# Phase Equilibrium Conditions for Krypton Clathrate Hydrate below the Freezing Point of Water

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The dissociation behavior of krypton (Kr) hydrate below the freezing point of water was characterized using optical scanning microscopy (OSM). The dissociation temperature was obtained in the pressure range of (0.10 to 1.42) MPa. The dissociation temperature of Kr hydrate at 0.1 MPa, which was inconsistent in previous reports, was 204.4 K. Using the Clausius−Clapeyron equation, the enthalpy of Kr hydrate dissociation was estimated to be approximately 18.5 kJ·mol$^{-1}$. This value agreed well with (19.54 ± 0.24) kJ·mol$^{-1}$, which was obtained from a previously reported calorimetric analysis.

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## 1. Introduction

Gas hydrates are crystalline clathrates in which gas molecules are stored in cages of hydrogen-bonded $H_2O$ molecules under certain temperature and pressure conditions.[1] Gas hydrates generally have one of three crystal structures: structure I, structure II, or structure H, depending mainly on the size of the stored gas molecules.[2] For example, a $CH_4$ gas molecule is approximately 4.4 Å in diameter, and the $CH_4$−water system forms a structure I hydrate. Gas hydrates have significant gas storage ability. A unit of gas hydrate can store approximately 170 times the volume of the guest gas molecules at normal conditions. Thus, gas hydrates are attractive new gas storage media,[3−5] and understanding their dissociation behavior is a key issue for their application as storage. A molecule of the noble gas krypton (Kr) is approximately 4.0 Å in diameter and can be stored in the cages of a gas hydrate. The crystal structure of Kr hydrate is structure II (sII).[2] Sugahara et al.[6] measured the hydrate−gas−liquid three-phase coexistence data for Kr hydrates in a wide temperature range of (274.4 to 320.0) K. Around the freezing point of water, the data in the literature were almost consistent at the Kr hydrate−gas−ice three-phase coexistence pressure, which is about 1.46 MPa.[1,6−9] Nevertheless, few Kr hydrate−gas−ice three-phase coexistence data have been reported, and they vary throughout the literature except around the freezing point of water. For example, the dissociation temperatures at approximately 0.1 MPa were reported as 248.2 K,[7] 245.4 K,[9] and 202.9 K (at 0.11 MPa).[10] In this paper, we report dissociation data for Kr hydrate below the freezing point of water in the pressure range of (0.10 to 1.42) MPa by optical scanning microscopy (OSM) observations. We compare our experimental data with that from the literature[7−10] and then evaluate the dissociation temperature of Kr hydrate at 0.1 MPa.

## 2. Experimental Methods

The crystal growth and dissociation of Kr hydrate on an ice surface were observed using an optical scanning microscope (1HD200, Lasertec Co., Japan). Figure 1 shows the configuration of a high-pressure vessel made of stainless steel 316 (SUS316) and the observation system. A digital camera (Coolpix 4500, Nikon Co., Japan) connected to a time-lapse video recorder was attached to the OSM for real-time observations. The sample cell was made of Cu with an inner diameter of 10 mm and a height of 5 mm. The maximum operating pressure of the vessel was 10 MPa in the temperature range of (173 to 298) K. The sample holder temperature was measured using a thermocouple (Type K, Chino Co., Japan). The thermocouple was calibrated using a thermo tracer (D641, Technol Seven Co. Ltd., Japan) and a thermistor thermometer (SXA-33, Technol Seven Co. Ltd., Japan). The uncertainty of the temperature measurements was estimated to be ± 0.06 K with a confidence level of approximately 95 %. The sample holder's temperature was maintained within ± 0.1 K by circulating liquid nitrogen, as shown in Figure 1. A cold jacket attached to the vessel was cooled to the same temperature as the sample holder by circulating ethanol or liquid nitrogen. The pressure was measured using two pressure transducers: AP-13S (Keyence Co., Japan) for the pressure range from (0.1 to 1.0) MPa and AP-14S (Keyence Co., Japan) for pressures above 1.0 MPa. The uncertainty of the pressure measurements was ± 0.005 MPa in the pressure range of (0.1 to 1.0) MPa and ± 0.05 MPa at pressures above 1.0 MPa, with a confidence level of approximately 95 %.

