conditions is crucial. Although equilibrium temperatures and pressures are well known and can be modeled with high accuracy [3], decomposition kinetics of some clathrate hydrates, including CO₂ clathrate hydrates, show an anomaly called “self-preservation”. Self-preservation refers to the clathrate hydrates ability to protect itself from decomposition by showing strongly reduced dissociation rates when placed outside the stability region. This is best seen in rapid depressurization experiments, where the clathrate hydrate is forced isothermally from stable pT-conditions to unstable pressures within seconds [1]. The formation of a protecting ice shield after an initial phase of dissociation is a popular hypothesis to explain this phenomenon [1]. However, until today there is no complete model which could explain the variety of pT-conditions for self-preservation as well as its dependence on particle size, clathrate preparation method, and experimental apparatus.

In contrast to generally high driving forces in rapid depressurization experiments, here we studied the self-preservation effect at very low driving forces in temperature-ramping experiments in a closed system. Samples with diameters of 0.5-2 mm were produced following a CO₂-H₂O vapor deposition process as described by Mitterdorfer et al. [4], and stored in liquid nitrogen afterwards. They were then loaded into a precooled sample cell containing dry nitrogen gas at 203 K and barometric pressure. The cell was tightly closed, and the pressure was monitored. After an initial waiting period at 203 K an equilibrium CO₂ partial pressure of approximately 200 mbar was attained by gas release of the decomposing clathrate hydrate. Subsequent heating of the sample at a rate of 1 K/min resulted in further dissociation. Gas release rates were high enough to attain equilibrium pressures at all temperatures until a significant decrease in gas release rates indicated the advent of self-preservation conditions. Remarkably, these conditions were found at several different temperatures in the range of 230-250 K corresponding to the sample size. That is, the larger the sample, the higher the temperature at which the gas release rate dropped to zero. Complete decomposition of the samples between 270-273 K showed that only about 10 wt% of the initial clathrate mass survived until melting. This is in contrast to the results obtained by Circone et al. [2], where 80 wt% of the clathrate hydrates survived until 270 K in similar experiments.

[1] Falenty et al., J. Phys. Chem. B, (2009)

[2] Circone et al., J. Phys. Chem. B, (2003)

[3] Sloan et al., CRC Press, (2007)

[4] Mitterdorfer et al., Phys. Chem. Chem. Phys. (2011)

Significance statement

Our results show the existence of the self-preservation effect at low driving forces. Furthermore, a particle size dependence of the self-preservation effect in CO₂ clathrate hydrates, not in accordance with the general notion that larger particles exhibit stronger self-preservation, was observed.

Author: Mr ARZBACHER, Stefan (Illwerke VKW Professorship for Energy Efficiency, Vorarlberg University of Applied Sciences)

Co-authors: Prof. OSTERMANN, Alexander (University of Innsbruck); Dr PETRASCH, Joerg (Illwerke VKW Professorship for Energy Efficiency, Vorarlberg University of Applied Sciences); Dr RAHMATIAN, Nima (Vorarlberg University of Applied Sciences); Prof. LOERTING, Thomas (Institute of Physical Chemistry, University of Innsbruck)

Presenter: Mr ARZBACHER, Stefan (Illwerke VKW Professorship for Energy Efficiency, Vorarlberg University of Applied Sciences)

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