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Kinetics of CO2-hydrate formation from ice powders: Data summary and modeling extended to low temperatures

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Abstract

The shrinking-core model of the formation of gas hydrates from ice spheres with a well-defined geometry gives experimental access to the gas permeation in bulk hydrates. Here we report on results obtained for CO2 clathration experiments in the temperature range from 185 to 272 K, extending earlier work to much lower temperature conditions. The activation energy deduced from the permeation coefficients changes its value from ~46 kJ/mol at higher temperatures to ~19 kJ/mol below 225 K. We compare our results with published molecular dynamics simulation as well as nuclear magnetic resonance studies and provide arguments that the rate limiting process at lower temperatures is the cage-to-cage jumping of CO2 molecules via a "hole-in-t-e-cage" mechanism involving extrinsic water vacancies in cage walls. The rate-limiting process at higher temperatures can be explained by the temperature-dependent creation of intrinsic water-vacancy-interstitial pairs. The results obtained for CO2-hydrate are compared to earlier results for CH4-hydrate formation. The permeation of CO2 molecules through bulk hydrate is found to be about three times faster when compared to the CH4 case. This explains the faster clathration reaction of CO2-hydrate in comparison to CH4-hydrate.

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