An ice sample was prepared from polycrystalline ice with large grains. Kr used in the experiment was of research grade (99.995 % purity) obtained from Takachiho Chemical Industrial Co., Ltd., Japan. All chemicals were used without further purification. In a cold room at 263 K, an ice sample with a flat surface was shaped into a disk-like form with a diameter and height of approximately 8 mm and 2 mm, respectively. The sample cell containing the ice sample was loaded into the high-pressure vessel while the temperature of the sample holder was controlled. Then, after eliminating air from the vessel, we pressurized it with Kr gas from an inlet at a designated

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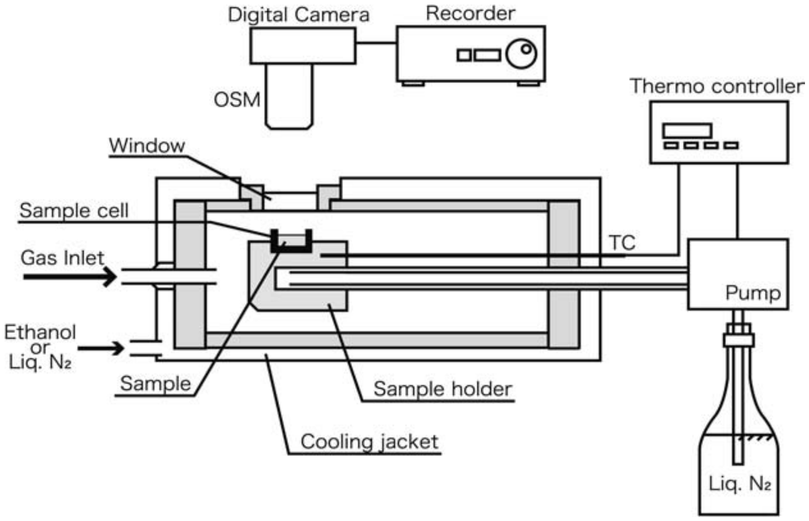

**Figure 1.** High-pressure vessel configuration and optical microscope configuration.

temperature. When the pressure–temperature combination conditions for Kr hydrate of the given experimental setup became stable, crystal growth was observed. In contrast, when the given condition was an unstable combination, the crystal morphology collapsed and/or the morphological surface changed. After Kr hydrate formed and grew on the flat ice surface, the dissociation temperature of Kr hydrate was visually determined by increasing the temperature in 0.1 K increments under constant pressure. The inner volume of the vessel shown in Figure 1 is about 20 $\text{cm}^3$. Compared with this volume, the total volume of hydrates formed on the ice surface is considered to be negligibly small. Therefore, when the pressure–temperature condition reaches the dissociation condition for hydrates as the temperature increases in 0.1 K increments, the hydrate particles on the ice surface would dissociate in a short amount of time to maintain the equilibrium pressure. Considering the inner volume of the vessel, we maintained the temperature at each temperature step for 30 min.

To confirm the reliability of our experimental method and the accuracy of the obtained data, we observed the dissociation of methane hydrate crystals and measured the dissociation pressure–temperature conditions. The methane gas used in the experiment was of research grade (99.9 % purity) obtained from Sumitomo Seika Chemicals Co., Ltd., Japan.

