

## Escape of helium from the crystal lattice of clathrate hydrate

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Gas hydrates enclathrate variety of gas molecules such as methane (CH<sub>4</sub>), which is the main component of natural gas, and their crystallographic structures change depending on the type and composition of the guest molecules. Small amount of helium (He) was detected in the hydrate-bound gases obtained from the dissociation of natural gas hydrates, but there are few studies on enclathrated He. Formation of pure He hydrate requires high pressure (e.g. 0.28 GPa at 220 K reported by Londono *et al.*, 1992). However, the crystallographic structure of He hydrate has not been reported, and there are many unknowns such as how the He is encapsulated in the crystal. On the other hand, it is possible that a small amount of He can be enclathrated in the mixed-gas hydrates.

We have established a technique to form synthetic mixed-gas hydrate composed of CH<sub>4</sub> and He and to separate the hydrate-bound gas from the residual gas (Kimura *et al.*, 2020; Moriya *et al.*, 2021). In these experiments, the hydrate sample was fixed at the temperature of liquid nitrogen and the residual gas in the cell was evacuated completely. Since the molecular size of He is small, He might diffuse through host water cages of gas hydrates and escape out of the crystals. In this study, we investigated how the concentration of He in the hydrate-bound gas changed with evacuation time for two types of gas hydrate systems: a CH<sub>4</sub>/He mixture (crystallographic structure I) and an argon (Ar)/He mixture (crystallographic structure II). The effect of temperature on the He concentration was also investigated.

The formation of the mixed-gas hydrates was carried out in the same method as reported by Moriya *et al.* (2021). CH<sub>4</sub> or Ar was introduced into the pressure cell together with appropriate amount of He. By fixing the gas composition and the amount of gas introduced, we aimed to obtain the same gas composition in the hydrate-bound gas. Hydrate samples formed by slowly raising the temperature of the pressure cell from 77 K to 273 K, to contact the mixed-gas with melting water of fine ice powder. The pressure cell was cooled to 77 K and evacuated without decomposing the gas hydrate crystals for several hours to completely discharge the residual gas (residual He and liquefied CH<sub>4</sub> or solid Ar) so that only the gas hydrate crystals remained in the pressure cell. The duration of the subsequent evacuation was set for each sample in the range of several hours to one month. After that, the gas hydrate samples were dissociated in the cell at room temperature, and the hydrate-bound gas was collected. These gas samples were immediately analyzed by a portable gas chromatograph (CP-4900, Varian) to determine the He concentration in the gas samples.

At the specific gas composition of the initial gas, the concentration of He in the hydrate-bound gas of the CH<sub>4</sub>/He mixture at 77 K varied from 0.7 to 1.1%, and that of the Ar/He mixture was about 0.2%. The concentration of He in the hydrate-bound gas did not decrease even though the vacuum was continued for up to one month. Therefore, it was confirmed that the He in the sample was maintained at a certain value at the temperature of liquid nitrogen for at least one month. On the other hand, as a result of the same experiment at 153 K, the concentration of He in the CH<sub>4</sub>/He mixture decreased to 0.2% in 6 hours, and the concentration of in the Ar/He mixture decreased drastically to the order of 0.001%. Accordingly, He is likely to escape more easily through the crystallographic structure II than structure I hydrate. This may be because the dodecahedral small cages of structure II hydrate are adjacent to each other.

### References

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