

Formation of porous gas hydrates from ice powders: Diffraction experiments and multistage model

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Abstract

Gas hydrates grown at gas-ice interfaces were examined by electron microscopy and found to have a submicron porous structure. In situ observations of the formation of porous CH₄- and CO₂-gas hydrates from deuterated ice Ih powders were made, using time-resolved neutron diffraction on the high-flux diffractometer D20 (ILL, Grenoble) at different pressures and temperatures. For the first time neutron diffraction experiments were also performed with methane in hydrogenated samples. The isotopic differences between H₂O and D₂O are found insignificant concerning the clathrate formation kinetics. At similar excess fugacities, the reaction of CO₂ was distinctly faster than that of CH₄. The transient formation of the CO₂-hydrate crystal structure II was also observed in coexistence with the usual type-I hydrate reaching a maximum of 5% after 5 h of the reaction at 272 K. A phenomenological model for the kinetics of the gas hydrate formation from ice powders is developed with special account of sample consolidation effects. It describes the initial stage (I) of hydrate film spreading over the ice surface and the two subsequent stages which are limited (II) by the clathration reaction at the ice-hydrate interface and (III) by the gas and water transport (diffusion) through the hydrate shells surrounding the shrinking ice cores. Comparable activation energies are found for stage II of the CH₄-hydrate formation in deuterated and hydrogenated ice with 8.1 and 9.5 kcal/mol, respectively. In the case of a diffusion-limited clathration (stage III) the activation energy in D₂O-ice powders can be estimated as 14.3 kcal/mol.