## 3. Results and Discussion

Figure 2 shows images of the dissociation of methane hydrate particles on an ice surface as the temperature increased from (272.2 to 272.4) K at 2.50 MPa. Each image was recorded after the designated temperature was maintained for 30 min. Agglomerated methane hydrate crystals were observed. At (272.2 and 272.3) K, hydrate crystals did not show any morphological changes. Then, the crystal morphology changed at 272.4 K; hydrate crystals became round, and the agglomerated particles were fragmented. Shimada et al.[11] reported that a change in the texture of hydrate particles did not appear before hydrate dissociation but was observed during dissociation. Therefore, the changes observed at 272.4 K are considered to be the result of ice formation during hydrate dissociation. From the morphology change shown in Figure 2c, we concluded that methane hydrate dissociated at 272.4 K under 2.50 MPa. The dissociation pressure–temperature conditions in our experiment are listed in Table 1 and plotted in Figure 3. The expanded uncertainty of the dissociation temperature was ± 0.2 K with a confidence level of approximately 95 %, taking into account the reproducibility of methane hydrate dissociation and including the uncertainty in the temperature measurement. Data from the literature[12−16] are also plotted in Figure 3. Our dissociation data in Figure 3 agree well with the literature and thus demonstrate the reliability of the data obtained by our visual observation method.

Figure 4 shows the images of typical crystal dissociation of Kr hydrate on an ice surface as the temperature increased from (269.0 to 269.2) K at 1.38 MPa. Faceted crystals, namely, Kr hydrates, clearly existed on the ice surface. Kr hydrates, as shown in Figure 4a,b, had facets as they grew. In a gas–water system, the morphology of hydrates depends on the degree of subcooling, which is the difference between the equilibrium and the experimental temperatures at a certain pressure.[17,18] Similarly, the morphology of hydrates in a gas–ice system depends on the degree of subcooling.[19] The thermal conductivity of ice is higher than that of a hydrate and Kr gas. Therefore, hydrate growth on an ice surface is considered to be controlled by mass transfer and growth kinetics. At a low degree of subcooling, hydrate growth would be controlled almost entirely by kinetics, and a single crystal plane would grow. A faceted Kr hydrate is believed to grow on the ice surface, as shown in Figure 4a, because the given pressure–temperature condition was close to the equilibrium condition.

The faceted hydrate crystals in Figure 4b are nearly the same as those in Figure 4a. Kr hydrate was seen to be stable at temperatures below 269.1 K. Figure 4c shows the sample surface at 269.2 K. Faceted Kr hydrate crystals gradually changed as a result of the temperature increase of 0.1 K and became round 30 min later, as shown in Figure 4c. In particular, the face of a rhombic-plate hydrate, indicated by the white arrow, collapsed. In our experiments, Kr hydrate was stable below 269.1 K at 1.38 MPa, because no surface morphology change was observed, as shown in Figure 4a,b. The surface change in hydrate particles at 269.2 K is considered to originate in Kr hydrate dissociation, like methane hydrate dissociation shown in Figure 2. As shown in Figure 4c, Kr hydrate dissociated at 269.2 K and 1.38 MPa. Kr hydrate has been reported to show a self-preservation effect.[20] Nevertheless, considering the result of methane hydrate dissociation shown in Figure 3, the self-preservation effect of the ice layer on Kr hydrate is considered to have a negligible influence on our result.

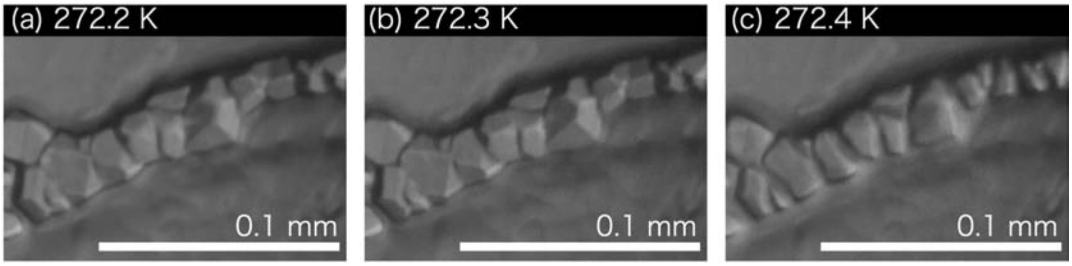

**Figure 2.** Still images of dissociation behavior of methane hydrate on an ice surface as a result of temperature increases from (272.2 to 272.4) K at 2.50 MPa.

