Experimental Report

27/06/2014

Proposal: **5-25-218** **Council:** 10/2012

Title: Diffusion constants and activationenergy of methane migration in bulk methane hydrate

This proposal is a new proposal

Researh Area: Other...

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Samples: CH4*6D2O

Instrument	Req. Days	All. Days	From	To
D20	3	3	28/06/2013	01/07/2013

Abstract:

We propose to determine the diffusion coefficients of methane in methane hydrate by following in-situ the formation of methane hydrate from well-characterized ice spheres via a shrinking-core modelling developed by us. Gas permeation through bulk hydrate is of major importance in geology and chemical engineering applications and it turns out that in-situ neutron diffraction is probably the most reliable way to establish this quantity. Absolute values of the diffusion constants will be derived and their temperature dependency will give access to the activation energy. Both, diffusion constants and activation energy, will be compared to results from molecular dynamics simulations, which will help to elucidate the mechanism of gas migration.

Diffusion constants and activation energy of methane migration in bulk methane hydrate

Permeation of gas molecules through the water host structure of clathrate hydrates plays a central role in SUGAR II (Submarine Gashydrat-Lagerstätten) project aiming on the recovery of methane from deposits of natural gas hydrates (GH) with the sequestration of anthropogenic CO_2. Although the spontaneous replacement of encaged methane with CO_2 has been confirmed by numerous experiments, the molecular scale mechanisms that enable this process remains obscure [1]. While small-size molecules like H_2, He or Ne [2] can freely travel between individual cavities, the majority of gas species is too large to pass through 5- and 6-membered rings of the clathrate cages and the migration process must be assisted by rearrangements of water molecules. Mobility of guest molecules is also needed for the formation of gas hydrates from water ice. During this process, after a rapid surface conversion, gas molecules can reach the reaction front only by penetrating the newly formed hydrate phase. Using this method we have successfully identified rate limiting gas permeation mechanisms for CO_2 hydrates using a modified shrinking core-modelling [3]. In this way we have found out that the permeation rate in bulk hydrate is about 3 times faster for CO_2 than for CH_4 [4]; this finding is of outmost importance for the exchange process but was identified only in a narrow temperature range between 270 and 250 K. With the experiment discussed here we attempted to firmly establish this difference and trace it down to 200 K via a combination of neutron diffraction experiments focused on the initial several hours of the reaction and several weeks' long pVT runs.

Long pVT experiments performed prior to the scheduled beam-time indicated very low transformation rates of only a several wt.% in a period of days to weeks within the targeted temperature region. They have also revealed, difficult to correct for, artefacts in the early stage of the reaction caused by the intrinsic temperature-pressure coupling. Since the *in-situ* neutron diffraction is unaffected by this issue we have modified the original experimental plan to pin down kinetic parameters this important region. We have performed two series of formation experiments with 88 and 17.8 µm size ice spheres, covering first several hours of the reactions where the transition between the initial nucleation and growth of the GH coating and diffusion

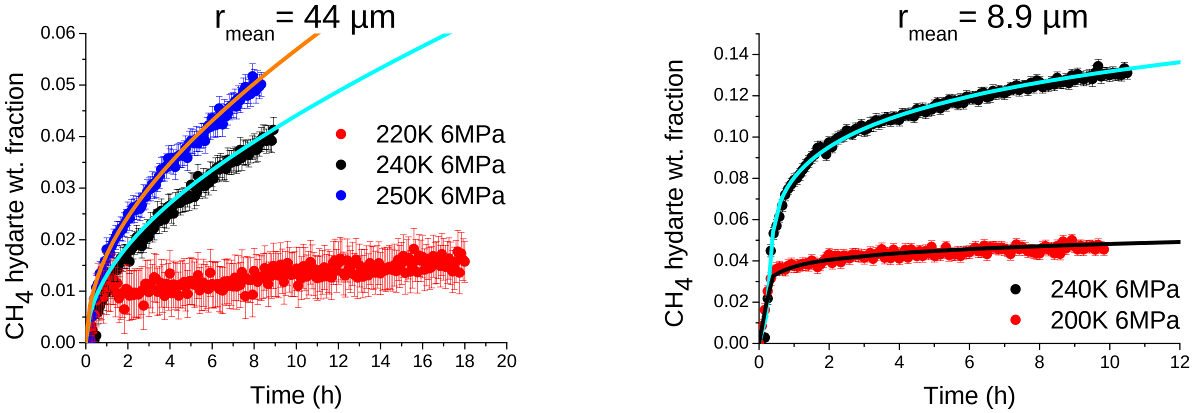

Figure 1. Formation kinetics of CH_4 hydrates from ice spheres with a mean radius of 44 µm (l.h.s) and 8.9 µm at selected temperatures (r.h.s) fitted with the "shrinking core" [3] model (solid lines).

controlled regime occurs. The first group has been performed at constant temperature of 240, 230, 220 K and constant methane pressure of 6 MPa. The refinement results (Figure 1 l.h.s) show less than ~ 5 wt.% of methane hydrate formed within the first 8h but due to the excellent precision and accuracy of acquired data we could pin down the diffusion-limited regime of the reaction. The slow reaction kinetics at 220 K is likely the consequence of an accidental warming and coarsening of the starting ice during the sample handling (also indicated by large deviations from the expected intensities of the ice reflections due to insufficient powder statistics)strongly affecting the spherical geometry of the starting material and reducing the surface available for the reaction. Unfortunately this issue was only recognized during the data treatment.

The exploration of diffusion constants at even lower temperatures by in-situ diffraction becomes increasingly challenging due to the beam-time limitation and intrinsic difficulty of separating fluctuations in the background from minute changes in the amount of the new substance during the full pattern Rietveld refinement. We attempted to circumvent this issue by enhancing the conversion rate during the initial coating stage with help of much finer ice powders. Indeed, the second group of runs taken at constant temperatures of 240 and 200 K and at constant pressure of 6 MPa (Figure 1 r.h.s) shows an initial rapid formation of CH_4 hydrates followed by a quick deceleration upon the transition to the diffusion controlled regime.

We were able to successfully treat both sets of the neutron diffraction data with our “shrinking core” [3] model (Figure 1 – solid lines) and currently work on much larger set on pVT experiments. First results will be presented at the upcoming International Conference on Gas Hydrates ICGH-8 in Beijing this summer.

[1] Falenty A, Murshed MM, Salamatin AN, Kuhs WF. Gas Replacement in Clathrate Hydrates during CO_2 Injection - Kinetics and Micro-Structural Mechanism. In: Tenth ISOPE Ocean Mining and Gas Hydrates Symposium, TheInternational Society of Offshore and Polar Engineers (ISOPE), Szczecin, Poland, 2013, 109-115.

[2] Falenty A, Hansen TC and Kuhs WF, *Formation and properties of an empty clathrate hydrate structure*, The final experimental report for proposal 5-25-217, (Full paper submitted to Nature on December 23rd, 2013)

[3] Falenty A, Salamatin AN and Kuhs WF, Kinetics of CO_2-Hydrate Formation from Ice Powders: Data Summary and Modeling Extended to Low Temperatures, Journal of Physical Chemistry C 2013, 117 (16), 8443-8457.

[4] Kuhs WF, Staykova DK and Salamatin AN, *Formation of Methane Hydrate from Polydisperse Ice Powders*, Journal of Physical Chemistry B 2006, 110, 13283-13295, DOI: 10.1021/jp061060f.