

Experimental studies on the formation of porous gas hydrates

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Abstract

Gas hydrates grown at gas-ice interfaces were examined by electron microscopy and found to have a sub-micrometer porous structure. In situ observations of the formation of porous CH₄- and CO₂-hydrates from deuterated ice Ih powders were made at different pressures and temperatures, using time-resolved neutron diffraction data from the high-flux D20 diffractometer (ILL, Grenoble) as well as in-house gas consumption measurements. The CO₂ experiments conducted at low temperatures are particularly important for settling the open question of the existence of CO₂ hydrates on Mars. We found that at similar excess fugacities, the reaction of CO₂ was distinctly faster than that of CH₄. A phenomenological model for the kinetics of the gas hydrate formation from powders of spherical ice particles is developed with emphasis on ice-grain fracturing and sample-consolidation effects due to the outward growth of gas hydrate. It describes (1) the initial stage of fast crack-filling and hydrate film spreading over the ice surface and the two subsequent stages which are limited by (2) the clathration reaction at the ice-hydrate interface and/or by (3) the diffusive gas and water transport through the hydrate shells surrounding the shrinking ice cores. In the case of CO₂-hydrate, the activation energies of the ice-surface coating in stage 1 are estimated to be 5.5 kJ/mol at low temperatures and 31.5 kJ/mol above 220 K, indicating that water molecule mobility at the ice surface plays a considerable role in the clathration reaction. Comparable activation energies of 42.3 and 54.6 kJ/mol are observed in the high temperature range for the reaction- and diffusion-limited stages 2 and 3, respectively.