**Table 1. Experimental Dissociation Conditions of Methane Hydrates**

| $T$/K[a] | $p$/MPa[b] |
|---|---|
| 243.7 | 1.00 |
| 254.7 | 1.45 |
| 264.3 | 1.94 |
| 265.8 | 2.03 |
| 267.6 | 2.19 |
| 270.1 | 2.35 |
| 272.4 | 2.50 |

[a] The expanded uncertainty of dissociation temperature was estimated to be ± 0.2 K with a confidence level of approximately 95 %. [b] Uncertainties of pressure measurements were estimated to be ± 0.05 MPa with a confidence level of approximately 95 %.

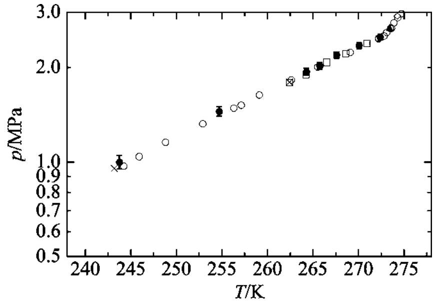

**Figure 3.** Dissociation pressure−temperature conditions of methane hydrates. ●, present study; ○, Yasuda and Ohmura;[12] □, Deaton and Frost;[13] ×, Makagon and Sloan;[14] ▲, Ohmura et al.;[15] ◇, Nakamura et al.[16] Error bar indicates the uncertainties of pressure measurements (± 0.05 MPa).

**Table 2. Experimental Dissociation Conditions of Kr Hydrates**

| $T$/K[a] | $p$/MPa[b] |
|---|---|
| 204.4 | 0.10 |
| 217.2 | 0.19 |
| 227.0 | 0.29 |
| 238.7 | 0.48 |
| 244.4 | 0.60 |
| 248.3 | 0.69 |
| 252.7 | 0.80 |
| 256.9 | 0.93 |
| 260.2 | 1.05 |
| 262.9 | 1.14 |
| 265.2 | 1.23 |
| 267.7 | 1.30 |
| 269.2 | 1.38 |
| 270.4 | 1.42 |

[a] The expanded uncertainty of dissociation temperature was estimated to be ± 0.2 K with a confidence level of approximately 95 %. [b] Uncertainties of pressure measurements were estimated to be ± 0.005 MPa at pressures below 1.0 MPa and ± 0.05 MPa at pressures above 1.0 MPa with a confidence level of approximately 95 %.

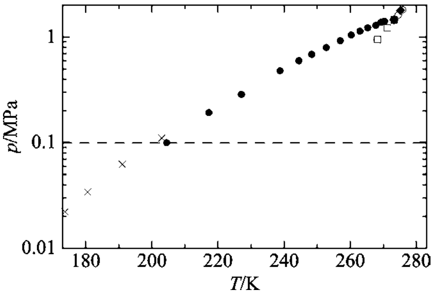

**Figure 5.** Dissociation pressure−temperature conditions of Kr hydrates. ●, present study; ○, Sugahara et al.;[6] ◆, de Forcrand;[7] □, Berecz and Balla-Achs;[8] ■, von Stackelberg;[9] ×, Barrer and Edge;[10] dashed line, 0.1 MPa.

Dissociation data at various pressures were obtained by temperature ramping, as described above. In our experiment, the dissociation temperature of Kr hydrate at 0.1 MPa was 204.4 K. Table 2 lists Kr hydrate dissociation conditions in our gas−ice system. The expanded uncertainty of the dissociation temperature was ± 0.2 K with a confidence level of approximately 95 %, taking into account the reproducibility and including the uncertainty in the temperature measurement. Figure 5 shows the dissociation pressure−temperature variation of Kr hydrate determined from our experimental results, together with experimental data from the literature.[6−10] Our experimental dissociation temperatures were lower than those reported by Berecz and Balla-Achs.[8] On the other hand, Barrer and Edge's data[10] were close to our experimental data. To assess the reliability of our data, we estimated the enthalpy of dissociation $\Delta H$ for hydrate to ice and gas using the Clausius−Clapeyron equation,

