

## Guest Migration Revealed in CO<sub>2</sub> Clathrate Hydrates

Salamatin A., Falenty A., Hansen T., Kuhs W.

*Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia*

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### Abstract

© 2015 American Chemical Society. The shrinking-core model of the formation of gas hydrates from ice spheres with well-defined geometry gives experimental access to the gas permeation in bulk hydrates which is relevant to their use as energy storage materials, their exploitation from natural resources, as well as to their role in flow assurance. Here we report on a new approach to model CO<sub>2</sub> clathration experiments in the temperature range from 230 to 272 K. We develop a comprehensive description of the gas permeation based on the diffusion along the network of polyhedral cages, some of them being empty. Following earlier molecular dynamics simulation results, the jump from a cage to one of its empty neighbors is assumed to proceed via a "hole-in-cage-wall" mechanism involving water vacancies in cage walls. The rate-limiting process in the investigated temperature range can be explained by the creation of water-vacancy-interstitial pairs. The gas diffusion leads to a time-dependent cage filling which decreases across the hydrate layer with the distance from the particle surface. The model allows a prediction of the time needed for a complete conversion of ice spheres into clathrate as well as the time needed for a full equilibration of the cage fillings. The findings essentially support our earlier results obtained in the framework of a purely phenomenological permeation model in terms of the overall transformation kinetics, yet it provides for the first time insight into the cage equilibration processes. The diffusion of CO<sub>2</sub> molecules through bulk hydrate is found to be about three to four times faster in comparison with the CH<sub>4</sub> case.

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