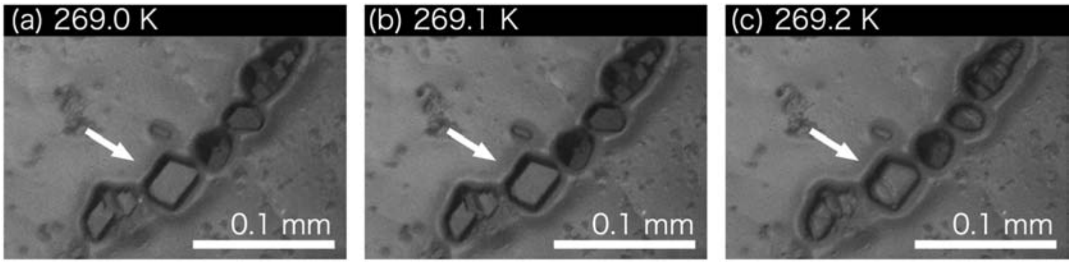

**Figure 4.** Still images of dissociation behavior of Kr hydrate on an ice surface as a result of temperature increases from (269.0 to 269.2) K at 1.38 MPa.

$$\frac{d \ln p}{d(1/T)} = -\frac{\Delta H}{zR}$$

where $p$, $T$, $z$, and $R$ are the pressure, temperature, compressibility factor, and gas constant, respectively. When $z$ is assumed to be 0.997, the value at 273.1 K and 1.46 MPa, $\Delta H$ is approximately 18.5 $\text{kJ} \cdot \text{mol}^{-1}$, from the slope of $\Delta H/zR$ in ln $p$ plotted against $1/T$. The $\Delta H$ value from our results agreed well with (19.54 ± 0.24) $\text{kJ} \cdot \text{mol}^{-1}$, which was obtained from an earlier calorimetric analysis.[21] On the other hand, Berecz and Balla-Achs's pressure−temperature data[8] indicated that $\Delta H =$ 52 $\text{kJ} \cdot \text{mol}^{-1}$. Assuming that the hydration number of Kr hydrate was 6.1, and considering an enthalpy of transition from ice to water of approximately 36.6 $\text{kJ} \cdot \text{mol}^{-1}$,[22] for $\Delta H = 19.5$ $\text{kJ} \cdot \text{mol}^{-1}$, the enthalpy of dissociation for Kr hydrate to liquid water and Kr gas was estimated to be approximately 56 $\text{kJ} \cdot \text{mol}^{-1}$. Thus, Berecz and Balla-Achs's data[8] were considered to be obtained in the liquid coexistence phase. Here the $\Delta H$ values of de Forcrand[7] and von Stackelberg[9] are (61 and 58) $\text{kJ} \cdot \text{mol}^{-1}$, respectively. Taking into account the $\Delta H$ value, de Forcrand's[7] and von Stackelberg's[9] values would be obtained by extrapolation from the enthalpy of dissociation above the freezing point of water. Thus, these values from the literature[7−9] were higher than our experimental results.

## 4. Conclusions

We reported Kr hydrate dissociation pressure−temperature data below the freezing point of water in the pressure range of (0.10 to 1.42) MPa via visual observation. The dissociation temperature data for Kr hydrate in our experiment were lower than those in the literature.[7−9] We obtained an enthalpy of dissociation, $\Delta H$, of approximately 18.5 $\text{kJ} \cdot \text{mol}^{-1}$ using the Clausius−Clapeyron equation. Our experimentally obtained dissociation data for Kr hydrate agreed well with the $\Delta H$ value obtained from calorimetric analysis.[21] This study showed that the dissociation temperature of Kr hydrate at 0.1 MPa was 204.4 K.

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